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INVESTIGATIONS ON THERMALLY HIGHLY STABLE EXPLOSIVES BASED ON NITROBENZENES AS REPLACEMENTS FOR HEXANITROSTILBENE (HNS)

vorgelegt von

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aus

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Erklärung

Diese Dissertation wurde im Sinne von §7 der Promotionsordnung vom 28. November 2011 von Herrn Prof. Dr. Thomas M. KLAPÖTKE betreut.

Eidesstattliche Versicherung

Diese Dissertation wurde eigenständig und ohne unerlaubte Hilfe erarbeitet.

München, den ……………………….

Michael Weyrauther

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Was wir wissen, ist ein Tropfen, was wir nicht wissen, ein Ozean.

Sir Isaac Newton (1643 – 1727)

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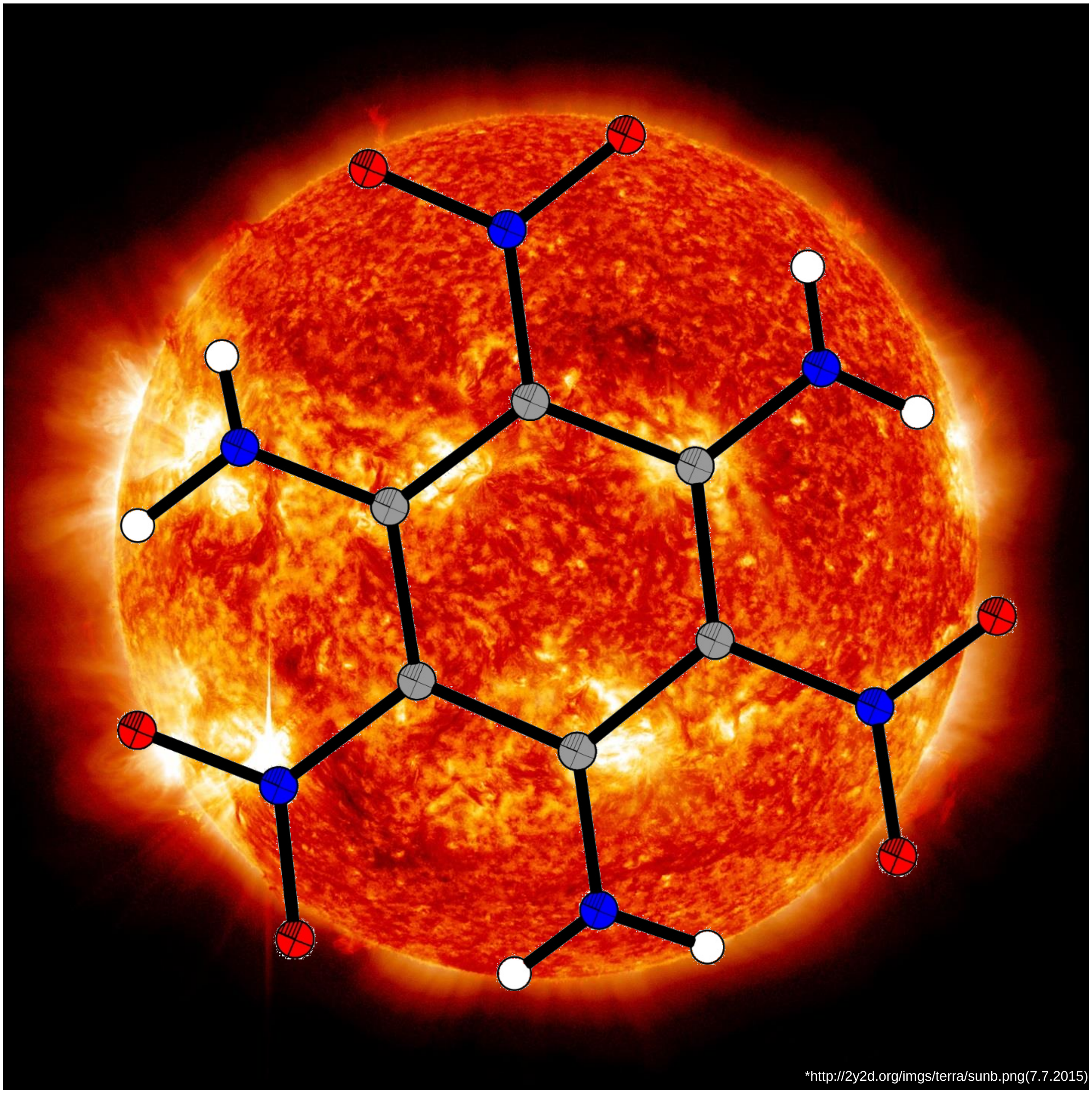

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1 Introduction

1.1 Historical overview

Albert Einstein once said: “The most beautiful thing we could experience was the mysterious.” Since the beginning mankind was fascinated by the mysterious. May it be the unknown or natural forces like flash, thunder, wind or fire. In early times these things were named after mystic creatures or gods. But as mankind went on and learned how to deal with it they took the advantages to improve their life.

One of these achievements was fire and the corresponding handling and implementation of energetic materials. It all began with a mixture containing pitch and sulphur in the 5th century BC, which was used with a stick as torch or fire arrow. In the 7th century AD the Byzantic Empire implemented the so called “Greek fire”, a mixture containing inter alia sulphur and saltpeter. In the next centuries this mixture was developed, updated further and a prequel to the today known black powder was invented. Black powder is a mixture containing potassium nitrate (75 % / oxidizer), sulfur (10 % / fuel) and charcoal (15 % / fuel), which even was known in China during the Han Dynasty (25-250 AD)[1] and used in first primitive rockets, called “Fire arrow” in the Sung-time (960-1279 AD).[2-4]

Although this composition was discovered in Asia so early in time, in Europe it got attention not until the 13th and 14th century. The knowledge of black powder was brought to Europe by Dutch sailors at the end of the 13th century. At the same time the English monk Roger Bacon and the franziscanian monk Berthold Schwarz autonomously experimented with the basic materials of black powder (Figure 1). By accident the monk Berthold Schwarz was able to discover the composition of today’s black powder.[2-4] A big mistake is the assumption that the name black powder (German: *Schwarzpulver*) was deduced by the monk Berthold Schwarz. Instead it has the name because of the color caused by the charcoal.[5]

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Figure 1: Left: Monument of Roger Bacon in the Oxford University Museum; right: Monument of Berthold Schwarz in Freiburg.

Since the discovery and the recognition of its very high potential for military usage black powder had become an effective weapon on the battlefield. After optimizing the production by Corning in the year 1425 it was used as propellant in guns and canons.[6]

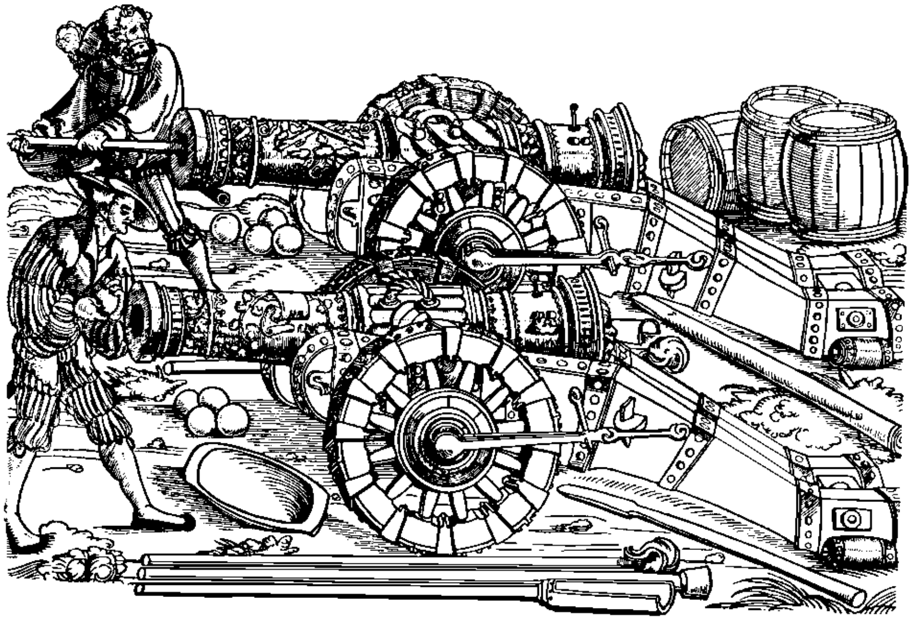

Figure 2: Woodcut by Erhard Schön.

Chapter 1: Introduction

Until 1846 black powder had been the only explosive in wide use. Then nitroglycerine (NG) was discovered by Ascanio Sobrero in Italy. In comparison to black powder, NG combines oxidizer (nitro groups) and fuel (C-H backbone) in one molecule. Soon the potential of nitrated compounds was recognized and other explosives like nitrocellulose (NC; 1846 by Schönbein and Böttger), Tetryl (CE; 1879 by Michler and Meyer) and pentaerythritol tetranitrate (PETN; 1891 by Tollens and Wigand) were developed.[7] One big disadvantage of NG was the very dangerous handling because of its high sensitivities. Also the initiation by black powder was very unreliable. Therefore in 1864 Alfred Nobel replaced black powder by mercury fulminate (MF), discovered by Edward Howard, which was the first compound used as a primary explosive. Later it was replaced by lead azide (LA) which is still used today. After his brother died in an explosion of their factory in the same year, he went on to make NG safer to handle. He finally solved the problem by pouring NG on kieselguhr. This combination is well known as Dynamite.[6]

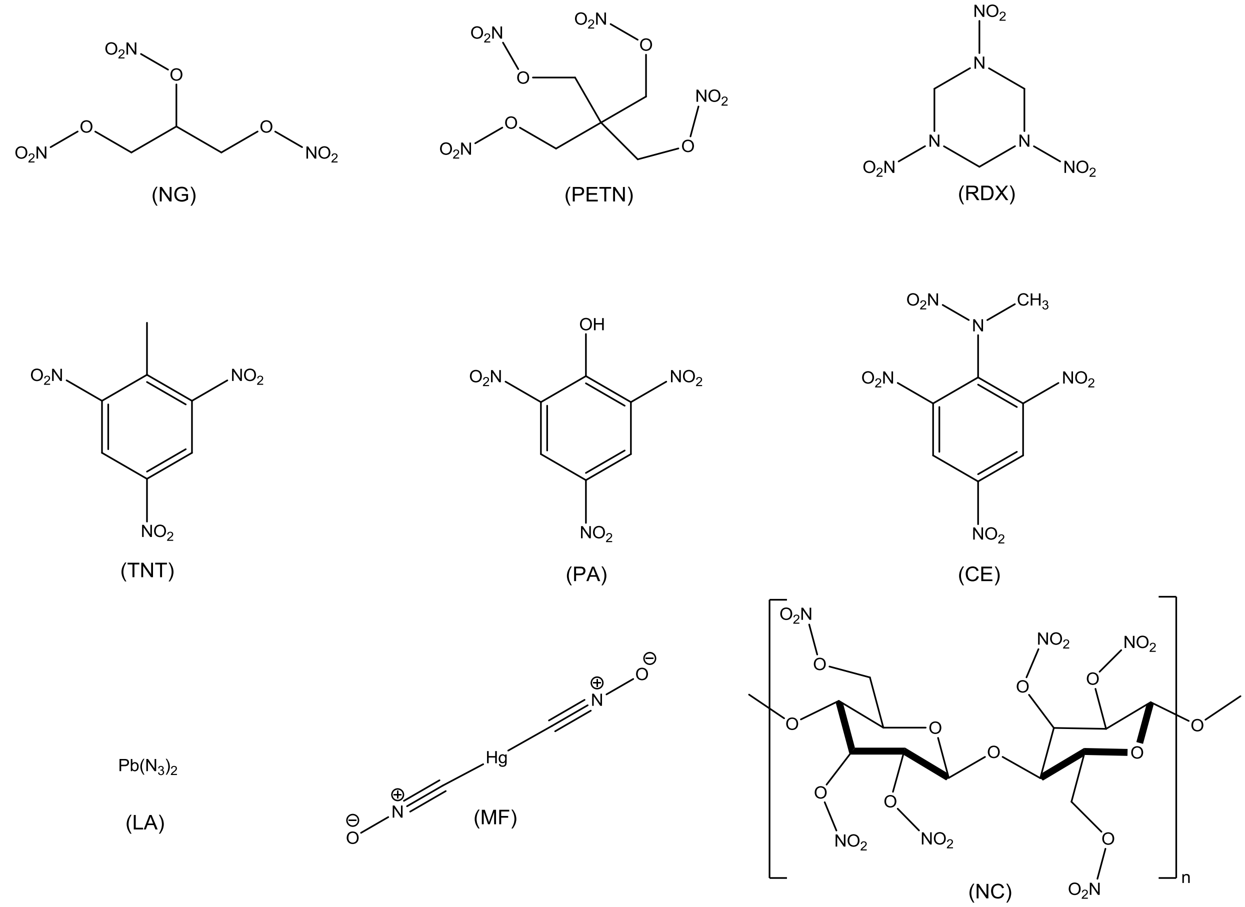

Figure 3: Molecular structures of nitroglycerine (NG), nitrocellulose (NC), picric acid (PA), trinitrotoluene (TNT), tetryl (CE), pentaerythritol tetranitrate (PETN), mercury fulminate (MF), hexogen (RDX) and lead azide (LA).

Dynamite never was used for military applications but found its way to civil applications like mining. Until the end of the 19th century black powder was used when it was replaced by picric acid (PA; 1771 by Woulfe). But the disadvantage of PA is the formation of very sensitive metal picrate salts and was therefore replaced soon by other explosive materials like TNT. In 1863 Joseph Wilbrand synthesized trinitrotoluene (TNT) and refined by Paul Hepp in 1888. Soon TNT became a replacement for PA.[6] In the same year triaminotrinitrobenzene (TATB) was synthesized by Jackson and Wing. But was described as an explosive not before 1978. TATB was one of the first high thermally stable explosives and exhibited very low sensitivities. Years before, in 1966 an also interesting high thermally stable explosive was investigated by Shipp, hexanitrostilbene (HNS).[8] In 1899 George Friedrich Henning synthesized hexogen which was well known as Royal Demolition Explosive (RDX). First it was investigated for medicine applications but soon its high potential for military application as an explosive was recognized and was finally used as a replacement for TNT. Still today it is the standard secondary explosive for military operations.[6]

1.2 Definition and classification

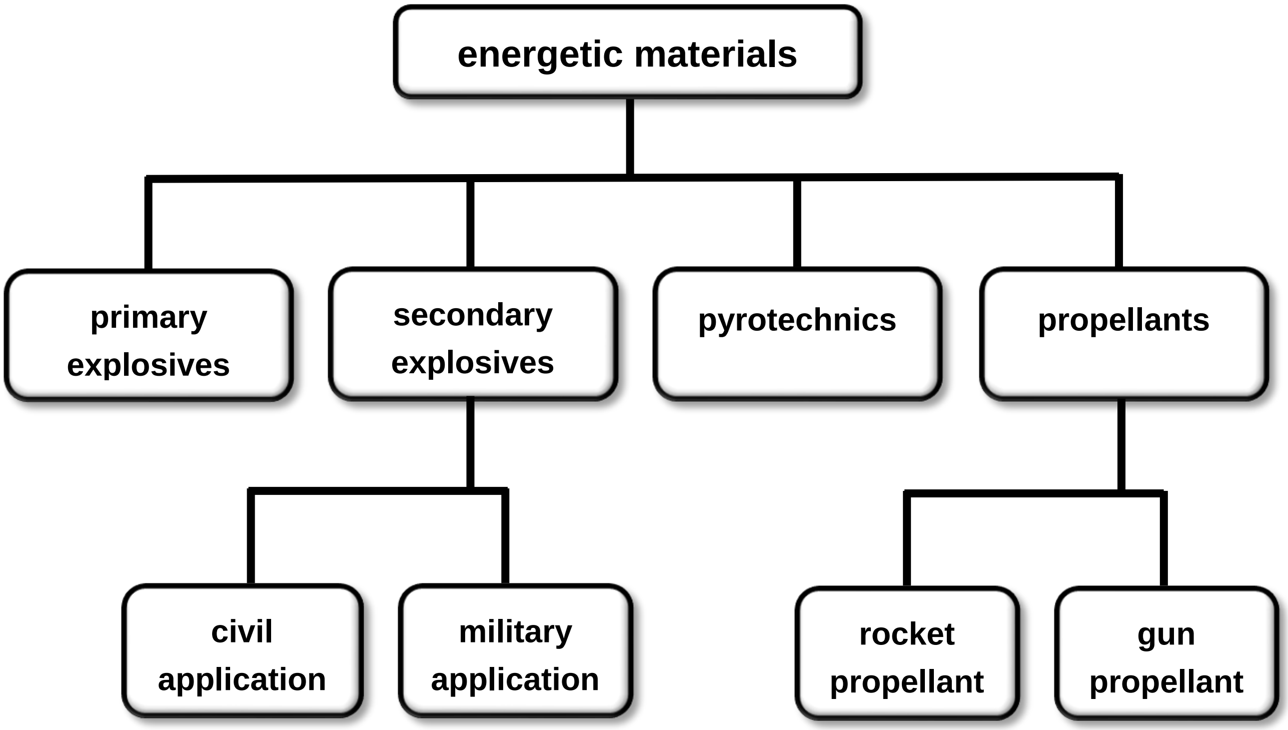

Figure 4: Classification of energetic material.

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The American Society for Testing and Materials (ASTM) defines *high energy density materials* (HEDM) as followed:

"*Energetic materials are defined as chemical compounds or compositions that contain both fuel and oxidizer and rapidly react to release energy and gas. Examples of energetic materials are high explosives, gun propellants, rocket and missile propellants, igniters, primers, initiators, and pyrotechnic (e.g. illuminants, smoke, delay, decoy, flare and incendiary) compounds and compositions. Energetic materials may be thermally, mechanically, and electrostatically initiated and do not require atmospheric oxygen to sustain the reaction.*"[6]

High energetic materials can by separated into four different parts: Primary as well as secondary explosives, pyrotechnics and propellants. Furthermore secondary explosives can be divided into civil and military applications and propellants into gun and rocket propellants.

Primary explosives were easily detonable and mostly highly sensitive towards friction, impact and electrical sparks. Therefore they are mainly used as initiator for secondary explosives which are not ignitable by heat or pressure.[6] Another difference of primary explosives from secondary explosives is a very rapid transition from burn to detonation. A huge problem of most primary explosives is the presence of heavy metals and the corresponding environmental impact. Commonly used primary explosives are lead azide, silver azide or mercury fulminate.[9, 10]

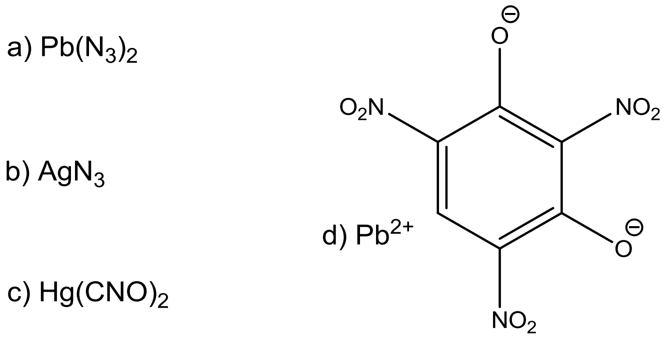


Figure 5: Common primary explosives: a) lead azide; b) silver azide; c) mercury fulminate; d) lead styphnate.

Secondary explosives are energy rich and stable components, which detonate or explode with higher detonation velocity and pressure under formation of a shockwave.[6] In difference to primary explosives they are slightly sensitive and kinetically stable. To ignite them, they have to be stimulated by the use of a detonator (primary explosive).

Commonly used secondary explosives are for example hexogen (RDX), octogen (HMX), hexanitrostilben (HNS) and 2,4,6-trinitrotoluene (TNT). All of them include oxidant as well as fuel in one molecule and have a high density. Secondary explosives (together with primary explosives) find applications as well in military and civil areas.

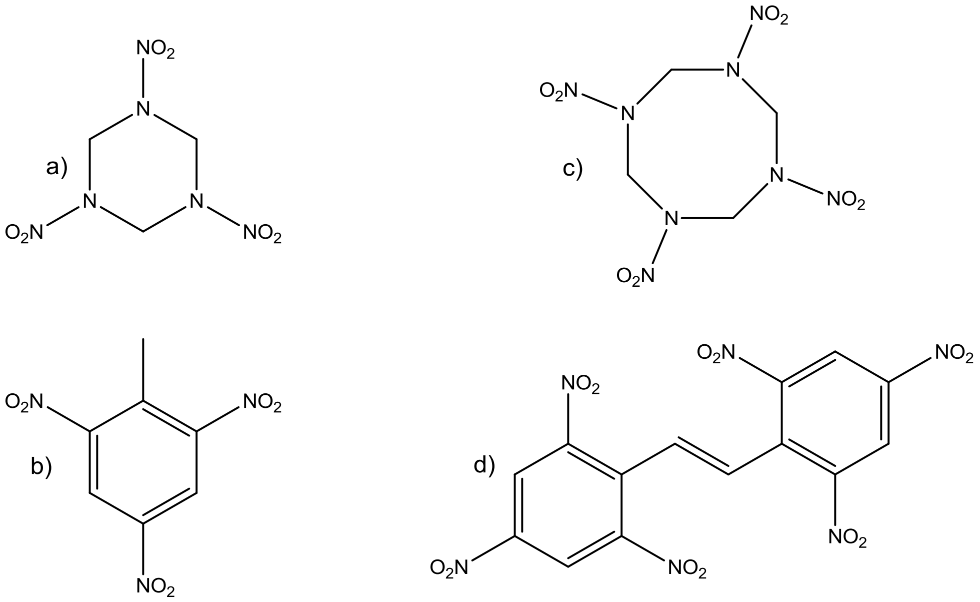


Figure 6: Common secondary explosives: a) RDX; b) TNT; c) HMX; d) HNS.

Table 1. Data of sensitivity and performance for primary and secondary explosives

	prim. expl.	LA	sec. expl.	RDX
sensitivity				
Impact / J	≤ 4	2.5–4	≥ 4	7.4
Friction / N	≤ 10	< 1	≥ 50	120
ESD / J	0.002–0.020	0.005	≥ 0.1	0.2
performance				
VOD / $m \cdot s^{-1}$	3500–5500	4600–5100	6500–9000	8750
p_{CJ} / kbar	343		120–390	347
Q / $kJ \cdot kg^{-1}$	1000–2000	1639	5000–6000	5277 (H_2O (g))

In Table 1 the typical and intended values for a primary or secondary explosive are listed together with a commonly used example for each. As illustrated primary explosives are much more sensitive towards impact, friction or electrical discharge (ESD) and exhibit lower performances relate to detonation velocity (VOD), detonation pressure (p_{CJ}) and heat of detonation (Q) than secondary explosives.[6]

Pyrotechnics (greek: pyros=fire; techne=art) are compositions which release their saved energy in form of light (fireworks), heat (decoy flare), smoke (signal flares) or gas. Pyrotechnics are mostly mixtures of chemicals that include at least one oxidizer and fuel, and are capable of undergoing self-contained and sustained exothermic chemical reactions.

Figure 7: Left: signal flare; right: smokeless firework.

Propellants are used in rocket engines, for example in space rockets or missiles, or as gun powders. They can be initiated by flame or sparks and impart an impulse to an object to accelerate it.[6] In best cases these materials/mixtures contain more oxygen than needed for the combustion. As in pyrotechnics the mostly used mixtures contain a fuel and an oxidizer. These materials can be liquids or solids. In contrast to explosives these materials should deflagrate then detonate. The most famous example for a propellant is black powder.

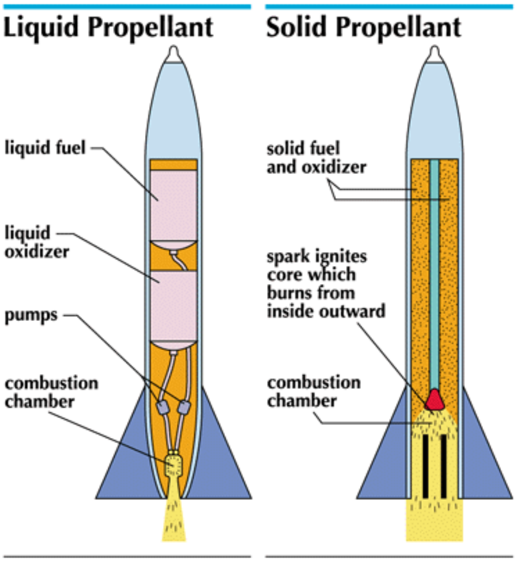


Figure 8: System of liquid and solid rockets.*

(*http://kids.britannica.com(7.7.2015))

1.3 High thermally stable explosives

A new field of secondary explosives was developed by the investigation of HNS by SHIPP and TATB by JACKSON and WING: “High thermally stable explosives”.

These kind of explosives mostly have lower energetic performances compared to RDX and would never replace it, but were highlighted by their characteristics of a very high decomposition point and a very high long time stability. Therefore on the one hand they exhibit a longer shelf life of munition as well as a higher safety towards initiation and on the other hand they open up attractive ways for special applications like developing new oil wells, renewable energy (geothermal energy) or space exploration.[11,12]

With the oil reserves on our planet shrinking, the drilling for new oil wells has to go deeper into earth. On the other hand the requirements and strains for compounds in these regions also get higher. In the first kilometers of earth crust the temperature increases strongly until it reaches at 120 kilometers a temperature of 1200°C. Within the crust each 1000 meters the temperature is almost doubled. After 20 – 30 kilometers temperatures around 400°C are already reached (Figure 9).

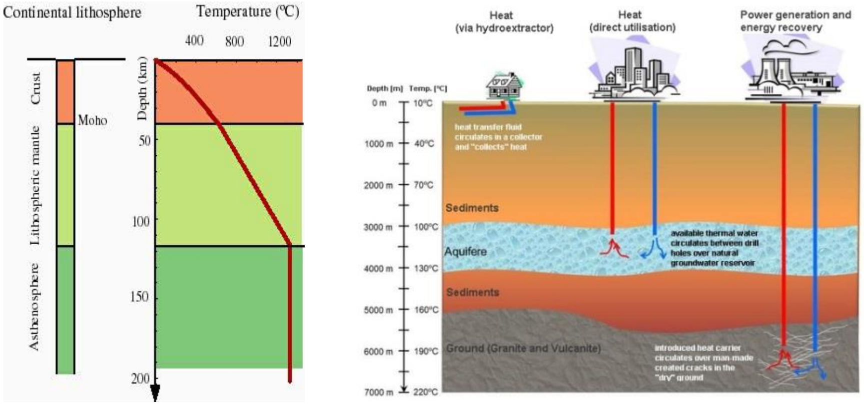


Figure 9: Effect of variation of temperature depending on the depth.* **(*http://www.geosci.usyd.edu.au/users/prey/ENG-1/HTML.Lect1/TempLitho.jpg / https://www.efzn.de/typo3temp/pics/52b62e012f.jpg(7.7.2015))**

With a high decomposition temperature of 350°C, TATB is a very interesting compound for these applications. But due to its higher costs in synthesis and its insensitivity it is mainly used in military application where extreme safety is required, such as the explosives used in nuclear weapons.[13-15] Instead HNS has a lower decomposition temperature of 320°C, but also lower synthesis costs. Therefore it became one of the commonly used explosive for civil applications in mining or drilling oil wells.[16]

Two interesting high thermally stable explosives were synthesized by Coburn. The *N*-(2,4,6-trinitrophenyl)-1H-1,2,4-triazol-3-amine (PATO) in 1969 and the 3,5-dinitro-*N*2,*N*6-bis(2,4,6-trinitrophenyl)pyridine-2,6-diamine (PYX) in 1972.[17-19]

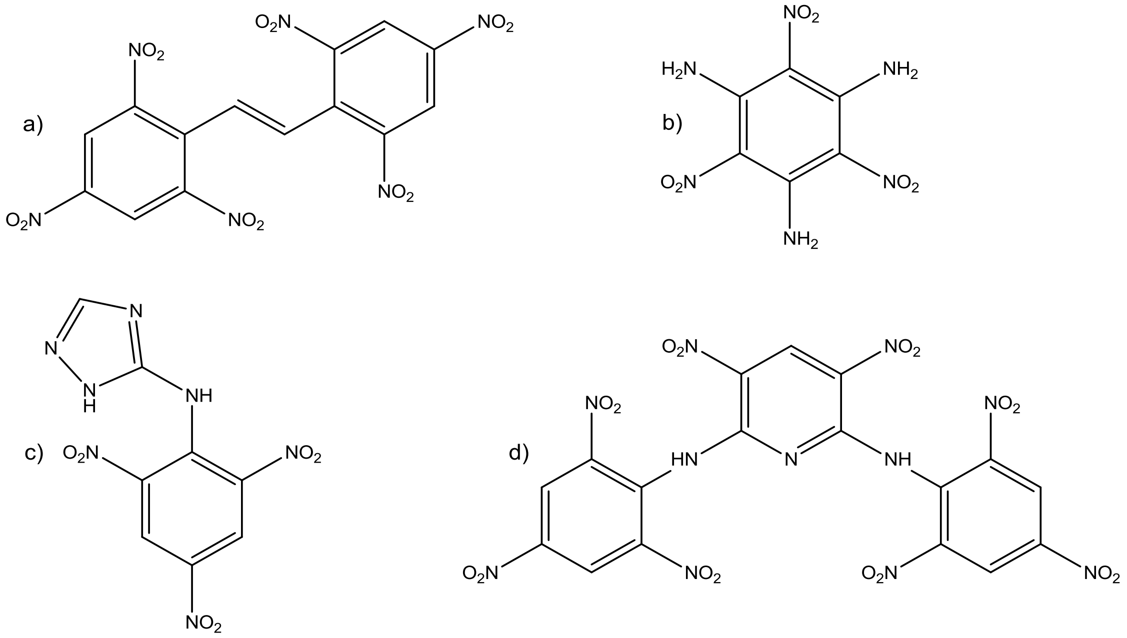


Figure 10: High thermally stable explosives: a) HNS; b) TATB; c) PATO; d) PYX.

As it could be recognized it is typical for those structures of thermally stable explosives, to combine aromatic systems – normally benzene – and nitro groups. The combination of both systems in one molecule could raise the thermal stability. Compared to RDX the decomposition temperature of HNS is about 111°C higher.

A short overview of their energetic performances is given in Table 2 in comparison to RDX.

Table 2. Energetic performance of RDX in comparison to HNS, TATB, PYX and PATO

	RDX	HNS	TATB	PYX	PATO
IS / J	7.5	5	50	25	8
FS / N	120	240	353	250	-
ESD / J	-	-	-	-	-
$T_{\text{Dec.}}$ /°C	210	320	350	350	310
ρ / g·cm^{-3}	1.806	1.74	1.80	1.757	1.94
EXPLO5 6.01 values:					
T_{det} / K	3800	3676	3526	3613	3185
P_{CJ} / kbar	352	243	296	252	313
V_{det} / m·s^{-1}	8815	7612	8310	7757	8477
V_o / L·kg^{-1}	792	602	700	633	624
F	1026	752	839	777	675

1.4 Concept and aims

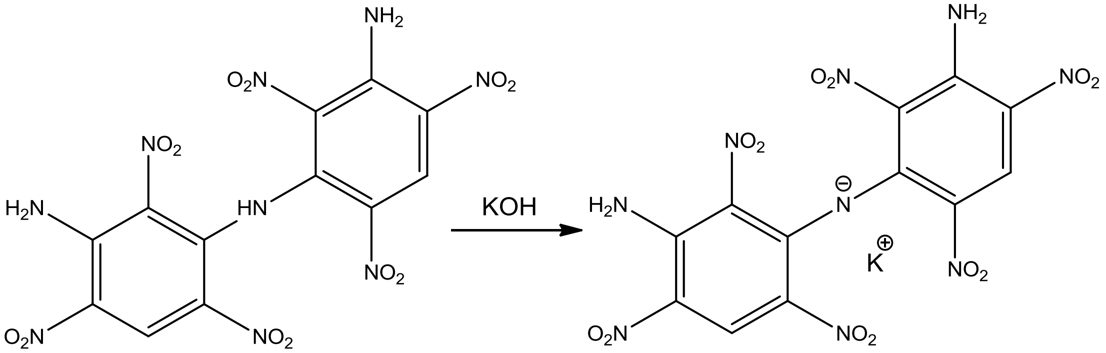
Most of the common explosives used as well as their decomposition products are very toxic. Because most of them include substances like perchlorate as well as heavy metals like lead they pollute the environment.[6,21-24]

The aim of the research in this thesis is focused on more environmentally friendly explosives and is to find replacements for explosives like lead azide as well as RDX and HNS. But the new compounds should not only be less toxic, they should also be safer to handle by increasing the thermal stability and lowering the sensitivity with a simultaneous increase of performance according to detonation velocity, detonation pressure and detonation heat.[6]

With the requirements to higher heat resistance explosives in the last years four general approaches have been proposed by AGRAWAL et al. to impart and increase the thermal stability.[25-27]

- Salt formation

Via salt formation the thermal stability can be enhanced. The formation of metal salts is a good methode to enhance the thermal stability (Figure 11).[17] But it should be mentioned that not all metals are environmentally friendly (e.g. copper (II))[28]. Instead of metal salts also salts of nitrogen-rich cations can be used. A good example is the guanidinium cation.[29,30]



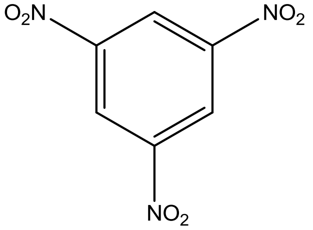
3,3'-Diamino-2,2',4,4'6,6'-hexanitrodiphenylamine
T_{dec} 237 °C

Potasium salt
T_{dec} 333 °C

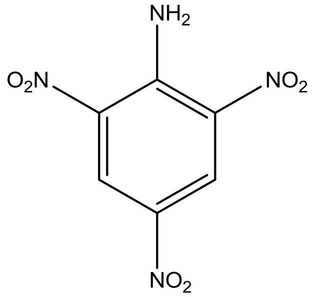
Figure 11: Salt formation of 3,3'-diamino-2,2',4,4',6,6'-hexanitrophenylamine with potassium hydroxide. The potassium salt obtains a significant higher decomposition temperature.

- Introduction of amino groups

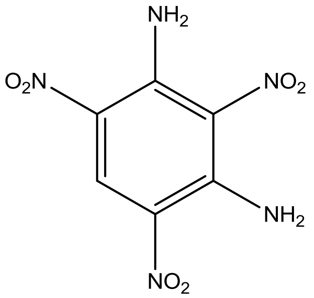
Introducing amino groups into nitrated benzene rings in the ortho position influences the thermal stability. It is one of the simplest and oldest approaches for enhancing the thermal stability of explosives. The "push-pull" effect, generated by the combination of electron withdrawing nitro groups next to electron donating amino groups, as well as the formation of hydrogen bonds among them is responsible for the great physical stability towards heat or other external stimuli like friction or impact. TATB and FOX-7 are two famous eaxmples of these insensitive materials.[31] A good illustration how amino groups influence the thermal stability is shown in figure 12 with the example of 1,3,5-trinitrobenzene.



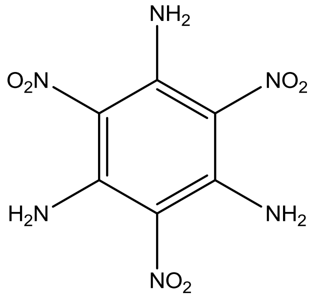
1,3,5-Trinitrobenzene
T_{dec} 122 °C



2,4,6-trinitroaniline (TNA)
T_{dec} 192 °C



1,3-Diamino-2,4,6-trinitrobenzene
T_{dec} 286 °C

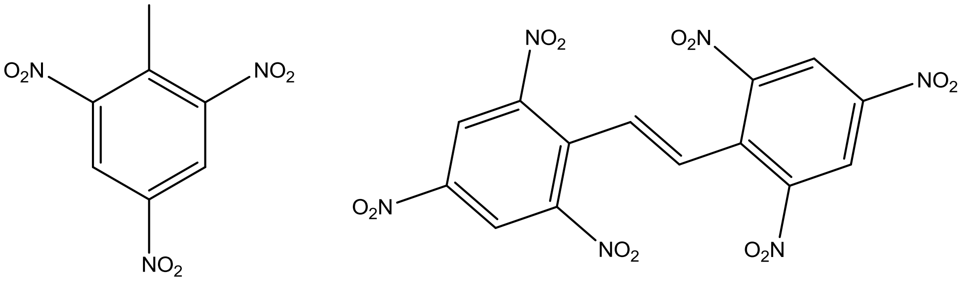


1,3,5-Triamino-2,4,6-trinitrobenzene
(TATB)
T_{dec} >320 °C

Figure 12: Effect on decomposition temperature by subsequent introduction of amino groups into 1,3,5-trinitrobenzene.

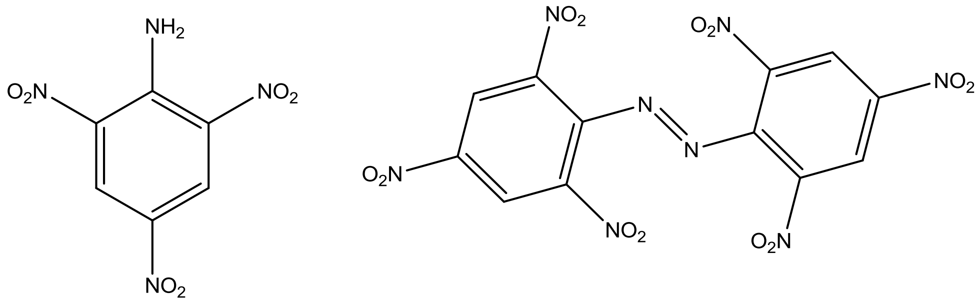
- Introduction of conjugation

A very good example for the introduction of conjugation in energetic molecules and how it imparts higher thermal stability is hexanitrostilbene (HNS). An other interesting explosive with a similar structure to HNS is hexanitroazobenzene (HNAB). Here also a conjugated system increases the thermal stability. In the following figure 13 these examples are shown. But not only nitrobenzenes influence the conjugated systems. Also the introduction of heterocyclic systems like tetrazines, triazoles or oxadiazoles can increase the thermal stability. Examples are BDATT, DANTNP or DAAzF shown in figure 14.[32-34]



2,4,6-trinitrotoluene (TNT)
T_{dec} 295 °C

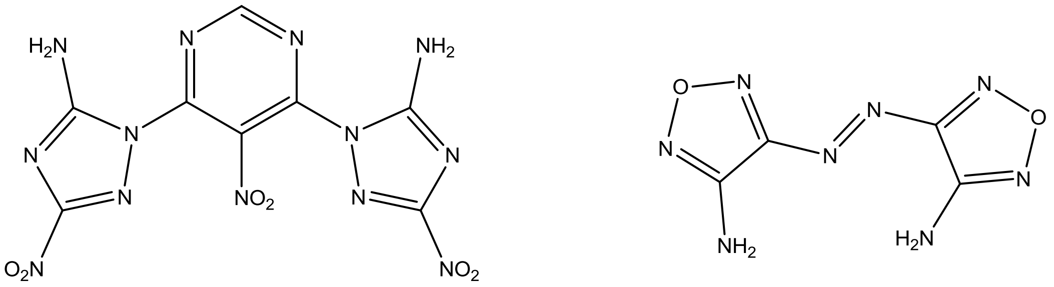
Hexanitrostilbene (HNS)
T_{dec} >320 °C



2,4,6-trinitroaniline (TNA)
T_{dec} 192 °C

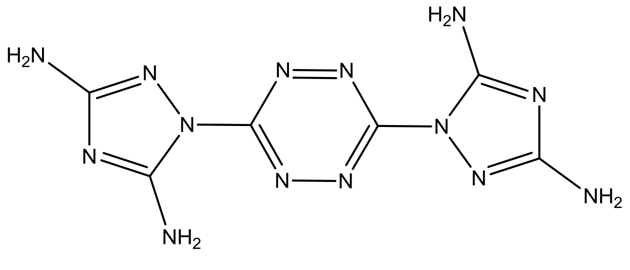
Hexanitroazobenzene (HNAB)
T_{dec} 215 °C

Figure 13: Effect on decomposition temperature by introduction of conjugation: monomer vs. oxidized dimer.



4,6-Bis(5-amino-3-nitro-1,2,4-triazolyl)-5-nitropyrimidine (DANTNP)
T_{dec} >330 °C

Diaminoazofurazane (DAAzF)
T_{dec} 320 °C

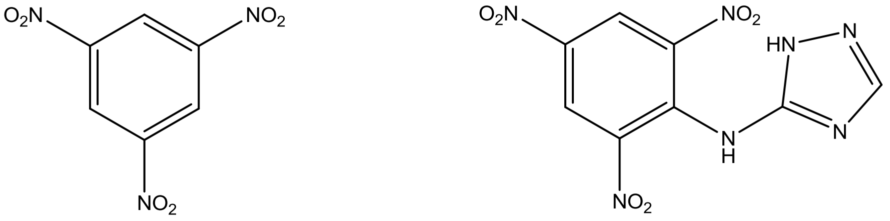


3,6-Bis(diaminotriazolyl-1,2,4,5-tetrazine) (BDATT)
T_{dec} 369 °C

Figure 14: Effect on decomposition temperature by introduction of conjugation: further molecules.

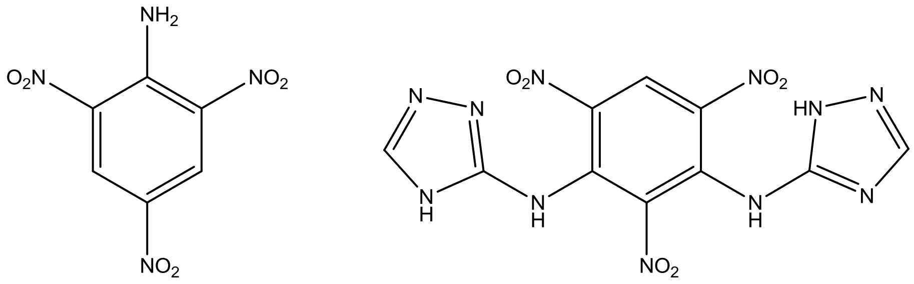
- Condensation with triazole rings

Various studies on the synthesis of picryl- and picrylamino substituted 1,2,4-triazoles by condensing 1,2,4-triazole or amino-1,2,4-triazole with picryl chloride (1-chloro-2,4,6-trinitrobenzene) were investigated in detail by COBURN & JACKSON.[17,18] One of these molecules is the already mentioned compound PATO (3-picrylamino-1,2,4-triazole), a well known, thermally stable explosive, which is obtained by the condensation of picryl chloride with 3-amino-1,2,4-triazole. A similar compound was prepared by AGRAWAL and co-workers.[35] 1,3-Bis(1',2',4'-triazol-3'-ylamino)-2,4,6-trinitrobenzene (BTATNB) was synthesized from the reaction of styphnyl chloride (1,5-dichloro-2,4,6-trinitrobenzene) with two equivalents of 3-amino-1,2,4-triazole. It exhibits a slightly higher thermal stability than PATO and is safer towards impact and friction.



1,3,5-Trinitrobenzene
T_{dec} 122 °C

3-Picrylamino-1,2,4-triazole (PATO)
T_{dec} 310 °C



2,4,6-trinitroaniline (TNA)
T_{dec} 192 °C

1,3-Bis(1',2',4'-triazol-3'-ylamino)-2,4,6-trinitrobenzene (BTATNB)
T_{dec} 320°C

Figure 14: Effect on decomposition temperature by condensation with triazole rings.

A combination of these approaches could lead to a much higher thermally stable compound with also higher performance. Suitable molecules for derivatization are PYX and PATO. Both molecules have the possibility to form ionic compounds and would then include the concepts of conjugation and salt formation. PATO also contains a triazole ring. This combination might lead to a very high thermal stability of over 350°C of the resulting derivatives, which might be used as replacements for HNS.

Compounds suitable for HNS replacements should have following specifications:

1) They should show a decomposition point over 300°C and a long time stability with no decomposition at 260°C for 100 h or mass loss of >1%.
2) The detonation velocity should be greater than 7500 $m \cdot s^{-1}$.
3) The specific energy should be greater than 975 $kJ \cdot kg^{-1}$. The specific energy is calculated according to:

   $\boldsymbol{F} = p_e \cdot V = \boldsymbol{n \cdot R \cdot T}$
   (n is the number of products of decomposition, R was the gas constant and T is the detonation temperature)

   The specific energies for RDX, HNS, TATB, PYX and PATO are given in Table 2.
4) They should exhibited sensitivities for impact of >7.4 J and for friction of >235 N. These specifications are higher as for RDX replacements (IS. >7 J; FS >120 N).
5) The total costs should not be greater than 500 Euro/kg.
6) The critical diameter should be smaller than that for HNS. The critical diameter indicates the minimum diameter of an explosive charge at which detonation could still take place. It also depends on the texture of an compound. In cast charges it is larger than in pressed ones.

Publications

The following chapters have been published in or are submitted to peer-reviewed scientific journals (*Chemistry – A European Journal; Crystals; Propellants, Explosives, Pyrotechnics*) and as poster contribution at the annual international seminar *New Trends in Research of Energetic Materials* in Pardubice, Czech Republic (2013). The published articles were slightly modified to properly fit in the thesis.

1.4.1 Generall methods and analytics

CAUTION! Most compounds prepared here are energetic compounds and sensitive to impact, friction and electrostatic discharge. Although there were no problems in synthesis and handling of the compounds described in this work proper protective measures (ear protection, Kevlar® gloves, face shield, body armor and earthed equipment) should be used at all times, especially when working with oftentimes highly sensitive silver salts.

Elemental analysis (EA): The percentage of hydrogen, nitrogen and carbon of a compound was detected in the laboratory for microanalysis owned by the department of chemistry and pharmacy of the Ludwig-Maximilians-University. The measurements were done with the complete automatically working analyzer *Elementar Vario EL.*

Differential scanning calorimetry (DSC): The preparation of the thermo grams was done with the institute's DSC calorimeter *LINSEIS DSC-PT 10*. About 1.5 – 2 mg of a compound was pressed in a crucible of aluminum and during a measurement an empty one was used as a reference sample. The measurements were done in a range of temperature from 25 – 400°C with a heating rate of 5°C/min and a nitrogen flow of 5 l/h.

Raman spectroscopy: The Raman spectra were obtained by the working group's *Bruker MultiRAM 1064 2000R FT* device including a Nd. YAG laser with a wavelength of 1064 nm. The spectra were obtained with 25 scans and a laser performance of 300 mW in a range from 4000 – 100 cm^{-1}.

Infrared spectroscopy (IR): The IR spectra were measured with the *Perkin Elmer FT-IR Spectrum BXII* device of the department of chemistry and pharmacy of the Ludwig-Maximilians-University including a *Smith ATR Dura Sample IRII* unit in the range from 4000 – 600 cm^{-1}. The general shortcuts were used for the characterization of the peaks: vw (very weak), w (weak), m (medium), s (strong), vs (very strong)

Mass spectrometry (MS): The mass spectra were obtained by the *JOEL Mstation JMS 700* device and the *Thermo Finnigan LTQ FT-ICR* device. Fast atom bombardment (FAB), electron ionization (EI/DEI) and electron spray ionization (ESI) were used as ionization methods.

Nuclear magnetic resonance spectroscopy (NMR): The NMR spectra were measured with the *JOELGSX 270 DELTA Eclipse*, the *JOEL EX 400 DELTA* or the *JOEL EX 400 Exlipse* device. The samples were dissolved in a deuterated solvent. The shifts of the signals were adjusted to the used solvent and given ppm. The general shortcuts were used for the multiplicities: s (singlet), d (doublet), t (triplet), m (multiplet).

Crystal structure analysis: The measurements were done at 173 K with a *Oxford Diffraction Xcalibur3* device using a *Spellman* generator (voltage 50 kV, amperage 40 mA) and a *Kappa* CCD detector. The data could be collected with the *CrysAllis* CCD software[36] and its reduction *CrysAllis Red* software[37]. The structures were solved with *SIR-92*[38] and *SHELXS-97*[39]*.* The refinement was also done with *SHELXS-97*[40]. The checking was done with *PLATON*[41]. The non hydrogen atoms were anisotropically refined. All hydrogen atoms were localized in the structure and also refined. The refinement of the absorption was done with the *SCALE 3 ABSPACK* multi scan method.[42]

Sensitivities: The sensitivities were determined by the following methods: Impact sensitivity: BAM drophammer (1 of 6); Friction sensitivity: BAM friction tester (1 of 6); Electrostatic Discharge: OZM small scale electrostatic discharge device with respect to the guidelines of the Bundesanstalt für Materialforschung und -prüfung (BAM).[43-48]

Energetic properties: The energetic properties have been calculated with the EXPLO5 V5.05 as well as V6.01 computer code[49-51] using the X-ray density and solid state heat of formation which was calculated using the *CBS-4M* atomization method.[52-62] Lattice enthalpy (U_L) and lattice enthalpy (ΔH_L) were calculated from the corresponding·molecular volume according to equations developed by Jenkins and Glasser.[54, 55] With these values the gas phase enthalpy was converted to the solid state (standard conditions) enthalpy of formation $\Delta_f H_m°$. And the standard molar enthalpy of formation (ΔH_m) was calculated into the molar solid state energy of formation (ΔU_m) according to Equation (1).

$$\Delta U_m = \Delta H_m - \Delta n\,RT \quad (1)$$

(Δn is the change of mol of gaseous components)

Lastly the specific energy (F) was calculated according to Equation (2).

$$F = p_e \cdot V = n \cdot R \cdot T \quad (2)$$

(n is the number of products of decomposition, R is the gas constant and T is the detonation temperature)

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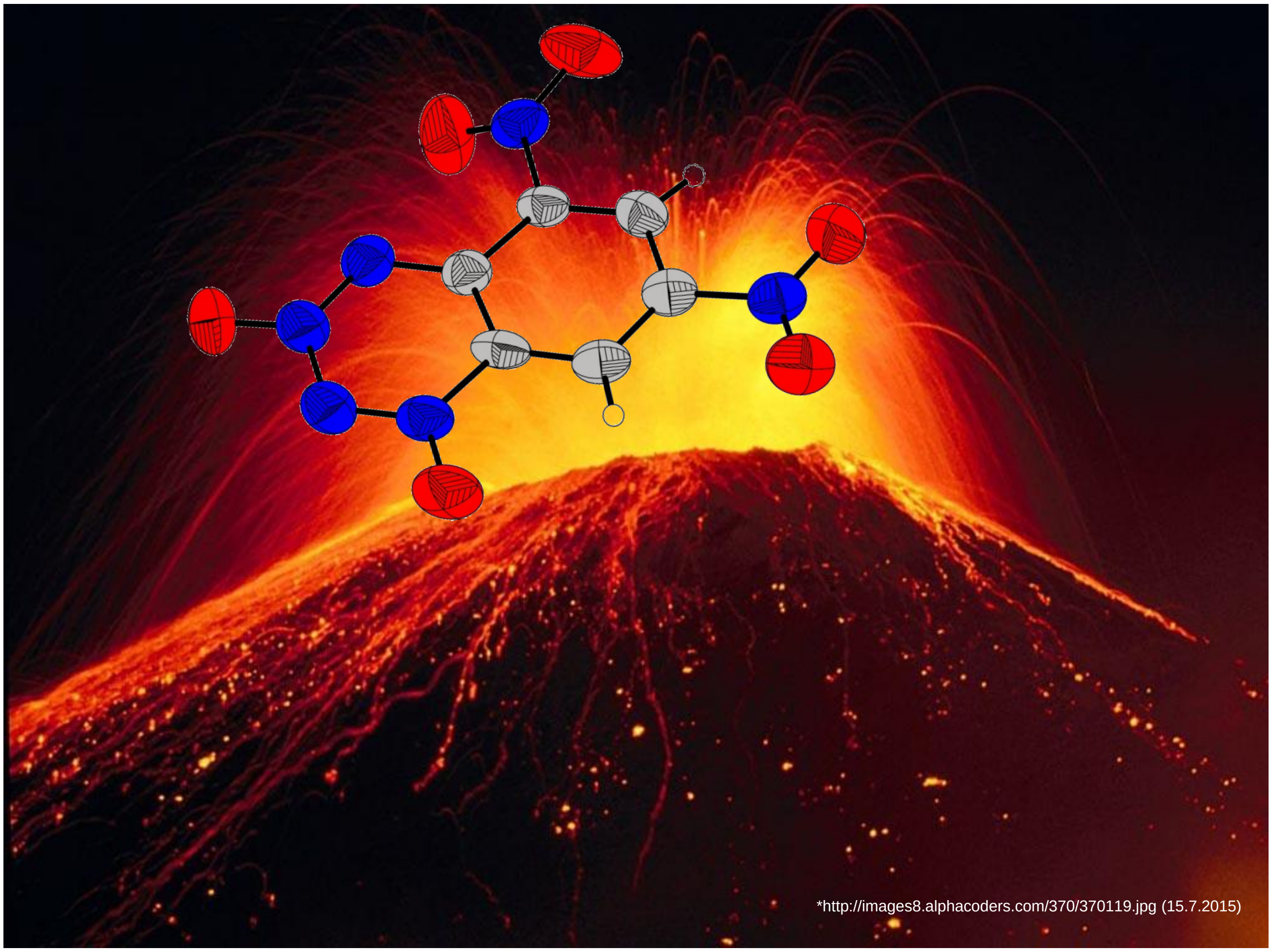
Chapter 2

1,2,3,4-tetrazine-1,3-dioxide



*http://images8.alphacoders.com/370/370119.jpg (15.7.2015)

2 The Synthesis and Energetic Properties of 5,7-Dinitrobenzo-1,2,3,4-tetrazine-1,3-dioxide (DNBTDO)

Thomas M. Klapötke, Davin G. Piercey, Jörg Stierstorfer and Michael Weyrauther

Propellants, Explosives, Pyrotechnics **2013**, *37*(5), 527-535

2.1 Introduction

High nitrogen heterocycles are a recurring pattern in the research of highly energetic materials.[1-5] The number of linked nitrogen atoms is directly correlated with the heat of formation of the compound, as a result of the energetically-favoured formation of dinitrogen gas. For example 1,1’-azobis(1,2,4-triazole) (676 kJ mol^{-1}) has a lower heat of formation than 1,1’-azobis(1,2,3-triazole) (962 kJ mol^{-1}) , both of which have lower heats of formation than 1,1’-azobis(tetrazole) (1030kJ mol^{-1}).[1,5] This is in contrast to classical explosives such as 1,3,5-trinitro-1,3,5-triazinane (RDX) and 1,3,5,7-tetranitro-1,3,5,7- tetrazocane (HMX) which derive their enthalpy of detonation through oxidation of the backbone. (Figure **1**)

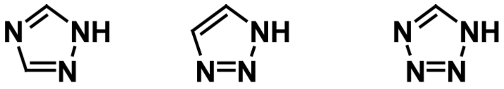


Figure 1: Structures of 1,2,4-triazole, 1,2,3-triazole, and 1,2,3,4-tetrazole respectively.

Currently used explosives suffer from problems ranging from high sensitivity to posing an environmental hazard. RDX is widely used in formulations with polymeric binders and plasticizers such as PBXN-107 (86/14 RDX/HTPB) or C4 (90/10: RDX/PIB). This use is despite concerns about the toxicity of RDX.[6,7] In order to be considered as a candidate explosive, a nitrogen-rich material requires sufficient performance (comparable to or greater than RDX), and sufficient thermal (T_{dec} above 180^{o}C) and mechanical stability (impact, friction, shock) while possessing a lower toxicity.[8,9]

1,2,4,5-tetrazine 1,2,3,4-tetrazine

Figure 2: structures of 1,2,4,5- and 1,2,3,4-tetrazine

Chapter 2: 1,2,3,4-tetrazine-1,3-dioxide

One of the currently pursued strategies in development of new advanced energetic materials are 1,2,4,5 and 1,2,3,4-tetrazines. (Figure **2**) The former class of compounds, as well as their 1,4-dioxides are well known and are high performing energetic materials, including LAX-112 (3,6-diamino-1,2,4,5-tetrazine-1,4-dioxide) which was once considered a prospective RDX replacement.[10] In contrast, 1,2,3,4-tetrazines are rarely reported in the literature, with only one known example being stable.[11a] However the oxidation product 1,2,3,4-tetrazine-1,3-dioxide moiety, is far more abundant in the literature and compounds with remarkable thermal stability have been reported, some members of this class of compounds decomposing above 200 °C.[11b,15] This stabilization is understood to result from the N-oxide removing lone pair electron density (increasing σ – π separation) that would otherwise destabilize the nitrogen system by donating electron density into antibonding orbitals.[12-14] Due to the zwitterionic character of the *N*-oxides, the densities of the 1,2,3,4-tetrazine-1,3-dioxides are often high, with short N-N bond lengths due to what has been termed “Alternating Positive Negative Charge” theory. (Figure **3**) Application of 1,2,3,4-tetrazine-1,3-dioxides in theoretical energetic materials has led to materials with calculated properties being among the most powerful explosives in existence such as DTTO.[16] (Figure **4**)

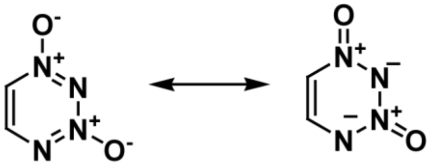


Figure 3: Isomerization as Described by APNC Theory

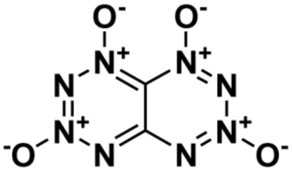
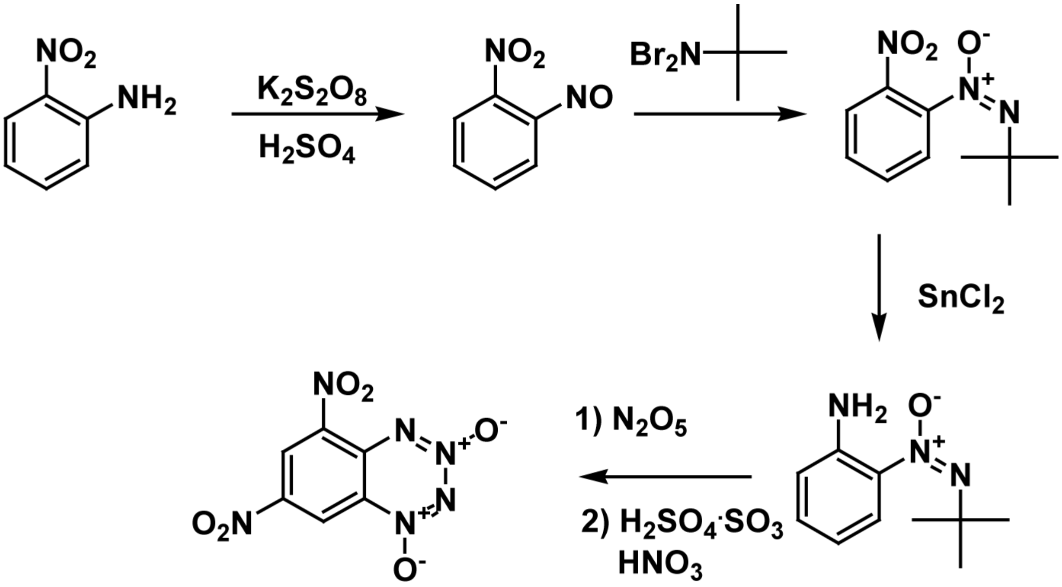


Figure 4: DTTO

Unfortunately the majority of 1,2,3,4-tetrazine-1,3-dioxides that have been prepared so far bear an annulated benzene ring.[11] However annulated pyridines and the more explosive furazan are also known.[17, 18] There is only one known non-annulated 1,2,3,4-tetrazine-1,3-dioxide which is the dicyano derivative.[19] Of the known tetrazine dioxides 5,7-dinitrobenzo-1,2,3,4-tetrazine-1,3-dioxide is one of the most facile prepared from the reaction of 2-tert-butyl-1-(2-anilino)-diazine-1-oxide (BADO) with N_2O_5 in dichloromethane, followed by nitration with nitric acid and oleum in a one-pot synthesis.

The precursor BADO is available from 2-nitro-aniline in a three step process (Scheme **1**).[20]



Scheme 1: Synthesis of DNBDTO

In this study we have prepared 5,7-dinitrobenzo-1,2,3,4-tetrazine-1,3-dioxide (DNBTDO), by the literature procedure[20] in 45% yield, and we report the full chemical (NMR, IR, Raman, mass spectra, and crystallographic proof) and explosive (impact, friction, static sensitivities and calculated performance) properties.

2.2 Experimental

All reagents and solvents were used as received (Sigma-Aldrich, Fluka and Acros Organics). 2-t-butyl-1-(2-anilino)-diazine-1-oxide was prepared by the literature procedure.[20] Decomposition temperature measurements were performed on a Linseis DSC at a heating rate of 5°C min^{-1} (under air). ^{1}H, ^{13}C, and ^{15}N NMR spectra were recorded using a Jeol Eclipse 400 instrument. All chemical shifts are in ppm relative to TMS(^{1}H, ^{13}C) or nitromethane (^{15}N). IR spectra were recorded using a Perkin Elmer Spectrum One FT-IR instrument. Raman spectra were measured using a Perkin Elmer Spectrum 2000R NIR FT-Raman instrument equipped with a Nd-YAG laser (1064 nm). Elemental analyses were performed on a Netzsch STA 429 Simultaneous Thermal Analyser.

Caution! The prepared compound is an explosive with sensitivity towards various stimuli. Although we had no problems during synthesis, proper protective *equipment(Kevlar gloves and wrist protectors, face shield, ear protection and thick leather coat) should be worn. Extra precautions should be taken when working on larger scale.*

Synthesis of 1,2,3,4-tetrazine-1,3-dioxide: 5,7-dinitrobenzo-1,2,3,4-tetrazine-1,3-dioxide

According to the literature procedure: 0.85 g (4.4 mmol) of 2-t-butyl-1-(2-anilino)-diazine-1-oxide was dissolved in 25 mL of dichloromethane and cooled to –20 °C. While maintaining this temperature, 2.7 g (25 mmol) of dinitrogen pentoxide was added under a nitrogen atmosphere. The temperature was allowed to rise to 0 °C over a half hour, and was stirred at this temperature for 15 minutes. To this was added a solution of 4 mL (95 mmol) of 100 % nitric acid in 6 mL of 20 % oleum. The mixture was heated to 80 °C and the temperature was maintained here for 2 hours to evaporate off the dichloromethane. After cooling to room temperature, the mixture was poured very slowly into an ice/water slurry. After this it was filtered and rinsed with water, followed by recrystallization from dichloroethane yielding 0.5 g (45 %) of DNBTDO as yellow crystals. **m.p.** 204 °C (dec.) (DSC, 5°Cmin$^{–1}$). **IR** (cm$^{–1}$): = 3099 (w), 1602 (m), 1541 (s), 1516 (s), 1474 (m), 1435. (m), 1336 (vs), 1267 (w), 1184 (m), 1080 (w), 993 (w), 915 (m), 860 (m), 800 (m), 776 (w), 735 (s), 708 (w), 671 (w); **Raman** (200 mW, cm$^{–1}$): 3078 (16), 1622 (83), 1548 (57), 1518 (55), 1477 (52), 1437 (57), 1370 (88), 1346 (100), 1191 (49), 1081 (57), 1056 (53), 992 (49), 938 (50), 756 (45), 711 (45), 330 (49), 99 (70); **^{1}H NMR** (acetone-d_6, 400.18 Mhz, 25°C, TMS): 9.42 (d, 1H, $^4J_{HH}$ = 2.40 Hz), 9.32 (d, 1H, $^4J_{HH}$=2.40Hz) **^{13}C NMR** (acetone-d_6, 100.63 Mhz, 25°C, TMS): 146.5 (1C), 142.0 (1C), 140.0 (1C), 127.3 (1C), 126.4 (1C), 119.2 (1C); **^{14}N NMR** (acetone-d_6, 40.55MHz, 25°C, acetone-d_6,) –17 (2N, NO_2), –36 (1N, N_4–O), –41 (1N, N2-O) **EA**: Calc for $C_6H_2N_6O_6$ (MW=254.12 g mol$^{–1}$): Calc.: C, 28.36; H, 0.79; N, 33.07. Found: C, 28.05; H, 0.83; N, 32.96; **MS** DEI+ *m/z* (%) 254.2 (30)[M$^+$] 209.1 (56)[M-NO_2], 181.1 (20)[M-N_2O_3], 120.1 (54)[M-NO_2-N_4O_2), 62.1 (68)[NO_3], 74.09 (66)[M-$_2NO_2$-N_4O_2], 30.1 (100)[NO]; **Impact sensitivity**: 5 J. **Friction Sensitivity:** 360 N**. Electrostatic Discharge Sensitivity**: 0.15 J.

2.3 Results and Discussion

2.3.1 X-Ray Structure

After recrystallization from dichloroethane, crystals of DNBTDO suitable for single crystal X-ray structure determination were obtained. The molecular structure of the crystalline DNBTDO is shown in Figure **5**.

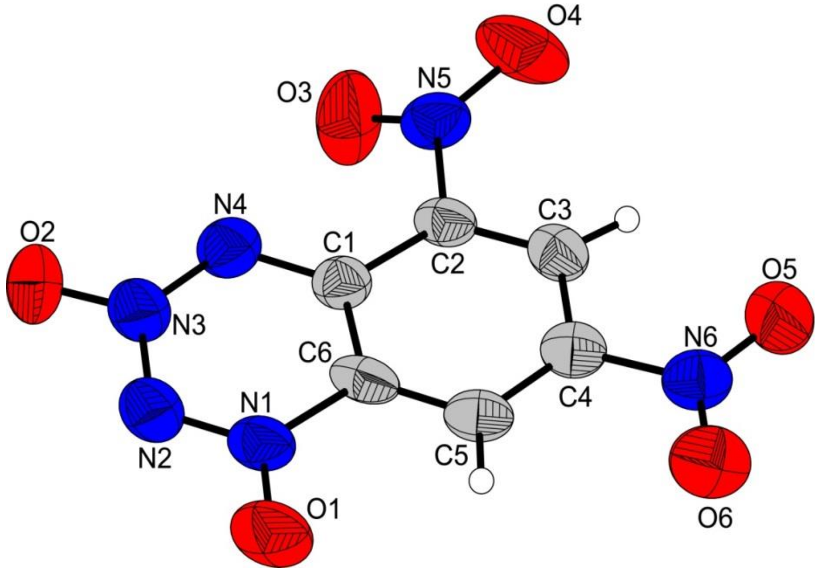


Figure 5: Molecular Structure of DNBTDO in the crystalline state. Non-hydrogen displacement ellipsoids are shown at the 50% probability level.

The molecular structure was determined using an Oxford Xcaliber3 diffractometer with a Spellman generator (voltage 50kV, 40mA current) and a KappaCCD detector. The data collection and reduction was performed using the CrysAlis Pro software.[21,22] The structure was solved using the SIR-92 program,[23] refined with SHELXL-97[24] and finally checked with PLATON software.[25] The hydrogen atoms were located and refined. Relevant data and parameters of the X-ray measurement and refinement is given in Table **1**.

Table 1. Crystal data and structure refinement parameters of DNBTDO.

Formula	$C_6H_2N_6O_6$
Formula Mass (g mol^{-1})	254.14
Crystal System	*Pca*2_1
Space group	orthorhombic
a (pm)	988.9 (2)
b (pm)	1785.9(3)
c (pm)	1023.4 (1)
α (°)	90
ß (°)	90
γ (°)	90
V (pm^3)	1.8075*10^9(5)
Z	8
ρ_{calc} (g cm^{-3})	1.868
T (K)	173
R_1 /wR_2 (all data)	0.0874/0.1586
R_1/wR_2 (I>2σ)	0.0583/0.1342
S	1.049
Device type	Oxford Xcalibur3 CCD
Solution	SIR-92
Refinement	SHELXL-97
Absorpt. Corr.	Multi-Scan
CCDC No.	854937

DNBTDO crystallizes in the space group *Pca*2_1 with eight formula units in the unit cell and a density of 1.868 g cm^{-3}. The bond lengths within the tetrazine ring and its *N*-oxides are as expected and lie between that of a single and double bond, however, the oxide bonds are generally closer to double-bond length and shorter than N-N bond distances in the tetrazine ring indicating the significant resonance contribution of the "Alternating Positive Negative Charge" resonance form as described above. The wave-like packing arrangement of DNBTDO within the unit cell is shown in Figure **6**. These results are in accordance with those in the literature.[20]

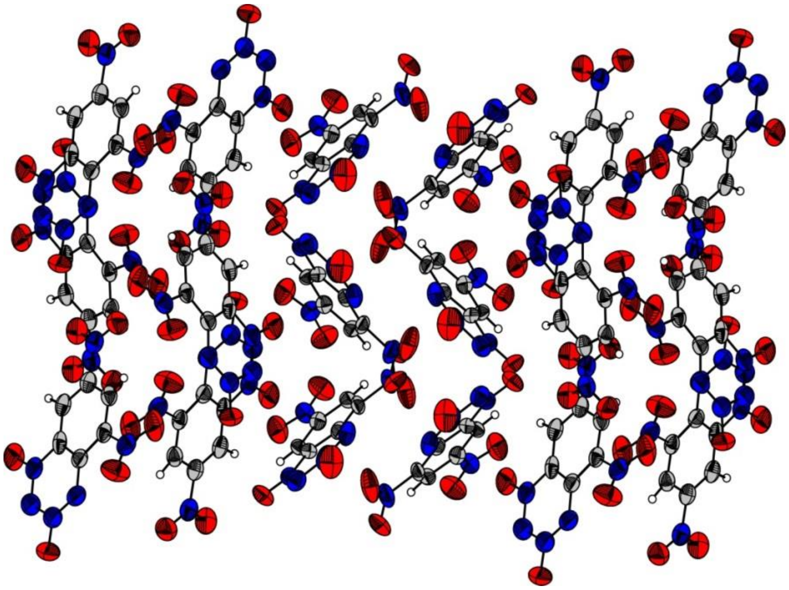


Figure 6: Wave-like packing arrangement of DNBTDO within the unit cell.

2.3.2 Infrared Spectroscopy

DNBTDO was analyzed by infrared spectroscopy. The strongest band occurs at 1333 cm^{-1} and is assigned to symmetric nitro group C-N stretching. The characteristic vibrations of the tetrazine dioxide system occur at 1516 and 1435 cm^{-1} (lit. 1520 and 1432cm^{-1}) and arise from the synphase and antiphase N=N vibrations.[11]

2.3.3 Mass spectra

The M+ peak was detected at 254.2 m/z during a DEI+ experiment. Loss of one nitro group, one nitro group and the tetrazine dioxide ring, and two nitro groups and the tetrazine dioxide ring are observed at 209.1, 120.1, and 74.09 m/z, respectively.

2.3.4 NMR Spectroscopy

2.3.4.1 ^{1}H NMR

The two protons in DNBTDO yield to resonances at 9.42 and 9.32 ppm. The shift difference between the two is too small to be able to definitely assign which shift belongs to which proton. The coupling constant between the two is 2.40 Hz.

2.3.4.2 ^{13}C NMR

The benzene ring of DNBTDO yields 6 separate peaks. The literature assignments for these carbon atoms are 146.5:C5, 142.0:C3, 140.0:C2, 127.3:C1, 126.4:C4, 119.2: C6.[11]

2.3.4.3 ^{14}N NMR

The spectrum shows three resonances, the first at –17 ppm ($\Delta v_{1/2}$=50 Hz) corresponds to the nitrogen of the aromatic nitro groups (N5, N6) while the remaining two resonances are resulting from the N-oxides of the tetrazine dioxide –36 ($\Delta v_{1/2}$= 40 Hz) and –41 ppm ($\Delta v_{1/2}$=40 Hz) for N4 and N2 respectively.[11] N1 and N3 are not observed.

2.3.5 Differential Scanning Calorimetry (DSC)

For determination of the decomposition temperature of DNBTDO, a differential scanning calorimetry (DSC) experiment was run at a heating rate of 5°C min^{-1}. Exothermic decomposition occurred beginning at 204°C. No melting event was observed prior to decomposition. A manual melting point determination was also performed and again no melting was observed prior to an onset of decomposition at 211.8°C

2.3.6 Explosive Properties

2.3.6.1 Experimental Sensitivities

For initial safety testing, impact, friction and electrostatic discharge sensitivities were determined. Impact sensitivity was carried out according to STANAG 4489[26] and modified according to Ref.[27] on a BAM drophammer.[28,29] Friction sensitivity was carried out in accordance with STANAG 4487[30] and modified according to Ref.[31] Sensitivity towards electrostatic discharge (ESD) was determined[32,33] on a small scale electric spark tester ESD 2010EN (OZM Research) operating with the “Winspark 1.15 software package.”[34] DNBTDO had its sensitivities determined at four particle sizes; <100 μm, 100-500 μm, 500-1000 μm, and >1000 μm. For these particle sizes the impact sensitivity was determined to be 6, 5, 4 and 4 J respectively, while the friction sensitivity was found to be constant at 360 N at all of these particle sizes. Electrostatic discharge sensitivity (ESD) was determined at 100-500 μm to be 0.15 J. According to the UN Recommendations on the Transport of Dangerous Goods, DNBTDO is classified as sensitive.[35]

2.3.6.2 Bomb Calorimetry

The heat of combustion of DNBTDO was determined to be 14846 kJ g^{-1} using a Parr 1356 bomb calorimeter. $\Delta_f H^o$ was calculated at 298.15 K using Hess' law and the following combustion reaction.

$$C_6H_2N_6O_{6(s)} + 3.5O_2 \rightarrow 6CO_{2(g)} + H_2O_{(l)} + 3N_2$$

The calculated solid state energy of formation for DNBTO is an endothermic +420 kJ mol^{-1}.

2.3.6.3 Computational Properties

2.3.6.3.1 Theoretical Calculations

All calculations were carried out using the Gaussian G09W (revision B.09) program package.[36] 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 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.[37] The enthalpies of the gas-phase species M were computed according to the atomization energy method (eq. 1) (Tables 2-4).[38]

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

Table 2. CBS-4M results

	point group	$-H^{298}$ / a.u.
DNBTDO	C_s	1008.059173
H		0.500991
C		37.786156
N		54.522462
O		74.991202

Table 3. Literature values for atomic $\Delta H°_f{}^{298}$ / kJ mol^{-1}

	NIST [39]
H	218.1
C	717.2
N	473.1
O	249.5

Table 4. Enthalpies of the gas-phase species M.

M	M	$\Delta_f H°$(g,M) / kJ mol^{-1}
DNBTDO	$C_6H_2N_6O_6$	515.0

The solid state energy of formation (Table **5**) of DNBTDO was calculated by subtracting the gas-phase enthalpy with the heat of sublimation (77.9 kJ mol^{-1}) obtained by the Troutman rule ($\Delta H_{sub} = 188 \cdot T_m$ [T_m = 204 °C]).[40] The molar standard enthalpy of formation (ΔH_m) was used to calculate the molar solid state energy of formation (ΔU_m) according to equation (2) (Table **5**).

$\Delta U_m = \Delta H_m - \Delta n\, RT$ (2) (Δn being the change of moles of gaseous components)

Table 5. Solid state energies of formation ($\Delta_f U°$)

	$\Delta_f H°$(s) / kJ mol^{-1}	Δn	$\Delta_f U°$(s) / kJ mol^{-1}	M / g mol^{-1}	$\Delta_f U°$(s) / kJ kg^{-1}
DNBTDO	475.3	-7	442.7	254.14	1741

The calculated solid state energy of formation of 442.7 kJ mol^{-1} agrees well with the value determined from bomb calorimetry of 420 kJ mol^{-1}.

2.3.6.3.2 Detonation Parameters

The calculation of the detonation parameters was performed with the program package EXPLO5 (version 5.04).[41] The program is based on the chemical equilibrium, steady-state model of detonation. It uses the Becker-Kistiakowsky-Wilson's equation of state (BKW EOS) for gaseous detonation products and Cowan-Fickett's equation of state for solid carbon [42]. The calculation of the equilibrium composition of the detonation products is done by applying modified White, Johnson and Dantzig's free energy minimization technique.

The detonation parameters calculated with the EXPLO5 program using the experimentally determined densities (X-ray) are summarized in Table **6**.

Table 6. Detonation parameters.

	DNBTDO	RDX
ρ / g cm^{-3}	1.868	1.80
Ω / %	–44.07	–21.61
Q_v / kJ kg^{-1}	–6306.7	–6125
T_{ex} / K	4659	4236
$p_{C\text{-}J}$ / GPa	33.0	34.9
V_{det} / m s^{-1}	8411	8748
V_0 / L kg^{-1}	576	739

DNBTDO has a calculated detonation velocity of 8411 m s^{-1} and pressure of 33.0 GPa. These values are both lower than those of RDX, however they are high for energetic materials containing the benzene ring, i.e. when compared to trinitrotoluene (TNT) and triaminotrinitrobenzene (TATB) both of which have detonation velocities below 7500 m s^{-1}. These results confirm the highly energetic nature of the 1,2,3,4-tetrazine-1,3-dioxide moiety.

2.3.6.3.3 Small-Scale Shock Reactivity Test

The Small-Scale Shock Reactivity Test (SSRT)[43] was introduced by researchers at IHDIV, DSWC (Indian Head Division, Naval Surface Warfare Center). The SSRT measures the shock reactivity (explosiveness) of energetic materials, often well-below critical diameter, without requiring a transition to detonation. The test setup combines the benefits from a lead block test[44] and a gap test.[45] In comparison to gap tests, the advantage is the use of a large smaller sample size of the tested explosive (ca. 500 mg). The sample volume V_s is recommended to be 0.284 mL (284 mm^3). For our test setup, shown in Figure **7a-c**, no possible attenuator (between detonator and sample) and air gap (between sample and aluminum block) was used. The used sample weight m_s (504 mg) was calculated by the formula V_s x ρ_{Xray} x 0.95. Several tests with commonly used explosives such as PETN, RDX and HMX were performed in order to get different dents within the aluminum plate. The dent sizes were measured by filling them with fine quartz sand and back-calculating the volume from the corresponding SiO_2 mass.

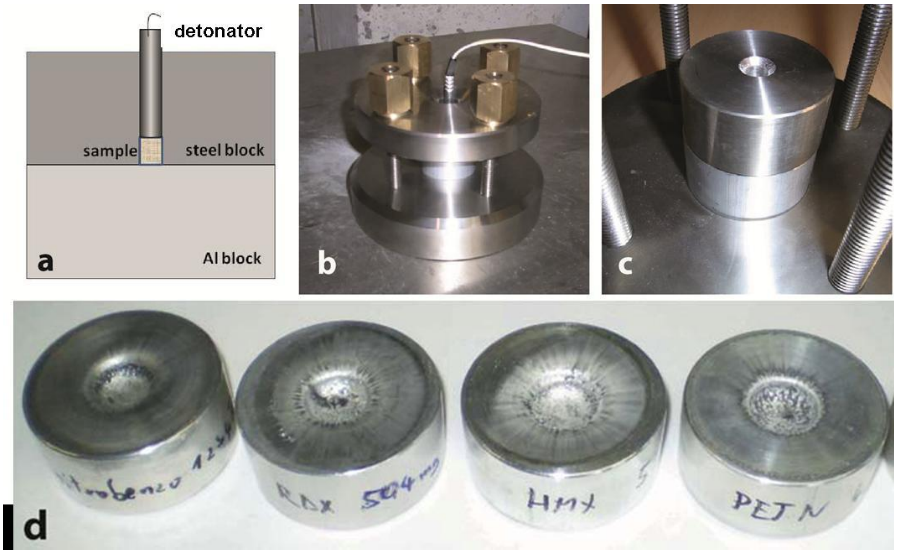


Figure 7: Small Scale Shock Reactivity Test (SSRT). a) Schematic setup; b) Picture of the overall setup; c) Steel cyclinder on top of the aluminum cyclinder; d) Test results.

As it can also be seen from Figure **7**, the dent resulted from **DNBTDO** is larger than that of **RDX** but smaller than that of **HMX** and **PETN**. Quantitative values have been summarized in Table **7**. Due to the large dent in the case of **PETN** we conclude that the obtained results also depend from the sensitivity of the explosive and also from the critical diameter. The lower these values the larger is the impact on the aluminum plate. From the SSRT it can be inferred that the explosiveness of **DNBTDO** is higher than that **RDX** but lower than those of **HMX** and **PETN**.

Table 7. Results from the Small Scale Shock Reactivity Test (SSRT).

Explosive	weight [mg]	dent [mg SiO_2]
DNBTDO	505	744
RDX	504	589
HMX	534	972
PETN	482	917

2.3.6.3.4 Cylinder Runs

As was already discussed extensively in the literature, it is not the detonation velocity that determines how quickly metal fragments are ejected from an explosive charge, but the so-called Gurney velocity.[46] This question was investigated in the work of Ronald W. GURNEY in 1943.[47] GURNEY suggested that there was a simple dependence relating the mass of the metal confinement (M) and the explosive (C) on the fragment velocity (V). The simple Gurney model developed in Aberdeen (MD) presumes the following:

- The energy released on detonation is essentially completely changed into the kinetic energy of the detonation gases <u>and</u> kinetic energy of the metal fragments;

- The energy used for the deformation or fragmentation of the confinement material can be essentially ignored;

- During detonation, the explosive is spontaneously ($\Delta t = 0$) transformed into homogeneous, chemically completely changed, gaseous products under high pressure;

- The gaseous detonation products expand with uniform density and a linear velocity gradient;

- The chemical detonation energy of the explosive is changed into kinetic energy, until the fragments have a steady-state velocity, from which the Gurney velocity can be calculated.

The fragment velocity is largely dependent on the shape of the charge. For cylindrical charges (which are a good approximation for most bomb and missile (rocket) warheads) the following equation is a good approximation:

$$\frac{V}{\sqrt{2E}} = \left(\frac{M}{C} + \frac{1}{2} \right)^{-0.5}$$

The constant $\sqrt{2E}$ is the so-called Gurney velocity (in km s^{-1}), which is dependent on the nature of the explosive. The Gurney velocity $\sqrt{2E}$ is decisive for the performance of the explosive used. It was only in 2002 that A. Koch *et al.* could show that the Gurney velocity $\sqrt{2E}$ and the detonation velocity (D) of an explosive can be described approximately using the following simple relationship[48]:

$$\sqrt{2E} = \frac{3\sqrt{3}}{16} D \approx \frac{D}{3.08}.$$

Of course, the Gurney velocity can also be determined experimentally using the measured fragment velocity V. It can be concluded that the relationship discussed above provides a good approximation, but that the Gurney velocity is also dependent on other factors including, for example, the material of the confinement used (in particular its density).

The cylinder test provides an experimental method to measure the effectiveness of an explosive. The radial expansion on detonation of a metallic cylinder (usually copper) filled with a high explosive is observed.[49] A streak camera or a laser method might be used. The detonation velocity is determined simultaneously. The equation of state (EOS) of the detonation products is derived using Gurney theory.

Using the Cheetah code[50], in the “cylinder runs” output section of the summary sheet, information on the adiabat is given. The term Cylinder run is used, because the cylinder test is the best experimental measurement of the adiabat. Relative V/V_0 volumes are shown along with the calculated energy. The energies are then compared to TATB at 1.83 g cm^{-3}, PETN at 1.76 g cm^{-3} and HMX at 1.89 g cm^{-3}. The comparison is given in terms of percentages, 100 percent indicating no difference. We calculated the cylinder energies (E_C) for DNBTDO and for RDX for comparison (Table **8**). It is evident from Table **8** that the cylinder energy for DNBTDO is comparable to but slightly larger than that of RDX which is also in accord with the result from the SSRT test (see above).

Table 8. Calculated cylinder energies (E_C) for DNBTDO and for RDX.

		% of standard			
compound V/V_0	E_C / kJ cm^{-3}	TATB	PETN	HMX	Cl-20
DNBTDO 2.2	-7.05	145	111	94	78
RDX 2.2	-6.94	143	109	93	77

2.4 Conclusions

From this combined experimental and theoretical study the following conclusions can be drawn

- 1,2,3,4-Tetrazine-1,3-dioxides are high-performance energetic materials even when the explosophoric tetrazine dioxide is “diluted” with low-performing aromatics.
- 1,2,3,4-Tetrazine-1,3-dioxides have the capability to be used in thermally stable energetic materials.
- Mechanical sensitivities and explosive performances of DNBTDO are higher than, and lower than those possessed by RDX respectively.
- DNBTDO shows a higher explosiveness in the SSRT (small-scale shock reactivity test) than RDX.
- DNBTDO has a slightly higher calculated cylinder energy than RDX.

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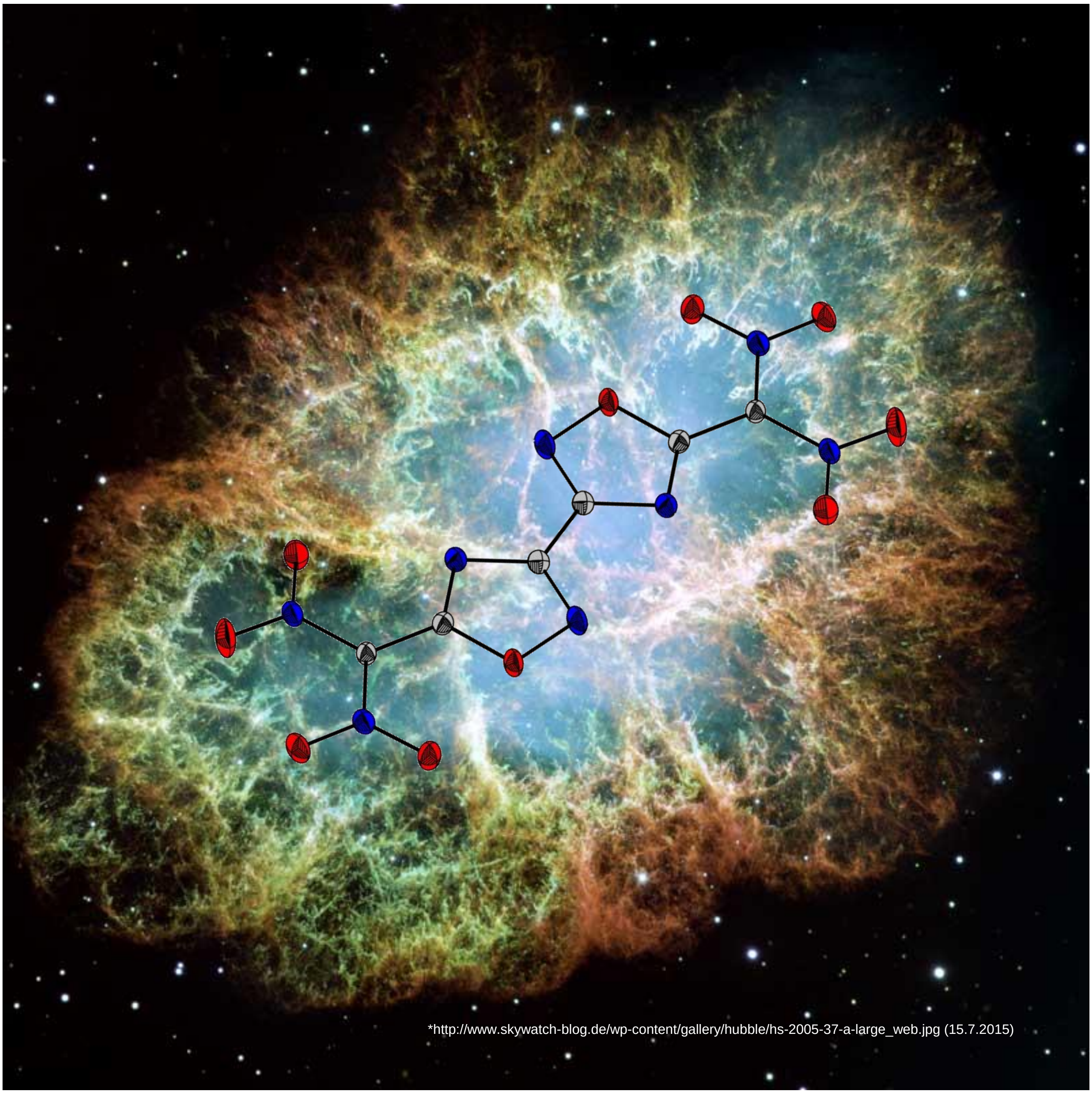
Chapter 3

5,5´-Dinitromethyl-3,3’-bis(1,2,4-oxadiazolate)



*http://www.skywatch-blog.de/wp-content/gallery/hubble/hs-2005-37-a-large_web.jpg (15.7.2015)

3 Maximum Compaction of Ionic Organic Explosives – Characterization of Bis(hydroxylammonium) 5,5´-Dinitromethyl-3,3'-bis(1,2,4-oxadiazolate)

Thomas M. Klapötke, Norbert Mayr, Jörg Stierstorfer and Michael Weyrauther

Chemistry - A European Journal **2014**, *20*(5), 1410-1417

3.1 Introduction

Most energetic materials in military use today, like RDX, TNT, PETN or lead azide, were developed in the 19th century[1]. These explosives have served their purpose well, but new research continues to provide materials with improved safety, performance, longevity[2] as well as environmentally compatibility. Most new materials[3] consist of nitrogen-rich compounds, often involving nitrogen-rich heterocycles, such as 1,2,3-triazoles[4], 1,2,4-triazoles[5], 1,2,3,4-tetrazoles[6] and 1,2,4,5-tetrazines[7] as well as 1,2,3,4-tetrazinedioxides[8]. Especially bistetrazoles[9] and their N-oxide homologous[10] and also bistriazoles[11] have been recently described as new energetic materials due to their high densities. Maximum densities are the main goal in order to get explosives with great detonation pressure and velocity. The replacement of one triazole nitrogen atom by an oxygen atom yields to the class of oxadiazoles which are also interesting backbones for new energetic materials. They consist of one oxygen, two nitrogen and two carbon atoms. Potential connection modes are given in Figure 1.

Oxadiazoles can be used used in dyes[12, 13], liquid crystals[14] and drugs[15], however, they are now getting more and more interesting in the design of new high energetic materials (HEDM). 3,5-Disubstitized 1,2,4-oxadiazoles can combine good performances with adequate stabilities. One example described in literature is methyl (3-nitro-1,2,4-oxadiazol-5-yl)amine[16].

Many 1,2,5-oxadiazole (A, furazane) based compounds have been published [17, 18] while 1,2,4-oxadiazoles (B) are rarely described.

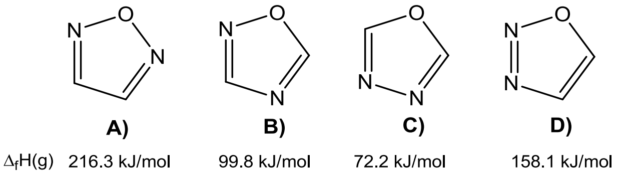
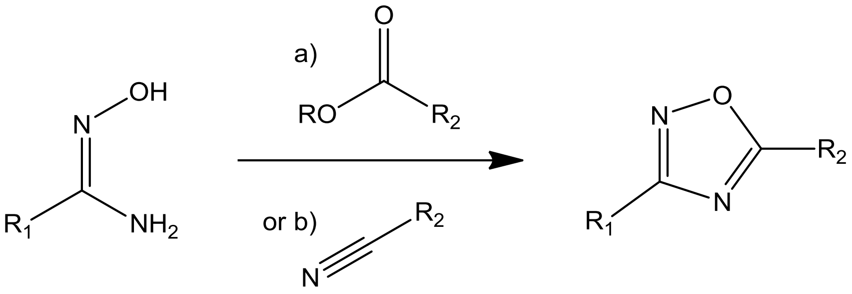


Figure 1: A) 1,2,5-Oxadiazole (Furazane); B) 1,2,4-Oxadiazole; C) 1,3,4-Oxadiazole; D) 1,2,3-Oxadiazole and their calculated gas phase heat of formations using the atomization method based on CBS-4M electronic enthalpies.

Obviously furazanes are better energetic materials in terms of their higher heat of formation. Even more uncommon are derivatives of C and D illustrated in Figure 1.

Oxadiazoles are synthesized in different ways. 1,2,3-Oxadiazole can be prepared by the reaction of α-amino-1,3-dicarbonyl-compounds with nitrous acid while 1,2,5-oxadiazole are synthesized by the dehydration of bis-oximes. 1,3,4-Oxadiazole are formed by the dehydration of diacylhydrazines with strong hydroscopic substances. 1,2,4-Oxadiazole can be synthesized in two ways starting with a N-hydroxyamidine (oximamide) which can be reacted with (a) carboxylic acid ester or (b) a nitrile compound.[19, 20]



Scheme 1: Synthesis for 1,2,4-oxadiazole compounds.

An promising approach towards dense energetic materials is the use of the good available 5,5'-bis-oxadiazole system with the dinitromethylene group connected to the carbon atom C3. Here we report on the synthesis of this promising new system as well as its deprotonation with nitrogen-rich bases. To the best of our knowledge the obtained hydroxylammonium salt shows the highest density of an ionic organic (only CHNO atoms) explosive. We also propose that the neutral trinitromethyl and dinitrofluoromethyl derivatives will have outstanding densities.

3.2 Results and Discussion

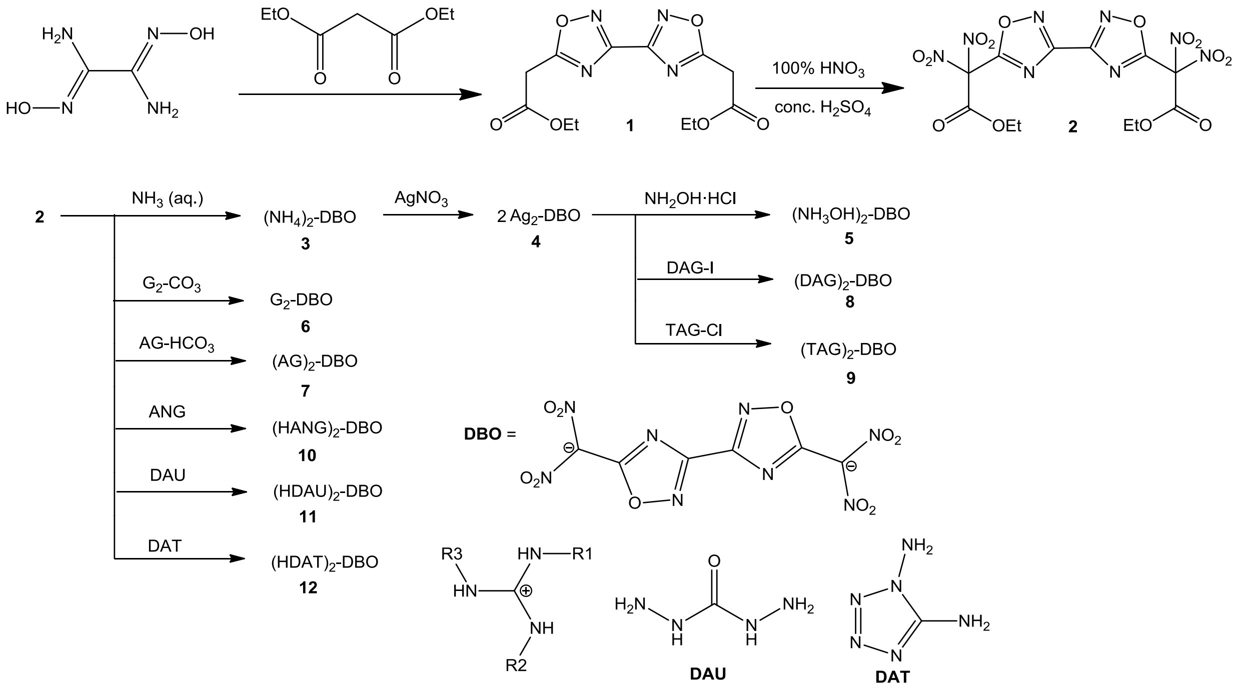
3.2.1 Synthesis

3,3'-Bis(1,2,4-oxadiazolyl)-5,5'-diacetic acid diethyl ester (**1**) was synthesized from the reaction of diaminoglyoxime in a solution of malonic acid diethyl ester (MADE) analogously to the literature.[21] The 3,3'-bis(1,2,4-oxadiazolyl)-5,5'-bis(2,2'-dinitro)-diacetic acid diethyl ester (**2**) was obtained by treatment of **1** with an excess of fuming nitric acid in conc. sulphuric acid. Reaction of **2** with bases lead to the decarboxylated compound 5,5'-dinitromethyl-3,3'-bis(1,2,4-oxadiazole) in its dianionic form.

Ten different nitrogen-rich salts, shown in Scheme 1, were synthesized, which are the ammonium (**3**), hydroxylammonium (**5**), guanidnium (**6**), aminoguanidinium (**7**), diaminoguanidinium (**8**), triaminoguanidinium (**9**), aminonitroguanidinium (**10**), diaminouronium (**11**), diaminotetrazolium (**12**) and hydrazinium (**13**) salt. The syntheses of the nitrogen-rich salts except for **5** are based on decarboxylation of **2**.

Salts **3**, **10**, **11**, **12** and **13** could be synthesized using the free bases in aqueous methanol solution; salts **6** and **7** were synthesized with the corresponding carbonates.

For the preparation of **5**, **8** and **9**, in the first step the ammonium salt **3** was reacted in a metathesis reaction using silver nitrate to precipitate the silver salt **4**. In the second step, **5**, **8** and **9** were synthesized by metathesis reactions using the respective halides.



Scheme 2: Syntheses of nitrogen-rich salts of 5,5’-dinitromethyl-3,3’-bis(1,2,4-oxadiazole) under different reaction conditions: a) aqueous NH_3, RT, 12h; b) $AgNO_3$, H_2O, RT, 2h; c) aqueous $NH_2OH \cdot HCl$, 30-40 ºC, 5 min; d) guanidinium carbonate, H_2O/MeOH, RT, 12h; e) aminoguanidinium bicarbonate, H_2O/MeOH, RT, 12h; f) 1) aqueous NH_3, RT, 12h; 2) $AgNO_3$, H_2O, RT, 2h; 3) diaminoguanidinium iodide, H_2O, 30-40 ºC, 5 min; g) 1) aqueous NH_3, RT, 12h; 2) $AgNO_3$, H_2O, RT, 2h; 3) triaminoguanidinium chloride, H_2O, 30-40 ºC, 5 min; h) aminonitroguanidine, H_2O/MeOH, RT, 12h; i) diamino urea, H_2O/MeOH, RT, 12h; j) 1,5-diaminotetrazole, H_2O/MeOH, RT, 12h; k) aqueous hydrazine hydrate, MeOH, RT, 12h.

3.2.2 Crystal Structures

Within this work we determined the X-ray structures of compounds **1**–**5** as well as **7**–**13**. The thermal expansion of **5** was explored at different XRD temperatures (92 K, 100 K, 173 K, 298K).

Data and parameters of the X-ray measurements and structure refinements are given in the Supplementary Information in Tables S1 and S2. The molecular structures of **1** as well as **7**–**13** can also be found in the Supplementary Information.

The structure of the backbone compound 3,3'-bis-1,2,4-oxadiazole has been described in the literature.[22]

Compound **2** crystallizes in the monoclinic space group $P2_1/n$ with two formula units in the unit cell and a density of 1.620 g cm^{-3} which is higher than its unnitrated precursor **1** (1.480 g cm^{-3}). The molecular structure is shown in Figure 2. The structures of **1** and **2** are similar to that of 5,5'-bis(azidomethyl)-3,3'-bi-1,2,4-oxadiazole.[23]

All of the ionic compounds contain the decarboxylated 5,5'-dinitromethyl-3,3'-bis(1,2,4-oxadiazole) dianion. In all structures very similar bond lengths and angles of the anion are obtained. However, significant differences in the position of the dinitromethyl unit to the oxadiazole ring system could be observed. A detailed comparison is given in the Supplementary Information in Table S3.

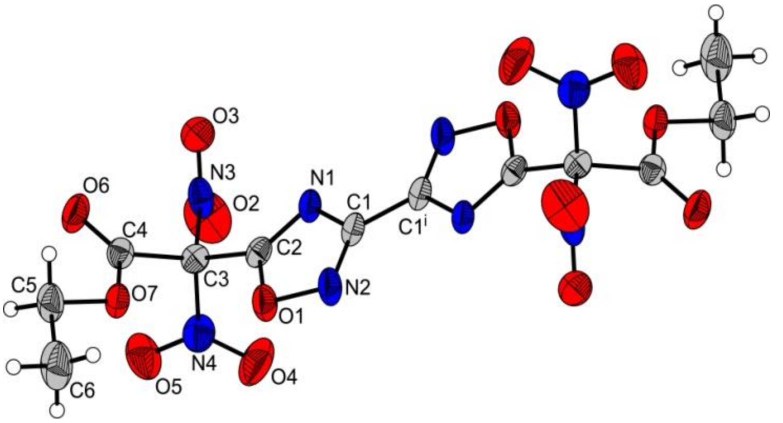


Figure 2: Molecular structure of 3,3'-bis(1,2,4-oxadiazolyl)-5,5'-bis(2,2'-dinitro)-diacetic acid diethyl ester (2). Thermal ellipsoids are drawn at the 50 % probability level. (i) −x, −y, −z.

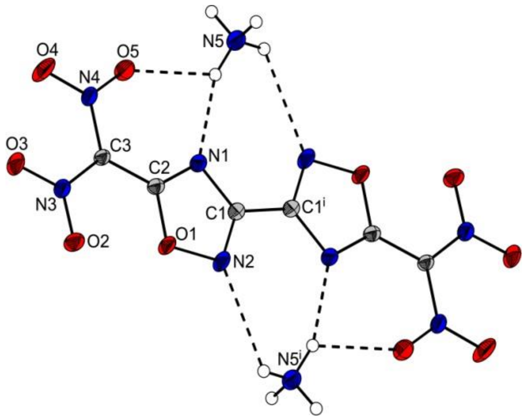


Figure 3: Molecular structure of compound 3. Thermal ellipsoids are drawn at the 50 % probability level. (i) 1−x, −y, 1−z.

Compound **3**, **4** and **5** crystallize in the triclinic space group *P-1* with one formula unit in the cell. The ammonium salt **3** has an astonishing high density of 1.951 g cm^{-3}. Usually ammonium salts of azoles show significantly lower densities mostly between 1.60 and 1.80 g cm^{-3}.[3,6c] The molecular structure is shown in Figure 3. The 5,5'-dinitromethyl-3,3'-bis(1,2,4-oxadiazole) anion is nearly planar, which can be seen by the O1–C2–C3–N3 torsion angle of 2.3(2)°. The structure of **3** is stabilized by various H-bonds involving all hydrogen atoms of the ammonium cation.

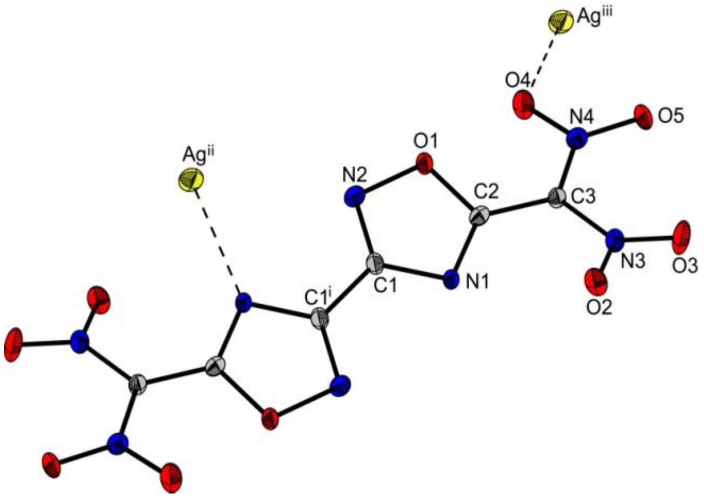


Figure 4: Structural motive of silver salt 4. Thermal ellipsoids are drawn at the 50 % probability level. (i) −x, −y, −z; (ii) 1+x, 1+y, z; (iii) −x, 1−y, 1−z.

A density of 3.087 g cm^{-3} is observed for the silver salt **4** (Figure 4). This is in agreement to other silver azoles in the literature e.g. silver 1-methyl-5-nitriminotetrazolate.[24] The molecular structure is shown in Figure 5. The torsion angle (–17.8(5)°) of the anion shows a significant derivation from planarity.

Single crystals of **5** were obtained from ethanol. Different crystals of **5** were measured at different temperatures (92, 100, 173 and 293 K) To the best of our knowledge the hydroxylammonium salt **5** shows the highest density (2.001 g cm^{-3} (92 K), 1.994 g cm^{-3} (100K), 1.986 g cm^{-3} (173 K), 1.946 g cm^{-3} (298 K)) ever observed for an energetic ionic CHNO compound. According to equation (1) an averaged coefficient of volume expansion α_V of $1.42 \cdot 10^{-4}$ K^{-1} was calculated for **5**. This is similar to other energetic materials like hexogen ($1.6 \cdot 10^{-4}$ K^{-1}) published in the literature.[25]

$$\rho_{298K} = \rho_T/(1+\alpha_V(298-T_0)) \quad (1)$$

Its molecular structure is depicted in Figure 5. The anion shows a nearly a planar structure (angle of torsion 2.8(2)°). No point of symmetry is observed at the centre of the inner C–C bond. The structure is stabilized by various hydrogen bonds involving all of the hydrogen atoms of the hydroxylammonium cations. In total more than 20 different H-bonds with a D–A distance <3.45 Å can be observed, which may be one reason for the high density. A second one is probably a conclusion of the bis-oxadiazolate moiety in connection with the dinitromethyl groups. This trend has also be observed for the corresponding triazol system. Dinitromethyl-bis-1,2,4-triazole dihydrate has a density of 1.95 g cm^{-3}.[11b] In **5** the dianions form a layer structure parallel to the *c* axis (Figure S9). The hydroxylammonium cations are arranged parallel to the *a* axis and connect the dianions with each other. No kind of nitro-nitro interactions could be observed. A very similar layer packing is observed for highly dense **3** (Figure S10).

The guanidinium derivatives **7**, **9**, **10** all crystallize in the triclinic space group *P-1* with one formula unit in the cell. Compound **8,** which has a lower density (1.696 g cm^{-3}) in comparison to **7** (1.742 g cm^{-3}) and **9** (1.769 g cm^{-3}) crystallizes in the orthorhombic space group *Pbca* with four formula units in the cell. Compounds **10** and **11** exhibit densities of 1.899 g cm^{-3} and 1.836 g cm^{-3}, respectively. In all compounds the structures are stabilized by various hydrogen bonds involving the respective cations. Compound **12** and the hydrazinium salt **13**, which could only be obtained crystalline with the inclusion of crystal water, both crystallize in the monoclinic space group $P2_1/n$ with two formula units in the cell and densities of 1.887 and 1.808 g cm^{-3}, respectively.

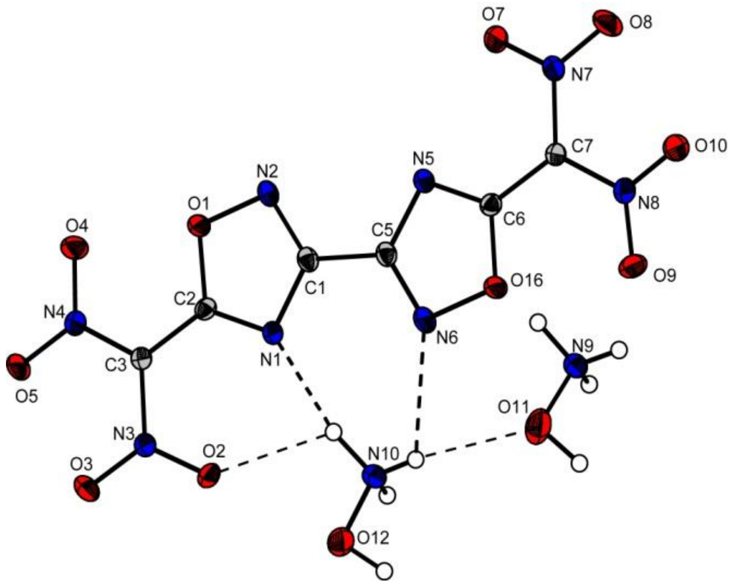


Figure 5: Depiction of the asymmetric unit structure of the crystal structure of compound 5. Thermal ellipsoids are drawn at the 50 % probability level.

3.2.3 NMR Spectroscopy

The ^{1}H, ^{13}C and ^{14}N NMR spectra of compounds **3**–**13** were recorded in DMSO-d_6 at room temperature. The resonance for the C1 carbon atom of the oxadiazole moiety is located at ~160.4 ppm, which is the same range observed for **2**. The resonance for the C2 carbon atom (C2) is observed at about 173.0–179.0, which is also similar for **2**. The ^{13}C resonance of the dinitromethyl signals (C3) are in a range of 154.1–158.4 ppm, which is (compared to **2** about 30 ppm) shifted to lower (at about 123 ppm) numbers. In the ^{1}H NMR spectra mostly broad signals caused by the N–H hydrogen atoms in the cations are observed. In the ^{14}N NMR the nitro groups can be observed at about –18 ppm while the amino groups are at about –300 ppm.

3.2.4 Sensitivities and Thermal Stabilities

Compounds **2–13** were tested for thermal capacity in DSC measurements (5 deg min^{-1}).[26] Compounds **2** and **4** show the highest decomposition temperatures of 286°C and 273°C. Compounds **3**, **6** and **9** also exhibit decomposition temperatures above 200°C. All the other compounds unfortunately decompose below 200°C which is the inofficial threshold value for the development of new military explosives. Compound **7** shows the lowest decomposition temperature of 141°C.

Also the sensitivities towards impact and friction were explored.[27-31] Compound **13** has the lowest sensitivity towards impact (40 J). This can be explained by the inclusion of crystal water. Also **6** is only very low sensitive. According to the UN guidelines [32] both are classified as *less sensitive*. **4**, **9** and **12** have the highest sensitivities (2 J) and are classified as *very sensitive*. Most of the other compounds exhibit sensitivities between 4 J and 7 J and are classified as *sensitive*. All compounds except **6**, **8** and **13** are slightly more sensitive than RDX (1,3,5-trinitro-1,3,5-triazacyclohexane, 7.5 J, 120 N).

In the BAM friction test **6** and **7** could not be initiated even with a force of 360 N and are therefore classified as *insensitive*. **5** and **12** have friction sensitivities of 108 N. Compound **10** is only slightly less sensitive (120 N). All three compounds are classified as *very sensitive*, which is in the range of commonly used secondary explosives like PETN (pentaerythritol tetranitrate) and RDX. The other compounds have sensitivities between 216 and 288 N and are classified as *sensitive*. As expected for a silver azole, **4** exhibits the highest sensitivity towards friction (60 N) and is therefore classified as *extremely sensitive*.

The sensitivities towards electrostatic discharge [32] range from 0.6 J (**6**) and 0.03 J (**9**). For comparison, RDX has ESD of 0.1 to 0.2 J, whereby those of primary explosives are 1000 times smaller.

Table 1. Energetic properties and detonation parameters of compounds 3–8.

	3	**4**	**5**	**6**	**7**	**8**
Formula	$C_6H_8N_{10}O_{10}$	$C_6N_8O_{10}Ag_2$	$C_6H_8N_{10}O_{12}$	$C_8H_{12}N_{14}O_{10}$	$C_8H_{14}N_{16}O_{10}$	$C_8H_{16}N_{18}O_{10}$
FW / g mol^{-1}	380.19	559.85	412.19	464.27	494.11	524.33
IS [J] [a]	6	2	4	35	6	20
FS [N] [b]	252	60	108	360	360	288
ESD [J] [c]	0.15	0.07	0.35	0.60	0.20	0.3
N [%] [d]	36.8	20.01	33.9	42.2	45.3	48.08
Ω [%] [e]	–25.25	–	–15.53	−41.35	−42.08	–42.72
$T_{Dec.}$ [°C] [f]	223	273	156	239	141	197
ρ_{173K} [g cm^{-3}] [g]	1.951	3.087	1.986	---	1.742	1.696
ρ_{298K} [g cm^{-3}] [h]	1.90	3.01	1.946§	1.75$^{\#}$	1.70	1.66
$\Delta_f H_m^{\circ}$ [kJ mol^{-1}] [i]	–91.6	–	41.1	–73.4	148.6	386.3
$\Delta_f U^{\circ}$ [kJ kg^{-1}] [j]	–149.7	–	189.9	–61.9	400.9	840.6
EXPLO5.05 values:						
$-\Delta_{Ex}U^{\circ}$ [kJ kg^{-1}] [k]	5307	–	6124	4630	4899	5166
T_{det} [K] [l]	3858	–	4359	3408	3542	3641
P_{CJ} [kbar] [m]	350	–	394	270	266	263
$V_{Det.}$ [m s^{-1}] [n]	8618	–	8935	8038	8078	8108
V_o [L kg^{-1}] [o]	689	–	682	721	747	769

Table 2. Energetic properties and detonation parameters of compounds 9–12 as well as PETN and RDX.

	9	**10**	**11**	**12**	**13·0.35 H_2O**	**PETN [34]**	**RDX [34]**
Formula	$C_8H_{18}N_{20}O_{10}$	$C_8H_{12}N_{18}O_{14}$	$C_8H_{14}N_{16}O_{12}$	$C_8H_{10}N_{20}O_{10}$	$C_6H_{10}N_{12}O_{10}$	$C_5H_8N_4O_{12}$	$C_3H_6N_6O_6$
FW / g mol^{-1}	554.36	584.29	526.3	546.29	410.22	316.14	222.12
IS [J] [a]	2	7	5	2	40	3	7.5
FS [N] [b]	216	120	252	108	288	60	120
ESD [J] [c]	0.03	0.07	0.10	0.15	0.30	0.20	0.20
N [%] [d]	50.53	43.15	42.6	51.3	40.9	17.72	37.84
Ω [%] [e]	−43.29	−21.9	−33.44	−32.21	–*	–10.12	–21.61
$T_{Dec.}$ [°C] [f]	204	149	197	178	135	141	210
ρ_{173K} [g cm^{-3}] [g]	1.769	1.899	1.836	1.887	1.808	1.845[35]	1.858 (90K)[37]
ρ_{298K} [g cm^{-3}] [h]	1.73	1.85	1.79	1.84	1.76	1.780[36]	1.806 [38]
$\Delta_f H_m^{\circ}$ [kJ mol^{-1}] [i]	595.1	593.1	188.5	920.5	–*	−538.6	66.9
$\Delta_f U^{\circ}$ [kJ kg^{-1}] [j]	1180.6	1108.2	457.0	1775.5	–*	–1610.7	401.8
EXPLO5.05 values:							
$-\Delta_{Ex}U^{\circ}$ [kJ kg^{-1}] [k]	-5368	-6091	-5381	-5632	–	6184	6110
T_{det} [K] [l]	368	4343	3810	4127	–	4317	4224
P_{CJ} [kbar] [m]	298	366	316	343	–	332	351
$V_{Det.}$ [m s^{-1}] [n]	8513	8872	8508	8744	–	8400	8763
V_o [L kg^{-1}] [o]	785	715	736	710	–	685	739

[a] Impact sensitivity (BAM drophammer,[29] 1 of 6). [b] Friction sensitivity (BAM friction tester,[29] 1 of 6). [c] Electrostatic discharge device (OZM).[33] [d] Nitrogen content. [e] Oxygen balance. [f] Decomposition temperature from DSC (β = 5 °C). [g] From X-ray diffraction at 173 K. [h] $\rho_{298K} = \rho_T/(1+\alpha_v(298\text{-}T))$,[25] $\alpha_v = 2.0\cdot10^{-4}$ K^{-1} (estimated); [i] Calculated (CBS-4M) heat of formation. [j] Energy of formation. [k] Energy of explosion. [l] Explosion temperature. [m] Detonation pressure. [n] Detonation velocity. [o] Assuming only gaseous products [*] not calculated due to water inclusion; § from X-ray diffraction at 298 K. $^{\#}$ measured by gas (He) pycnometry at 298 K.

3.2.5 Heat of Formation

The heats of formation were computed theoretically using the Gaussian G09 program package.[39] To obtain very accurate energies the enthalpies (*H*) were calculated by the CBS-4M method. The enthalpies of the gas phase species M were computed according to the atomization energy method[40] (Equation (2)) described e.g. in the literature.[41]

$$\Delta_f H^\circ_{(g,M,298)} = H_{(M,298)} - \Sigma H^\circ_{(atoms,298)} + \Sigma \Delta_f H^\circ_{(atoms,298)} \quad (2)$$

All single values of the calculations are given in the Supporting Information. Lattice enthalpies (U_L) and lattice enthalpies (ΔH_L) were calculated from the corresponding molecular volumes (taken from low temperature X-ray structures) according to equations developed by Jenkins and Glasser.[42] With these values the gas phase enthalpies were converted to the solid state (standard conditions) enthalpy of formation $\Delta_f H_m^\circ$ (Table 1). Lastly, the standard molar enthalpies of formation (ΔH_m) were calculated into the molar solid state energies of formation (ΔU_m) according to Equation (3).

$$\Delta U_m = \Delta H_m - \Delta n\, RT \quad (3)$$

(Δn is the change of mol of gaseous components)

The compound with the highest heat of formation is **12** (910 kJ mol^{-1}) followed by **9** (585 kJ mol^{-1}) and **10** (583 kJ mol^{-1}). Except for compounds **3** (−104 kJ mol^{-1}) and **6** (–85 kJ mol^{-1}) the remaining compounds were calculated to be formed endothermically. In comparison RDX has a calculated heat of formation of 86 kJ mol^{-1} by using the same theoretical method.

3.2.6 Detonation Parameters

Detonation parameters were calculated by EXPLO5 V5.05 as well as V6.01 computer code.[43] The input for EXPLO5.05 needs sum formula, densities and heats of formation. The calculations were performed using the maximum densities according to the low temperature (173K) crystal structures. These are lower by ~0.04 g cm^{-3} in comparison to the real room temperature densities and yield an increase in calculated performance e.g. about 200-300 m s^{-1} for the detonation velocity. The density of **6** was measured by gas pycnometry at room temperature (1.751 g cm^{-3}).

The most important criteria of a high explosive are its detonation velocity V_{Det}, its detonation pressure p_{CJ} and its energy of explosion $\Delta_{Ex}U^\circ$. Commonly used explosives like TNT, HNS or RDX, were also calculated with the EXPLO5.05 code. (V_{Det}: TNT: 7450, HNS: 7436, RDX: 8983 ms^{-1}; p_{CJ}: TNT: 234, HNS: 242, RDX: 380 kbar; $\Delta_{Ex}U°$: TNT:– −5261, HNS: −5476, RDX: −6190 kJ kg^{-1})

In terms of detonation velocity, compounds **3**, **5**–**12** reached the level of commonly used secondary explosives such as RDX. Compounds **5** and **10** even exceed the calculated detonation velocities of RDX. The reason for their great performance is based of course on their great densities.

3.3 Conclusions

From this experimental and theoretical study the following conclusions can be drawn:

- Ten different nitrogen-rich salts, ammonium (**3**), hydroxylammonium (**5**), guanidinium (**6**), aminoguanidinium (**7**), diaminoguanidinium (**8**), triaminoguanidinium (**9**), aminonitroguanidinium (**10**), diaminouronium (**11**), diaminotetrazolium (**12**) and hydrazinium (**13**), of 5,5'-dinitromethyl-3,3'-bis(1,2,4-oxadiazole) were synthesized out of 3,3'-bis(1,2,4-oxadiazolyl)-5,5'-diacetic acid diethyl ester (**2**) by decarboxylation with additional deprotonation and metathesis reactions involving the silver salt and the corresponding nitrogen rich halides.

- To the best of our knowledge hydroxylammonium 5,5'-dinitromethyl-3,3'-bis(1,2,4-oxadiazolate) is the most dense (X-ray density of 2.00 g cm^{-3} at 92K, 1.98 g cm^{-3} at 173 K, 1.95 g cm^{-3} at room temperature) ionic organic CHNO explosive investigated yet. Also the ammonium salts has an astonishing high density of 1.95 g cm^{-3} at 173K.

- The precursors **1** and **2** as well as the salts **3–5**, **7–13** were characterized by single-crystal X-ray diffraction. The precursors **1** and **2** crystallize in the monoclinic space groups $P2_1/n$. The salts crystallize in the mononoclinic, triclinic and orthorhombic space groups $P2_1/n$ (**12**, **13**), *P–1* (**3-7**, **9-11**) and *Pbca* (**8**). The precursors show densities of 1.480 g cm^{-3} (**1**) and 1.620 g cm^{-3} (**2**) while the nitrogen-rich salts exhibit densities between 1.70 and 2.00 g cm^{-3}. Silver salt **4** has a density of 3.087 g cm^{-3}.

- Regarding the thermal stabilities the investigated compounds mostly decompose at temperatures below 200°C (exception compounds **2**, **3**, **4**, **6** and **9**).

- The impact and friction sensitivities of the nitrogen-rich salts were determined. According to UN recommendations they are classified as less sensitive (**6**, **13**), sensitive (**3**, **5**, **7**, **8**, **10** and **11**) or very sensitive (**4**, **9** and **12**) towards impact and insensitive (**6** and **7**), sensitive (**3**, **4**, **8**, **9**, **10**, **11** and **13**) or very sensitive (**5** and **12**) towards friction. - The silver salt **4** turned out to be a potential primary explosive.

- Based on the crystal densities and calculated (mostly endothermic) enthalpies of formation, several detonation parameters were calculated. Salts **5**, **10** and **12** show the highest values regarding the detonation velocity (**5**: 8935 ms^{-1}). With a detonation pressure of 413 kbar compound **5** exceeds also the value of RDX (394 kbar) With respect to their performance data compounds **3**, **5**, **10** and **12** could be of interest as high explosives.

3.4 Experimental Section

CAUTION! Although we had no problems in synthesis and handling of the compounds described in this work they are nevertheless energetic materials with sensitivity to various stimuli. Proper protective measures (face shield, ear protection, body armor, Kevlar gloves, and earthed equipment) should be used at all times.

General Procedures and description of the analytical methods are given in the Supplementary Information.

3,3'-Bis(1,2,4-oxadiazolyl)-5,5'-diacetic acid diethyl ester (1)

3,3'-Bis(1,2,4-oxadiazolyl)-5,5'-diacetic acid diethyl ester was prepared according to the literature procedure.[21]

Nitration of 3,3'-bis(1,2,4-oxadiazolyl)-5,5'-diacetic acid diethyl ester (1) to 3,3'-bis(1,2,4-oxadiazolyl)-5,5'-bis(2,2'-dinitro)-diacetic acid diethyl ester (2): 3,3`-bis(1,2,4-oxadiazolyl)-5,5`-diacetic acid diethyl ester (12 mmol) was dissolved in a solution of 96 % H_2SO_4 (34 mL) at 0 ºC. After cooling to -5 ºC a solution of 100% nitric acid (14 mL) was added dropwise. The reaction mixture was warmed up to 10 ºC and stirred for 3 h at 10-15 ºC. After cooling to -15 ºC, filtering, washing with trifluoro acetic acid and iced water, the product was yielded as colorless solid. Yield 5.70 g (97%), colorless solid. M.p. (DSC, 5 deg min-1): 72 ºC (mp), 286 ºC (dec.); Raman: $\tilde{\nu}$ = 2993 (13), 2979 (17), 2950 (32), 2931 (12), 2878 (4), 1780 (13), 1602 (100), 1581 (44), 1474 (4), 1455 (10), 1447 (10), 1423 (44), 1352 (5), 1306 (6), 1246 (4), 1121 (7), 1022 (10), 995 (12), 974 (18), 946 (29), 849 (20), 810 (4), 793 (6), 769 (4), 705 (5), 649 (2), 622 (4), 525 (13), 437 (6), 389 (40), 317 (8), 286 (5), 251 (18), 222 (6), 101 (82) cm^{-1}. IR: $\tilde{\nu}$ = 3007 (w), 2948 (w) 1780 (vs), 1739 (w), 1605 (vs), 1592 (vs), 1559 (m), 1472 (w), 1456 (w), 1445 (w), 1415 (w), 1368 (w), 1351 (w), 1299 (m), 1280 (m), 1236 (s), 1220 (vs), 1159 (m), 1107 (w), 1087 (m), 1025 (m), 987 (m), 972 (s), 915 (m), 849 (s), 840 (vs), 817 (s), 795 (s), 724 (m), 693 (m), 665 (m) cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6, 25 °C, ppm): δ= 1.06 (t, J = 6.87 Hz, 6H, $C\mathit{H}_3$), 3.38(q, J = 6.87, 7.15 Hz, 4H, $C\mathit{H}_2CH_3$). ^{13}C NMR (101 MHz, DMSO-d_6, 25 °C, ppm): δ= 19.0 (s, 2C, $\mathit{C}H_3$), 56.5 (s, 2C, $\mathit{C}H_2CH_3$), 124.7 (s, 2C, $\mathit{C}(NO_2)_2$), 160.4 (s, 2C, *CC*), 172.9 (s, 2C, $\mathit{C}C(NO_2)_2$), 173.2 (s, 2C, *C*O). ^{14}N NMR (29 MHz, DMSO-d_6, 25 °C, ppm): δ= −18 (s, 4N, *N*O$_2$). MS (DEI$^+$): m/z (%) = 490.4 [M$^+$] (5), 474.3 [M$^+$-O] (3), 444.4 [M$^+$-NO$_2$] (47), 445.4 [M$^+$-OEt] (10), 400.3 [M$^+$-2OEt] (5), 429.3 [M$^+$-O,-OEt] (22). $C_{12}H_{10}N_8O_{14}$ (490.25): calc. C 29.40, H 2.06, N 22.86, found: C 28.91, H 1.98, N 22.40.

Preparation of ammonium-5,5'-dinitromethyl-3,3'-bis(1,2,4-oxadiazolyl) (3): Compound **2** (2.628 mmol) was dissolved in 15 mL methanol and conc. ammonia (0.4 mL, 21 mmol) was added drop wise. The mixture was stirred for 12 h. After filtering the product was given as a yellow solid. Yield 243 mg 97%, yellow solid. M.p. (DSC, 5 deg min^{-1}): 223ºC (dec.); Raman: $\tilde{\nu}$ =1602 (44), 1541 (32), 1481 (3), 1452 (24), 1350 (70), 1285 (9), 1198 (100), 1153 (16), 1089 (4), 965 (63), 938 (11), 837 (36), 782 (7), 751 (2), 711 (2), 564 (4), 462 (6), 430 (3), 366 (4), 128 (23) cm^{-1}. IR: $\tilde{\nu}$ = 3241 (m), 3021 (w), 1738 (w), 1532 (s), 1484 (w), 1456 (m), 1401 (vs), 1352 (s), 1290 (m), 1247 (s), 1179 (vs), 1141 (vs), 1065 (vs), 999 (w), 964 (vs), 925 (m), 834 (s), 778 (s), 751 (vs), 743 (m) cm^{-1}. ^{1}H NMR (400 MHz, DMSO-*d*$_6$, 25°C, ppm): δ= 7.06 (t, J = 51.23 Hz, 8H, N*H*$_4$). ^{13}C{^{1}H} NMR (101 MHz, DMSO-*d*$_6$, 25 °C, ppm): δ= 122.9 (s, 2C, *C*(NO$_2$)$_2$), 160.5 (s, 2C, *CC*), 172.9 (s, 2C, *C*C(NO$_2$)$_2$). ^{14}N NMR (29 MHz, DMSO-*d*$_6$, 25 °C, ppm): δ= −18 (s, 4N, *N*O$_2$), −353 (s, 2N, *N*H$_4$). MS (FAB$^+$): m/z (%) = 18 [NH$_4^+$]$^+$ (4). MS (FAB$^-$) m/z (%): 345 [M-N$_2$H$_7$]$^-$ (16), 282 [M-N$_3$H$_8$O$_3$]$^-$ (6), 242.3 [M-N$_2$H$_8$-NO$_2$]$^-$ (5). $C_6H_8N_{10}O_{10}$ (380.19): calc. C 18.95, H 2.12, N 36.84, found: C 19.23, H 2.08, N 36.24.

Preparation of silver-5,5'-dinitromethyl-3,3'-bis(1,2,4-oxadiazolate) (4): Silver nitrate (0.894 mmol) was dissolved in 2 mL water and carefully added to a solution of **3** (0.447 mmol) in 3 mL water. The mixture was stirred for 2 h. After filtrating the product was obtained as a yellow solid. Yield 235 mg (94%), yellow solid. M.p. (DSC, 5 deg min^{-1}): 273ºC (dec.); Raman: $\tilde{\nu}$ = 1615 (56), 1544 (81), 1477 (14), 1444 (75), 1381 (4), 1336 (70), 1290 (31), 1226 (100), 1145 (30), 1097 (2), 1040 (3), 973 (75), 938 (14), 828 (46), 781 (7), 763 (2), 749 (2), 704 (4), 569 (5), 483 (10), 441 (2), 416 (3), 367 (7), 305 (8), 241 (6), 141 (24), 129 (19), 88 (17) cm^{-1}. IR: $\tilde{\nu}$ = 1532 (m), 1477 (m), 1462 (m), 1381 (m), 1344 (m), 1292 (w), 1193 (vs), 1131 (s), 1071 (s), 965 (s), 924 (m), 823 (s), 776 (s), 747 (vs), 731 (m), 725 (s) cm^{-1}. ^{13}C{^{1}H} NMR (101 MHz, DMSO-*d*$_6$, 25 °C, ppm): δ= 123.2 (s, 2C, *C*(NO$_2$)$_2$), 160.3 (s, 2C, *CC*), 172.9 (s, 2C, *C*C(NO$_2$)$_2$). ^{14}N NMR (29 MHz, DMSO-*d*$_6$, 25°C, ppm): δ= −18 (s, 4N, *N*O$_2$). MS (FAB$^+$): m/z (%) = 107.1 [Ag$^+$]$^+$ (20). MS (FAB$^-$) m/z (%):451 [M-Ag]$^-$ (3). $C_6N_8O_{10}Ag_2$ (559.85): calcd. C 12.87, H 0.00, N 20.01, found: C 12.70, H 0.32, N 19.72.

Preparation of bis-hydroxylammonium 5,5'-dinitromethyl-3,3'-bis(1,2,4-oxadiazolate) (5): Hydroxylamine-hydrochloride (1.214 mmol) was dissolved in 2 mL water and **4** (0.607 mmol) dissolved in 5 mL water is added. The mixture was filtered warm and the solution was evaporated to dryness. A yellow solid was remained. Yield 178 mg (71%). M.p. (DSC, 5 deg min-1): 156ºC (dec.); Raman: $\tilde{\nu}$ = 1601 (46), 1541 (48), 1448 (82), 1354 (56), 1286

(15), 1246 (26), 1221 (53), 1170 (19), 1147 (35), 1089 (9), 1013 (13), 1001 (3), 965 (100), 937 (11), 840 (35), 785 (9), 711 (3), 568 (4), 473 (8), 428 (4), 373 (5), 319 (5), 212 (11), 112 (40), 91 (40) cm^{-1}. IR: $\tilde{\nu}$ = 3150 (w), 2969 (w), 1737 (s), 1586 (w), 1544 (m), 1518 (m), 1454 (s), 1409 (m), 1354 (s), 1292 (w), 1270 (m), 1226 (vs), 1161 (m), 1139 (m), 1066 (m), 1010 (m), 965 (s), 911 (w), 835 (m), 775 (m), 752 (s), 734 (m), 698 (w) cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6, 25°C, ppm): δ= 10.06 (s, 6H, NH_3), 3.46 (s, 2H, OH). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6, 25 °C, ppm): δ= 122.9 (s, 2C, $C(NO_2)_2$), 160.4 (s, 2C, CC), 172.9 (s, 2C, CC$(NO_2)_2$). ^{14}N NMR (29 MHz, DMSO-d_6, 25 °C, ppm): δ= −18 (s, 4N, NO_2), −353 (s, 2N, NH_3). MS (FAB$^+$): m/z (%) = 34 $[NH_4O^+]^+$ (3). MS (FAB$^-$) m/z (%): 345 $[M\text{-}N_2O_2H_7]^-$ (66), 378 $[M\text{-}NOH_4]^-$ (4), 282 $[M\text{-}N_3H_8O_5]^-$ (12), 266 $[M\text{-}N_3H_8O_6]^-$ (7). $C_6H_8N_{10}O_{12}$ (412.19): calc. C 17.48, H 1.96, N 33.98, found: C 18.12, H 1.87, N 32.98.

*The experimental part of compounds **6–13** can be found in the Supplementary Information.*

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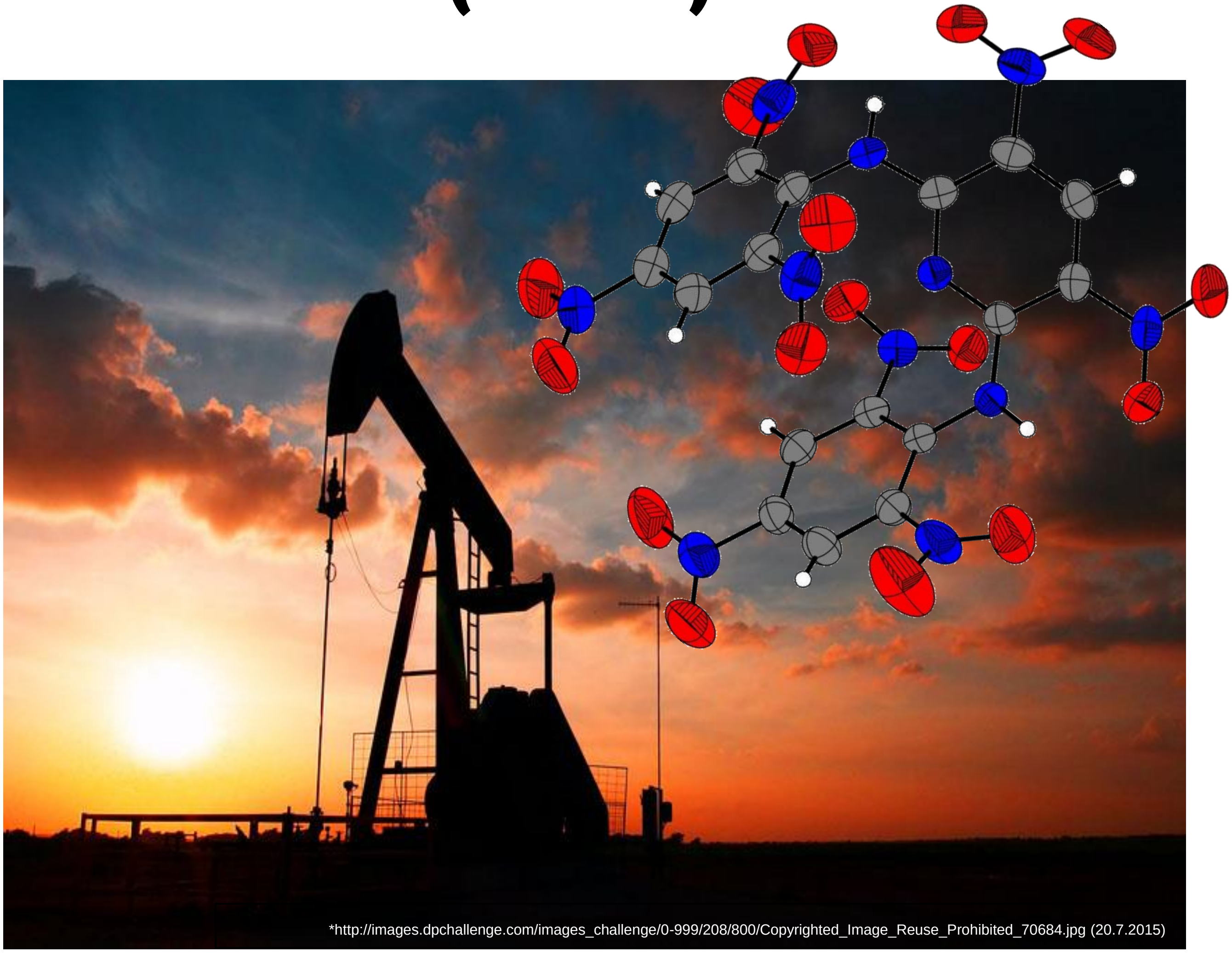
Chapter 4

2,6-Bis(picrylamino)-3,5-dinitropyridine (PYX)



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4 Studies on explosives with high thermal stabilities: 2,6-bis(picrylamino)-3,5-dinitropyridine (PYX) and its salts

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4.1 Introduction

The investigation of triamino-trinitrobenzene (TATB) by Jackson and Wing in 1888 and hexanitrostilbene (HNS) by Shipp in 1964[1] opened up a new field of explosives: Explosives with high thermal stabilities. The most characteristic feature of these explosives are the high decomposition points in the range of 300 – 350 °C. Despite its higher synthetic cost, since TATB is extremely insensitive, it is used in military applications where extreme safety is required, such as in nuclear weapons.[2-4] Hexanitrostilbene (HNS) is cheaper to synthesize and shows a high heat resistance and a wide temperature range for applications (–200 to 320 °C), however its performance is significantly lower than that of RDX (hexogen). Therefore HNS is one of today's commonly used high explosives and is used for example, in space exploration as well as for drilling deeper oil-wells.[5-7] But the search went on for new more thermal stable and powerfull explosives. With the synthesis of 2,6-bis(picrylamino)-3,5-dinitropyridine (PYX), another interesting and highly thermally stable explosive was described by Coburn in 1972.[8,9] Salt formation can increase the thermal stability. In this paper 2,6-bis(picrylamino)-3,5-dinitropyridine was investigated and the formation of salts based on 2,6-bis(picrylamino)-3,5-dinitropyridine is shown to result in an increase in the thermal stability (scheme 1).

4.2 Results and Discussion

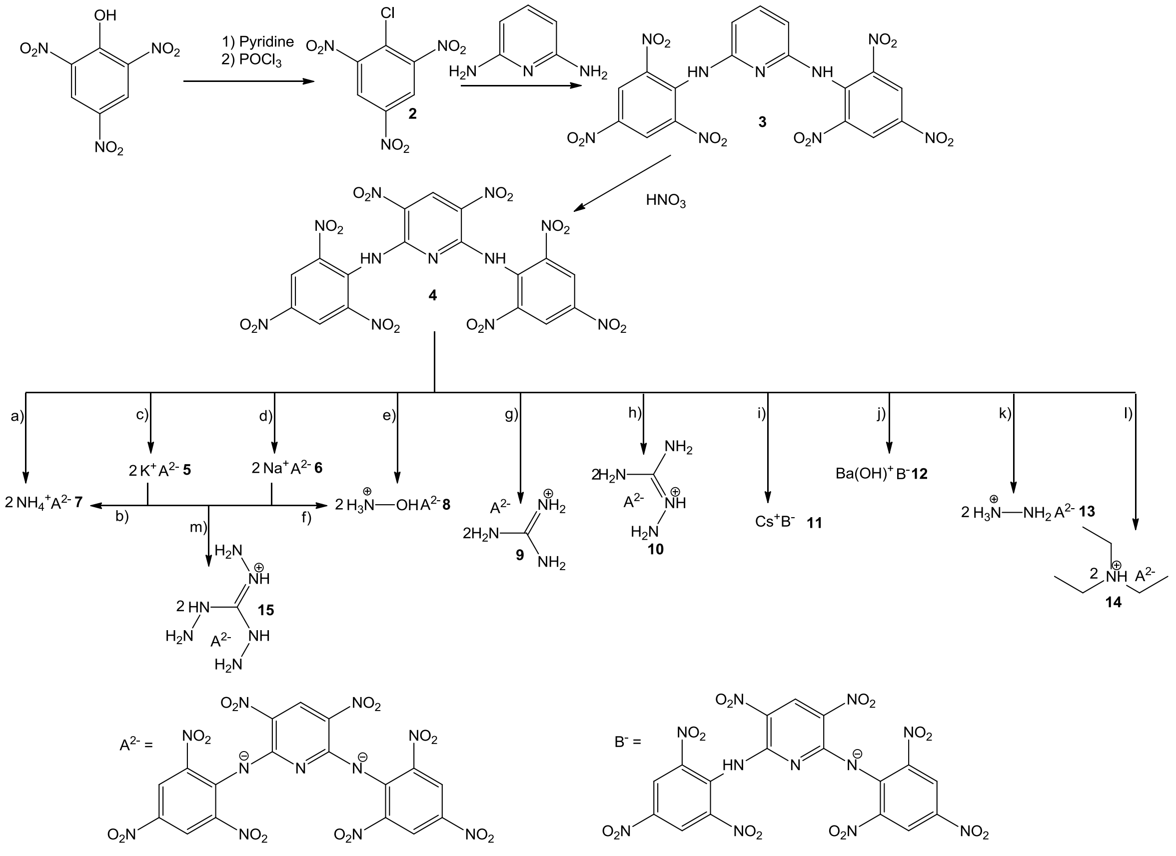
4.2.1 Synthesis

2,6-bis(picrylamino)-3,5-dinitropyridine (PYX) (**4**) was synthesized according to the literature.[8-12] Picrylchloride (**2**) was synthesized from picric acid by the literature method.[10] 2,6-bis(picrylamino)pyridine (**3**) was synthesized from the reaction of diaminopyridine with picrylchloride in DMF. 2,6-bis(picrylamino)-3,5-dinitropyridine (PYX) (**4**) was obtained by the treatment of **3** with an excess of fuming nitric acid. Reaction of **4** with bases resulted in the formation of salts containing the monoanion or dianion. All compounds were analyzed using ^{1}H, ^{13}C and ^{14}N NMR spectroscopy, mass spectrometry as well as Raman and IR spectroscopy and elemental analysis.

The eleven different nitrogen-rich and metal salts, shown in Scheme 1, which were synthesized, are the potassium (**5**), sodium (**6**), ammonium (**7**), guanidinium (**8**), aminoguanidinium (**9**), cesium (**10**), barium (**11**), hydrazinium (**12**), triethylammonium (**13**), hydroxylammonium (**14**) and triaminoguanidinium (**15**) salts.

Salts **5**, **6**, **7, 8, 11, 12, 13** and **14** were synthesized using the free bases or MOH in water or aqueous ethanol or methanol solution; salts **9** and **10** were synthesized from the corresponding carbonates and bicarbonates respectively.

Salts **15, 7** and **8** were synthesized by metathesis reactions using the respective halides.



Scheme 1: Synthesis of salts of 2,6-bis(picrylamino)-3,5-dinitropyridine (PYX) under different reaction conditions: a) aqueous NH_3, MeOH, 5h, RT; b) NH_4Cl, MetOH, 5h, RT; c) KOH, EtOH, 3h, reflux; d) NaOH, EtOH, 3h, reflux; e) hydroxylamine, EtOH, 3h, reflux; f) NH_3OHCl, water, 2h, 100 ºC; g) guanidinium carbonate, EtOH, 3h, reflux; h) aminoguanidinium bicarbonate, EtOH, 3h, reflux; i) CsOH hydrate, EtOH, 3h, reflux; j) $Ba(OH)_2$ octahydrate, EtOH, 3h, reflux, k) hydrazinium hydrate, EtOH, 3h, reflux; l) TEA, water, 5h, RT; m) triaminoguanidinium chloride, EtOH, 2h, 100 ºC.

4.2.2 Crystal Structures

The X-ray structures of compounds **3, 4, 9** and **11** were determined.

All of the compounds contain a similar 2,6-bis(picrylamino)-3,5-dinitropyridine moiety. All of the structures show similar bond lengths and angles. In each structure, the picryl moieties are twisted with respect to one other due to the pyridine moiety. Differences between the monoanion and dianion can be observed in the salt crystal structures.

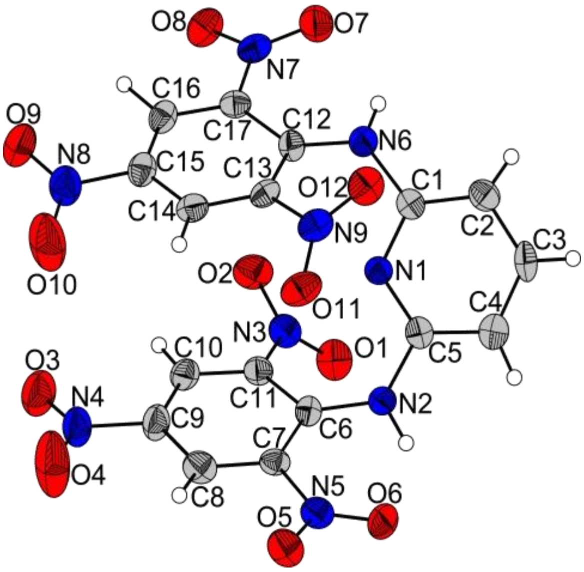


Figure 1: Molecular structure of compound 3. Thermal ellipsoids are drawn at the 50 % probability level.

Compound **3** crystallizes in the monoclinic space group $P2_1$ with four formula units in the cell and a density of 1.698 g cm^{-3}. The nitrated compound **4** crystallizes in the orthorombic space group $P2_12_12_1$ with eight formula units in the cell and a density of 1.757 g cm^{-3}.

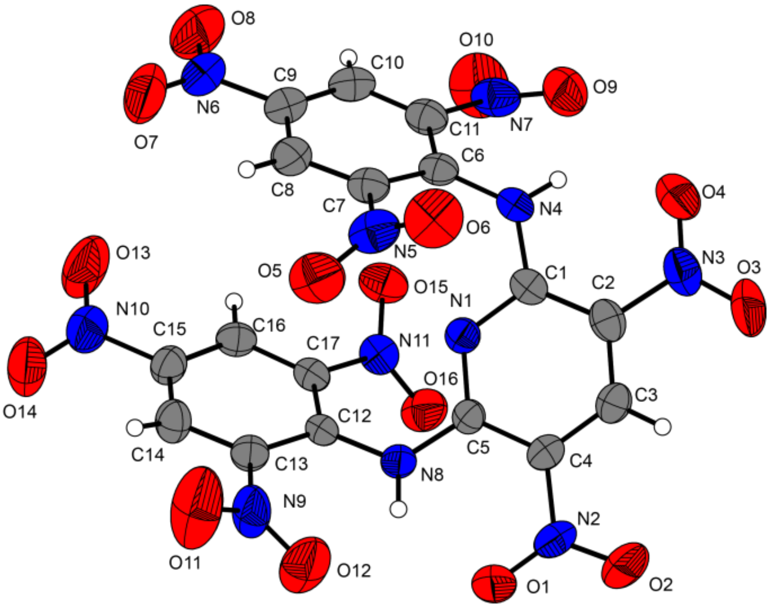


Figure 2: Molecular structure of compound 4. Thermal ellipsoids are drawn at the 50 % probability level.

Compound **9**, which could only be obtained as crystals with the inclusion of crystal water, crystallizes in the triclinic space group *P-1* with two formula units in the cell and a density of 1.714 g cm^{-3}.

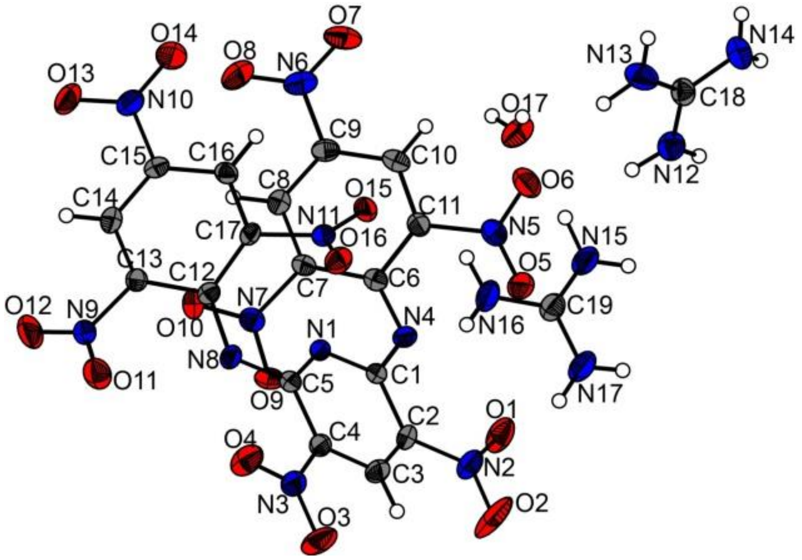


Figure 3: Molecular structure of compound 9. Thermal ellipsoids are drawn at the 50 % probability level.

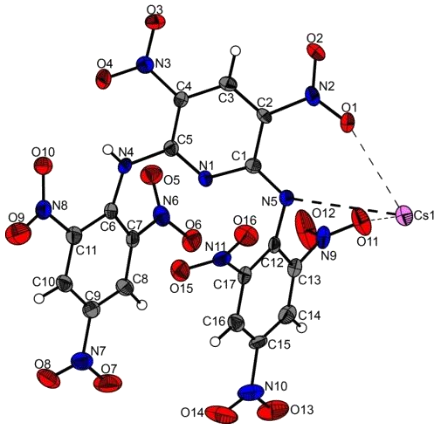


Figure 4: Molecular structure of compound 11. Thermal ellipsoids are drawn at the 50 % probability level.

Compound **11** crystalizes in the monoclinic space group $P2_1/c$ with four formular units in the cell and a density of 2.077 g cm^{-3}.

According to equation (1) an averaged coefficient of volume expansion α_V of $1.42 \cdot 10^{-4}$ K^{-1} was calculated for **4** to calculated its density at room temperature. This is similar to other energetic materials like hexogen ($1.6 \cdot 10^{-4}$ K^{-1}) published in the literature.[13]

$$\rho_{298K} = \rho_T/(1+\alpha_V(298-T_0)) \quad (1)$$

4.2.3 NMR Spectroscopy

The ^{1}H, ^{13}C and ^{14}N NMR spectra of compounds **4** – **15** were recorded in DMSO-d_6 at room temperature. The resonance in the neutral compound **4** for the C6/C12 carbon atoms of the picryl moieties is observed at 144.4 ppm and for the C1/C5 carbon atoms of the pyridine moiety at 161.2 ppm. In the salts containing the dianions, the signals of the C6/C12 carbon atoms are shifted to low field (159.5 – 151.3 ppm), while the signals of the C1/C5 carbon atoms are shifted to high field (136.4 – 130.7 ppm). In the neutral compound **4** the resonance for the carbon atoms C7/C11/C13/C17 in the picryl moiety is observed at 137.7 ppm while in the salts the resonance is shifted to low field (143.0 ppm). It is only in compounds **7** and **13** that this signal is shifted to high field (131.0 ppm). The same trend is observed for the carbon atoms C2/C4 of the pyridine moiety. In the neutral compound **4** they are located at 124.0 ppm, while in the salts the signals are shifted to low field (132.6 – 128.0 ppm). Only compound **13** shows a shift to high field (120.7 ppm) for this signal. The carbon atoms of the CH group of the picryl moiety are located at 124.0 ppm for the neutral molecule as well as for the salts. The signal for the carbon atom of the pyridine-CH group is located at 131.2 ppm in compound **4,** while for the salts it is shifted to high field (126.0 ppm). In the ^{1}H NMR spectra the signal for the protons of the picryl moiety is located at 8.86 ppm in the neutral compound **4,** while in the salts the signal is slightly shifted to high field (8.81 – 8.34 ppm). The signal is shifted to low field (9.04 ppm) only in compound **7**. The proton signal of the pyridine moiety is located at 9.15 ppm in the neutral compound and is shifted to high field (9.08 – 8.68 ppm) in the salts. The broad signal caused by the N–H hydrogen atoms is located at 11.25 ppm in the neutral compound **4** and is absent in the bianion salts as a result of the double deprotonation of **4** which has occurred. For the monoanion salts the signal is shifted slightly to high field (10.0 ppm). In the ^{14}N NMR spectra the nitro groups are observed at –15 ppm, while the amino groups are found at –370 ppm.

The NMR signals for the mono-anion compounds **11** and **12** are in the range of the neutral compound **4** for the non deprotonated moiety while for the protonated moiety the signals are in the range of the salts.

4.2.4 Sensitivities and Thermal Stability

Compounds **3** – **15** were tested for thermal capacity in DSC measurements (5 deg min^{-1}).[14] Precursor **3** exhibits a decomposition temperature of 287°C and compound **4** exhibits a substantially higher decomposition temperature of 373°C. The aminoguanidinium salt **10** exhibits the lowest decomposition temperature of the compounds which were investigated of 183°C. The other salts decompose in the range 205 – 353°C. A decomposition temperature at over 200°C is the unofficial minimum threshold value for new military explosives. With a decomposition temperature of 333°C the hydroxylammonium salt **8** shows the highest decomposition temperature of all of the nitrogenrich salts which were investigated in this work and is also slightly higher then the decomposition temperature of HNS (T$_{dec}$:310 – 330°C).

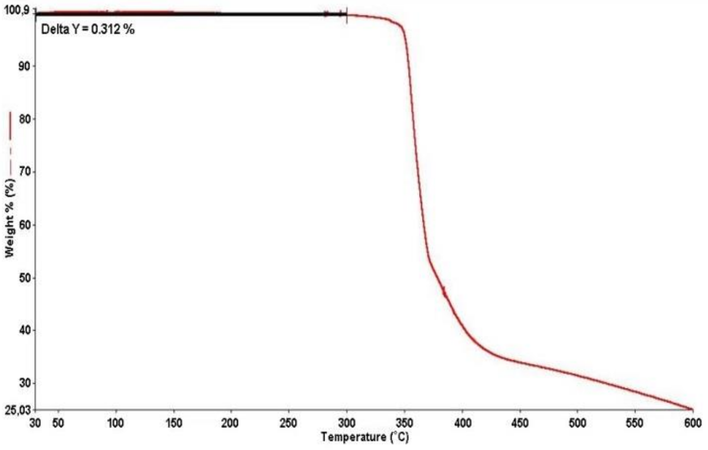


Figure 5: TGA measurement of compound

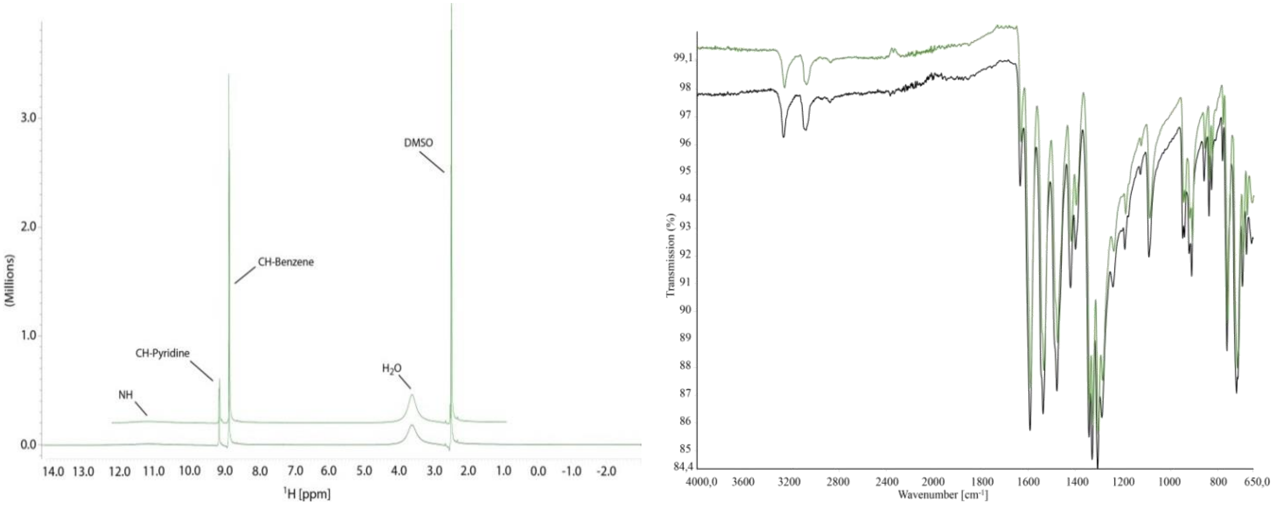


Figure 6: ^{1}H NMR spectra (left) and IR spectra (right): before and after the long time stability test for compound 4.

In addition to DSC, a TGA measurement as well as a long term stability test were performed on compound **4**. The TGA measurement showed a loss of mass of only 0.3 % for the first 300 °C. In the long term stability test, no change in the IR and ^{1}H NMR spectra (Figure 6) were observed after 100 h at 260°C. Only a change of color (yellow to brown) and a loss of mass of about 4 % were observed.

The sensitivities of the compounds towards impact and friction were explored.[15-19] Precursor **3** is declared as *sensitive* towards friction (324 N) and impact (20 J) according to the UN guidelines.[20] Compound **4** is classified as *insensitive* towards friction (360 N) and *sensitive* towards impact (10 J). Compounds **5** – **7** and **9** – **15** are declared as *insensitive* towards friction (360 N), whereas compound **8** is declared as being *sensitive* towards friction (324 N). Compounds **7**, **9** and **10** are classified as being *insensitive* (40 J), compound **14** as *less sensitive* (35 J) and compounds **5**, **6**, **8**, **11**, **12**, **13** and **15** as *sensitive* (3 – 20 J) towards impact.

The sensitivities towards electrostatic discharge were also measured for compounds **3, 4** and **13** (0.5, 0.5 and 0.35 J). For comparison, RDX has an ESD of 0.1 to 0.2 J and HNS has a ESD of 0.8 J. The ESDs of primary explosives are 1000 times higher.

Compounds **5, 6, 11** and **12** are measured as water adduct and compound **7** as methanol adduct.

4.2.5 Heat of Formation

The heats of formation were computed theoretically using the Gaussian G09 program package.[21] To obtain very accurate energies the enthalpies (*H*) were calculated by the

CBS-4M method. The enthalpies of the gas phase species M were computed according to the atomization energy method (Equation (2)) described e.g. in the literature.[22-25]

$$\Delta_f H°_{(g,M,298)} = H_{(M,298)} - \Sigma H°_{(atoms,298)} + \Sigma \Delta_f H°_{(atoms,298)} \quad (2)$$

All single values of the calculations are given in the Supporting Information. Lattice enthalpies (U_L) and lattice enthalpies (ΔH_L) were calculated from the corresponding molecular volumes (taken from low temperature X-ray structures) according to equations developed by Jenkins and Glasser.[26,27] With these values the gas phase enthalpies were converted to the solid state (standard conditions) enthalpy of formation $\Delta_f H_m°$ (Table 1). Lastly, the standard molar enthalpies of formation (ΔH_m) were calculated into the molar solid state energies of formation (ΔU_m) according to Equation (3).

$$\Delta U_m = \Delta H_m - \Delta n\, RT \quad (3)$$

(Δn is the change of mol of gaseous components)

The compound with the highest heat of formation is **15** (794.4 kJ mol^{-1}) followed by **13** (553.9 kJ mol^{-1}). All of the compounds were calculated to show positive heats of formation (i.e. are endothermic). Except compounds **14** (–92.9 kJ mol^{-1}) and **9** (–244.6 kJ mol^{-1}). In comparison, RDX has a calculated heat of formation of 70.3 kJ mol^{-1} and HNS a calculated heat of formation of 78.2 kJ mol^{-1} using the same theoretical method.

4.2.6 Detonation Parameters

Detonation parameters were calculated using the EXPLO5 V6.01 computer code.[28,29] The input for EXPLO5.06 needs the sum formula, densities and heats of formation. The calculations were performed using the maximum densities obtained form the pycnometric measurement.

The most important properties of a high explosive are its detonation velocity V_{Det}, detonation pressure p_{CJ} and energy of explosion $\Delta_{Ex}U°$. Commonly used explosives like TNT, HNS and RDX, were also calculated with the EXPLO5.06 code. (V_{Det}: TNT: 7450, HNS: 7612, RDX: 8815 ms^{-1}; p_{CJ}: TNT: 234, HNS: 243, RDX: 352 kbar; $\Delta_{Ex}U°$: TNT: −5261, HNS: −5142, RDX: −5734 kJ kg^{-1})

In terms of the detonation velocity, compounds **4**, **7**, **8**, **10**, **13** and **15** reached the detonation velocities of commonly used high thermally stable secondary explosives such as HNS. Compounds **7, 8** and **13** even exceed the calculated detonation velocity of HNS. Compounds **7** and **8** exceed the calculated detonation velocities of the neutral compound **4** (PYX), and compound **8** almost reached the 8000 ms^{-1}.

Table 1. Energetic properties and calculated detonation parameters of compounds 4, 7-10 and 13-15 as well as HNS

	HNS	**PYX (4)**	**(7)**	**(8)**	**(9)**	**(10)**	**(13)**	**(14)**	**(15)**
Formula	$C_{14}H_6N_6O_{12}$	$C_{17}H_7N_{11}O_{16}$	$C_{17}H_{13}N_{13}O_{16}$	$C_{17}H_{13}N_{13}O_{18}$	$C_{19}H_{17}N_{17}O_{16}$	$C_{19}H_{19}N_{19}O_{16}$	$C_{17}H_{15}N_{15}O_{16}$	$C_{29}H_{37}N_{13}O_{16}$	$C_{19}H_{23}N_{23}O_{16}$
FW / g mol^{-1}	450.1	621.34	655.4	687.4	739.4	769.5	685.4	823.7	829.2
IS [J] [a]	5 [30]	8	40	5	40	40	10	35	20
FS [N] [b]	240 [30]	360	360	324	360	360	360	360	360
ESD [J] [c]	0.8	1	n.d.	n.d.	n.d.	n.d.	0.35	n.d.	n.d.
N [%] [d]	18.67	24.80	27.8	26.5	32.2	34.6	30.7	22.1	38.8
Ω [%] [e]	−67.6	−55.36	−59.8	−52.4	−65.9	−65.5	−59.5	−117.5	−64.6
$T_{Dec.}$ [°C] [f]	320 [30]	373	276	333	227	183	205	276	233
ρ / g cm^{-3}[g]	1.74[30]	1.725§	1.72#	1.71#	1.62#	1.67#	1.65#	1.43#	1.62#
$\Delta_f H_m°$ [kJ mol^{-1}] [h]	78.2	43.7	273.5	382.1	−244.6	378.5	553.9	−92.9	794.4
$\Delta_f U°$ [kJ kg^{-1}] [i]	239.76	138.2	496.7	635.1	−247.1	578.8	891.3	−13.5	1050.1
EXPLO5_601 values:									
$-\Delta_{Ex}U°$ [kJ kg^{-1}] [j]	5142	4842	5176	5533	4624	4814	5376	4560	5085
T_{det} [K] [k]	3676	3624	3606	3852	3298	3341	3722	2854	3456
P_{CJ} [kbar] [l]	243	241	256	268	205	229	241	134	224
$V_{Det.}$ [m s^{-1}] [m]	7612	7644	7839	7949	7354	7672	7739	6400	7686
V_o [L kg^{-1}] [n]	602	640	676	687	712	722	713	717	760
F / kJ kg^{-1} [o]	752	788	829	899	799	820	903	696	894

[a] Impact sensitivity (BAM drophammer,[17] 1 of 6). [b] Friction sensitivity (BAM friction tester,[17] 1 of 6). [c] Electrostatic discharge device (OZM).[31] [d] Nitrogen content. [e] Oxygen balance. [f] Decomposition temperature from DSC (β = 5 °C). [g] From X-ray diffraction at 173 K or pycnometry at 298 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 [o] specific energy; § Recalculated density at 298 K. # measured by gas (He) *pycnometry at 298 K.*

To determine the energetic properties a small scale reactivity test was performed for compound **4** and the values compared to those of in comparison to HNS and TNT. Compound **4** which is thermally more stable than HNS, still has essentially the same power.

Table 2. small scale shock reactivity test

Substance	Net weight substance[mg]	Capacity SiO_2 [mg]
TNT	450	761
HNS	474	703
PYX	477	701

4.3 Conclusions

From this experimental and theoretical study the following conclusions can be drawn:

- 2,6-Bis(picrylamino)-3,5-dinitropyridine (**4**) as well as its starting materials could be synthesized in a facile and inexpensive method.
- eleven different metal and nitrogen-rich salts (potassium (**5**), sodium (**6**), ammonium (**7**), hydroxylammonium (**8**), guanidinium (**9**), aminoguanidinium (**10**), cesium (**11**), barium (**12**), hydrazinium (**13**), triethylammonium (**14**) and triaminoguanidinium (**15**)) of 2,6-bis(picrylamino)-3,5-dinitropyridine were synthesized from 2,6-bis(picrylamino)-3,5-dinitropyridine (**4**) by deprotonation, followed by metathesis reactions involving the potassium or sodium salt with the corresponding nitrogen-rich halide.
- Precursors **3** and **4** as well as salts **9** and **11** were characterized using single-crystal X-ray diffraction. The precursors show densities of 1.698 g cm^{-3} (**3**) and 1.757 g cm^{-3} (**4**), while the nitrogen-rich salt (**9**) exhibits a density of 1.714 g cm^{-3} and the cesium salt **11** a density of 2.077 g cm^{-3}. Whereas **9** contains the dianion of 2,6-bis(picrylamino)-3,5-dinitropyridine compound **11** contains only the monoanion.
- The investigated compounds show similar thermal stabilities and decompose at temperatures below 300°C (exceptions **4**, **6**, **8**, **11** and **12**). A TGA measurement

showed a loss of mass of only 0.3 % for the first 300 °C for compound **4,** and in the long term stability test (RADEX) no changes after 100 h at 260°C in the IR and ^{1}H NMR spectra were occurred.

- The impact and friction sensitivities of the precursors and salts were determined. According to UN recommendations **7**, **9** and **10** are classified as insensitive, **14** as less sensitive and **3** – **6**, **8**, **11** – **13** and **15** as sensitive towards impact. Compounds **4** – **7,** and **9** – **15** are classified as insensitive whereas **3** and **8** as sensitive towards friction.
- Based on the crystal or pycnometric densities and calculated (mostly endothermic) enthalpies of formation, several detonation parameters were calculated. Compound **4** as well as salts **7, 8** and **13** show the highest values regarding the detonation velocity (**8**: 7949 ms^{-1}). Compounds **4**, **7** and **8** also exceed the value for the detonation pressure of HNS (243 kbar). With respect to their performance data compounds **4**, **7** and **8** could be of interest as explosives with high thermal stabilities. Based on the decomposition temperature and calculated energetic properties compound **8** seems to be most promising.
- To illustrated the energetic properties a SSRT-test was undertaken for compound **4** and compared to that for HNS which showed almost the same values.

4.4 Experimental Section

CAUTION! Although we had no problems in the synthesis and handling of the compounds described in this work, they are nevertheless energetic materials with sensitivity to various stimuli. Proper protective measures (face shield, ear protection, body armor, Kevlar gloves, and earthed equipment) should be used at all times.

General Procedures and description of the analytical methods are given in the Supplementary Information. The values of the elemental analysis differ slightly due to variable numbers of solvent adduct.

2,6-Bis(picrylamino)-3,5-dinitropyridine (4)

2,6-Bis(picrylamino)-3,5-dinitropyridine was prepared according to the literature procedure.[8-12]

Preparation of potassium 2,6-bis(picrylamino)-3,5-dinitropyridine (5): 2,6-bis(picrylamino)-3,5-dinitropyridine (222.7 mg,0.36 mmol) and KOH (40.2 mg, 0.72

mmol) were dissolved in 10 mL EtOH and heated to reflux for 3 hours. After cooling and filtering the product was obtained as a red solid. Yield : 180.3 mg (0.26 mmol; 72%), red solid; M.p. (DSC, 5 deg min^{-1}): 280ºC (dec.); EA ($C_{17}H_5N_{11}O_{16}K_2$, 697.48 g/mol); found (calc.) [%]: C: 29.05 (29.27), H: 1.26 (0.72), N: 21.65 (22.09). EA ($C_{17}H_5N_{11}O_{16}K_2$*H_2O, 715.50 g/mol); found (calc.) [%]: C: 29.05 (28.85), H: 1.26 (0.99), N: 21.65 (21.53). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3084 (w), 2892 (vw), 2349 (vw), 2281 (vw), 1840 (vw), 1611 (w), 1594 (w), 1564 (m), 1528 (s), 1485 (m), 1444 (m), 1345 (m), 1321 (m), 1296 (s), 1274 (vs), 1216 (s), 1192 (s), 1168 (s), 1119 (m), 1088 (m), 961 (vw), 937 (w), 922 (m), 910 (w), 857 (vw), 846 (vw), 824 (w), 802 (vw), 780 (vw), 755 (m), 738, (vw), 730 (vw), 720 (s), 704 (vw), 678 (m). Raman (300 mW, 25 scans): $\tilde{\nu}$ [cm^{-1}] = 3084 (2), 1613 (18), 1595 (19), 1578 (34), 1535 (18), 1501 (20), 1432 (14), 1359 (58), 1343 (54), 1323 (100), 1300 (58), 1270 (34), 1243 (36), 1203 (38), 1174 (25), 1120 (21), 1081 (12), 945 (11), 827 (76), 803 (6), 753 (11), 741 (14), 720 (11), 208 (37), 189 (39), 94 (76).MS (FAB$^+$, m/z): 39.0 [K^+] (8); (FAB$^-$, m/ z): 620.6 [$C_{17}H_6N_{11}O_{16}^-$] (48), 604.0 [$C_{17}H_5N_{11}O_{16}^-{-}O$] (12), 573.5 [$C_{17}H_5N_{11}O_{16}^-{-}NO_2$] (15), 557.0 [$C_{17}H_5N_{11}O_{16}^-{-}NO_3$] (5), 511.0 [$C_{17}H_5N_{11}O_{16}^-{-}N_2O_5$] (6), 46.1 [$C_{17}H_5N_{11}O_{16}^-{-}C_{17}H_5N_{10}O_{14}$] (18). ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, ppm): δ = 8.75 (s, 1H, CH), 8.34 (s, 4H, CH).^{13}C NMR (101 MHz, DMSO-d_6, 25 °C, ppm): δ = 151.3 (2C, CN), 144.1 (2C, CNO_2), 143.0 (4C, CNO_2), 134.4 (2C, CN), 134.0 (2C, CNO_2), 124.2 (1C, CH),123.0 (4C, CH).^{14}N NMR (29 MHz, DMSO-d_6, 25 °C, ppm): δ = −32 (8N, NO_2). BAM Impact sensitivity test: 10 J; Friction sensitivity test: 360 N.

Preparation of sodium 2,6-bis(picrylamino)-3,5-dinitropyridine (6): 2,6-bis(picrylamino)-3,5-dinitropyridine (467.0 mg, 0.75 mmol) and NaOH (60.1 mg, 1.50 mmol) were dissolved in 10 mL EtOH and heated to reflux for 3 hours. After cooling and filtering the product was obtained as a bright red solid. Yield : 297.3 mg (0.45 mmol, 60 %), red solid; M.p. (DSC, 5 deg min^{-1}): 349ºC (dec.); EA ($C_{17}H_5N_{11}O_{16}Na_2$, 665.27 g/mol); found (calc.) [%]: C: 30.36 (30.69), H: 1.09 (0.76), N: 22.63 (23.16). EA ($C_{17}H_5N_{11}O_{16}Na_2$*$H_2O$, 683.28 g/mol); found (calc.) [%]: C: 30.36 (29.88), H: 1.09 (1.03), N: 22.63 (22.55). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3084 (w), 2289 (vw), 1607 (m), 1556 (m), 1520 (s), 1504 (m), 1466 (w), 1443 (w), 1413 (w), 1346 (s), 1266 (vs), 1185 (vs), 1166 (vs), 1126 (s), 1087 (s), 940 (m), 931 (m), 914 (m), 848 (w), 826 (w), 806 (vw), 782 (vw), 769 (w), 755 (m), 738 (m), 719 (vs), 678 (m). Raman (300 mW, 25 scans): $\tilde{\nu}$ [cm^{-1}] = 3088 (2), 1612 (28), 1541 (19), 1441 (14), 1368 (67), 1340 (86), 1325 (92), 1309 (57), 1292 (60), 1233 (33), 1187 (100), 1131 (20), 1091 (9), 945 (6), 916 (7), 832 (52), 769 (12), 739 (16), 720 (25), 385 (9), 190 (21), 170 (25), 85 (68).MS (FAB$^+$, m/z): 23.1 [Na^+] (3); (FAB$^-$, m/ z): 621.6 [$C_{17}H_7N_{11}O_{16}^-$] (20) , 604.0 [$C_{17}H_5N_{11}O_{16}^-{-}O$] (10), 573.5

$[C_{17}H_5N_{11}O_{16}^{-}-NO_2]$ (13), 557.0 $[C_{17}H_5N_{11}O_{16}^{-}-NO_3]$ (4), 511.0 $[C_{17}H_5N_{11}O_{16}^{-}-N_2O_5]$ (1), 46.1 $[C_{17}H_5N_{11}O_{16}^{-}-C_{17}H_5N_{10}O_{14}]$ (12).^{1}H NMR (400 MHz, DMSO-d$_6$, 25 °C, ppm): δ = 8.74 (s, 1H, CH), 8.34 (s, 4H, CH).^{13}C NMR (101 MHz, DMSO-d$_6$, 25 °C, ppm): δ = 153.5 (2C, CN), 145.6 (2C, CNO_2), 143.6 (4C, CNO_2), 134.0 (2C, CN), 131.2 (2C, CNO_2), 126.0 (1C, CH),122.9 (4C, CH).^{14}N NMR (29 MHz, DMSO-d$_6$, 25 °C, ppm): δ = −20 (8N, NO_2). BAM Impact sensitivity test: 3 J; Friction sensitivity test: 360 N

Preparation of ammonium 2,6-bis(picrylamino)-3,5-dinitropyridine (7): Methode 1 The sodium or potassium salt of 2,6-bis(picrylamino)-3,5-dinitropyridine ((5): 535.5 mg; (6) 561.5 mg, 0.81 mmol) was dissolved in 10 mL MeOH and ammonium chloride (86.1 mg, 1.61 mmol) was added to the solution. After heating to reflux for 3 hours, or stirring at room temperature for 5 h the solution was filtered and the product obtained as a brown solid. Methode 2 2,6-bis(picrylamino)-3,5-dinitropyridine (4) (1.00 g, 1.61 mmol) was dissolved in 10 mL MeOH and a ammonia solution (25% in water, 1.00 mL, 45.3 mmol) was added to the solution. After heating to reflux for 3 hours or stirring at room temperature for 5 h the solution was filtered and the product was obtained as a brown solid. Yield : 396.8 mg (0.61 mmol, 39 %), brown solid; M.p. (DSC, 5 deg min^{-1}): 276ºC (dec.); EA ($C_{17}H_{13}N_{13}O_{16}$, 654.38 g/mol), found (cal.) [%]: C: 31.99 (31.16), H: 2.07 (2.00) N: 26.64 (27.78). EA ($C_{17}H_{13}N_{13}O_{16}$*MeOH, 687.40 g/mol), found (cal.) [%]: C: 31.99 (31.45), H: 2.07 (2.49) N: 26.64 (26.49). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3436 (w), 3326 (w), 3085 (w), 1633 (m), 1580 (m), 1523 (m), 1455 (m), 1419 (m), 1346 (m), 1269 (vs), 1161 (m), 1089 (m), 1039 (m), 933 (m), 897 (m), 827 (m), 777 (w), 763 (m), 738 (m), 727 (s), 707 (m), 689 (m). Raman (300 mW, 25 scans): $\tilde{\nu}$ [cm^{-1}] = 2620 (20), 1628 (32), 1530 (38), 1338 (81), 1282 (55), 1224 (36), 1166 (33), 1092 (32), 1055 (30), 940 (42), 829 (70), 101 (135). MS (FAB^{+}, m/z): 18.0 $[NH_4^{+}]$ (10); (FAB^{-}, m/ z): 620.6 $[C_{17}H_6N_{11}O_{16}^{-}]$ (50), 604 $[C_{17}H_5N_{11}O_{16}^{-}-O]$ (14), 573.5 $[C_{17}H_5N_{11}O_{16}^{-}-NO_2]$ (17), 557 $[C_{17}H_5N_{11}O_{16}^{-}-NO_3]$ (4), 511 $[C_{17}H_5N_{11}O_{16}^{-}-N_2O_5]$ (7), 46.1 $[C_{17}H_5N_{11}O_{16}^{-}-C_{17}H_5N_{10}O_{14}]$ (23). ^{1}H NMR (400 MHz, DMSO-d$_6$, 25 °C, ppm): δ = 9.04 (s, 4H, CH), 8.98 (s, 1H, CH), 7.14 (s, 4H, NH_4). ^{13}C NMR (101 MHz, DMSO-d$_6$, 25 °C, ppm): δ = 154.7 (2C, CN), 143.6 (2C, CNO_2), 134.2 (4C, CNO_2), 132.6 (2C, CN), 128.0 (2C, CNO_2), 125.2 (1C, CH), 120.2 (4C, CH). ^{14}N NMR (29 MHz, DMSO-d$_6$, 25 °C, ppm): δ = −18 (8N, NO_2), −355 (1N, NH_4). BAM Impact sensitivity test: 40 J; Friction sensitivity test: 360 N.

Preparation of hydroxylammonium 2,6-bis(picrylamino)-3,5-dinitropyridine (8): Methode 1 The sodium salt of 2,6-bis(picrylamino)-3,5-dinitropyridine (5) (501 mg, 0.75 mmol) or the potassium salt of 2,6-bis(picrylamino)-3,5-dinitropyridine (6) (523 mg, 0.75 mmol) were dissolved in H_2O (10 mL) and hydroxyamine-chloride (103 mg, 1.50 mmol) was added. After heating to 100 °C for 2 h, the hot mixture was filtered and the product obtained as a yellow-brown solid. Methode 2 2,6-bis(picrylamino)-3,5-dinitropyridine (4) (466 mg, 0.75 mmol) was dissolved in 10 mL EtOH and hydroxylamine (1.00 mL, 36.6 mmol) was added to the solution. After heating to reflux for 3 hours or stirring at room temperature for 5 h the solution was filtered and the product obtained as a yellow-brown solid. Yield : 201.0 mg (0.29 mmol, 39 %), yellow-brown solid; M.p. (DSC, 5 deg min^{-1}): 333ºC (dec.); EA ($C_{17}H_{13}N_{13}O_{18}$, 686.38 g/mol), found (cal.) [%]: C: 29.05 (29.71), H: 1.43 (1.91), N: 26.38 (26.49). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3270 (vw), 3089 (vw), 1635 (w), 1593 (vs), 1538 (s), 1480 (s), 1422 (m), 1400 (m), 1343 (vs), 1330 (vs), 1330 (vs), 1307 (vs), 1290 (s), 1243 (m), 1193 (w), 1091 (m), 948 (m), 921 (w), 910 (m), 858 (vw), 837 (w), 826 (w), 779 (vw), 761 (m), 720 (s), 695 (m), 678 (w). Raman (300 mW, 25 scans): $\tilde{\nu}$ [cm^{-1}] = 3263 (3), 3102 (4), 1627 (62), 1605 (18), 1542 (20), 1524 (19), 1483 (12), 1357 (84), 1347 (89), 1333 (100), 1309 (43), 1293 (64), 1293 (65), 1267 (29), 1177 (14), 942 (7), 838 (27), 827 (13), 640 (6), 332 (14), 286 (13), 205 (21), 96 (38). MS (FAB^+, m/z): 33.0 [NH_3OH^+] (10); (FAB^-, m/z): 620.6 [$C_{17}H_6N_{11}O_{16}^-$] (76), 604 [$C_{17}H_5N_{11}O_{16}^-{-}O$] (23), 573.5 [$C_{17}H_5N_{11}O_{16}^-{-}NO_2$] (31), 557 [$C_{17}H_5N_{11}O_{16}^-{-}NO_3$] (10), 511 [$C_{17}H_5N_{11}O_{16}^-{-}N_2O_5$] (13), 46.1 [$C_{17}H_5N_{11}O_{16}^-{-}C_{17}H_5N_{10}O_{14}$] (27). ^1H NMR (400 MHz, DMSO-d_6, 25 °C, ppm): δ = 9.05 (s, 1H, CH), 8.85 (s, 4H, CH), 4.55 (br, s, 4H, NH_3OH). ^{13}C NMR (101 MHz, DMSO-d_6, 25 °C, ppm): δ = 149.1 (2C, CN), 145.6 (2C, CNO_2), 142.8 (4C, CNO_2), 136.4 (2C, CN), 127.3 (2C, CNO_2), 124.5 (1C, CH), 122.4 (4C, CH). ^{14}N NMR (29 MHz, DMSO-d_6, 25 °C, ppm): δ = −18 (N, NO_2), −292 (N, NH_3). BAM Impact sensitivity test: 5 J; Friction sensitivity test: 324 N.

Preparation of guanidinium 2,6-bis(picrylamino)-3,5-dinitropyridine (9): 2,6-bis(picrylamino)-3,5-dinitropyridine (4) (420.1 mg , 0.68 mmol) and guanidinium carbonate (121.8 mg, 0.68 mmol) were dissolved in 10 mL EtOH and heated to reflux for 3 hours. After cooling and filtering the product was obtained as a dark red solid. Yield : 153 mg (0.21 mmol; 61 %), red solid; M.p. (DSC, 5 deg min^{-1}): 227ºC (dec.); EA ($C_{19}H_{17}N_{17}O_{16}$, 739.4 g/mol); found (calc.) [%]: C: 30.13 (30.13), H: 2.51 (2.53), N: 31.27 (31.44). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3604 (vw), 3436 (w), 3360 (w), 3190 (w), 3080 (w), 2360 (vw), 2341 (vw),1668 (m), 1006 (w), 1540 (m), 1521 (s), 1496 (m),1464 (w), 1439 (w), 1415 (w), 1341 (m), 1267 (s), 1203 (s), 1165 (s), 1084 (m), 932 (m), 924 (m), 906 (w), 824 (w), 766 (vw), 758 (w), 718 (m), 700 (vw), 683 (w), 668 (vw). Raman (300 mW, 25 scans): $\tilde{\nu}$ [cm^{-1}] = 3087 (1), 1609 (23), 1573 (7), 1535 (17), 1469 (2), 1435 (11), 1364 (53), 1327 (100), 1230 (40), 1202 (58), 1173 (20), 1124 (18), 1087 (7), 1010 (3), 943 (3), 827 (39), 771 (8), 741 (8), 719 (8), 520 (5), 381 (7), 334 (6), 195 (9), 121 (27). MS (FAB$^+$, m/z): 60.1 [$CN_3H_6^+$] (24); (FAB$^-$, m/z): 619.5 [$C_{17}H_5N_{11}O_{16}^-$] (18), 573.5 [$C_{17}H_5N_{11}O_{16}^-{-}NO_2$] (4), 393 [$C_{17}H_5N_{11}O_{16}^-{-}C_6H_2N_4O_6$] (6), 228 [$C_{17}H_5N_{11}O_{16}^-{-}C_{11}H_3N_7O_6$] (35), 212.2 [$C_{17}H_5N_{11}O_{16}^-{-}C_{11}H_3N_8O_{10}$] (7), 46.1 [$C_{17}H_5N_{11}O_{16}^-{-}C_{17}H_5N_{10}O_{14}$] (12). ^{1}H NMR (400 MHz, DMSO-d$_6$, 25 °C, ppm): δ = 8.82 (s 1H, CH), 8.66 (s, 4H, CH), 6.90 (s, br, 6H, NH_2). ^{13}C NMR (101 MHz, DMSO-d$_6$, 25 °C, ppm): δ = 158.4 (2C, C-NH_2), 154.1 (2C, C-N), 145.3 (2C, C-NO_2), 143.1 (4C, C-NO_2), 134.5 (2C, C-N), 132.6 (2C, C-NO_2), 125.7 (1C, CH), 123.9 (4C, CH). ^{14}N NMR (29 MHz, DMSO-d$_6$, 25 °C, ppm): δ = −15 (8N, NO_2), −364 (6N, NH_2). BAM Impact sensitivity test: 40 J; Friction sensitivity test: 360 N.

*The experimental part of compounds **10–15** can be found in the Supplementary Information.*

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[20] Impact: insensitive >40 J, less sensitive ≈ 35 J, sensitive ≈ 4 J, very sensitive ≈ 3 J. Friction: insensitive > 360 N, less sensitive ≈ 360 N, sensitive < 360 N, very sensitive > 80 N, extremely sensitive > 10 N. According to the UN Recommendations on the Transport of Dangerous Goods, (+) indicates “Not safe for transport”.

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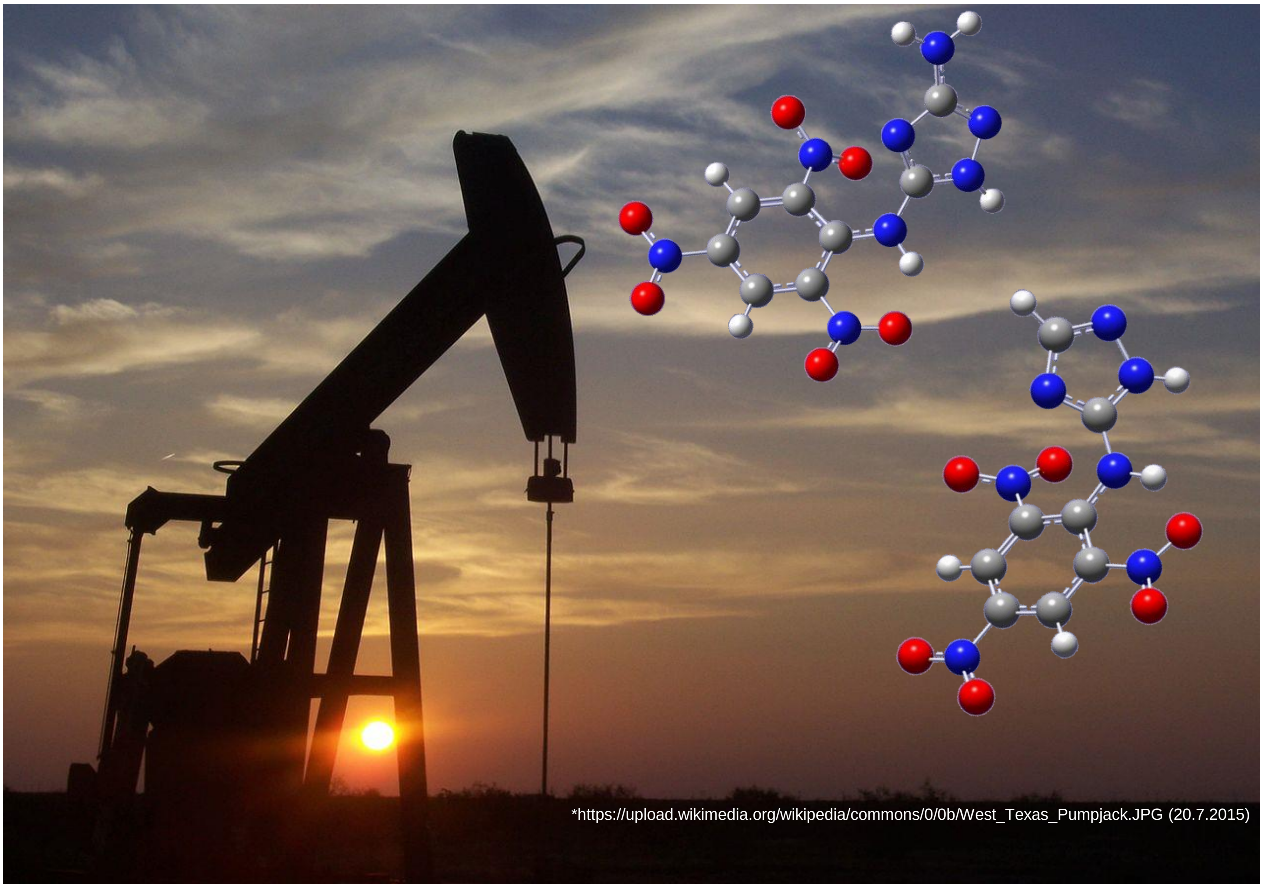
Chapter 5

3-Picrylamino-1,2,4-triazole (PATO) and 3-Amino-5-picryl-amino-1,2,4-triazole (APATO)



*https://upload.wikimedia.org/wikipedia/commons/0/0b/West_Texas_Pumpjack.JPG (20.7.2015)

5 (Picrylamino)-1,2,4-triazole derivatives: thermally stable explosives

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5.1 Introduction

Hexanitrostilbene (HNS) was developed by SHIPP in 1964[1] by treating TNT with sodium hypochlorite and is one of the today's commonly used explosives with a high thermal stability. The most characteristic aspect of high thermally stable explosives is the high decomposition point in the range of 300 – 400 ºC. Therefore HNS is used for example in space explorations as well as for drilling deeper oil-wells.[2-4] With the synthesis of 2,6-bis(picrylamino)-3,5-dinitropyridine (PYX), another interesting and high thermally stable explosive was described by Coburn in 1972.[5,6] Years before, Coburn synthesized two other interesting high thermally stable explosive: 3-(Picrylamino)-1,2,4-triazole (PATO) and 3-amino-5-(picrylamino)-1,2,4-triazole (APATO).[7,8] Both compounds consist of a nitro benzene ring and a triazole ring which are two typical building blocks for explosives. To increase the thermal stability the formation of salts is a suitable strategy. In this paper 3-(picrylamino)-1,2,4-triazole (PATO) as well as the 3-amino-5-(picrylamino)-1,2,4-triazole (APATO) were investigated and the formation of salts based on both compounds are described (scheme 1).

5.2 Results and Discussion

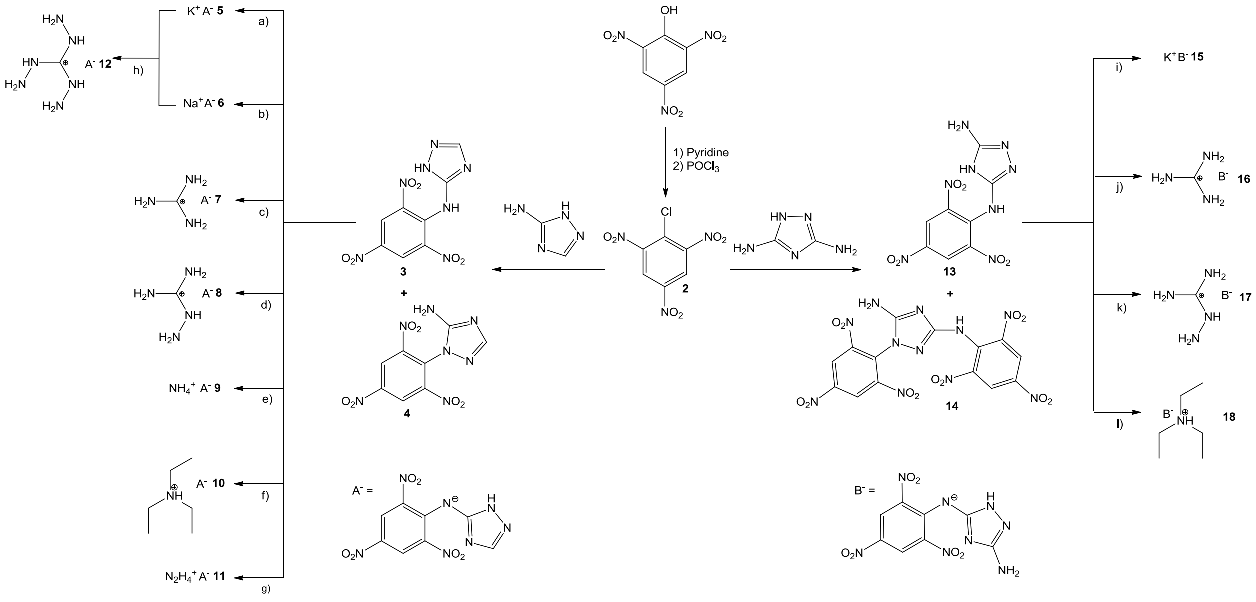
5.2.1 Synthesis

3-(Picrylamino)-1,2,4-triazole (PATO) (**3**) and 3-amino-5-(picrylamino)-1,2,4-triazole (APATO) (**13**) were synthesized according to the literature.[7,8] Picrylchloride (**2**) was synthesized from picric acid according to literature.[9] Picrylchloride was then reacted with 3-amino-1,2,4-triazole or 3,5-diamino-1,2,4-triazole in DMF to obtain 3-(picrylamino)-1,2,4-triazole (PATO) (**3**) and 3-amino-5-(picrylamino)-1,2,4-triazole (APATO) (**13**). Further more a side product **4** could be identified by XRD and NMR spectroscopy. Another side product **14** could by identified via XRD but could not be solved properly yet why it is not discussed here. Reaction of **3** and **13** with bases resulted in the formation of salts containing the anions of 3-(picrylamino)-1,2,4-triazole and 3-amino-5-(Picrylamino)-1,2,4-triazole. All compounds were analyzed using ^{1}H, ^{13}C and ^{14}N NMR spectroscopy, mass spectrometry as well as Raman and IR spectroscopy and elemental analysis.

The eight different salts, shown in Scheme **1**, which were synthesized of compound **3**, are the potassium (**5**), sodium (**6**), guanidinium (**7**), aminoguanidinium (**8**), ammonium (**9**), triethylammonium (**10**), hydroxylammonium (**11**) and triaminoguanidinium (**12**) salts. The four different salts, which were synthesized of compound **13**, are the potassium (**15**), guanidinium (**16**), aminoguanidinium (**17**) and triethylammonium (**18**) salts.

Salts **5**, **6**, **9** – **11, 15** and **18** were synthesized using the free bases or the corresponding hydroxides in water or aqueous ethanol or methanol solution. Salts **7, 8, 16** and **17** were synthesized from the corresponding carbonates and bicarbonates respectively.

Salt **12** was synthesized by metathesis reactions using the respective halide.



Scheme 1: Synthesis of ionic (picrylamino)-1,2,4-triazole derivates under different reaction conditions: a) KOH, EtOH, 3h, reflux; b) NaOH, EtOH, 3h, 70 ºC; c) guanidinium carbonate, EtOH, 1h, 70 ºC; d) aminoguanidinium bicarbonate, EtOH, 3h, 70 ºC; e) aqueous NH_3, EtOH, 3h, RT; f) TEA, EtOH, 2h, 100 ºC; g) hydrazinium hydrate, EtOH, 3h, RT; h) triaminoguanidinium chloride, EtOH, 3h, reflux; i) KOH, EtOH, 3h, 100 ºC; j) guanidinium carbonate, EtOH, 3h, 100 ºC; k) aminoguanidinium bicarbonate, MeOH, 3h, 100 ºC; l) TEA, EtOH, 3h, 100 ºC.

5.2.2 Crystal Structures

The X-ray structures of compounds **4** and **7** were determined.

All of the structures show similar bond lengths and angles. In each structure the picryl moieties are twisted with respect to the triazole ring plane.

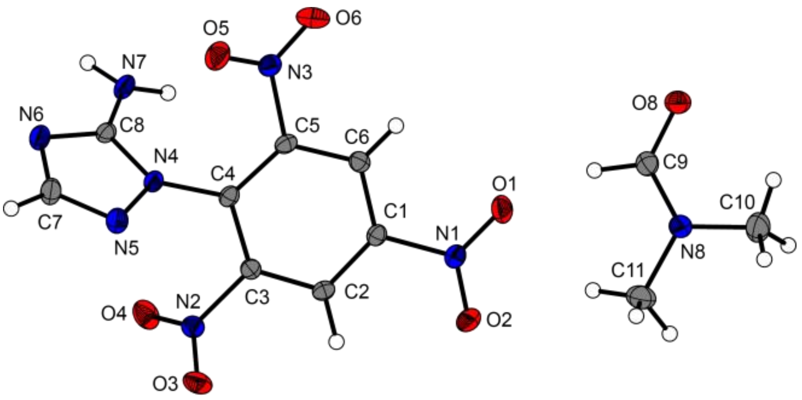


Figure 1: Molecular structure of compound 4. Thermal ellipsoids in cell crystal structures are drawn at the 50 % probability level.

Compound **4** includes one molecule of DMF in the structure and crystalizes in the triclinic space group *P*-1 with two formula units in the cell and a density of 1.557 g cm^{-3} at –100°C.

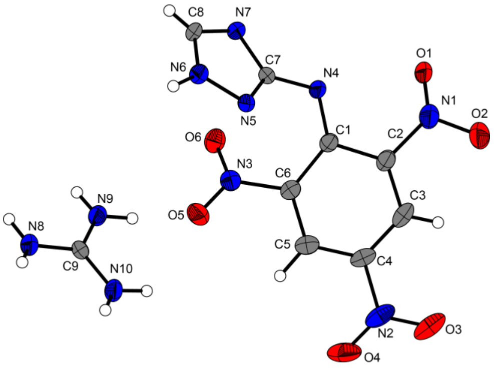


Figure 2: Molecular structure of compound 7.

Salt **7** crystallizes in the monoclinic space group *C*2/c with eight formula units in the cell and a density of 1.697 g cm^{-3} at –100°C.

According to equation (1) an averaged coefficient of volume expansion α_V of 1.42·10^{-4} K^{-1} was calculated for **7** to calculated its density at room temperature. This is similar to other energetic materials like hexogen (1.6·10^{-4} K^{-1}) published in the literature.[10]

$$\rho_{298K} = \rho_T/(1+\alpha_V(298-T_0)) \quad (1)$$

5.2.3 NMR Spectroscopy

The ^{1}H, ^{13}C and ^{14}N NMR spectra of compounds **3** – **13** and **15** – **18** were recorded in DMSO-d_6 at room temperature. The resonance in the neutral compound **3** for the carbon atom of the picryl moiety next to the bridging nitrogen is observed at 136.0 ppm while in the side product **4** the signal is observed at 128.7 ppm. In compound **13** the same carbon signal is observed at 130.1 ppm. In compound **3** the signal for the carbon atom of the triazole moiety next to the bridging nitrogen is observed at 157.9 ppm while for compound **13** the signal is located at 153.9 ppm. The signals for the carbon atoms in the picryl moieties in the corresponding salts are shifted slightly to higher fields (135.8 – 125.7 ppm) compared to compound **3**. Only in compound **6** this signal is shifted to lower fields to 141.4 ppm. The signals for the carbon atoms of the triazole moieties are observed at 161.3 – 155.7 ppm. The signals for the carbon atoms in the picryl moieties of the corresponding salts of compound **13** show a shift to low field (142.7 – 140.2 ppm) compared to compound **13**. The signals for the carbon atoms of the triazole moieties are observed between 159.5 – 148.2 ppm. In the ^{1}H NMR spectra the signal for the protons of the picryl moiety of the neutral compounds **3, 4** and **13** are located at about 8.89 ppm (**3**), 9.22 ppm (**4**) and 8.83 ppm (**13**). Salts **6, 7, 9** – **12** show signals shifted slightly to high field (8.86 – 8.40 ppm) compared to compound **3**. In salt **8** the signal show a shift to low field (9.34 ppm). Salts **15** – **18** show a shift for the signals to high field (8.70 – 8.30 ppm) compared to compound **13**, too. The broad signals caused by the N–H hydrogen atoms in the neutral compounds (**3**) and (**13**), of the bridging nitrogens, are located at 10.45 (**3**) and 11.81 ppm (**13**) and are absent in the salts. Compound **4** shows a signal for the amine group at 6.94 ppm, while the amine group in compound **13** exhibits a signal at 6.28 ppm. In the ^{14}N NMR the nitro groups can be observed at about –12 ppm while the NH groups are located at about –200 and the amino groups at about –350ppm.

5.2.4 Sensitivities and Thermal Stability

Compounds **3**–**18** were tested for thermal capacity in DSC measurements (5 deg min^{-1}).[11] Precursor **3** exhibits a melting point at 178°C and a decomposition temperature of 316°C which is slightly higher as given in literature (310°C).[7,8] Compound **4** instead exhibits a substantially lower decomposition temperature of 306°C. With a decomposition point of 143°C compound **11** exhibits the lowest decomposition point of all salts of compound **3,** which were investigated. The other salts decompose in the range of 195 – 317°C. Compound **13** decomposes at 261°C. With a decomposition point of 145°C compound **17** exhibits the lowest decomposition point of all salts of compound **13,** which were investigated. The other salts decompose in the range of 205 – 266°C. A decomposition temperature at over 200°C is the unofficial minimum threshold value for new military explosives.

The sensitivities of the compounds **3**, **5** – **13** and **15** – **18** toward impact and friction were explored.[12-16] The neutral compounds **3** and **13** are assumed as *insensitive* towards friction (360 N) and *insensitive* (**3**) and *sensitive* (**13**) toward impact (40 and 25 J) according to the UN guidelines.[17] Salts **5** – **10, 12** and **15** – **18** are assumed as *insensitive* (360 N) and compound **11** is declared as *sensitive* (288 N) toward friction.

Regarding the impact sensitivity compounds **7** – **10**, **12** and **16** – **18** are classified as *insensitive* (40 J), compounds **5**, **6** and **11** as *sensitive* (7 – 15 J) and compound **15** as *very sensitive* (3 J).

5.2.5 Heat of Formation

The heats of formation were computed theoretically using the Gaussian G09 program package.[19] To obtain very accurate energies the enthalpies (H) were calculated by the CBS-4M method. The enthalpies of the gas phase species M were computed according to the atomization energy method (Equation (2)) described e.g. in the literature.[19-22]

$$\Delta_f H^\circ_{(g,M,298)} = H_{(M,298)} - \Sigma H^\circ_{(atoms,298)} + \Sigma\Delta_f H^\circ_{(atoms,298)} \quad (2)$$

All single values of the calculations are given in the Supporting Information. Lattice enthalpies (U_L) and lattice enthalpies (ΔH_L) were calculated from the corresponding molecular volumes (taken from low temperature X-ray structures) according to equations developed by Jenkins and Glasser.[23,24] With these values the gas phase enthalpies were converted to the solid state (standard conditions) enthalpy of formation $\Delta_f H_m^\circ$ (Table 1). Lastly, the standard molar enthalpies of formation (ΔH_m) were calculated into the molar solid state energies of formation (ΔU_m) according to Equation (3).

$$\Delta U_m = \Delta H_m - \Delta n\ RT \quad (3)$$

(Δn is the change of mol of gaseous components)

The compound with the highest heat of formation is **12** (512.4 kJ mol^{-1}) followed by **11** (386.9 kJ mol^{-1}) and **8** (303.4 kJ mol^{-1}). All of the compounds were calculated to show positive heats of formation (i.e. are endotherm). In comparison, RDX has a calculated heat of formation of 70.3 kJ mol^{-1} and HNS a calculated heat of formation of 78.2 kJ mol^{-1} using the same theoretical method.

5.2.6 Detonation Parameters

Detonation parameters were calculated using the EXPLO5 V6.01 computer code.[25,26] The input for EXPLO needs the sum formula, densities and heats of formation. The calculations were performed using the densities obtained from the low temperature (173K) crystal structures recalculated to room temperature (298K) and the pycnometric measurement.

The most important properties of a high explosive are its detonation velocity V_{Det}, detonation pressure p_{CJ} and energy of explosion $\Delta_{Ex}U^\circ$. Commonly used explosives like

TNT, HNS and RDX, were also calculated with the EXPLO5_601 code. (V_{Det}: TNT: 7450, HNS: 7612, RDX: 8815 ms^{-1}; p_{CJ}: TNT: 234, HNS: 243, RDX: 352 kbar; $\Delta_{Ex}U°$: TNT: −5261, HNS: −5142, RDX: −5734 kJ kg^{-1})

In terms of the detonation velocity, compounds **3**, **7**, **8**, **9**, **11**, **13** and **17** reached the detonation velocity of commonly used high thermally stable secondary explosives such as HNS. Compounds **3**, **8**, **9** and **13** even exceed the calculated detonation velocity of HNS. The calculated salts showed lower values than the neutral compounds **3** and **13**. Only compound **9** is in the range of its neutral compound **3**. Compounds **3, 8, 9** and **13** even reached more then 8000 ms^{-1}.

Table 1. Energetic properties and calculated detonation parameters of compounds 3, 7 – 13, 16 – 18 as well as HNS

	HNS	**PATO (3)**	**(7)**	**(8)**	**(9)**	**(10)**	**(11)**	**(12)**	**APATO (13)**	**(16)**	**(17)**	**(18)**
Formula	$C_{14}H_6N_6O_{12}$	$C_8H_5N_7O_6$	$C_9H_{10}N_{10}O_6$	$C_9H_{11}N_{11}O_6$	$C_8H_8N_8O_6$	$C_{14}H_{20}N_8O_6$	$C_8H_9N_9O_6$	$C_9H_{13}N_{13}O_6$	$C_8H_6N_8O_6$	$C_9H_{11}N_{11}O_6$	$C_9H_{12}N_{12}O_6$	$C_{14}H_{21}N_9O_6$
FW / g mol^{-1}	450.1	295.17	354.2	369.26	312.2	396.15	327.1	399.29	310.19	369.09	384.10	411.16
IS / J	5 [27]	40	40	40	40	40	7	40	25	40	40	40
FS / N	240 [27]	360	360	360	360	360	288	360	360	360	360	360
ESD / J	0.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N / %	18.67	33.22	39.5	41.7	35.9	28.3	38.5	45.6	36.12	41.73	43.74	30.64
Ω / %	−67.6	−67.7	−76.8	−75.8	−71.7	−129.2	−70.9	−74.1	−67.1	−75.8	−74.9	−126.4
$T_{\text{Dec.}}$ /°C	320 [27]	316	240	209	270	263	143	195	261	205	145	266
ρ / g cm^{-3}	1.74[27]	1.94[7]	1.666§	1.80$^{\#}$	1.84$^{\#}$	1.53$^{\#}$	1.62$^{\#}$	1.59$^{\#}$	1.85 [7]	1.59$^{\#}$	1.66$^{\#}$	1.50$^{\#}$
$\Delta_f H_m$°/kJ mol^{-1}	78.2	147.1	197.5	303.4	245.9	68.6	386.9	512.4	147.4	154.8	260.6	25.9
$\Delta_f U$°/kJ kg^{-1}	239.76	573.9	648.5	915.6	875.2	279.5	1273.4	1382.6	554.9	513.1	775.0	171.4
EXPLO5_601 values:												
-$\Delta_{Ex}U$°/kJ kg^{-1}	5142	4608	4391	4619	4931	4148	5137	4850	4473	4173	4379	3933
T_{det} / K	3676	3185	3037	3050	3247	2537	3462	3229	3142	2947	2989	2460
P_{CJ} / kbar	243	313	211	268	289	158	220	208	278	185	214	151
$V_{Det.}$ / m s^{-1}	7612	8477	7543	8302	8400	6937	7640	7597	8178	7209	7657	6802
V_o / L kg^{-1}	602	624	732	742	697	716	745	782	664	753	764	731
F / kJ kg^{-1}	752	675	756	769	769	618	877	859	709	755	777	611

[a] Impact sensitivity (BAM drophammer,[14] 1 of 6). [b] Friction sensitivity (BAM friction tester,[14] 1 of 6). [c] Electrostatic discharge device (OZM).[28] [d] Nitrogen content. [e] Oxygen balance. [f] Decomposition temperature from DSC (β = 5°C). [g] From X-ray diffraction at 173 K or pycnometry at 298 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 [o] specific energy; § Recalculated to 298 K. $^{\#}$ measured by gas (He) pycnometry at 298 K.

5.3 Conclusions

From this experimental and theoretical study the following conclusions can be drawn:

- The neutral compounds 3-(picrylamino)-1,2,4-triazole (**3**) and 3-amino-5-(picrylamino)-1,2,4-triazole (**13**) as well as its starting materials could be synthesized in a facile and inexpensive method. Also two interesting side products could be identified.

- Eight different salts (potassium (**5**), sodium (**6**), guanidinium (**7**), aminoguanidinium (**8**), ammonium (**9**), triethylammonium (**10**), hydrazinium(**11**) and triaminoguanidinium (**12**)) of 3-(picrylamino)-1,2,4-triazole were synthesized from 3-(picrylamino)-1,2,4-triazole (**3**) by deprotonation, followed by metathesis reactions involving the potassium or sodium salt with the corresponding nitrogen-rich halide.

- Four different salts (potassium (**15**), guanidinium (**16**), aminoguanidinium (**17**) and triethylammonium (**18**)) of 3-amino-5-(picrylamino)-1,2,4-triazole were synthesized from 3-amino-5-(picrylamino)-1,2,4-triazole (**13**) by deprotonation.

- Two different side products **4** as well as salt **7** were characterized using single-crystal X-ray diffraction. The side product shows a density of 1.557 g cm^{-3} (**4**) while the nitrogen rich salt (**7**) exhibits a density of 1.697 g cm^{-3}.

- The investigated compounds show similar thermal stabilities and decompose at temperatures below 300°C (exception compound **3**).

- The impact and friction sensitivities of the precursors and salts were determined. According to UN recommendations **3, 5** – **10, 12, 13** and **15** – **18** are classified as insensitive and **11** as sensitive towards friction. Towards impact **3, 7** – **10, 12** and **16** – **18** are classified as insensitive, **5, 6** and **13** as sensitive or **15** as very sensitive.

- Based on the crystal or pycnometric densities and calculated (all endothermic) enthalpies of formation, several detonation parameters were calculated. Compounds **3, 8, 9** and **13** show the highest values regarding the detonation velocity (**3**: 8477 ms^{-1}). Compounds **3, 8, 9** and **13** also exceed the value for the detonation pressure of HNS (243 kbar). With respect to their performance data compounds **3, 8, 9** and **13** could be of interest as explosive with high thermal stabilities. Based on the decomposition temperature and calculated energetic properties compound **3** seems to be most promising.

5.4 Experimental Section

CAUTION! Although we had no problems in the synthesis and handling of the compounds described in this work they are nevertheless energetic materials with sensitivity to various stimuli. Proper protective measures (face shield, ear protection, body armor, Kevlar gloves, and earthed equipment) should be used at all times.

General Procedures and description of the analytical methods are given in the Supplementary Information. The values of the elemental analysis differ slightly due to variable numbers of solvent adduct.

Picryl chloride (2)

Picryl chloride was prepared according to the literature procedure.[12]

Synthesis of 3-(Picrylamino)-1,2,4-triazole (3) and 1-(2,4,6-trinitrophenyl)-1H-1,2,4-triazol-3-amine (4)

A mixture of 5-Amino-1,2,4-triazole (570.0 mg, 6.79 mmol) and Picrylchloride (1.68 g, 6.79 mmol) in 50 mL DMF was stirred for 5 h at 100°C. After cooling and pouring into ice water the yellow solid was filtered. The product mixture was dissolved in $CHCl_3$, filtered and product **3** could be obtained as bright yellow solid while product **4** was in solution. After evaporating product **4** could be obtained as light orange-brown solid. Yield (complete): 1.64 mg (82%); EA ($C_8H_5N_7O_6$, 295.17 g/mol); found (calc.) [%]: C: 32.75 (32.55), H: 1.75 (1.71), N: 33.45 (33.22). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3443 (m), 3338 (m), 3250 (m), 3170 (m), 3139 (m), 3087 (s), 2865 (m), 2360 (w), 2337 (w), 1858 (w), 1712 (w), 1697 (m), 1644 (s), 1615 (s), 1592 (s), 1520 (vs), 1427 (s), 1401 (m), 1389 (m), 1335 (vs), 1311 (s), 1292 (s), 1275 (s), 1254 (s), 1234 (vs), 1202 (s), 1168 (s), 1092 (s), 1051 (m), 979 (s), 958 (m), 949 (m), 942 (m), 924 (s), 919 (s), 858 (s), 824 (m), 815 (m), 785 m), 779 (m), 766 (m), 740 (m), 732 (s), 717 (s), 712 (vs), 667 (s), 660 (s). Raman (300 mW, 25 Scans): $\tilde{\nu}$ [cm^{-1}] = 2939 (5), 1621 (25), 1576 (13), 1548 (26), 1497 (8), 1434 (6), 1402 (12), 1350 (100), 1315 (32), 1294 (33), 1206 (6), 1175 (13), 1094 (5), 1018 (3), 981 (4), 945 (10), 867 (5), 825 (17), 735 (4), 663 (3), 393 (7), 337 (11), 290 (7), 238 (10), 202 (20), 161 (24), 96 (57). MS (DEI^+, m/z): 295.2 [M^+] (100), 249.2 [M^+-NO_2] (21), 229 [$M^+-C_2HN_3$] (30), 212 [$M^+-C_2H_3N_4$] (30), 203 [$M^+-(NO_2)_2$] (20), 84 [$M^+-C_6O_6N_3$] (16). **(3)** Yield: 1.06 g (53%), yellow solid; M.p. (DSC, 5 deg min^{-1}): 178 ºC (melt.), 316ºC (dec.); ^1H NMR (400 MHz, DMSO-d_6, 25°C, ppm): δ = 13.83 (s, 1 H, NH), 10.45 (s, 1 H, NH), 8.89 (s, 2 H, CH), 8.35 (s, 1 H, C H). ^{13}C NMR (101 MHz, DMSO-d_6, 25°C, ppm): δ = 157.9 (1 C, C-N), 144.0 (1 C, N-C-N), 140.4 (2 C, C-NO_2), 138.0 (1

C,C-NO_2), 136.0 (1 C, C-NH), 126.6 (2 C, C-H). ^{14}N NMR (29 MHz, DMSO-d_6, 25°C, ppm): δ = −12 (1N, *N*O_2), −269 (2N, *N*H). BAM Impact sensitivity test: 40 J; Friction sensitivity test: 360 N. **(4)** Yield: 560 mg (28%), orange brown solid; M.p. (DSC, 5 deg min^{-1}):, 306ºC (dec.); ^1H NMR (400 MHz, DMSO-d_6, 25°C, ppm): δ = 9.22 (s, 2 H, C-H), 7.66 (s, 1 H, C-H), 6.94 (s, 2 H, -NH2). ^{13}C NMR (101 MHz, DMSO-d_6, 25°C, ppm): δ = 162.8 (1 C, C-NH_2), 157.2 (1 C, N-C-N), 147.5 (1 C, C-NO_2), 147.1 (2 C,C-NO_2), 128.7 (1 C, C-N), 125.1 (2 C, C-H). ^{14}N NMR (29 MHz, DMSO-d_6, 25°C, ppm): δ = −10 (1N, *N*O_2), −349 (1N, *N*H_2).

Synthesis of guanidinium-3-(Picrylamino)-1,2,4-triazole (7)

3-(Picrylamino)-1,2,4-triazole (**3**) (415 mg, 1.4 mmol) was dissolved in 10 mL EtOH and guanidinium carbonate (127.1 mg, 0.71mmol) was added. The mixture was heated for 1h at 70°C. After cooling and evaporating the solvent, product (**7**) could be obtained as a dark red solid. Yield: 395.0 mg (1.11 mmol, 79 %), dark red solid; M.p. (DSC, 5 deg min^{-1}): 240ºC (dec.); EA ($C_9H_{10}N_{10}O_6$, 354.24 g/mol); found (calc.) [%]: C: 30.51 (30.52), H: 3.06 (2.85), N: 38.77 (39.54). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3473 (w), 3408 (m), 3254 (m), 3202 (m), 3084 (w), 2806 (w). 2360 (w), 2341 (w), , 1651 (s) 1607 (m), 1558 (s), 1476 (m), 1427 (m), 1386 (w), 1363 (m), 1318 (s), 1247 (s), 1159 (m), 1112 (m), 1077 (m), 1008 (w), 966 (w), 932 (m), 910 (m), 882 (w), 838 (w), 823 (w), 789 (m), 744 (m), 712 (s), 668 (w). Raman (300 mW, 25 Scans): $\tilde{\nu}$ [cm^{-1}] = 3394 (2), 3264 (2), 3142 (2), 3082 (2), 2855 (2), 1803 (3), 1529 (57), 1500 (37), 1441 (7), 1339 (49), 1296 (100), 1270 (93), 1187 (7), 1083 (7), 1010 (10), 976 (4), 944 (10), 870 (82), 821 (32), 741 (10), 713 (6), 532 (10), 496 (8), 458 (7), 338 (13), 239 (15), 117 (42). MS (FAB^+, m/z): 60.1 [$CH_6N_3^+$] (70) ; (FAB^-, m/ z): 294.0 [$C_8H_4N_7O_6^-$] (100) , 228.0 [$C_8H_4N_7O_6^-$−$C_2H_2N_3$] (10), 199 [$C_8H_4N_7O_6^-$−$C_2H_2N_4O$] (60), 151 [$C_8H_4N_7O_6^-$−$C_2H_2N_5O_3$] (60), 122 [$C_8H_4N_7O_6^-$−$C_2H_2N_6O_4$] (10), 46 [$C_8H_4N_7O_6^-$−$C_8H_4N_6O_4$] (7). ^1H NMR (400 MHz, DMSO-d_6, 25°C, ppm): δ = 12.77 (s, 1 H, NH), 8.40 (s, 2 H, CH), 7.42 (s, 1 H, CH); 6.90 (s, 6 H, -NH_2). ^{13}C NMR (101 MHz, DMSO-d_6, 25°C, ppm): δ = 160.0 (1C, C-NH_2), 158.5 (1 C, C-N), 149.5 (1 C, C-H), 145.8 (2 C, C-NO_2), 141.4 (1C,C-NO_2), 125.8 (1 C,C-N), 124.3 (2 C, C-H). ^{14}N NMR (29 MHz, DMSO-d_6, 25°C, ppm): δ = −14 (3N, *N*O_2), −187 (1N, NH), −366 (1N, *N*H_2). BAM Impact sensitivity test: 40 J; Friction sensitivity test: 360 N.

Synthesis of ammonium-3-(Picrylamino)-1,2,4-triazole (9)

3-(Picrylamino)-1,2,4-triazole (**3**) (500 mg, 1.69 mmol) was dissolved in 10 mL ethanol and an aqueous ammonia solution (1.00 mL, 45.3 mmol, 25% in water) was added. The mixture was stirred for 3 h at room temperature. After cooling the mixture was filtered and the solvent was removed. The product could be obtained as a brown solid. Yield: 323.0 mg (1.03 mmol; 64 %), brown solid; M.p. (DSC, 5 deg min^{-1}): 270ºC (dec.); EA ($C_8H_8N_8O_6$, 312.20 g/mol), found (cal.) [%]: C: 31.73 (30.78), H: 2.32 (2.58), N: 34.73 (35.89). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3434 (m), 3321 (m), 3085 (w), 1620 (m), 1591 (s), 1523 (vs), 1454 (m), 1419 (m), 1348 (s), 1269 (vs), 1235 (vs), 1163 (m), 1090 (m), 1044 (m), 980 (m), 933 (m), 898 (m), 828 (m), 777 (m), 737 (s), 728 (s), 710 (s), 684 (m). Raman (300 mW, 25 scans): $\tilde{\nu}$ [cm^{-1}] = 1632 (15), 1530 (43), 1340 (100), 1167 (16), 1093 (6), 942 (13), 823 (21), 711 (6), 341 (10), 86 (40). MS (FAB$^+$, m/z): 18.1 [NH_4^+] (20); (FAB$^-$, m/z): 294.3 [M$^-$] (89), 278 [M$^-$−O] (25), 247 [M$^-$−NO_2] (13), 228 [M$^-$−$C_2H_2N_3$] (22), 212 [M$^-$−$C_2H_2N_4$] (7), 46.1 [M$^-$−$C_8H_4N_6O_4$] (34). ^{1}H-NMR (400 MHz, DMSO-d_6, 25°C, ppm): δ = 9.05 (s, 2H, CH), 8.86 (s, 1H, CH), 8.26 (s, 1H, NH), 7.69 (s, br,4H, NH_4). ^{13}C-NMR (101 MHz, DMSO-d_6- 25°C, ppm): δ = 155.7 (1C, C-N), 145.1 (1C, C-H), 143.6 (2C, C-NO_2), 140.3 (1C, C-NO_2), 134.2 (1C,C-N), 125.5 (2C, C-H). ^{14}N NMR (29 MHz, DMSO-d_6, 25°C, ppm): δ = −15 (N, NO_2), −271 (N, NH), −364 (N, NH_4). BAM Impact sensitivity test: 40 J; Friction sensitivity test: 360 N.

Synthesis of 3-Amino-5-picrylamino-1,2,4-triazole (13)

A mixture of 3,5-Diamino-1,2,4-triazole (2.00 g, 20.2 mmol) and picrylchloride (5.00 g, 20.2 mmol) in 20 mL DMF was stirred for 5 h at 100°C. After cooling and pouring into ice water a orange solid was filtered. The product mixture was dissolved in ethanol, filtered and product **13** could be obtained as orange solid, while product **14** was still in solution. Yield: 3.65 g (11.7 mmol, 58 %), orange solid; M.p. (DSC, 5 deg min^{-1}):, 261ºC (dec.); EA ($C_8H_6N_8O_6$, 310.19 g/mol), found (cal.) [%]: C: 30.40 (30.98), H: 2.14 (1.95), N: 36.20 (36.12). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3471 (w), 3389 (w), 3265 (vw), 3090 (w), 2094 (m), 1675 (w), 1624 (m), 1575 (m), 1553 (m), 1534 (s), 1515 (vs), 1449 (w), 1411 (w), 1395 (w), 1347 (vs), 1297 (m), 1284 (m), 1174 (w), 1096 (vw), 1082 (m), 927 (m), 863 (vw), 829 (vw), 756 (w), 734 (s), 718 (m). Raman (300 mW, 25 Scans): $\tilde{\nu}$ [cm^{-1}] = 3088 (6), 2218 (5), 2124 (5), 1623 (27), 1583 (12), 1556 (27), 1540 (27), 1397 (11), 1351 (100), 1300 (56), 1283 (40), 1175 (23), 1086 (9), 946 (17), 830 (30), 735 (8), 375 (26), 337 (33), 278 (28), 205 (47), 121 (90), 92 (92). MS (DEI$^+$, m/z): 310.1 [M$^+$] (10), 264.1 [M$^+$−NO_2] (10), 228.0 [M$^+$−$C_2H_3N_4$] (90), 213.1 [M$^+$−$C_2H_3N_5$] (80),198.3 [M$^+$−$C_2H_3N_5O$] (45), 136.1 [M$^+$−$C_2H_3N_6O_4$] (14), 120.1 [M$^+$−$C_2H_2N_7O_4$] (20), 73.1 [M$^+$−$C_2H_4N_8O_4$] (90), 44.1 [M$^+$−$C_8H_6N_7O_4$] (60). ^{1}H NMR (400 MHz, DMSO-d_6, 25°C, ppm): δ = 11.81 (br, s, 1H, NH), 10.21 (br, s, 1H, NH), 8.83 (s, 2H, CH), 6.28 (br, s, 2H, NH_2). ^{13}C NMR (101 MHz, DMSO-d_6, 25°C, ppm): δ = 160.7 (1C, C-NH_2), 153.9 (1C, C-N), 142.6 (2C, C-NO_2), 139.8 (1C, C-NO_2), 130.1 (1C, C-N), 125.7 (2C, CH). ^{14}N NMR (29 MHz, DMSO-d_6, 25°C, ppm): δ = −9 (3N, NO_2), −235 (2N, NH), −322 (1N, NH_2). BAM Impact sensitivity test: 25 J; Friction sensitivity test: 360 N.

Synthesis of guanidinium-3-Amino-5-picrylamino-1,2,4-triazole (16)

3-Amino-5-picrylamino-1,2,4-triazole (**13**) (420.0 mg, 1.35 mmol) was dissolved in 10 mL ethanol and guanidinium carbonate (243.96 mg, 1.35 mmol) was added. The mixture was stirred for 3 h at 100°C. After cooling, filtering and evaporating the solvent, product (**16**) could be obtained as a dark red solid. Yield: 476 mg (1.29 mmol, 95%), red solid; M.p. (DSC, 5 deg min^{-1}):, 205ºC (dec.); EA ($C_8H_5N_7O_6$, 369.25 g/mol); found (calc.) [%]: C: 27.69 (29.27), H: 3.79 (3.00), N: 39.64 (41.73). EA ($C_8H_5N_7O_6$*H_2O); found (calc.) [%]:C: 27.69 (27.91), H: 3.79 (3.38), N: 39.64 (39.78). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3329 (m), 3090 (m), 2770 (m), 1656 (s), 1601 (m), 1536 (s), 1427 (w), 1380 (m), 1343 (vs), 1256 (vs), 1164 (vs), 1077 (s), 918 (M), 879 (m), 801 (S), 737 (m), 718 (s), 665 (s). Raman (300 mW, 25 Scans): $\tilde{\nu}$ [cm^{-1}] = 3091 (2), 2116 (2), 1542 (64), 1486 (30), 1341 (72), 1306 (87), 1279 (100), 1167 (14), 1083 (13), 1009 (8), 949 (12), 868 (4), 823 (55), 727 (17), 507 (12), 390 (10), 328 (6), 229 (11), 97 (39). MS (FAB$^+$, m/z): 60.1 [G^+] (22); (FAB$^-$, m/z): 309.1 [M^-] (26), 228.0 [$M^- - C_2H_3N_4$] (10), 199.3 [$M^- - C_2H_3N_5O$] (45), 168.2 [$M^- - C_2HN_5O_3$] (50), 153.2 [$M^- - C_2HN_6O_3$] (50), 122 [$M^- - C_2H_3N_7O_4$] (22), 46 [$M^- - C_8H_5N_7O_4$] (38). ^{1}H NMR (400 MHz, DMSO-d_6, 25°C, ppm): δ = 8.68 (br, s, 1H, NH), 8.35 (s, 2H, CH), 7.29 (br, s, 6H, NH_2), 4.96 (br, s, 2H, NH_2). ^{13}C NMR (101 MHz, DMSO-d_6, 25°C, ppm): δ = 162.8 (1C, C-NH_2), 159.5 (1C, C-N), 158.4 (1C, C-NH_2), 144.5 (2C,C-NO_2), 142.7 (1C, C-N), 141.1 (1C, C-NO_2), 124.2 (1C, C-H). ^{14}N NMR (29 MHz, DMSO-d_6, 25°C, ppm): δ = −15 (3N, NO_2), −181 (1N, NH), −370 (4N, NH_2) . BAM Impact sensitivity test: 40 J; Friction sensitivity test: 360 N.

*The experimental part of compounds **5, 6, 8, 10–12, 15, 17** and **18** can be found in the Supplementary Information.*

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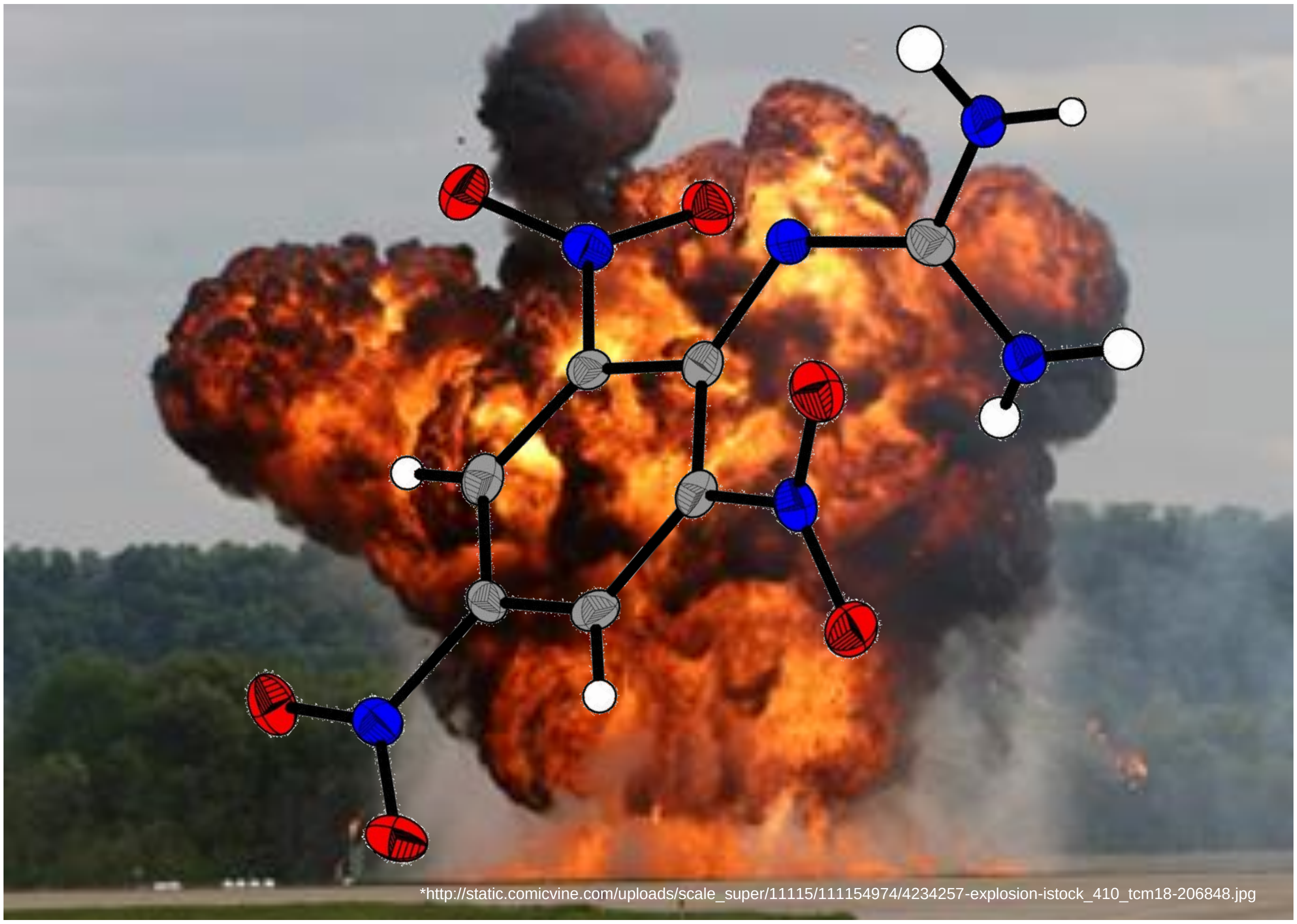
Chapter 6

Picrylguanidine (PCG)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6 Studies on energetic salts based on (2,4,6-trinitrophenyl)guanidine

Thomas M. Klapötke, Frank Mieskes, Jörg Stierstorfer and Michael Weyrauther

Submitted to Propellants, Explosives, Pyrotechnics

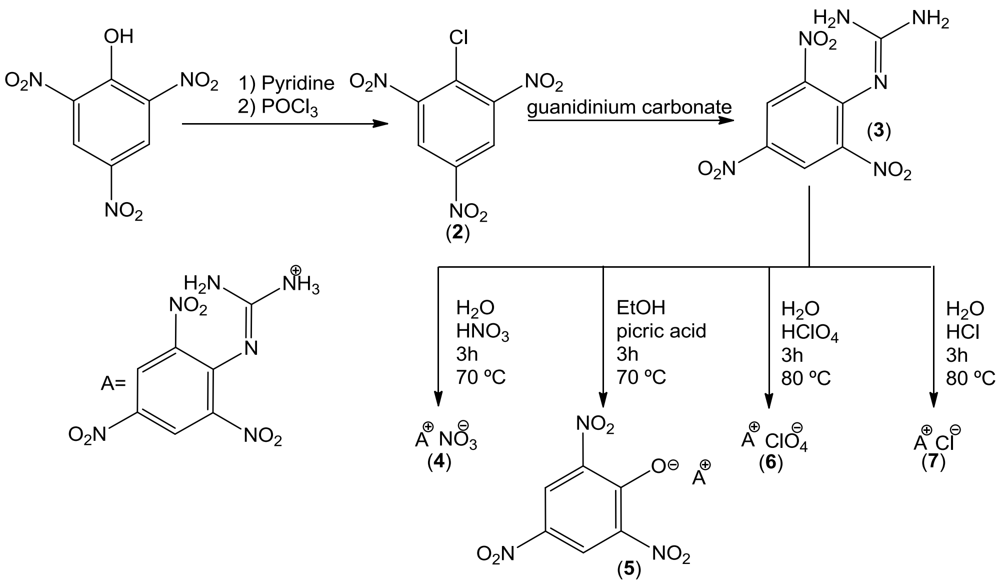
6.1 Introduction

Most of the today used secondary explosives consist of heterocycles like triazoles[1,2] or tetrazoles[3] but also nitron benzenes have a wide range of applications. Some examples for those explosives are trinitrotoluene (TNT), picric acid or hexanitrostilbene (HNS). HNS, invented by Shipp in 1964[4] by threating TNT with sodium hypochlorite, has a high conjugated system which results in a higher thermal stability than for its parental monomer TNT or RDX (HNS: 320°C; TNT: 295°C; RDX: 210°C). Unfortunately its energetic performances are significant lower compared to RDX which has a higher nitrogen content why HNS never found its way to a military explosive. A compound which could combine both advantages is the (2,4,6-Trinitrophenyl)guanidine.[5] With a high conjugates system as well as high nitrogen content it could be a good replacement for HNS and RDX. With salt formation the thermal stability could be increased, too. In this paper the properties of (2,4,6-Trinitrophenyl)guanidine were investigated using several methods. The formation of salts of (2,4,6-trinitrophenyl)guanidine is reported to result in compounds with higher thermal stabilities than that of (2,4,6-trinitrophenyl)guanidine (scheme 1).

6.2 Results and Discussion

6.2.1 Synthesis

Picrylchloride (**2**) was synthesized according to the literature procedure.[6] (2,4,6-Trinitrophenyl)guanidine (**3**) was obtained using a similar method of that described in the literature by treating **2** with an excess of guanidinium carbonate in ethanol.[5] Reaction of **3** with various acids resulted in protonation of (**3**) and the formation of the corresponding salts. The salts could be synthesized by using the free acid in aqueous ethanol solution or just water. Four different salts containing the (2,4,6-trinitrophenyl)guanidinium cation, shown in Scheme 1, were synthesized. These are the nitrate (**4**), picrate (**5**), perchlorate (**6**) and chloride (**7**) salts. The compounds were investigated using ^{1}H, ^{13}C and ^{14}N NMR spectroscopy, mass spectrometry as well as Raman and IR spectroscopy and elemental analysis.



Scheme 1: Synthesis of salts containing the (2,4,6-Trinitrophenyl)guanidinium cation by protonation of (3) using various BrØsted acids.

6.2.2 Crystal Structures

The X-ray structures of compounds **4** – **7** were determined.

The structure of the neutral parent compound (2,4,6-Trinitrophenyl)guanidine has been described previously in the literature.[5]

All of the salts (**4** – **7**) contain the protonated form of the (2,4,6-Trinitrophenyl)guanidine cation. In structures (**4** – **7**) very similar bond lengths and angles are observed for the cation. In each structure the guanidinium layer is twisted to the benzene layer. A detailed comparison is given in the Supplementary Information in Table S2.

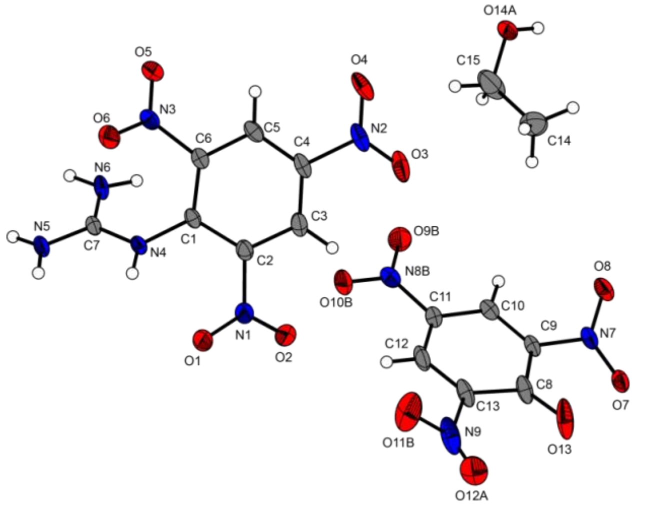


Figure 1: Molecular structure of compound 5 Thermal ellipsoids are drawn at the 50 % probability level.

Compound **5** was only obtained as crystalline material with the inclusion of ethanol in the crystal lattice, and has a low density of 1.664 g cm^{-3}.

Compounds **4**, **6** and **7** all crystallize in the orthorhombic space group *Pbca* and show high densities of 1.819 g cm^{-3} (**4**), 1.854 g cm^{-3} (**6**) and 1.796 g cm^{-3} (**7**), respectively. All densities of **4**, **6** and **7** are higher than the density of the neutral compound (2,4,6-Trinitrophenyl)guanidine (1.794 g cm^{-3}).[5]

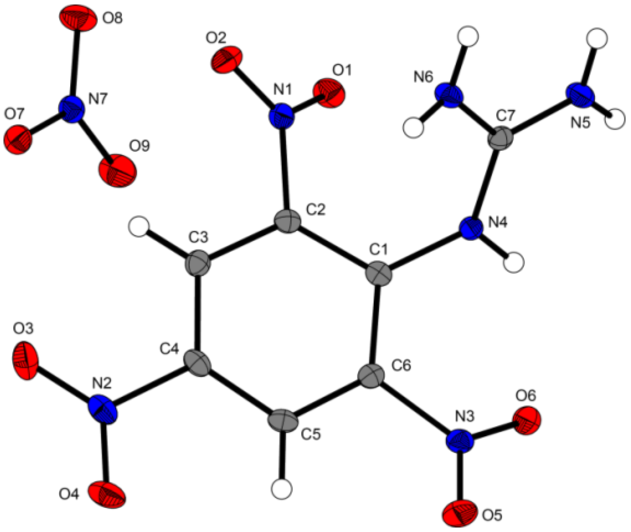


Figure 2: Molecular structure of compound 4. Thermal ellipsoids are drawn at the 50 % probability level.

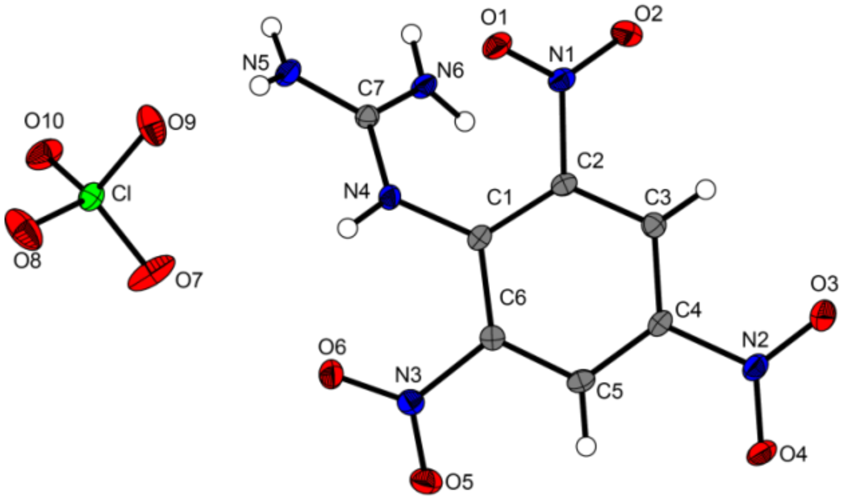


Figure 3: Molecular structure of compound 6. Thermal ellipsoids are drawn at the 50 % probability level.

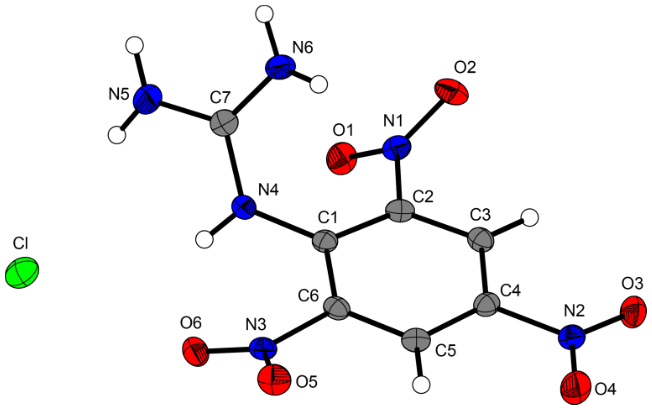


Figure 4: Molecular structure of compound 7. Thermal ellipsoids are drawn at the 50 % probability level.

Compound **3** exhibits only intermoleculare hydrogen bonds.[5] With the additional protonated nitrogen (N4) the salts form also intramoleculare hydrogen bonds. These bonds stabilises the molecule and increases the thermal stabilitie.

According to equation (1) an averaged coefficient of volume expansion α_V of $1.42 \cdot 10^{-4}$ K^{-1} was calculated for salt **4**, **6** and **7** to calculated their densities at room temperature. This is similar to other energetic materials like hexogen ($1.6 \cdot 10^{-4}$ K^{-1}) published in the literature.[7]

$$\rho_{298K} = \rho_T/(1+\alpha_V(298-T_0)) \quad (1)$$

6.2.3 NMR Spectroscopy

The ^{1}H, ^{13}C and ^{14}N NMR spectra of compounds **3** – **7** were recorded in DMSO-d_6 at room temperature. The resonance for the C7 carbon atom of the guanidine moiety is located at 158.4 ppm in the neutral compound **3**, however in the salts, the signal of the C7 carbon atom is shifted to low field (161.2 – 161.1 ppm). The resonance for the C1 carbon atom is observed at 134.7 ppm for compound **3** while in the salts this resonance is observed between 142.3 – 130.6 ppm. In the ^{1}H NMR spectra the protons of the benzene ring are located at 8.62 – 8.96 ppm. The signals corresponding to the N–H and N-H_2 hydrogen atoms overlap and are located at 7.23 – 7.54 ppm in **4** – **7.** The N-H_2 signals are shifted to low field compared to the N-H_2 signal of compound **3** which is located at 6.89 ppm. In the ^{14}N NMR spectra the nitro groups are located at about –10 ppm while the amino groups are found at approximately –300 ppm.

6.2.4 Sensitivities and thermal stability

The thermal behavior of compounds **3** – **7** were investigated using DSC measurements (5 deg min^{-1}).[8] The neutral compound **3** exhibits a decomposition temperature of

232°C. The nitrate salt **4** exhibits a slightly lower decomposition temperature (215°C) while the three other salts **5** – **7** exhibit decomposition temperatures in the range of 279 – 293°C. All of the compounds which were investigated decompose at temperatures above 200°C which is the unofficial threshold value for the development of new military explosives.

The sensitivities of **3** – **7** towards impact and friction were determined.[9-13] Compounds **3** – **7** are all classified as *insensitive* towards friction (360 N) according to the UN guidelines.[14] Compound **6** has the highest sensitivity towards impact (10 J) and is classified as *sensitive*. Compounds **4** and **5** are also classified as *sensitive* (15 J), whereas compounds **3** and **7** are classified as *insensitive* (40 J). Compounds **3** – **7** are less sensitive than RDX (1,3,5-trinitro-1,3,5-triazacyclohexane, 7.5 J, 120 N) or HNS (hexanitrostilbene, 5 J, 240 N).

The sensitivity towards electrostatic discharge was also measured for compound **6** (0.7 J). For comparison, RDX has ESD of 0.1 to 0.2 J and HNS has a ESD of 0.8 J, whereby those of primary explosives are 1000 times smaller.

6.2.5 Heat of Formation

The heats of formation were computed theoretically using the Gaussian G09 program package.[15] To obtain very accurate energies the enthalpies (H) were calculated by the CBS-4M method. The enthalpies of the gas phase species M were computed according to the atomization energy method (Equation (1)) described e.g. in the literature.[16-19]

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

All single values of the calculations are given in the Supporting Information. Lattice enthalpies (U_L) and lattice enthalpies (ΔH_L) were calculated from the corresponding molecular volumes (taken from low temperature X-ray structures) according to equations developed by Jenkins and Glasser.[20,21] With these values the gas phase enthalpies were converted to the solid state (standard conditions) enthalpy of formation $\Delta_f H_m°$ (Table 1). Lastly, the standard molar enthalpies of formation (ΔH_m) were calculated into 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 is the change of mol of gaseous components)

The compound with the highest heat of formation is **7** (118.5 kJ mol^{-1}) followed by **6** (43.4 kJ mol^{-1}) and **3** (32.3 kJ mol^{-1}). Except for compounds **5** (–104.6 kJ mol^{-1}) and **4**

(–89.7 kJ mol$^{–1}$) the remaining compounds were calculated to be formed endothermically. In comparison RDX has a calculated heat of formation of 86 kJ mol^{-1} by using the same theoretical method.

6.2.6 Detonation parameters

Detonation parameters were calculated using EXPLO5 V6.01 computer code.[22,23] The input for EXPLO5.06 requires the sum formula, densities and heats of formation. The calculations were performed using the maximum densities according to the low temperature (173K) crystal structures. For compound **5** the density was measured by pycnometry.

Table 1. Energetic properties and calculated detonation parameters of compounds 3 – 7 as well as HNS and RDX

	(3)	**(4)**	**(5)**	**(6)**	**(7)**	**HNS**	**RDX**
Formula	$C_7H_6N_6O_6$	$C_7H_7N_7O_9$	$C_{13}H_9N_9O_{13}$	$C_7H_7N_7O_{10}Cl$	$C_7H_7N_6O_6Cl$	$C_{14}H_6N_6O_{12}$	$C_3H_6N_6O_6$
FW / g mol$^{–1}$	270.16	333.1	499.26	370.6	306.64	450.1	222.1
IS [J] [a]	40	15	40	10	40	5[24]	7.5[24]
FS [N] [b]	360	360	360	360	360	240[24]	120[24]
ESD [J] [c]	n.d.	n.d.	n.d.	0.7	n.d.	0.8	-
N [%] [d]	31.11	29.4	23.12	22.6	27.4	18.67	37.84
Ω [%] [e]	−65.1	−40.8	−56.08	−30.2	-57.4	−67.6	−21.6
$T_{\text{Dec.}}$ [°C] [f]	232	215	293	279	290	320[24]	210[24]
ρ / g cm$^{–3}$[g]	1.794[5]	1.786§	1.63#	1.820§	1.763§	1.74[24]	1.806[24]
$\Delta_f H_m°$ [kJ mol$^{–1}$] [h]	−13.6	−58.4	−90.7	−12.4	12.8	78.2	70.3
$\Delta_f U°$ [kJ kg$^{–1}$] [i]	32.3	−89.7	−104.6	43.4	118.5	239.76	401.8
EXPLO5.601 values:							
$−\Delta_{Ex}U°$ [kJ kg$^{–1}$] [j]	4524	5124	4782	5292	4323	5142	5734
T_{det} [K] [k]	3161	3562	3513	3895	3251	3676	3800
P_{CJ} [GPa] [l]	26.2	29.4	21.6	29.9	22.8	24.3	35.2
$V_{Det.}$ [m s$^{–1}$] [m]	7955	8216	7378	8152	7484	7612	8815
V_o [L kg$^{–1}$] [n]	674	705	686	709	696	602	792
F / kJ kg$^{–1}$ [o]	725	854	820	939	770	752	1026

[a] Impact sensitivity (BAM drophammer,[11] 1 of 6). [b] Friction sensitivity (BAM friction tester,[11] 1 of 6). [c] Electrostatic discharge device (OZM).[25] [d] Nitrogen content. [e] Oxygen balance. [f] Decomposition temperature from DSC (β = 5 °C). [g] From X-ray diffraction at 173 K or pycnometry at 298 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 [o] specific energy; § from X-ray diffraction at 173 K. # measured by gas (He) pycnometry at 298 K.

The most important criteria of high explosives are the detonation velocity V_{Det}, its detonation pressure p_{CJ} and energy of explosion $\Delta_{\mathrm{Ex}}U°$. Commonly used explosives like TNT, HNS or RDX, were also calculated with the EXPLO5.06 code. (V_{Det}: TNT: 7450, HNS: 7612, RDX: 8815 ms^{-1}; p_{CJ}: TNT: 23.4, HNS: 24.3, RDX: 35.2 GPa; $\Delta_{\mathrm{Ex}}U°$: TNT: −5261, HNS: −5142, RDX: −5734 kJ kg^{-1})

In terms of the detonation velocity, compounds **3**, **4**, **6** and **7** show similar or higher values with those of commonly used secondary explosives such as HNS, but are lower than that of RDX. Compounds **3**, **4** and **6** exceeded the calculated detonation velocity of HNS. The detonation temperatures of compounds **3** – **7** exceed that of RDX, but are lower than that of for HNS.

6.3 Experimental Section

CAUTION! Although we had no problems in the synthesis and handling of the compounds described in this work they are nevertheless energetic materials with sensitivity to various stimuli. Proper protective measures (face shield, ear protection, body armor, Kevlar gloves, and earthed equipment) should be used at all times.

General Procedures and a description of the analytical methods are given in the Supplementary Information.

Picryl chloride (2)

Picryl chloride was prepared according to the literature procedure.[11]

Synthesis of (2,4,6-Trinitrophenyl)guanidine (3)

Guanidinium carbonate (1.20 g, 6.66 mmol) and picryl chloride (1.38 g, 5.54 mmol) were dissolved in ethanol (40 mL), and the mixture was heated for 4h. After cooling, the solution was poured into a crystallization dish to crystallize. A brown – red solid was obtained.

Yield : 1.34 mg (4.96 mmol, 89%), M.p. (DSC, 5 deg min^{-1}): 232ºC (dec.); EA ($C_7H_6N_6O_6$, 270.17 g/mol); found (calc.) [%]: C: 30.95 (31.12), H: 2.34 (2.24), N: 31.13 (31.11). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3482 (w), 3427 (w), 3345 (w), 3245(w), 3071 (vw), 1649 (s), 1606 (s), 1561 (s), 1502 (s), 1428 (w), 1319 (vs), 1266 (vs), 1161 (m), 1078 (s), 923 (m), 910 (m), 821 (w), 789 (m), 744 (s), 735 (m), 714 (vs), 683 (m). Raman (300 mW, 25 Scans): $\tilde{\nu}$ [cm^{-1}] = 3389 (1), 3082 (1), 1608 (6), 1525 (9), 1462 (2), 1344 (9), 1308 (100), 1173 (13), 1084 (6), 943 (3), 930 (2), 826 (10), 780 (2), 750 (2), 630 (5), 590 (3), 426 (3), 386 (2), 322 (2), 287 (4), 210 (3), 180 (3), 180 (3), 136 (3), 111 (22), 88 (5). MS (DEI$^+$, m/z): 270.7 [M^+] (100), 240.2 [$M^+{-}H_2N_2$] (10), 228.1 [$M^+{-}CH_2N_3$] (6), 224.2 [$M^+{-}NO_2$] (4), 178.2 [$M^+{-}N_2O_4$] (6), 132.2 [$M^+{-}N_3O_6$] (6), 43.1 [$M^+{-}C_6H_3N_4O_6$] (55). ^{1}H

NMR (400 MHz, DMSO-d_6, 25 °C, ppm): δ = 8.62 (s,1H, CH), 6.89 (br, s, 4H, NH_2). ^{13}C NMR (101 MHz, DMSO-d_6, 25 °C, ppm): δ = 158.4 (1C, C-$(NH_2)_2$), 145.1 (2C, C-NO_2), 143.6 (1C, C-NO_2), 134.7 (1C, C-N), 123.4 (2C, C-H). ^{14}N NMR (29 MHz, DMSO-d_6, 25 °C, ppm): δ = −7 (3N, NO_2), −272 (1N, N=C), −298 (2N, NH_2) . BAM Impact sensitivity test: 40 J; Friction sensitivity test: 360 N.

General synthesis of (2,4,6-trinitrophenyl)guanidinium salts (4 – 7)

(2,4,6-trinitrophenyl)guanidine (**3**) was dissolved in 10 mL H_2O or EtOH and the corresponding acid was added at room temperature. The mixture then was heated to 70 – 80 °C for 3 h. After cooling and filtering the products were obtained as orange – yellow solids. Yields: 60-94%

6.4 Conclusion

From this experimental and theoretical study the following conclusions can be drawn:

- The nitrate (**4**), picrate (**5**), perchlorate (**6**) and chloride (**7**) salts containing the (2,4,6-Trinitrophenyl)guanidinium cation were synthesized from (2,4,6-Trinitrophenyl)guanidine (**3**) by protonation with the corresponding acid.

- Salts **4** – **7** were characterized by single-crystal X-ray diffraction. Compounds **4** – **7** crystallize with densities of 1.819 (**4**), 1.664 (**5**), 1.854 (**6**) and 1.796 (**7**) g cm^{-3}. The density of compound (**5**) without ethanol trapped in the crystal lattice was measured using pycnometry and corresponds to a density of 1.63 g cm^{-3}.

- Compounds **3** – **7** show good thermal stabilities with the investigated compounds decomposing at temperatures over 210 °C and below 300 °C. The decomposition of **3** – **7** are all higher than that of RDX (210 °C).

- The impact and friction sensitivities of the precursor and salts were determined. According to UN recommendations all should be classified as insensitive (**3** – **7**) towards friction and insensitive (**3**, **5** and **7**) or sensitive (**4** and **6**) towards impact.

- Using the crystal or pycnometric densities and calculated (mostly endothermic) enthalpies of formation, several detonation parameters were calculated. Salts **4** and **6** show the highest detonation velocities (**4**: 8330 ms^{-1}; **6**: 8258 ms^{-1}) followed by compound **3** (**3**: 7955 ms^{-1}). Compounds **3**, **4** and **6** also exceed the value for the detonation pressure of HNS (24.3 GPa). With respect to their performance data compounds **3** – **7** could be of interest as replacements for HNS and RDX.

6.5 References

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Conclusion

7 Summary and Conclussion

In this thesis the general goal was the synthesis of new high thermally stable explosives as replacement for hexanitrostilbene (HNS). The main focus was located on 1,3,5-trinitrobenzene derivatives with high conjugated systems and additional salt formation. Further more 1,2,3,4-tetrazine and 1,2,4-oxadiazole systems were investigated. (All compound numbers are related to the compounds in each chapter)

In **Chapter 2** the interesting compound 5,7-dinitrobenzo-1,2,3,4-tetrazine-1,3-dioxide is described. Although already reported in literature, the compound was poorly characterized. 5,7-dinitrobenzo-1,2,3,4-tetrazine-1,3-dioxide was synthesized and comprehensively characterized. Single crystal X-ray diffraction was used to determine the structure of 5,7-dinitrobenzo-1,2,3,4-tetrazine-1,3-dioxide. With a high conjugated system and “Alternating Positive Negative Charge” the 5,7-dinitrobenzo-1,2,3,4-tetrazine-1,3-dioxide was a promising candidate as high thermally stable compound. But measurements showed a lower thermal stability then expected (211°C). A bomb calorimetric measurement as well as a small-scale shock reactivity test were made. 5,7-dinitrobenzo-1,2,3,4-tetrazine-1,3-dioxide exhibited a higher explosiveness than RDX. With mechanical sensitivities and explosive performances higher than RDX, 5,7-dinitrobenzo-1,2,3,4-tetrazine-1,3-dioxide seams to be a promising candidate for replacing RDX.

In **Chapter 3** the new compound 3,3’-bis(1,2,4-oxadiazolyl)-5,5’-diacetic acid diethyl ester (**2**) was synthesized and comprehensively characterized. Additionally ten different nitrogen-rich salts, ammonium (**3**), hydroxylammonium (**5**), guanidinium (**6**), aminoguanidinium (**7**), diaminoguanidinium (**8**), triaminoguanidinium (**9**), aminonitroguanidinium (**10**), diaminouronium (**11**), diaminotetrazolium (**12**) and hydrazinium (**13**), of 5,5’-dinitromethyl-3,3’-bis(1,2,4-oxadiazole) were synthesized and comprehensively characterized. The precursors **1** and **2** as well as the salts **3–5**, **7–13** were characterized by single-crystal X-ray diffraction. The hydroxylammonium salt (**5**) exhibited a very high density which is the best of our knowledge most dense (X-ray density of 2.00 g cm^{-3} at 92 K, 1.98 g cm^{-3} at 173 K, 1.95 g cm^{-3} at room temperature) ionic organic CHNO explosive investigated yet. Also the ammonium salts (**3**) has an astonishing high density of 1.95 g cm^{-3} at 173 K. The impact and friction sensitivities of the nitrogen-rich salts were determined. According to UN recommendations they are classified as less sensitive (**6**, **13**), sensitive (**3**, **5**, **7**, **8**, **10** and **11**) or very sensitive (**4**, **9** and **12**) towards impact and insensitive (**6** and **7**), sensitive (**3**, **4**, **8**, **9**, **10**, **11** and **13**) or very sensitive (**5** and **12**) towards friction. - The silver salt **4** turned out to be a potential primary explosive. Regarding the thermal stabilities the investigated compounds mostly decompose at temperatures below 200°C (exception compounds **2**, **3**, **4**, **6** and **9**). Only compounds **4** and **6** exhibited higher decomposition temperatures as the precursor **2** but they were still lower as 300°C (**4**: 273°C; **6**: 239°C). Maybe other metal salts like sodium or potassium could reach the 300°C. Based on these results the compounds again were only compared to RDX. The energetic performances were calculated with EXPLO5.05. Salts **5**, **10** and **12** show the highest values regarding the detonation velocity (**5**: 8935 ms^{-1}; **10**: 8872 ms^{-1}; **12**: 8744 ms^{-1}). With a detonation pressure of 413 kbar compound **5** exceeds also the value of RDX (394 kbar) With respect to their performance data compounds **3**, **5**, **10** and **12** could be of interest as high explosives and replacements for RDX.

Chapter 4 reports the interesting, but poorly analyzed in literature, high thermally stable explosive 2,6-bis(picrylamino)-3,5-dinitropyridine (**4**) also know as PYX. Additionally to the synthesis and comprehensive characterization eleven different metal and nitrogen-rich salts were synthesized and characterized, too. The salts (potassium (**5**), sodium (**6**), ammonium (**7**), hydroxylammonium (**8**), guanidinium (**9**), aminoguanidinium (**10**), cesium (**11**), barium (**12**), hydrazinium (**13**), triethylammonium (**14**) and triaminoguanidinium (**15**)) were synthesized from 2,6-bis(picrylamino)-3,5-dinitropyridine (**4**) by deprotonation, followed by metathesis reactions involving the potassium or sodium salt with the corresponding nitrogen-rich halide. Precursors **3** and **4** as well as salts **9** and **11** were characterized using single-crystal X-ray diffraction. Whereas **9** contains the dianion of 2,6-bis(picrylamino)-3,5-dinitropyridine compound **11** contains only the monoanion. The impact and friction sensitivities of the precursors and salts were determined. According to UN recommendations **7**, **9** and **10** are classified as insensitive, **14** as less sensitive and **3** – **6**, **8**, **11** – **13** and **15** as sensitive towards impact. Compounds **4** – **7**, and **9** – **15** are classified as insensitive whereas **3** and **8** as sensitive towards friction. With a very high thermal stability (373°C) and energetic properties, which were calculated with EXPLO5_601, similar to HNS, PYX is a very promising candidate as replacement for HNS. For a better comparison a TGA as well as a long term stability test were made. The TGA measurement showed a loss of mass of only 0.3 % for the first 300°C and in the long term stability test no changes after 100 h at 260°C in the IR and ^{1}H NMR spectra were occurred. To illustrated the energetic properties a SSRT-test was undertaken for compound **4** and compared to that for HNS which showed almost the same values. With salt formation the thermal stability should be increased but most of the salts decompose at temperatures below 300°C. Exceptions **6** (349°C), **8** (333°C), **11** (337°C) and **12** (353°C) decompose over 300°C but below the decomposition point of the precursor **4**. The detonation temperature of salt **8** is of interest, because hydroxylammonium salts mostly decompose at very low temperatures. Instead here the hydroxylammonium salt exhibited one of the highest. Compared to the energetic properties salts **7, 8** and **13** showed the highest values regarding the detonation velocity (**7**: 7839 ms^{-1}; **8**: 7949 ms^{-1}; **13**: 7739 ms^{-1}).

Compounds **4**, **7** and **8** also exceed the value for the detonation pressure of HNS. With respect to their performance data compounds **4**, **7** and **8** could be of interest as explosives with high thermal stabilities. Based on the decomposition temperature and calculated energetic properties compound **8** seemed to be most promising. Unfortunately almost all metal salts were all hydrates and proper dehydration was unsuccessful.

In **Chapter 5** the synthesis and characterization of 3-(picrylamino)-1,2,4-triazole (**3**) and 3-amino-5-(picrylamino)-1,2,4-triazole (**13**) is reported. During both synthesis two unknown side products could be identified. Side product **4** could be analyzed further by single-crystal X-ray diffraction. Side product **14** could only be identified by single-crystal X-ray diffraction. The thermal analysis exhibited a slightly higher stability for compound **3** as given in literature (316°C). Based on the decomposition temperature and calculated energetic properties, calculated with EXPLO5_601, compound **3** seemed to be a very promising replacement for HNS. Even the calculated detonation velocity is about 1000 ms^{-1} higher as for HNS (**3**: 8477 ms^{-1}). Unfortunately compound **13** exhibited a lower thermal stability as expected (261°C) but the calculated detonation parameters exhibited also better values as for HNS especially the detonation velocity (**13**: 8178 ms^{-1}). To increase the thermal stability eight different salts (potassium (**5**), sodium (**6**), guanidinium (**7**), aminoguanidinium (**8**), ammonium (**9**), triethylammonium (**10**), hydrazinium (**11**) and triaminoguanidinium (**12**)) of 3-(picrylamino)-1,2,4-triazole were synthesized from 3-(picrylamino)-1,2,4-triazole (**3**) by deprotonation, followed by metathesis reactions involving the potassium or sodium salt with the corresponding nitrogen-rich halide. Additionally four different salts (potassium (**15**), guanidinium (**16**), aminoguanidinium (**17**) and triethylammonium (**18**)) of 3-amino-5-(picrylamino)-1,2,4-triazole were synthesized from 3-amino-5-(picrylamino)-1,2,4-triazole (**13**) by deprotonation. All salts were comprehensively characterized. Salt **7** was characterized using single-crystal X-ray diffraction. The impact and friction sensitivities of the precursors and salts were determined. According to UN recommendations **3, 5** – **10, 12, 13** and **15** – **18** are classified as insensitive and **11** as sensitive towards friction. Towards impact **3, 7** – **10, 12** and **16** – **18** are classified as insensitive, **5, 6** and **13** as sensitive or **15** as very sensitive. All investigated salts showed similar thermal stabilities and decomposed at temperatures below 300°C. For most of the salts the detonation parameters were calculated using EXPLO5_601. Compounds **8** and **9** showed the highest values regarding the detonation velocity (**8**: 8302 ms^{-1}; **9**: 8400 ms^{-1}).

In **Chapter 6** the synthesis of (2,4,6-Trinitrophenyl)guanidine (**3**) was slightly optimized. Compound **3** which was analyzed in literature only by single-crystal X-ray diffraction, was comprehensively characterized. Additionally the nitrate (**4**), picrate (**5**), perchlorate (**6**) and chloride (**7**) salts containing the (2,4,6-Trinitrophenyl)guanidinium cation were synthesized from (2,4,6-Trinitrophenyl)guanidine (**3**) by protonation with the corresponding acid and comprehensively characterized. Salts **4** – **7** were characterized by single-crystal X-ray diffraction. The impact and friction sensitivities of the precursor and salts were determined. According to UN recommendations all compounds are classified as insensitive (**3** – **7**) towards friction and insensitive (**3**, **5** and **7**) or sensitive (**4** and **6**) towards impact. The thermal stabilities of compounds **3** – **7** exhibited decomposition points over 210 °C and below 300 °C. Several detonation parameters were calculated using EXPLO5_601. Salts **4** and **6** showed the highest detonation velocities (**4**: 8330 ms^{-1}; **6**: 8258 ms^{-1}) followed by compound **3** (7955 ms^{-1}). With respect to their performance data compounds **3** – **7** could be of interest as replacements for HNS and RDX.

General Conclusion and Outlook: Overall it can be concluded that the concept described in the introduction represents a good approach to increase the thermal stability of energetic molecules. The neutral compounds PYX and PATO have the capability to form high thermally stable explosives which might serve as replacement for HNS. But salt formation to increase the thermal stability leads to the opposite effect and lowers the thermal stability. Insertion of amino groups probably can increase the thermal stability. This would be an interesting topic for future theoretical and experimental investigations. Nevertheless the hydroxylammonium salt of PYX should be investigated further. With a higher thermal stability and higher detonation performances it is a promising replacement for HNS. (2,4,6-Trinitrophenyl)guanidine instead could increase the thermal stability mostly by salt formation. (2,4,6-Trinitrophenyl)guanidine as well as its salts have the capability to form secondary explosives. Here also the insertion of amino groups probably can increase the thermal stability and should be investigated further. Most of the invested compounds and salts would probably neither replace HNS but could be of interest as RDX replacements. Especially the nitrogen-rich salts of 5,5'-dinitromethyl-3,3'-bis(1,2,4-oxadiazole), mostly the ammonium and hydroxylammonium salts, could be of interest as replacement for RDX and should be further investigated. Maybe a salt formation of 5,5'-dinitromethyl-3,3'-bis(1,2,4-oxadiazole) with metal salts like potassium or sodium could lead to higher thermal stabilities, which then could be of interest for HNS replacements.

Supplementary Informations

8 Supplementary Information for Chapter 3

8.1 X-ray Diffraction

For all compounds, an Oxford Xcalibur3 diffractometer with a CCD area detector was employed for data collection using Mo-$K\alpha$ 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 $F2$ (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]. DIAMOND2 plots are shown with thermal ellipsoids at the 50% probability level.

Supplementary Information

Table S1. X-ray data and parameters for 1-5.

	1	**2**	**3**	**4**	**5 (92K)**
CCDC	940819	940820	940821	940823	963558
Formula	$C_{12}H_{14}N_4O_6$	$C_{12}H_{10}N_8O_{14}$	$C_6H_8N_{10}O_{10}$	$C_6N_8O_{10}Ag_2$	$C_6H_8N_{10}O_{12}$
FW / g mol^{-1}	310.27	490.28	380.19	559.85	412.19
Crystal system	monoclinic	monoclinic	triclinic	triclinic	triclinic
Space Group	*P2$_1$/n* (No. 14)	*P2$_1$/n* (No 14)	*P-1* (No. 2)	*P-1* (No. 2)	*P-1* (No. 2)
Color / Habit	colorless plate	colorless plate	yellow plate	yellow plate	colorless plate
Size [mm]	0.20 x 0.10 x 0.05	0.35 x 0.21 x 0.07	0.21 x 0.2 x 0.02	0.10 x 0.15 x 0.20	0.20 x 0.25 x 0.30
a [Å]	8.8524(8)	10.4829(18)	4.6929(5)	4.8147(4)	8.5300(7)
b [Å]	8.1381(6)	7.2700(7)	7.6985(9)	7.3772(5)	8.8114(7)
c [Å]	9.6626(8)	13.740(2)	9.7159(12)	9.3569(6)	9.3578(7)
α [°]	90.00	90.00	69.484(11)	106.138(5)	94.929(6)
β [°]	90.687(8)	106.253(19)	79.857(10)	101.275(6)	102.071(7)
γ [°]	90.00	90.00	85.919(9)	101.725(7)	92.044(7)
V [Å^3]	696.06(10)	1005.3(3)	323.60(6)	301.16(4)	684.21(10)
Z	2	2	1	1	2
$\rho_{calc.}$ [g cm^{-3}]	1.480	1.620	1.951	3.087	2.001
μ [mm^{-1}]	0.121	0.150	n.d.	3.344	0.193
F(000)	324	500	194	266	420
T [K]	100	100	173	173	92
Θ Min-Max [°]	4.2-28.8	4.2-25.5	4.19-26.74	4.4-25.0	4.1- 26.8
Dataset [h; k; l]	−10:12; −10:10; −13:11	−12:9; −5:8; −12:16	−5:5; −9:9; −12:12	−5:5; −8:8; −10:11	−10:10; −11:11; −9:11
Reflection collected	4799	3690	3494	2807	3796
Independent reflection	1615	1859	1370	1060	2881
R_{int}	0.041	0.066	0.029	0.047	0.019
Observed reflection	885	681	990	955	2381
No. parameters	128	174	134	118	285
R_1 (obs)[a]	0.0414	0.0401	0.0331	0.0216	0.0356
wR_2 (all data)[b]	0.0945	0.0461	0.0798	0.0449	0.0946
S [c]	0.819	0.606	0.931	1.007	1.06
Min./Max. Resd. [e Å^{-3}]	−0.17 / 0.25	−0.18 / 0.20	−0.27 / 0.28	−0.40 / 0.58	−0.32, 0.30
Device type	Oxford Xcalibur3	Oxford Xcalibur3	Oxford Xcalibur3	Oxford Xcalibur3	Oxford Xcalibur3
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
Solution	SIR-92	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

[a] $R_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. [b] $wR_2 = [\Sigma[w(Fo^2 - Fc^2)^2]/\Sigma[w(Fo)^2]]^{1/2}$; $w = [\sigma c^2(Fo^2) + (xP)^2 + yP]^{-1}$ and $P = (Fo^2 + 2Fc^2)/3$. [c] $S = [\Sigma\{w(Fo^2 - Fc^2)^2\}/(n - p)]^{1/2}$ (n = number of reflections; p = total number of parameters).

Table S2. X-ray data and parameters for 5-8.

	5 (100 K)	**5 (173 K)**	**5 (293 K)**	**7**	**8**
CCDC	963559	940826	963557	940822	941545
Formula	$C_6H_8N_{10}O_{12}$	$C_6H_8N_{10}O_{12}$	$C_6H_8N_{10}O_{12}$	$C_8H_{14}N_{16}O_{10}$	$C_8H_{16}N_{18}O_{10}$
FW / g mol^{-1}	412.19	412.19	412.19	494.11	524.33
Crystal system	triclinic	triclinic	triclinic	triclinic	orthorhombic
Space Group	*P-1* (No. 2)	*P-1* (No. 2)	*P-1* (No. 2)	*P-1* (No. 2)	*Pbca* (No. 61)
Color / Habit	colorless plate	colorless plate	colorless plate	colorless plate	colorless plate
Size [mm]	0.20 x 0.20 x 0.30	0.20 x 0.25 x 0.30	0.14 x 0.22 x 0.29	0.16 x 0.27 x 0.34	0.31 x 0.18 x 0.15
a [Å]	8.5328(12)	8.5453(5)	8.5752(8)	6.8571(6)	7.7925(3)
b [Å]	8.8358(13)	8.8726(5)	9.0234(8)	8.0950(9)	11.3001(6)
c [Å]	9.3536(13)	9.3499(6)	9.3513(8)	8.7754(8)	23.3226(11)
α [°]	95.009(11)	95.176(5)	84.367(7)	104.341(9)	90
β [°]	101.845(12)	102.177(5)	77.766(8)	90.935(8)	90
γ [°]	91.955(12)	91.314(5)	89.773(7)	92.690(8)	90
V [Å^3]	686.57(17)	689.48(7)	703.63(11)	471.21(8)	2053.70(17)
Z	2	1	2	1	4
$\rho_{calc.}$ [g cm^{-3}]	1.994	1.986	1.946	1.742	1.696
μ [mm^{-1}]	0.192	n.d.	0.188	0.157	0.152
F(000)	420	420	420	254	1080
T [K]	100	173	293	173	173
Θ Min-Max [°]	4.5-27.0	4.14-26.75	4.2-26.5	4.2-26.0	4.1-26.0
Dataset [h; k; l]	-10:10; -9:11; -10:11	−10:10; −11:11; −11:11	-10:10; -11:11; -11:11	−8:8; −9:9; −10:9	-7:9; -11:13; -28:28
Reflection collected	3881	7475	9787	2455	9804
Independ.reflection	2950	2930	2906	1822	2006
R_{int}	0.035	0.025	0.030	0.012	0.034
Observed reflection	1900	1981	2138	1323	1587
No. parameters	285	285	286	182	187
R_1 (obs)[a]	0.0567	0.0321	0.0406	0.0348	0.0326
wR_2 (all data)[b]	0.1306	0.0750	0.1127	0.0860	0.0854
S[c]	1.05	0.872	1.03	0.917	1.03
Min./Max. Resd. [e Å^{-3}]	-0.35 / 0.34	−0.31 / 0.23	-0.22 / 0.24	−0.27 / 0.20	−0.21 / 0.22
Device type	Oxford Xcalibur3	Oxford Xcalibur3	Oxford Xcalibur3	Oxford Xcalibur3	Oxford Xcalibur3
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
Solution	SHELXS-97	SHELXS-97	SIR-92	SHELXS-97	SIR-92
Refinement	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97
Absorp. correction	multi-scan	multi-scan	multi-scan	multi-scan	

[a] $R_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. [b] $wR_2 = [\Sigma[w(Fo^2 - Fc^2)^2]/\Sigma[w(Fo)^2]]^{1/2}$; $w = [\sigma c^2(Fo^2) + (xP)^2 + yP]^{-1}$ and $P = (Fo^2 + 2Fc^2)/3$. [c] $S = [\Sigma\{w(Fo^2 - Fc^2)^2\}/(n - p)]^{1/2}$ (n = number of reflections; p = total number of parameters).

Table S3. X-ray data and parameters for 10-13.

	9	**10**	**11**	**12**	**$13\cdot0.35\ H_2O$**
CCDC	940827	940828	940825	940824	
Formula	$C_8H_{18}N_{20}O_{10}$	$C_8H_{12}N_{18}O_{14}$	$C_8H_{14}N_{16}O_{12}$	$C_8H_{10}N_{20}O_{10}$	$C_6H_{10}N_{12}O_{10}$
FW / g mol^{-1}	554.36	584.29	526.3	546.29	410.22
Crystal system	triclinic	triclinic	triclinic	monoclinic	monoclinic
Space Group	*P-1* (No. 2)	*P-1* (No. 2)	*P-1* (No. 2)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
Color / Habit	yellow block	colorless plate	light yellow plate	colorless plate	Light yellow block
Size [mm]	0.10 x 0.20 x 0.35	0.4 x 0.35 x 0.3	0.24 x 0.28 x 0.32	0.11 x 0.44 x 0.58	0.10 x 0.31 x 0.32
a [Å]	7.4992(4)	7.1349(12)	4.8254(11)	7.4113(6)	10.9662(12)
b [Å]	7.9402(5)	7.8632(12)	10.509(2)	8.2789(7)	9.6820(11)
c [Å]	9.0013(5)	10.548(2)	10.530(2)	15.7253(13)	7.2254(9)
α [°]	81.453(5)	71.481(19)	111.701(17)	90	90
β [°]	80.812(5)	86.720(17)	97.863(18)	94.784(8)	93.729(10)
γ [°]	82.844(5)	66.005(15)	100.230(19)	90	90
V [$Å^3$]	520.43(5)	510.87(18)	476.12(19)	961.50(14)	765.53(15)
Z	1	1	1	2	2
$\rho_{calc.}$ [g cm^{-3}]	1.769	1.899	1.836	1.887	1.808
μ [mm^{-1}]	0.158	0.178	0.169	0.170	0.170
F(000)	286	298	270	556	427
T [K]	173	173	173	173	173
Θ Min-Max [°]	4.6-26.5	4.2-26.4	4.3-26.5	4.4-26.5	4.2-26.0
Dataset [h; k; l]	−9:9; −9:9; −11:11	−5:8; −9:9; −13:12	−6:6; −13:13; −13:13	−9:9; −6:10; −18:19	−13:13; −11:11; −8:8
Reflection collected	7886	2724	4918	5001	10994
Independent reflection	2135	2055	1930	1981	1498
R_{int}	0.024	0.028	0.037	0.023	0.043
Observed reflection	1681	1487	1216	1524	1246
No. parameters	208	205	191	192	159
R_1 (obs)[a]	0.0302	0.0864	0.0339	0.0323	0.0354
wR_2 (all data)[b]	0.0803	0.2294	0.0672	0.0839	0.0980
S [c]	1.009	1.23	0.815	1.014	1.05
Min./Max. Resd. [e $Å^{-3}$]	−0.24 / 0.22	−0.44 / 0.49	−0.20 / 0.24	−0.27 / 0.21	−0.25 / 0.33
Device type	Oxford Xcalibur3	Oxford Xcalibur3	Oxford Xcalibur3	Oxford Xcalibur3	Oxford Xcalibur3
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
Solution	SHELXS-97	SHELXS-97	SHELXS-97	SIR-92	SHELXS-97
Refinement	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan

[a] $R_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. [b] $wR_2 = [\Sigma[w(Fo^2 - Fc^2)^2]/\Sigma[w(Fo)^2]]^{1/2}$; $w = [\sigma c^2(Fo^2) + (xP)^2 + yP]^{-1}$ and $P = (Fo^2 + 2Fc^2)/3$. [c] $S = [\Sigma\{w(Fo^2 - Fc^2)^2\}/(n - p)]^{1/2}$ (n = number of reflections; p = total number of parameters).

Table S4. Angle of torsion for compounds 3–5,7-13

Compound	**3**	**4**	**5 (173K)**	**7**	**8**	**9**	**10**	**11**	**12**	**13·0.35 H_2O**
angle of torsion / ° [a]	2.25 (22)	−17.77 (51)	2.79 (22)	59.83 (19)	87.5 (17)	−27.29 (18)	−54.75 (79)	−74.28 (23)	49.46 (19)	−31.92 (22)

[a] distortion angle between nitro C–N bond towards oxadiazole ring plane.

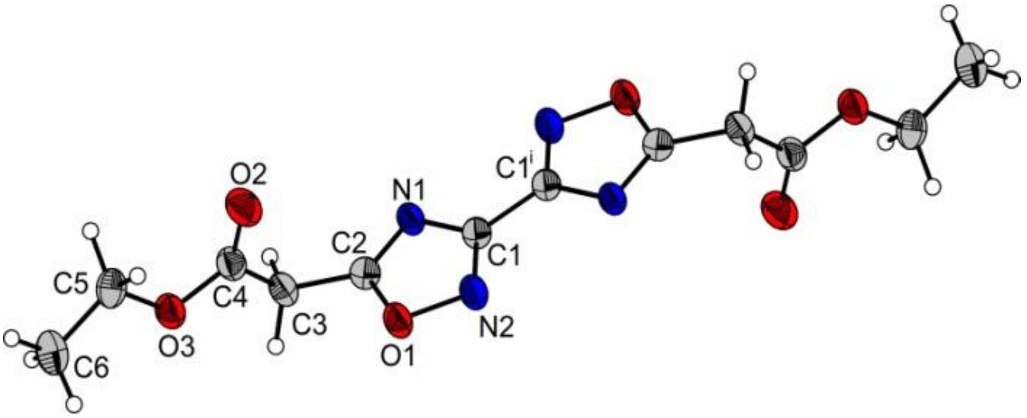

Figure S1: Molecular structure of 3,3`-bis(1,2,4-oxadiazolyl)-5,5`-diacetic acid diethyl ester (1). Thermal ellipsoids are drawn at the 50 % probability level. (i) −x, −y, −z.

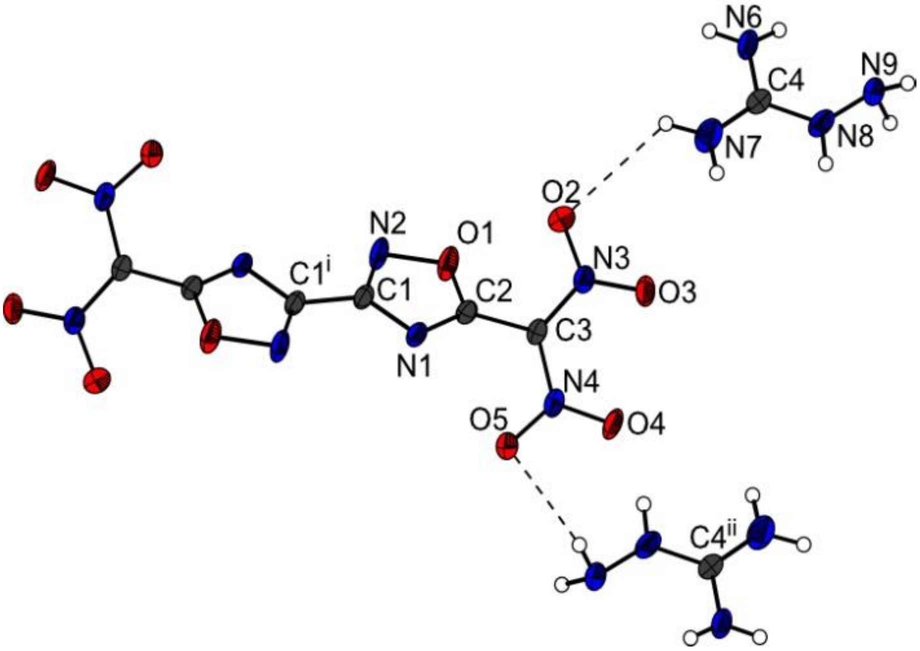

Figure S2: Depiction of the molecular unit in the crystalline solid state structure of compound 7. Thermal ellipsoids are drawn at the 50 % probability level. (i) 1−x, 3−y, 1−z; (ii) 1−x, 1−y, −z.

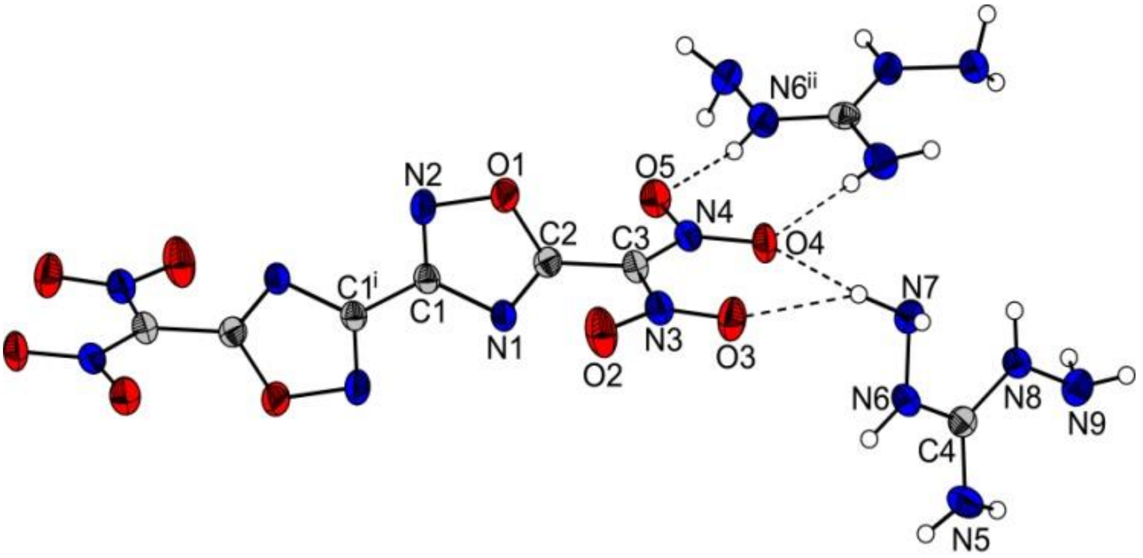

Figure S3: Representation of the molecular moiety of 8. Thermal ellipsoids are drawn at the 50 % probability level. (i) 2−x, 1−y, −z; (ii) 1-x, 0.5+y, 0.5−z.

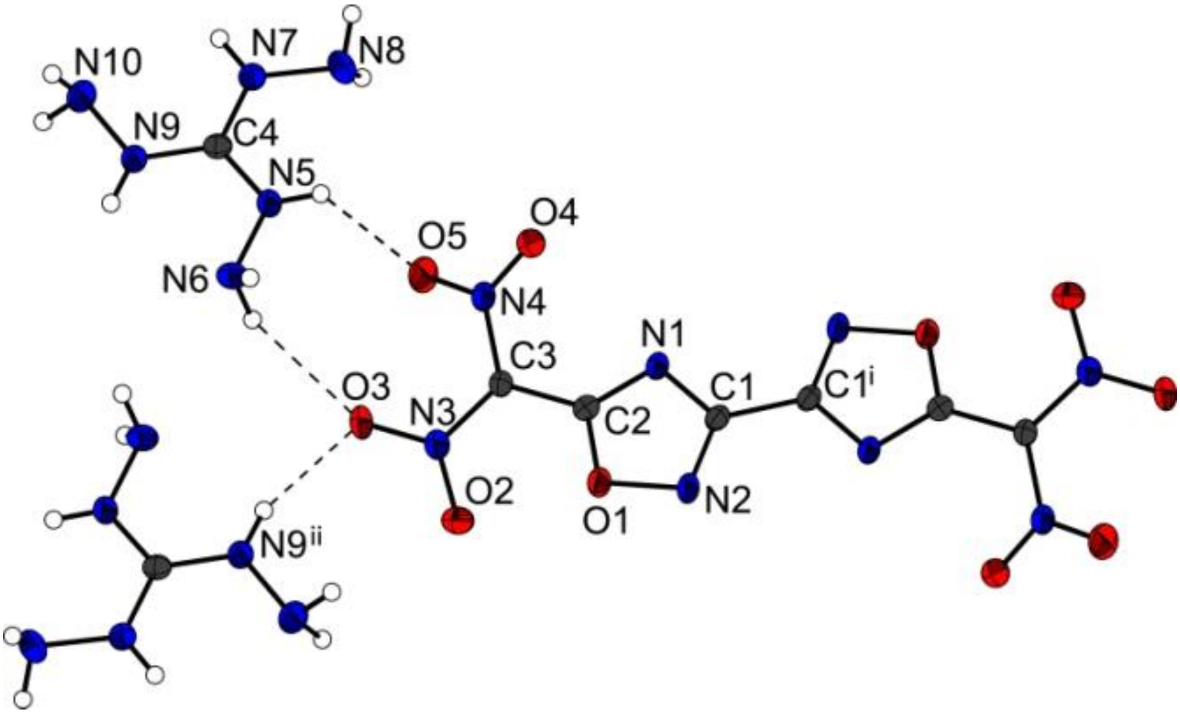

Figure S4: Molecular moiety of compound 9; Thermal ellipsoids are drawn at the 50 % probability level. (i) −x, 1−y, 2−z; (ii) 1−x, 1−y, −z.

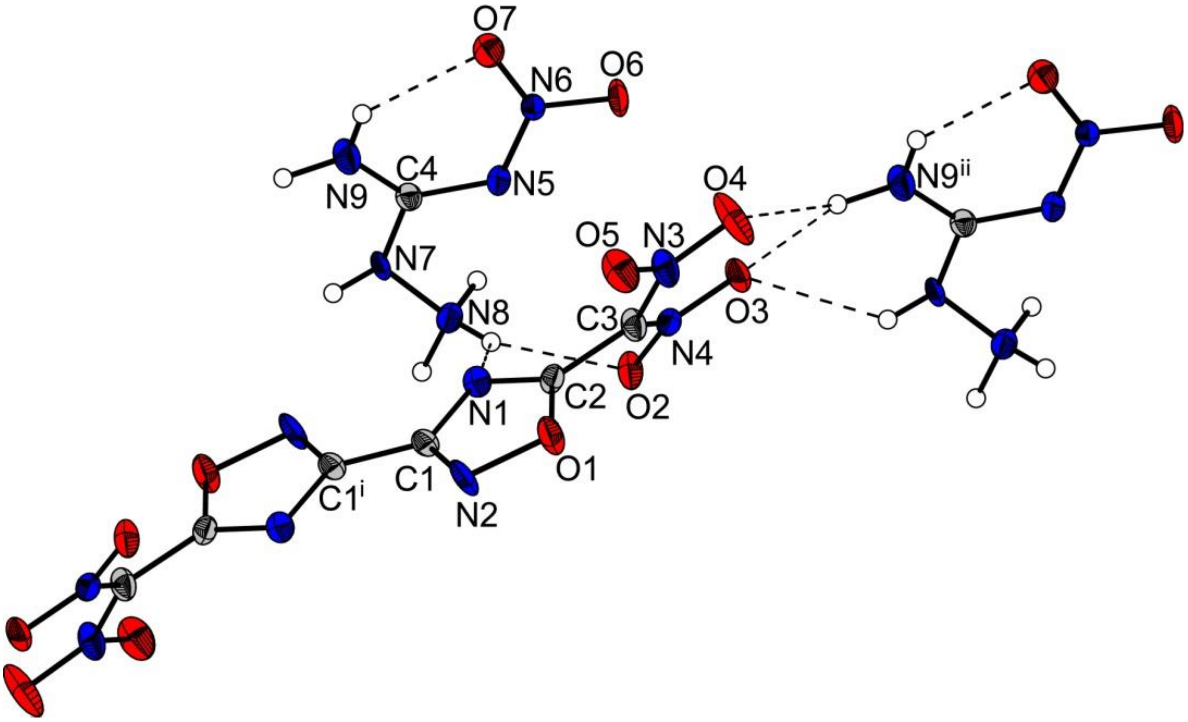

Figure S5: Molecular moiety of compound 10; (i) 2−x, −y, 1-z; (ii) −1+x, 1+y, z.

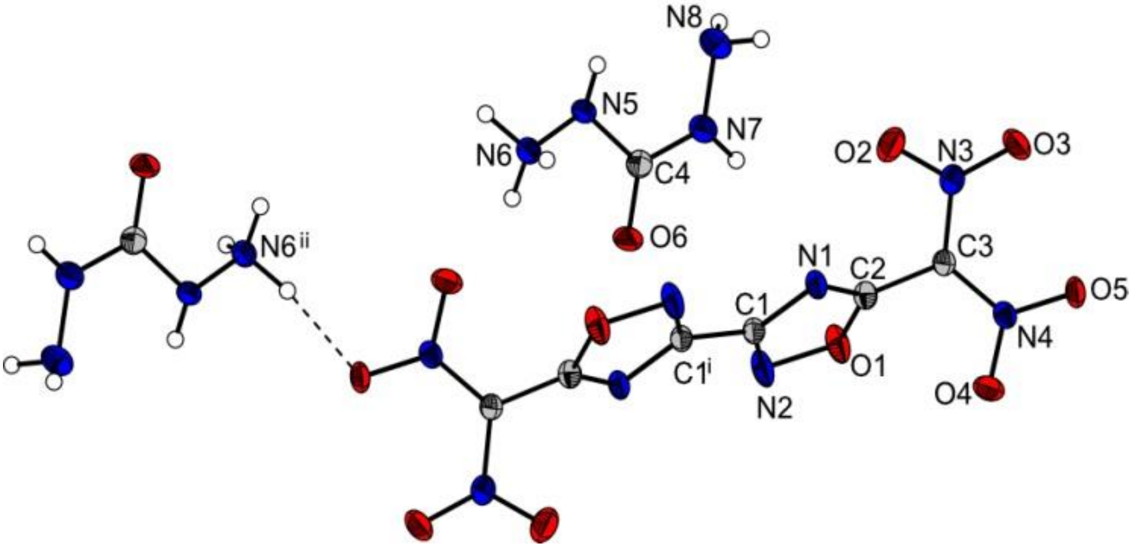

Figure S6: Molecular moiety of compound 11. Thermal ellipsoids are drawn at the 50 % probability level; (i) 2−x, 1−y, 1−z; (ii) 1−x, 1−y, 2−z.

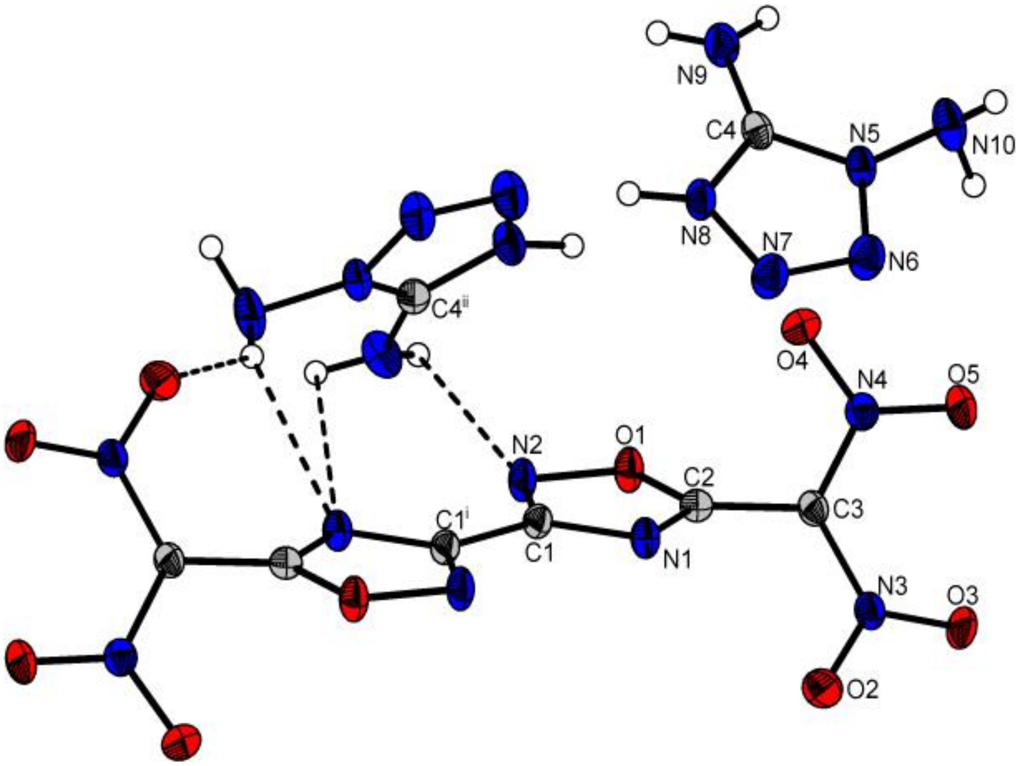

Figure S7: Molecular moiety of compound 12. Thermal ellipsoids are drawn at the 50 % probability level. (i) 2−x, 1−y, 1−z; (ii) 2−x, 0.5+y, 0.5−z.

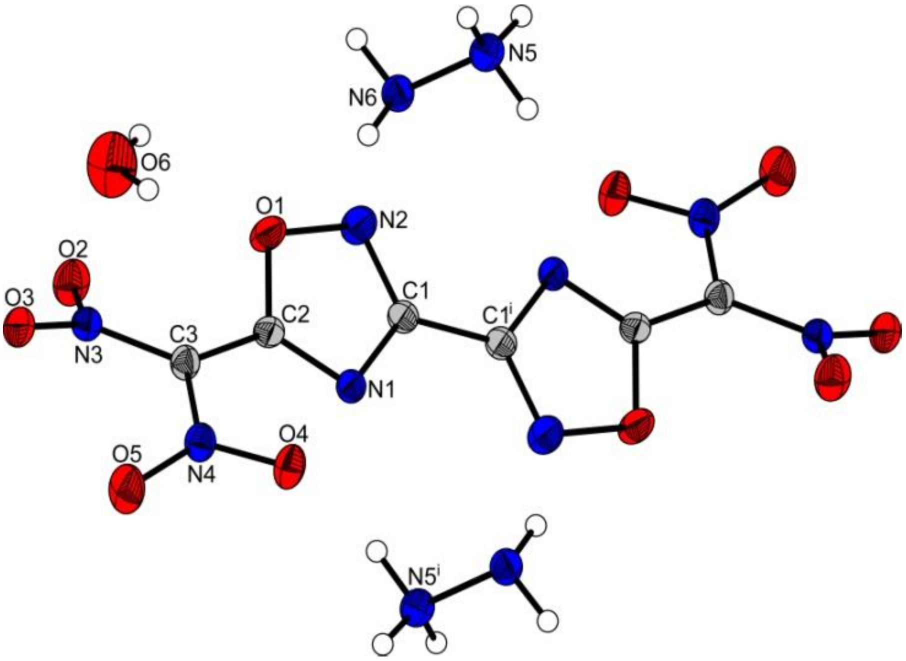

Figure S8: Crystal structure of compound 13·0.35 H_2O; Thermal ellipsoids are drawn at the 50 % probability level; (i): 1−x, 1−y, 1−z.

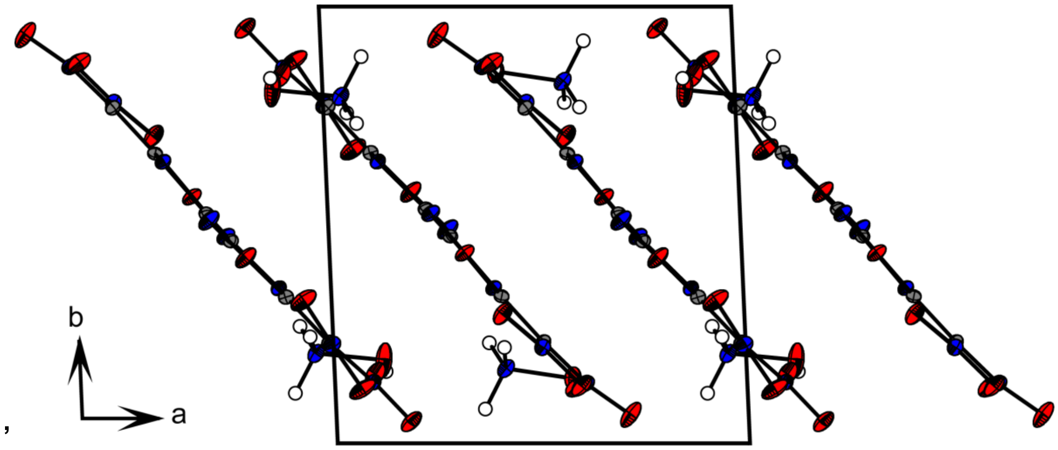

Figure S9: View on the unit cell of 5 along the *c* axes.

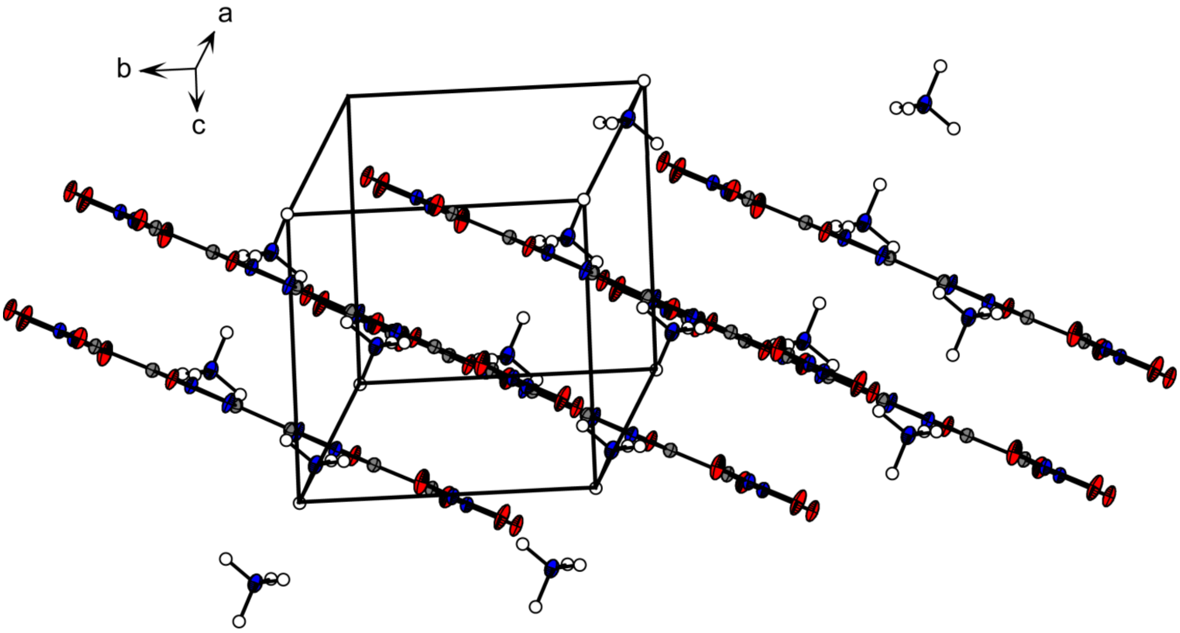

Figure S10: View on the unit cell of 3.

8.2 Computations

All calculations were carried out using the Gaussian G09W (revision A.02) program package. 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 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).

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

Table S5. CBS-4M results and calculated gas-phase enthalpies

	M	$-H^{298}$ / a.u.	$\Delta_f H^\circ(g,M)$ / kcal mol^{-1}
BOD^{2-}	$C_6N_8O_{10}^{2-}$	1416.875738	–24.3
NH_4^+	NH_4^+	56.796608	151.9
NH_4O^+	NH_4O^+	131.863249	164.1
G^+	$CH_6N_3^+$	205.453192	136.6
AG^+	$CH_7N_4^+$	260.701802	160.4
DAG^+	$CH_8N_5^+$	315.949896	184.5
TAG^+	$CH_7N_4^+$	371.197775	208.8
ANG^+	$CH_6N_5O_2^+$	464.914496	209.5
DAU^+	$CH_7N_4O^+$	335.781212	164.7
DAT^+	$CH_5N_6^+$	368.793548	251.6

Table S6. CBS-4M values and literature values for atomic $\Delta H^{\circ}{}_{f}^{298}$ / kcal mol^{-1}

	$-H^{298}$ / a.u.	NIST [S8]
H	0.500991	52.1
C	37.786156	171.3
N	54.522462	113.0
O	74.991202	59.6

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. With the calculated lattice enthalpy (Table 8) the gas-phase enthalpy of formation (Table 7) was converted into the solid state (standard conditions) enthalpy of formation (Table 8). 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 S7. Calculated gas phase heat of formation, molecular volumes, lattice energies and lattice enthalpies of 3 as well as 5–12.

	$\Delta_f H^{\circ}$(g,M) / kcal mol^{-1}	V_M / nm^3	U_L / kJ mol^{-1}	ΔH_L / kJ mol^{-1}
3	279.4	0.324	1265.8	1273.3
5	303.9	0.345	1235.7	1243.1
6	248.8	0.447	1118.3	1125.8
7	296.5	0.471	1095.7	1103.2
8	344.7	0.513	1059.8	1067.3
9	393.3	0.520	1054.2	1061.7
10	394.6	0.511	1061.9	1069.3
11	305.0	0.476	1091.3	1098.8
12	478.2	0.481	1087.3	1094.7

Table S8. 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}
3	–24.7	–103.5	14	–68.8	380.2	–180.9
5	7.0	29.5	15	66.6	412.2	161.7
6	–20.0	–83.9	18	–39.2	464.3	–84.5
7	33.0	138.1	20	187.7	494.3	379.7
8	89.8	376.2	22	430.7	524.3	821.3
9	139.7	585.0	24	644.5	554.4	1162.4
10	139.2	582.9	22	637.4	584.3	1090.8
11	42.5	178.1	21	230.2	526.3	437.3
12	217.4	910.1	20	959.7	546.3	1756.5

Notes: Δn being the change of moles of gaseous components when formed.

8.3 Experimental Part

General Procedures

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, all samples were measured at 25 °C. Mass spectrometric data were 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. [S19] The impact sensitivities were tested according to STANAG 4489modified 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". Additionally all compounds were tested for sensitivity towards electrical discharge using an Electric Spark Tester ESD 2010 EN. Energetic properties have been calculated with the EXPLO5.05 as well as the EXPLO5.601 computer code] using the 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 suite] using the CBS-4M method.

Preparation of diaminoguanidinium-5,5'-dinitromethyl-3,3'-bis(1,2,4-oxadiazolyl) (8): Diaminoguanidinium iodide (0.477 mmol) was dissolved in 2 mL water and **4** (0.954 mmol) dissolved in 5 mL water is added. The mixture was filtered warm and the solution was evaporated to dryness. A yellow solid was given. Yield 152 mg 61%, yellow solid. M.p. (DSC, 5 deg min-1): 197 ºC (dec.); Raman: $\tilde{\nu}$ = 3353 (5), 3300 (5), 1672 (3), 1579 (83), 1547 (26), 1528 (29), 1508 (17), 1474 (44), 1418 (12), 1391 (51), 1343 (43), 1290 (39), 1260 (42), 1219 (95), 1188 (25), 1087 (3), 1024 (5), 966 (100), 934 (13), 838 (38), 782 (4), 708 (2), 660 (2), 545 (5), 464 (6), 362 (5), 336 (4), 318 (5), 253 (9), 163 (17), 93 (44) cm^{-1}. IR: $\tilde{\nu}$ = 3854 (m), 3746 (m), 3568 (w), 3413 (w), 3338 (w), 2360 (s), 2341 (s), 1792 (w), 1772 (w), 1717 (m), 1684 (vs), 1654 (vs), 1617 (m), 1576 (m), 1559 (s), 1538 (vs), 1504 (vs), 1473 (s), 1458 (m), 1419 (m), 1394 (m), 1340 (m), 1292 (s), 1261 (s), 1247 (vs), 1178 (m), 1142 (w), 1062 (m), 966 (s), 834 (m), 780 (m), 750 (s), 668 (m) cm^{-1}. ^{1}H NMR (400 MHz, DMSO-*d*$_6$, 25 °C, ppm): δ= 4.53 (s, 4H, NHN*H*$_2$), 7.08 (s, 2H, CN*H*$_2$), 8.49 (s, 2H, N*H*NH$_2$). ^{13}C{^{1}H} NMR (101 MHz, DMSO-*d*$_6$, 25 °C, ppm): δ= 122.9 (s, 2C, *C*(NO$_2$)$_2$), 160.2 (s, 2C, *C*C), 160.5 (s 2C, *C*(NH)$_2$), 173.0 (s, 2C, *C*C(NO$_2$)$_2$). ^{14}N NMR (29 MHz, DMSO-*d*$_6$, 25 °C, ppm): δ= −18 (s, 4N, *N*O$_2$), −353 (s, 2N, *N*H$_3$). Ms (FAB$^+$): m/z (%) = 90.1 $[CH_8N_5^{+}]^{+}$ (42). MS (FAB$^-$) m/z (%): 434 $[M\text{-}CH_8N_5]^-$ (20), 345 $[M\text{-}C_2H_{15}N_{10}]^-$ (60), 282 $[M\text{-}C_2N_{11}H_{16}O_3]^-$ (33), 266 $[M\text{- }C_2N_{11}H_{16}O_4]^-$ (10). $C_8H_{16}N_{18}O_{10}$ (524.33): calc. C 18.33, H 3.08, N 48.08, found: C 17.99, H 3.45, N 46.26.

Preparation of Triaminoguanidinium-5,5'-dinitromethyl-3,3'-bis(1,2,4-oxadiazolyl) (9): Triaminoguanidinium chloride (0.896mmol) was dissolved in 2 mL water and **4** (0.450 mmol) dissolved in 5 mL water is added. The mixture was filtered warm and the solution was evaporated to dryness. A yellow solid was obtained. Yield 166 mg 66%, yellow solid. M.p. (DSC, 5 deg min-1): 204 ºC (dec.); Raman: $\tilde{\nu}$ = 3345 (5), 3268 (8), 1684 (2), 1599 (64), 1561 (44), 1502 (13), 1463 (58), 1422 (8), 1371 (10), 1280 (24), 1154 (8), 1032 (3), 958 (100), 930 (7), 891 (6), 828 (31), 781 (9), 728 (3), 705 (2), 647 (3), 564 (4), 467 (9), 411 (9), 348 (8), 304 (12), 191 (20), 103 (53) cm^{-1}. IR: $\tilde{\nu}$ = 3341 (m), 3240 (m), 2969 (m), 1737 (vs), 1685 (m), 1609 (w), 1548 (m), 1492 (m), 1453 (m), 1416 (w), 1365 (vs), 1276 (w), 1229 (vs), 1216 (vs), 1182 (w), 1126 (s), 1071 (m), 955 (s), 925 (s), 824 (s), 775 (s), 742 (vs) cm^{-1}. ^{1}H NMR (400 MHz, DMSO-*d*$_6$, 25 °C, ppm): δ= 3.34 (s, 18H, N*H*$_2$, N*H*). ^{13}C{^{1}H} NMR (101 MHz, DMSO-*d*$_6$, 25 °C, ppm): δ= 31.2 (s, 2C, *C*(NH)$_3$), 159.5 (s, 2C, *C*(NO$_2$)$_2$), 160.5 (s, 2C, *CC*), 173.0 (s, 2C, *C*C(NO$_2$)$_2$). ^{14}N NMR (29 MHz, DMSO-*d$_6$*, 25 °C, ppm): δ= −16 (s, 4N, *N*O$_2$), −168 (br, s, 6N, *N*H), −350 (br, s, 6N, *N*H$_2$). MS (FAB$^+$): m/z (%) = 105.1 [$CN_6H_9^+$]$^+$ (39), 555 [M+H]$^+$ (2). MS (FAB$^-$) m/z (%):345.2 [M-$N_{12}C_2H_{17}$]$^-$ (31), 449 [M-$N_6CH_9^+$]$^-$ (9), 282 [M-$N_{13}H_{18}O_3$]$^-$ (11), 266 [M-$N_{13}H_{18}O_4$]$^-$ (3). $C_8H_{18}N_{20}O_{10}$ (554.36): calc. C 17.33, H 3.27, N 50.53, found: C 17.58, H 3.06, N 50.23.

Preparation of 5,5'-dinitromethyl-3,3'-bis(1,2,4-oxadiazolyl) salts (6, 7, 10-13): Compound **2** (0.538 mmol (**6**), 0.506 mmol (**7**), 0.428 (**10**), 0.475 mmol (**11),** 0.458 mmol (**12**), 0.609 mmol (**13**)) was dissolved in 3 ml methanol and the base (guanidinium carbonate 1.076 mmol (**6**), aminoguanidinium carbonate 1.012 mmol (**7**), ANG 0.856 mmol (**10**), DAU 0.950 mmol (**11),** DAT 0.916 mmol (**12**), hydrazine hydrate 0.1 mL (**13**)) dissolved in 2 mL water was added drop wise. The mixture was stirred for 12 h. After filtration the product was obtained as light yellow to yellow solid.

Guanidinium-5,5'-dinitromethyl-3,3'-bis(1,2,4-oxadiazolyl) (6): Yield 130 mg 52%, yellow solid. M.p. (DSC, 5 deg min-1): 239 ºC (dec.); Raman: $\tilde{\nu}$ = 1600 (70), 1550 (100), 1446 (91), 1371 (60), 1287 (30), 1259 (52), 1235 (52), 1157 (12), 1093 (2), 1014 (36), 964 (66), 958 (52), 934 (8), 830 (47), 779 (16), 748 (3), 731 (2), 703 (3), 563 (7), 541 (16), 475 (7), 418 (3), 368 (6), 305 (17), 126 (66), 97 (51) cm^{-1} IR: $\tilde{\nu}$ = 3638 (w), 3411 (m), 3347 (m), 3269 (m), 3206 (m), 1737 (m), 1656 (s), 1540 (vs), 1476 (m), 1449 (m), 1416 (m), 1369 (s), 1292 (m), 1227 (vs), 1146 (s), 1065 (s), 969 (s), 961 (m), 926 (w), 826 (m), 775 (m), 747 (vs), 730 (w), 700 (w) cm^{-1}. ^{1}H NMR (400 MHz, DMSO-*d$_6$*, 25 °C, ppm): δ= 2.07 (s, 12H, N*H$_2$*). ^{13}C{^{1}H} NMR (101 MHz, DMSO-*d$_6$*, 25 °C, ppm): δ= 31.2 (s, 2C, *C*(NH$_2$)$_3$), 158.4 (s, 2C, *C*(NO$_2$)$_2$), 160.5 (s, 2C, *CC*), 173.0 (s, 2C, *C*C(NO$_2$)$_2$). ^{14}N NMR (29 MHz, DMSO-*d$_6$*, 25 °C, ppm): δ= −18.84 (s, 4N, *N*O$_2$), −337.33 (br, s, 6N, *N*H$_2$). MS (FAB$^+$): m/z (%) = 60.1 [$CN_3H_6^+$]$^+$ (11). MS (FAB$^-$) m/z (%):345.2 [M-$N_6C_2H_{11}$]$^-$ (15), 404.3 [M-$N_3CH_6^+$]$^-$ (4), 282 [M-$N_7H_{12}O_3$]$^-$ (8), 250 [M- $N_6C_2H_{12}$-2NO$_2$] (2). $C_8H_{12}N_{14}O_{10}$ (464.27): calc. C 20.70, H 2.61, N 42.24, found: C 20.74, H 2.59, N 40.44 .

Aminoguanidinium-5,5'-dinitromethyl-3,3'-bis(1,2,4-oxadiazolyl) (7): Yield 145 mg 58%, light yellow solid. M.p. (DSC, 5 deg min-1): 141 ºC (dec.); Raman: $\tilde{\nu}$ = 3348 (3), 3281 (3), 1596 (54), 1577 (77), 1490 (5), 1434 (44), 1397 (9), 1364 (100), 1281 (19), 1235 (25), 1214 (22), 1153 (14), 1101 (25), 1025 (10), 1002 (7), 974 (98), 828 (72), 758 (7), 745 (5), 702 (7), 656 (6), 563 (3), 495 (6), 458 (18), 413 (10), 375 (12), 338 (5), 313 (9), 283 (9), 190 (13), 120 (95), 107 (92), 85 (87) cm^{-1}. IR: $\tilde{\nu}$ = 3430 (m), 3341 (m), 2969 (w), 2009 (w), 1738 (m), 1661 (m), 1560 (m), 1480 (m), 1429 (w), 1397 (m), 1365 (m), 1291 (m), 1230 (vs), 1203 (vs), 1146 (vs), 1073 (s), 1000(s), 980 (vs), 933 (s), 825 (s), 784 (s), 748 (vs), 719 (m), 660 (m) cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, ppm): δ= 2.07 (s, 12H, NH_2), 3.31 (s, 2H, N*H*). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6, 25 °C, ppm): δ= 31.2 (s, 2C, *C*(NH$_2$)$_2$), 159.2 (s, 2C, *C*(NO$_2$)$_2$), 160.5 (s, 2C, *CC*), 173.0 (s, 2C, *C*C(NO$_2$)$_2$). ^{14}N NMR (29 MHz, DMSO-d_6, 25 °C, ppm): δ= −19 (s, 4N, *N*O$_2$), −264 (br, s, 2N, *N*H), −328 (br, s, 6N, *N*H$_2$). MS (FAB$^+$): m/z (%) = 75.1 $[CN_4H_7^+]^+$ (18). MS (FAB$^-$) m/z (%):345.1 $[M\text{-}N_8C_2H_{13}]^-$ (17), 419 $[M\text{-}N_4CH_7^+]^-$ (5), 282 $[M\text{-}N_9H_{14}O_3]^-$ (11), 266 $[M\text{-}N_9H_{14}O_4]^-$ (3). $C_8H_{14}N_{16}O_{10}$ (494.11): calcd. C 19.44, H 2.85, N 45.34, found: C 19.70, H 2.72, N 44.93 .

Aminonitroguanidinium-5,5’-dinitromethyl-3,3’-bis(1,2,4-oxadiazolyl) (10): Yield 163 mg 65%, colorless solid. M.p. (DSC, 5 deg min-1): 149 ºC (dec.); Raman: $\tilde{\nu}$ = 3287 (2), 1643 (4), 1606 (74), 1589 (54), 1511 (7), 1490 (8), 1474 (5), 1438 (59), 1398 (14), 1346 (10), 1300 (100), 1261 (47), 1200 (17), 1149 (5), 1099 (19), 1029 (8), 1011 (13), 974 (65), 961 (10), 938 (9), 924 (13), 829 (41), 796 (15), 786 (11), 764 (4), 753 (11), 738 (7), 699 (7), 625 (16), 564 (5), 494 (5), 465 (17), 443 (9), 419 (21), 375 (18), 317 (10), 285 (10), 192 (24), 160 (58), 132 (68), 111 (83), 100 (100), 74 (31) cm^{-1}. IR: $\tilde{\nu}$ = 3383 (w), 3270 (w), 3028 (w), 2683 (w), 2360 (w), 2333 (w), 1645 (m), 1575 (m), 1510 (s), 1446 (w), 1387 (m), 1347 (m), 1307 (s), 1245 (vs), 1229 (vs), 1196 (vs), 1142 (s), 1117 (w), 1075 (s), 1010 (m), 978 (s), 966 (m), 922 (s), 824 (s), 795 (w), 772 (w), 752 (s), 721 (m), 703 (s), 668 (m) cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, ppm): δ= 9.46 (s, br, 1H, N*H*NH$_3^+$), 8.25 (s, 3H, NHNH_3^+), 6.11 (s, br, 1H, CNH_2). ^{13}C NMR (101 MHz, DMSO-d_6, 25 °C, ppm): δ= 122.9 (s, 2C, *C*(NO$_2$)$_2$), 159.9 (s, 2C, *CC*), 160.5 (s 2C, *C*(NH)$_2$), 173.0 (s, 2C, *C*C(NO$_2$)$_2$). ^{14}N NMR (29 MHz, DMSO-d_6, 25 °C, ppm): δ= −10 (s, 2N, *N*O$_2$), −18 (s, 4N, *N*O$_2$), −354 (s, 2N, *N*H$_3$). MS (FAB$^+$): m/z (%) = 120 $[CH_6N_5O_2^+]^+$ (19). MS(FAB$^-$) m/z (%): 345 $[M\text{-}CN_5O_2H_7]^-$ (10), 46 $[NO_2]^-$ (31). $C_8H_{12}N_{18}O_{14}$ (584.29): calc. C 16.44, H 2.07, N 43.15, found: C 16.52, H 2.13, N 43.26.

Diaminouronium-5,5’-dinitromethyl-3,3’-bis(1,2,4-oxadiazolyl) (11): Yield 189 mg 76%, light yellow solid. M.p. (DSC, 5 deg min-1): 197 ºC (dec.); Raman: $\tilde{\nu}$ = 1708 (3), 1608 (28), 1594 (33), 1479 (7), 1438 (33), 1396 (44), 1352 (12), 1288 (53), 1259 (100), 1196 (8), 1146 (14), 1104 (11), 1025 (8), 979 (67), 943 (8), 822 (89), 788 (5), 752 (4), 697 (11), 582 (5), 461 (21), 413 (12), 386 (6), 313 (11), 277 (6), 179 (4), 123 (90) cm^{-1}. IR: $\tilde{\nu}$ = 3366 (m), 2970 (m), 1709 (m), 1616 (m), 1591 (m), 1573 (w), 1495 (s), 1427 (m), 1369 (m), 1351 (m), 1290 (m), 1224 (vs), 1173 (m), 1157 (w), 1130 (vs), 1077 (vs), 982 (vs), 961 (m), 929 (s), 819 (s), 780 (m), 746 (s), 714 (m), 655 (m) cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, ppm): δ= 3.13 (s, 4H, NH_2), 4.03 (s, 4H, N*H*), 8.26 (br, s, 6H, NH_3). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6, 25 °C, ppm): δ= 122.8 (s, 2C, *C*O(NH)$_2$), 159.5 (s, 2C, *C*(NO$_2$)$_2$), 160.4 (s, 2C, *CC*), 172.9 (s, 2C, *C*C(NO$_2$)$_2$). ^{14}N NMR (29 MHz, DMSO-d_6, 25 °C, ppm): δ= −18 (s, 4N, NO_2). MS (FAB^-) m/z (%):345.2 $[M\text{-}O_2N_8C_2H_{13}]^-$ (12), 282 $[M\text{-}N_9H_{14}O_5]^-$ (5), 329 $[M\text{-}O_3N_8C_2H_{13}]^-$ (9). $C_8H_{14}N_{16}O_{12}$ (526.3): calc. C 18.26, H 2.68, N 42.58, found: C 17.80, H 2.64, N 41.17.

Diaminotetrazol-5,5'-dinitromethyl-3,3'-bis(1,2,4-oxadiazolyl) (12): Yield 213 mg (85%), light yellow solid. M.p. (DSC, 5 deg min-1): 178 ºC (dec.); Raman: $\tilde{\nu}$ = 3334 (4), 3267 (4), 1717 (5), 1601 (68), 1581 (47), 1565 (47), 1488 (10), 1434 (70), 1404 (11), 1368 (81), 1316 (21), 1281 (24), 1214 (32), 1158 (19), 1140 (8), 1098 (21), 1056 (13), 1042 (12), 1024 (12), 972 (100), 954 (10), 833 (45), 788 (27), 772 (9), 744 (14), 705 (10), 695 (11), 560 (10), 493 (10), 464 (18), 443 (9), 426 (14), 369 (11), 315 (15), 305 (13), 286 (16), 251 (13), 195 (13), 134 (78), 114 (100) cm^{-1}. IR: $\tilde{\nu}$ = 3440 (w), 3334 (m), 3266 (w), 2977 (m), 2870 (w), 1709 (s), 1621 (m), 1556 (s), 1479 (s), 1443 (w), 1399 (m), 1350 (vs), 1314 (s), 1285 (m), 1214 (vs), 1153 (vs), 1136 (m), 1074 (s), 1058 (m), 1042 (m), 1008 (m), 978 (s), 929 (vs), 831 (m), 795 (m), 764 (s), 750 (s), 724 (s), 705 (s), 691 (s), 658 (m) cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6, 25 °C, ppm): δ= 5.30 (br, s, 10H, N*H*, NH_2). $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6, 25 °C, ppm): δ= 152.5 (s, 2C, *C* NH_2), 154.1 (s, 2C, $C(NO_2)_2$), 160.4 (s, 2C, *CC*), 172.9 (s, 2C, $CC(NO_2)_2$). ^{14}N NMR (29 MHz, DMSO-d_6, 25 °C, ppm): δ= −18 (s, 4N, NO_2). MS (FAB^+): m/z (%) = 101.1 $[CN_6H_5^+]^+$ (10). MS (FAB^-) m/z (%):345.2 $[M\text{-}N_{12}C_2H_9]^-$ (100) 282.3 $[M\text{-}N_{13}H_{10}O_3]^-$ (55), 266.2 $[M\text{-}N_{13}H_{10}O_4]^-$ (9). $C_8H_{10}N_{20}O_{10}$ (546.29): calc. C 17.59, H 1.85, N 51.28, found: C 17.97, H 1.85, N 51.18.

Hydrazinium-5,5'-dinitromethyl-3,3'-bis(1,2,4-oxadiazolyl) (13): Yield 240 mg 96%, yellow solid. M.p. (DSC, 5 deg min-1): 135 ºC (dec.); Raman: $\tilde{\nu}$ = 3203 (10), 2483 (15), 1595 (77), 1567 (35), 1553 (51), 1493 (29), 1478 (30), 1449 (84), 1361 (55), 1285 (52), 1256 (86), 1154 (20), 1083 (20), 973 (33), 958 (100), 920 (20), 834 (51), 781 (23), 745 (15), 708 (16), 560 (17), 461 (21), 416 (20), 353 (20), 307 (22), 101 (88) cm^{-1}. IR: $\tilde{\nu}$ = 3355 (m), 3220 (w), 2984 (w), 1720 (m), 1622 (w), 1531 (s), 1478 (m), 1452 (m), 1424 (s), 1354 (s), 1289 (s), 1232 (vs), 1124 (m), 1088 (m), 1057 (s), 965 (m), 954 (m), 913 (m), 831 (s), 777 (s), 744 (s), 732 (s) cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6, 25 °C, ppm): δ= 5.21 (br, s, 10H, NH_2, NH_3). $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6, 25 °C, ppm): δ= 158.9 (s, 2C, $C(NO_2)_2$), 160.5 (s, 2C, *CC*), 173.0 (s, 2C, $CC(NO_2)_2$). ^{14}N NMR (29 MHz, DMSO-d_6, 25 °C, ppm): δ= −18 (s, 4N, NO_2), −322 (br, s, 4N, NH_2, NH_3). MS (FAB^+): m/z (%) = 33.1 $[N_2H_5^+]^+$ (5). MS (FAB^-) m/z (%):345.1 $[M\text{-}N_4H_9]^-$ (88), 377 $[M\text{-}N_2H_5]^-$ (9), 266 $[M\text{-}N_5H_{10}O_4]^-$ (17), 282 $[M\text{-}N_5H_{10}O_3]^-$ (38), 329 $[M\text{-}N_5H_{10}O]^-$ (23). $C_6H_{10}N_{12}O_{10}$ (410.22): calc. C 17.57, H 2.46, N 40.97, found: C 16.85, H 3.02, N 40.43.

8.4 References

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9 Supplementary Information for Chapter 4

9.1 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]. DIAMOND2 plots are shown with thermal ellipsoids at the 50% probability level.

Supplementary Information

Table S1. X-ray data and parameters for 3,4,9 and 11.

	3	**4**	**9**	**11**
CCDC	1429071	1429070	1429065	1429064
Formula	$C_{17}H_9N_9O_{12}$	$C_{17}H_7N_{11}O_{16}$	$C_{19}H_{17}N_{17}O_{16}$	$C_{17}H_6CsN_{11}O_{16}$
FW / g mol^{-1}	531.33	621.34	757.51	753.24
Crystal system	Monoclinic	Orthorombic	Triclinic	Monoclinic
Space Group	$P2_1$ (No. 4)	$P2_12_12_1$ (No. 19)	$P{-}1$ (No. 2)	$P2_1/c$ (No. 14)
Color / Habit	yellow block	yellow needles	orange-red plate	dark-red plate
Size [mm]	0.03 x 0.25 x 0.30	0.06 x 0.07 x 0.12	0.05 x 0.16 x 0.26	0.01 x 0.10 x 0.32
a [Å]	7.9956(10)	14.5179(11)	7.3620(6)	11.2965(5)
b [Å]	16.571(3)	17.6612(13)	12.2385(7)	11.2478(6)
c [Å]	15.733(2)	18.3198(14)	16.6602(12)	19.1003(9)
α [°]	90	90	96.862(5)	90
β [°]	94.268(12)	90	99.492(6)	96.921(4)
γ [°]	90	90	91.796(5)	90
V [Å^3]	2078.8(5)	4697.3(6)	1467.93(18)	2409.2(2)
Z	4	8	2	4
$\rho_{calc.}$ [g cm^{-3}]	1.698	1.757	1.714	2.077
μ [mm^{-1}]	0.148	0.159	0.152	1.646
F(000)	1080	2512	776	1472
T [K]	173	298	173	173
Θ Min-Max [°]	4.1-30.0	4.3-26.3	4.2-26.0	4.1-26.0
Dataset [h; k; l]	−7:11;−23:23;−17:22	−12: 18;−21:17;−22:18	−9:9;−15:14;−18: 20	−13:13;−13:13;−23:18
Reflection collected	14319	24673	10311	19656
Independent reflection	6198	5204	5728	4699
R_{int}	0.110	0.049	0.042	0.075
Observed reflection	3046	3692	3593	3438
No. parameters	757	849	554	410
R_1 (obs)[a]	0.0617	0.0502	0.0515	0.0393
wR_2 (all data)[b]	0.1417	0.1441	0.1047	0.0682
S [c]	0.96	1.04	0.99	1.01
Min./Max. Resd. [e Å^{-3}]	−0.29/ 0.46	−0.20/ 0.27	−0.26/ 0.32	−0.55/ 0.86
Device type	Oxford Xcalibur3	Oxford Xcalibur3	Oxford Xcalibur3	Oxford Xcalibur3
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073
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

[a] $R_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. [b] $wR_2 = [\Sigma[w(Fo^2 - Fc^2)^2]/\Sigma[w(Fo)^2]]^{1/2}$; $w = [\sigma c^2(Fo^2) + (xP)^2 + yP]^{-1}$ and $P = (Fo^2 + 2Fc^2)/3$. [c] $S = [\Sigma\{w(Fo^2 - Fc^2)^2\}/(n - p)]^{1/2}$ (n = number of reflections; p = total number of parameters).

9.2 Computations

All calculations were carried out using the Gaussian G09W (revision A.02) program package. 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 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).

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

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

	M	$-H^{298}$ / a.u.	$\Delta_f H^\circ$(g,M) / kcal mol^{-1}
PYX^{2-}	$C_{17}H_5N_{11}O_{16}^{2-}$	2453.04651	–8.9
NH$_4^+$	NH_4^+	56.796608	151.9
NH$_4$O$^+$	NH_4O^+	131.863249	164.1
G$^+$	$CH_6N_3^+$	205.453192	136.6
AG$^+$	$CH_7N_4^+$	260.701802	160.4
TAG$^+$	$CH_7N_4^+$	371.197775	208.8
N$_2$H$_4^+$	$N_2H_5^+$	112.030523	185.1
TEA$^+$	$C_6H_{16}N_1^+$	292.237586	102.9

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

	$-H^{298}$ / a.u.	NIST [S8]
H	0.500991	52.1
C	37.786156	171.3
N	54.522462	113.0
O	74.991202	59.6

Supplementary Information

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. With the calculated lattice enthalpy (Table 8) the gas-phase enthalpy of formation (Table 7) was converted into the solid state (standard conditions) enthalpy of formation (Table 8). 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. Calculated gas phase heat of formation, molecular volumes, lattice energies and lattice enthalpies of 7-10 as well as 13-15.

	$\Delta_f H°(g,M)$ / kcal mol^{-1}	V_M / nm^3	U_L / kJ mol^{-1}	ΔH_L / kJ mol^{-1}
7	294.8	0.678	949.9	960.8
8	319.3	0.684	946.6	955.0
9	264.3	0.723	926.5	937.4
10	311.9	0.743	916.5	927.4
13	360.9	0.686	946.0	956.9
14	196.9	0.763	906.8	917.7
15	408.7	0.765	905.9	916.8

Table S5. 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}
7	65.3	273.5	21	325.6	655.4	496.7
8	91.3	382.1	22	436.6	687.4	635.1
9	40.4	169.0	25	231.0	739.5	312.4
10	90.4	378.5	27	445.4	769.6	548.8
13	132.3	553.9	22	610.9	685.5	891.3
14	–22.2	–92.9	33	–11.1	823.8	–13.5
15	189.7	794.4	31	871.3	829.7	1050.2

Notes: Δn being the change of moles of gaseous components when formed.

9.3 Experimental Part

General Procedures

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, all samples were measured at 25 °C. Mass spectrometric data were 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 4489modified 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". Additionally all compounds were tested for sensitivity towards electrical discharge using an Electric Spark Tester ESD 2010 EN. Energetic properties have been calculated with the EXPLO5.05 as well as the EXPLO5.601 computer code] using the 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 suite] using the CBS-4M method.

Synthesis of aminoguanidinium 2,6-bis(picrylamino)-3,5-dinitropyridine (10): 2,6-bis(picrylamino)-3,5-dinitropyridine (403.7 mg , 0.65 mmol) and aminoguanidinium bicarbonate (177.0 mg, 1.30 mmol) were dissolved in 10 ml EtOH and heated to reflux for 3 hours. After cooling and filtering the product was obtained as a brown-red solid. Yield : 308.7 mg (0.40 mmol; 62 %); M.p. (DSC, 5 deg min^{-1}): 183ºC (dec.); EA ($C_{19}H_{19}N_{19}O_{16}$, 769.47 g/mol); found (calc.) [%]: C: 29.61 (29.66), H: 2.31 (2.49), N: 34.71 (34.59). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3334 (w), 3082 (w), 2280 (vw), 1682 (w), 1666 (m), 1625 (m), 1572 (m), 1527 (s), 1497 (m), 1444 (w), 1389 (w), 1344 (s), 1310 (s), 1289 (s), 1247 (m), 1184 (m), 1116 (m), 1081 (m), 957 (m), 938 (m), 924 (m), 857 (w), 923 (m), 767 (vw), 758 (m), 717 (m), 685 (m). Raman (300 mW, 25 scans): $\tilde{\nu}$ [cm^{-1}] = 3065 (8), 2748 (7), 1617 (32), 1581 (78), 1503 (49), 1456 (13), 1368 (73), 1346 (100), 1317 (43), 1298 (46), 1242 (66), 1174 (41), 1119 (52), 1082 (28), 946 (10), 824 (70), 747 (21), 363 (20), 329 (22), 393 (19), 200 (46), 90 (55). MS (ESI, m/z): 620.0 $[C_{17}H_6N_{11}O_{16}^-]$ (100), 573.0$[C_{17}H_5N_{11}O_{16}^- - NO_2]$ (80), 557.0 $[C_{17}H_5N_{11}O_{16}^- - NO_3]$ (2); MS (FAB^+, m/z): 75.1 $[CN_4H_7^+]$ (30); (FAB^-, m/ z): 620.1 $[C_{17}H_5N_{11}O_{16}^-]$ (25), 573.0 $[C_{17}H_5N_{11}O_{16}^- - NO_2]$ (6), 557.0 $[C_{17}H_5N_{11}O_{16}^- - NO_3]$ (3), 195.0 $[C_{17}H_5N_{11}O_{16}^- - C_{12}H_4N_6O_{12}]$ (30), 167.0 $[C_{17}H_5N_{11}O_{16}^- - C_{12}H_4N_8O_{12}]$ (24), 46.1 $[C_{17}H_5N_{11}O_{16}^- - C_{17}H_5N_{10}O_{14}]$ (32). ^1H NMR (400 MHz, DMSO-d_6, 25 °C, ppm): δ = 8.75 (s, 1H, CH), 8.58 (s, br, 2H, NH) 8.34 (s, 4H, CH), 7.26 (s, br, 2H, N-NH_2), 6.79 (s, br, 4H, NH_2). ^{13}C NMR (101 MHz, DMSO-d_6, 25 °C, ppm): δ = 159.2 (2C, C-NH_2), 153.4 (2C, C-N), 145.5 (2C, C-NO_2), 143.6 (4C, C-NO_2), 134.0 (2C, C-N), 131.2 (2C, C-NO_2), 126.0 (1C, CH), 122.9 (4C, CH). ^{14}N NMR (29 MHz, DMSO-d_6, 25 °C, ppm): δ = −20 (8N, NO_2), −264 (2N, NH) −369 (6N, NH_2). BAM Impact sensitivity test: 40 J; Friction sensitivity test: 360 N.

Synthesis of cesium salt of 2,6-bis(picrylamino)-3,5-dinitropyridine (11): 2,6-bis(picrylamino)-3,5-dinitropyridine (351.0 mg, 0.57 mmol) was dissolved in ethanol (10 ml) and $CsOH \cdot H_2O$ (0.05 ml, 1.13 mmol, ρ = 3.68 g·cm^{-3}) was dropped slowly to the mixture. After heating for 3 hours and filtering the product was obtained as a dark purple to black solid from the residue. Yield: 377.1 mg (0.43 mmol; 75 %); M.p. (DSC, 5 deg min^{-1}): 337°C (dec.); EA ($C_{17}H_6N_{11}O_{16}Cs$, 753.20 g/mol); found (calc.) [%]: C: 26.36 (27.11), H: 1.08 (0.80), N: 19.55 (20.46). EA ($C_{17}H_6N_{11}O_{16}Cs*H_2O$, 771.21 g/mol); found (calc.) [%]: C: 26.36 (26.48), H: 1.08 (1.05), N: 19.55 (19.98). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3083 (vw), 1608 (w), 1550 (s), 1525 (s), 1479 (m), 1448 (w), 1425 (w), 1343 (m), 1326 (s), 1255 (vs), 1213 (s), 1166 (s), 1086 (m), 936 (w), 920 (w), 908 (w), 857 (vw), 836 (vw), 824 (w), 779 (vw), 756 (m), 717 (s), 695 (m), 678 (m), 660 (m). Raman (300 mW, 25 scans): $\tilde{\nu}$ [cm^{-1}] = 3240 (8), 2563 (17), 2269 (12), 2242 (14), 2221 (16), 2208 (17), 2185 (19), 2158 (21), 2136 (24), 2092 (22), 2075 (20), 2059 (21), 2043 (18), 2023 (22), 1925 (22), 1796 (22), 1625 (29), 1328 (66), 1204 (35), 1123 (34), 1090 (22), 826 (40), 723 (36), 641 (42), 98 (100). MS (FAB^+, m/z): 131.1 $[M^+]$ (79); (FAB^-, m/ z): 620.5 $[M^-]$ (88), 604 $[M^- - O]$ (20), 573.4 $[M^- - NO_2]$ (23), 557.0 $[M^- - NO_3]$ (9), 511 $[M^- - N_2O_5]$ (11), 46.1 $[M^- - C_{17}H_5N_{10}O_{14}]$ (8). ^1H-NMR (400 MHz, DMSO-d_6, 25 °C, ppm): δ = 10.80 (br, 1H, NH), 8.83 (s, 1H, CH), 8.71 (s, 4H, CH). ^{13}C-NMR (101 MHz, DMSO-d_6- 25 °C, ppm): δ = 163.5 (1C, CN^-), 153.9 (1C, CNH), 148.9 (2C, CNO_2), 148.5 (1C, CN^-), 144.3 (1C, C NO_2), 143.2 (2C, CNO_2), 139.9 (1C, CNO_2), 138.6 (1C, CNH), 134.1 (1C, CNO_2), 128.5 (1C, CH), 125.7 (1C, CNO_2), 124.7 (2C, CH), 122.9 (2C, CH). ^{14}N

NMR (29 MHz, DMSO-d$_6$, 25 °C, ppm): δ = −3 (8N, CNO$_2$), −231 (1N, CNH). BAM Impact sensitivity test: 5 J; Friction sensitivity test: 360 N

Synthesis of barium salt of 2,6-bis(picrylamino)-3,5-dinitropyridine (12): A mixture of 2,6-bis(picrylamino)-3,5-dinitropyridine (410.6 mg, 0.66 mmol) and $Ba(OH)_2 \cdot 8H_2O$ (104.3 mg, 0.33 mmol) was stirred under reflux in 10 mL ethanol for 3 hours. After cooling, the suspension was filtered and the product was obtained as a brown solid. Yield: 436.2 mg (0.32 mmol; 49 %); M.p. (DSC, 5 deg min^{-1}): 353ºC (dec.); EA ($C_{17}H_5N_{11}O_{16}BaOH$, 774.91 g/mol); found (calc.) [%]: C: 26.03 (26.36), H: 1.53 (0.91), N: 19.12 (19.89). EA ($C_{17}H_5N_{11}O_{16}BaOH{*}H_2O$, 792.64 g/mol); found (calc.) [%]: C: 26.03 (25.76), H: 1.53 (1.14), N: 19.12 (19.44). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3561 (vw), 3476 (vw), 3359 (vw), 3082 (w), 2361 (vw), 1624 (m), 1592 (m), 1573 (m), 1532 (s), 1499 (m), 1443 (m), 1413 (m), 1344 (s), 1308 (s), 1283 (s), 1242 (s), 1190 (s), 1176 (s), 1115 (m), 1087 (m), 940 (m), 922 (m), 858 (w), 824 (m), 758 (m), 718 (s), 704 (m), 656 (w). MS (FAB$^+$, m/z): 136.0 [M$^+$] (16); (FAB$^-$, m/ z): 620.6 [M$^-$] (57), 604 [$M^- - O$] (20), 573.5 [$M^- - NO_2$] (12), 511 [$M^- - N_2O_5$] (13), 46.1 [$M^- - C_{17}H_5N_{10}O_{14}$] (14). ^{1}H NMR (400 MHz, DMSO-d6, 25 °C, ppm): δ = 9.59 (br, s, 1H, NH), 9.00 (s, 1H, CH), 8.79 (s, 2H, CH), 8.54 (s, 2H, CH), 3.53 (1H, OH). ^{13}C NMR (101 MHz, DMSO-d6- 25 °C, ppm): δ = 155.2 (1C, CNH), 153.9 (1C, CN$^-$), 151.1 (1C, CN$^-$), 144.2 (2C, CNO$_2$), 143.0 (1C, CNO$_2$), 142.2 (1C, CNO$_2$), 135.6 (1C, CNH), 134.1 (12C, CNO$_2$), 125.1 (1C, CNO$_2$), 124.7 (1C, CH), 123.8 (1C, CNO$_2$), 123.4 (2C, CH), 120.6 (2C, CH). ^{14}N NMR (29 MHz, DMSO-d$_6$, 25 °C, ppm): δ = −24 (8N, CNO$_2$), −221 (1N, CNH). BAM Impact sensitivity test: IS: 6 J; Friction sensitivity test: 360 N

Synthesis of hydrazinium salt of 2,6-bis(picrylamino)-3,5-dinitropyridine (13): 2,6-Bis(picrylamino)-3,5-dinitropyridine (453.5 mg, 0.73 mmol) was dissolved in 10 ml ethanol. Aqueous hydrazine (0.07 ml, 1.46 mmol) were added drop-wise to the mixture. The mixture was heated under reflux for 3 hours. After cooling and filtering the product was obtained as a red to brown solid. Yield : 331.3 mg (4.8 mmol; 66 %); M.p. (DSC, 5 deg min^{-1}): 205ºC (dec.); EA ($C_{17}H_{15}N_{15}O_{16}$, 685.69 g/mol); found (calc.) [%]: C: 28.99 (29.79), H: 2.72 (2.21), N: 36.64 (30.65). EA ($C_{17}H_{15}N_{15}O_{16}{*}N_2H_4$); found (calc.) [%]: C: 28.99 (28.46), H: 2.72 (2.67), N: 36.64 (33.19). MS (FAB$^+$, m/z): 33.1 [$N_2H_5^+$] (17); (FAB$^-$, m/ z): 619.1 [$C_{17}H_5N_{11}O_{16}^-$] (10), 527.0 [$C_{17}H_5N_{11}O_{16}^- - N_2O_4$] (21), 449.4 [$C_{17}H_5N_{11}O_{16}^- - N_4O_7$] (32), 433.0 [$C_{17}H_5N_{11}O_{16}^- - N_4O_8$] (5), 373.4 [$C_{17}H_5N_{11}O_{16}^- - N_5O_{11}$] (25), 224.2 [$C_{17}H_5N_{11}O_{16}^- - C_{11}H_5N_7O_{10}$] (95), 153.2 [$C_{17}H_5N_{11}O_{16}^- - C_{12}H_4N_8O_{13}$] (90), 46.1 [$C_{17}H_5N_{11}O_{16}^- - C_{17}H_5N_{10}O_{14}$] (19). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3474 (m), 3357 (m), 3088 (w), 2840 (vw), 2740 (vw), 2648 (vw), 2360 (vw), 1606 (vs), 1552 (w) 1526 (w), 1508 (m), 1455 (m), 1436 (m), 1389 (w) 1373 (m), 1328 (s), 1281 (s), 1269 (vw), 1217 (vs), 1180 (m), 1330 (w), 1106 (vw), 1086 (m), 1060 (vw), 1036 (s), 944 (vw), 934 (m), 922 (vw), 902 (w), 877 (vw), 864 (vw), 828 (w), 802 (m), 742 (m), 717 (m), 706 (m), 684 (vw). Raman (300 mW, 25 scans): $\tilde{\nu}$ [cm^{-1}] = 3347 (8), 3297 (6), 3085 (7), 2476 (7), 1598 (17), 1554 (12), 1358 (13), 1323 (86), 1253 (9), 1185 (17), 1111 (5), 1061 (7), 1010 (5), 805 (12), 791 (7), 751 (7), 726 (6), 381 (17), 348 (6), 87 (43). ^{1}H NMR (400 MHz, DMSO-d$_6$, 25 °C, ppm): δ = 8.97 (s, 1H, CH), 8.81 (s, 4H, CH), 7.31 (br, 10H, NH_2/NH_3). ^{13}C NMR (101 MHz, DMSO-d$_6$, 25 °C, ppm): δ = 155.2 (2C, C-N), 139.2 (2C, C-NO_2), 135.8 (2C, C-N), 130.7 (4C, C-NO_2), 120.7 (2C, C-NO_2), 117.6 (1C, CH), 116.7 (4C, CH). ^{14}N NMR (29 MHz, DMSO-d$_6$, 25 °C, ppm): δ = −15 (8N, CNO_2), −359 (4N, NH_2). BAM Impact sensitivity test: 10 J; Friction sensitivity test: 360 N; Electrostatic discharge: 0.35 J.

Synthesis of the triethylammonium salt of 2,6-bis(picrylamino)-3,5-dinitropyridine (14): 2,6-Bis(picrylamino)-3,5-dinitropyridine (500 mg, 0.81 mmol) and triethylamine (2.00 ml, 14.3 mmol) were dissolved in H_2O (10 ml) and heated to 100°C for 2 h, or stirred at room temperature for 5 h. The mixture was filtered and the product was obtained as a dark brown solid. Yield : 207.0 mg (0.25 mmol, 31 %); M.p. (DSC, 5 deg min^{-1}): 276ºC (dec.); EA ($C_{29}H_{37}N_{13}O_{16}$, 823.68 g/mol), found (cal.) [%]: C: 41.94 (42.29), H: 4.52 (4.53), N: 22.84 (22.11). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3472 (w), 3439 (w), 3350 (w), 3316 (w), 3089 (w), 2705 (w), 1604 (m), 1576 (m), 1558 (m), 1531 (m), 1501 (m), 1443 (m), 1388 (m), 1368 (m), 1316 (s), 1269 (s), 1209 (vs), 1137 (m), 1100 (m), 1078 (m), 1017 (m), 943 (m), 912 (m), 848 (m), 820 (m), 796 (m), 736 (m), 736 (m), 717 (s). MS (FAB^{+}, m/z): 102.2 [TEA^{+}] (100); (FAB^{-}, m/ z): 620.6 [$C_{17}H_6N_{11}O_{16}^{-}$] (43), 604 [$C_{17}H_5N_{11}O_{16}^{-}$−O] (35), 573.5 [$C_{17}H_5N_{11}O_{16}^{-}$−$NO_2$] (27), 557 [$C_{17}H_5N_{11}O_{16}^{-}$−$NO_3$] (14), 511 [$C_{17}H_5N_{11}O_{16}^{-}$−$N_2O_5$] (9), 46.1 [$C_{17}H_5N_{11}O_{16}^{-}$−$C_{17}H_5N_{10}O_{14}$] (18). ^{1}H NMR (400 MHz, DMSO-d$_6$, 25 °C, ppm): δ = 8.82 (s, 1H, CH), 8.66 (s, 4H, CH), 7.82 (br, s, 2H, NH), 3.08 (q, 12H, J = 7.3 Hz, CH_2), 1.17 (t, 18H, J = 7.3 Hz, CH_3). ^{13}C NMR (101 MHz, DMSO-d$_6$, 25 °C, ppm): δ = 154.7 (2C, CN), 144.3 (2C, CNO_2), 142.5 (4C, CNO_2), 135.6 (2C, CN), 133.9 (2C, CNO_2), 125.2 (1C, CH),123.3 (4C, CH), 45.8 (6C, CH_2), 8.7 (6C, CH_3). ^{14}N NMR (DMSO-d$_6$, 25 °C, ppm): δ = −10 (8N, NO_2), −250 (2N, NH). BAM Impact sensitivity test: 35 J; Friction sensitivity test: 360 N.

Synthesis of triaminoguanidinium salt of 2,6-bis(picrylamino)-3,5-dinitropyridine (15): The sodium salt of 2,6-bis(picrylamino)-3,5-dinitropyridine (501 mg, 0.75 mmol) or the potassium salt of 2,6-bis(picrylamino)-3,5-dinitropyridine (523 mg, 0.75 mmol) and triaminoguanidinium chloride (211 mg, 1.50 mmol, 2 eq) were dissolved in ethanol (10 ml) and heated to 100 °C for 2 h. The hot mixture was filtered and the product was obtained as a brown-red solid. Yield : 300.4 mg (0.43 mmol, 48 %); M.p. (DSC, 5 deg min^{-1}): 233ºC (dec.); EA ($C_{19}H_{23}N_{23}O_{16}$, 829.53 g/mol); found (calc.) [%]: C: 27.84 (27.51), H: 3.55 (2.79), N: 38.90 (38.84). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3319 (vw), 3193 (w), 3082 (w), 1681 (w), 1623 (m), 1583 (m), 1531 (s), 1500 (m), 1439 (m), 1412 (m), 1348 (vs), 1306 (vs), 1251 (s), 1200 (s), 1130 (m), 1093 (w), 1056 (w), 945 (m), 931 (m), 913 (m), 858 (w), 825 (w), 758 (m), 721 (s), 684 (m). MS (FAB$^+$, m/z): 105.2 [$CN_6H_{10}^+$] (70); (FAB$^-$, m/ z): 620.6 [$C_{17}H_6N_{11}O_{16}^-$] (73), 604 [$C_{17}H_5N_{11}O_{16}^-{-}O$] (13), 573.5 [$C_{17}H_5N_{11}O_{16}^-{-}NO_2$] (15), 557 [$C_{17}H_5N_{11}O_{16}^-{-}NO_3$] (25), 511 [$C_{17}H_5N_{11}O_{16}^-{-}N_2O_5$] (12), 46.1 [$C_{17}H_5N_{11}O_{16}^-{-}C_{17}H_5N_{10}O_{14}$] (27). ^{1}H NMR (400 MHz, DMSO-d$_6$, 25 °C, ppm): δ = 8.81 (s, 4H, CH), 8.68 (s, 1H, CH), 8.59 (br, s, 6H, NH), 4.49 (br, s, 12H, NH_2). ^{13}C NMR (101 MHz, DMSO-d$_6$, 25 °C, ppm): δ = 160.9 (1C, C-NH), 159.5 (2C, CN), 144.7 (2C, CNO_2), 134.1 (4C, CNO_2), 130.7 (2C, CN), 124.7 (2C, CNO_2), 123.5 (1C, CH), 114.5 (4C, CH). ^{14}N NMR (DMSO-d$_6$, 25 °C, ppm): δ = −19 (8N, NO_2), −170 (6N, NH), −279 (6N, NH_2). BAM Impact sensitivity test: 20 J; Friction sensitivity test: 360 N.

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10 Supplementary Information for Chapter 5

10.1 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 hydrogen atoms were located and freely refined. The absorptions were corrected by a Scale3 Abspack multiscan method.[S6]. Diamond2 plots are shown with thermal ellipsoids at the 50% probability level.

Supplementary Information

Table S1. X-ray data and parameters for 4,7 and 14.

	4· DMF	**7**
CCDC	1433585	1433586
Formula	$C_8H_5N_7O_6$	$C_9H_{10}N_{10}O_6$
FW / g mol^{-1}	368.29	354.27
Crystal system	Triclinic	Monoclinic
Space Group	*P*−1 (No. 2)	*C*2/c (No. 15)
Color / Habit	yellow block	dark-red block
Size [mm]	0.10 x 0.35 x 0.40	0.06 x 0.19 x 0.26
a [Å]	7.9131(6)	23.1666(16)
b [Å]	8.7171(6)	8.4540(4)
c [Å]	12.4208(10)	14.6023(9)
α [°]	77.277(6)	90
β [°]	78.960(7)	104.165(6)
γ [°]	71.483(7)	90
V [Å^3]	785.60(11)	2772.9(3)
Z	2	8
$\rho_{calc.}$ [g cm^{-3}]	1.557	1.697
μ [mm^{-1}]	0.132	0.144
F(000)	380	1456
T [K]	173	173
Θ Min-Max [°]	4.5-26.0	4.2-26.5
Dataset [h; k; l]	−9: 9; −10: 10; −15: 15	−27: 28; −10: 9; −15: 18
Reflection collected	6007	5754
Independent reflection	3068	2863
R_{int}	0.020	0.031
Observed reflection	2483	2021
No. parameters	283	285
R_1 (obs)[a]	0.0361	0.0540
wR_2 (all data)[b]	0.0955	0.1461
S [c]	1.03	1.04
Min./Max. Resd. [e Å^{-3}]	−0.19/0.21	−0.35/0.52
Device type	Oxford Xcalibur3	Oxford Xcalibur3
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073
Solution	SIR-92	SIR-92
Refinement	SHELXL-97	SHELXL-97
Absorption correction	multi-scan	multi-scan

[a] $R_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. [b] $wR_2 = [\Sigma[w(Fo^2 - Fc^2)^2]/\Sigma[w(Fo)^2]]^{1/2}$; $w = [\sigma c^2(Fo^2) + (xP)^2 + yP]^{-1}$ and $P = (Fo^2 + 2Fc^2)/3$. [c] $S = [\Sigma\{w(Fo^2 - Fc^2)^2\}/(n - p)]^{1/2}$ (n = number of reflections; p = total number of parameters).

10.2 Computations

All calculations were carried out using the Gaussian G09W (revision A.02) program package. 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 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).

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

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

	M	$-H^{298}$ / a.u.	$\Delta_f H^\circ$(g,M) / kcal mol^{-1}
PATO$^-$	$C_8H_4N_7O_6^-$	1140.218604	15.9
APATO$^-$	$C_8H_5N_8O_6^-$	1195.521432	5.8
NH_4^+	NH_4^+	56.796608	151.9
G$^+$	$CH_6N_3^+$	205.453192	136.6
AG$^+$	$CH_7N_4^+$	260.701802	160.4
TAG$^+$	$CH_7N_4^+$	371.197775	208.8
$N_2H_4^+$	$N_2H_5^+$	112.030523	185.1
TEA$^+$	$C_6H_{16}N_1^+$	292.237586	102.9

Table S3. CBS-4M values and literature values for atomic $\Delta H^{\circ}{}_{f}^{298}$ / kcal mol^{-1}

	$-H^{298}$ / a.u.	NIST [S8]
H	0.500991	52.1
C	37.786156	171.3
N	54.522462	113.0
O	74.991202	59.6

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. With the calculated lattice enthalpy (Table 8) the gas-phase enthalpy of formation (Table 7) was converted into the solid state (standard conditions) enthalpy of formation (Table 8). 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)

Table S4. Calculated gas phase heat of formation, molecular volumes, lattice energies and lattice enthalpies of 7-12 as well as 16-18.

	$\Delta_f H^{\circ}$(g,M) / kcal mol^{-1}	V_M / nm^3	U_L / kJ mol^{-1}	ΔH_L / kJ mol^{-1}
7	152.6	0.346	437.8	441.3
8	176.4	0.366	431.6	435.1
9	167.8	0.303	453.2	456.7
10	118.9	0.386	425.8	429.3
11	200.9	0.310	450.6	454.1
12	224.8	0.389	425.3	428.8
16	142.3	0.347	437.8	441.2
17	166.2	0.367	431.6	435.1
18	108.7	0.387	425.8	429.3

Table S5. 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}
7	47.2	197.5	13	229.7	354.2	648.5
8	72.5	303.4	14	338.1	369.3	915.6
9	58.7	245.9	11	273.2	312.2	875.2
10	16.4	68.6	17	110.8	396.4	279.5
11	92.4	386.9	12	416.7	327.2	1273.4
12	122.4	512.4	16	552.0	399.3	1382.6
16	36.9	154.8	14	189.5	369.3	513.1
17	62.3	260.6	15	297.8	384.3	775.0
18	6.2	25.8	18	70.5	411.4	171.4

Notes: Δn being the change of moles of gaseous components when formed.

10.3 Experimental Part

General Procedures

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, all samples were measured at 25 °C. Mass spectrometric data were 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 4489modified 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". Additionally all compounds were tested for sensitivity towards electrical discharge using an Electric Spark Tester ESD 2010 EN. Energetic properties have been calculated with the EXPLO5.05 as well as the EXPLO5.601 computer code] using the 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 suite] using the CBS-4M method.

Synthesis of potassium salt of 3-(Picrylamino)-1,2,4-triazole (5) A mixture of 3-(Picrylamino)-1,2,4-triazole (**3**) (442.9 mg, 1.50 mmol) and KOH (84.2 mg, 1.76 mmol) in 10 ml ethanol was stirred under reflux for 3 hours. After cooling, the mixture was filtered. After removing the solvent of the filtrate, a dark red solid was obtained as product. Yield: 495.0 mg (1.49 mmol; 99 %); M.p. (DSC, 5 deg min^{-1}): 125ºC (melt.), 278ºC (dec.); EA ($C_8H_4N_7O_6K$, 333.26 g/mol); exp. (calc.) [%]: C: 25.43 (28.83), H: 2.32 (1.21), N: 27.65 (29.42). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3352 (w), 3086 (w), 2763 (vw), 2689 (vw), 2360 (vw), 2341 (vw), 1604 (m), 1544 (m), 1519 (m), 1478 (m), 1436 (w), 1386 (w), 1338 (s), 1310 (s), 1262 (vs), 1203 (m), 1163 (m), 1084 (m), 1050 (s), 964 (m), 928 (s), 888 (m), 825 (m), 811 (m), 766 (m), 752 (m), 736 (s), 722 (m), 706 (m), 683 (m). Raman (300 mW, 25 scans): $\tilde{\nu}$ [cm^{-1}] = 3100 (1), 1583 (27), 1525 (40), 1494 (30), 1349 (47), 1276 (100), 1207 (9), 1082 (12), 949 (10), 862 (3), 827 (30), 814 (5), 739 (5), 708 (10), 659 (4), 540 (3), 505 (8),446 (2), 406 (4), 340 (3), 289 (3), 162 (10), 103 (23). MS (FAB$^+$, m/z): 39.0 [M^+] (22); (FAB$^-$, m/z): 294.3 [M^-] (100), 278 [$M^-{-}O$] (13), 247 [$M^-{-}NO_2$] (12), 228 [$M^-{-}C_2H_2N_3$] (20), 212 [$M^-{-}C_2H_2N_4$] (5), 46.1 [$M^-{-}C_8H_4N_6O_4$] (20). ^{1}H-NMR (400 MHz, DMSO-d$_6$, 25 °C, ppm): δ = 12.73 (s, 1H, NH); 8.35 (s, 2H, CH); 7.42 (s, 1H, CH). ^{13}C-NMR (101 MHz, DMSO-d$_6$- 25 °C, ppm): δ = 163.0 (1C, C-N), 159.4 (1C, C-H), 157.9 (2C, C-NO_2), 148.7 (1C, C-NO_2), 141.5 (1C,C-N), 126.6 (2C, C-H). ^{14}N NMR (29 MHz, DMSO-d$_6$, 25 °C, ppm): δ = −12 (3N, *N*O_2), −182 (1N, NH). BAM Impact sensitivity test: 15 J; Friction sensitivity test: 360 N

Synthesis of sodium salt of 3-(Picrylamino)-1,2,4-triazole (6) 3-(Picrylamino)-1,2,4-triazole (**3**) (465.3mg, 1.58 mmol) was dissolved in 10 ml EtOH and NaOH (63.1 mg, 1.58 mmol) was added. The mixture was heated for 3h at 70 °C. After cooling , filtering and evaporating product **6** was obtained as a red solid. Yield: 331 mg (0.93 mmol; 67 %); M.p. (DSC, 5 deg min^{-1}): 317ºC (dec.); EA ($C_8H_4N_7O_6Na$, 317.15 g/mol); found (calc.) [%]: C: 30.53 (30.30), H: 2.74 (1.27), N: 24.68 (30.91). EA ($C_8H_4N_7O_6Na{*}2H_2O{*}EtOH$, 317.15 g/mol); found (calc.) [%]: C: 30.53 (30.08), H: 2.74 (3.53), N: 24.68 (24.56). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3250 (w), 3088 (w), 2338 (w), 1637 (w), 1617 (m), 1560 (m), 1514 (s), 1429 (m), 1341 (s), 1277 (s), 1236 (s), 1164 (m), 1099 (m), 960 (m), 921 (m), 970 (w), 789 (m), 736 (m), 712 (s), 679 (m), 667 (s). Raman (200 mW, 25 Scans): $\tilde{\nu}$ [cm^{-1}] = 3094 (3), 2930 (5), 1608 (20), 1565 (55), 1497 (37), 1438

(12), 1350 (99), 1313 (100), 1276 (89), 1206 (28), 1174 (21), 1083 (8), 947 (20), 876 (7), 824 (46), 739 (16), 712 (17), 541 (16), 504 (21), 338 (36), 276 (33), 203 (44), 99 (89). MS (FAB$^+$, m/z): 23.1 [Na$^+$] (10) ; (FAB$^-$, m/ z): 294.2 $[C_8H_4N_7O_6^-]$ (100), 228.1 $[C_8H_4N_7O_6^- - C_2H_2N_3]$ (90), 46.1 $[C_8H_4N_7O_6^- - C_8H_4N_6O_4]$ (14). ^{1}H NMR (400 MHz, DMSO-d$_6$, 25 °C, ppm): δ = 12.76 (s, br, 1H, NH), 8.40 (s, 2H, CH); 7.47 (s, 1H, CH). ^{13}C NMR (101 MHz, DMSO-d$_6$, 25 °C, ppm): δ = 159.1 (2C, C-N), 148.3 (1C, C-H), 144.4 (1C, C- NO_2), 142.3 (1C, C-NO_2), 141.4 (1C, C-N), 124.6 (2C, CH). ^{14}N NMR (29 MHz, DMSO-d$_6$, 25 °C, ppm): δ = −16 (3N, *N*O$_2$), −179 (1N, NH). BAM Impact sensitivity test: 10 J; Friction sensitivity test: 360 N.

Synthesis of aminoguanidinium salt of 3-(Picrylamino)-1,2,4-triazole (8) 3-(Picrylamino)-1,2,4-triazole (**3**) (399.7 mg, 1.35 mmol) was dissolved in 10 ml EtOH and aminoguanidinium bicarbonate (184.3 mg , 1.35 mmol) was added. The mixture was heated for 3h at 70 °C. After cooling and evaporating, product (**8**) was obtained as a brown solid. Yield: 228.4 mg (0.35 mmol, 46 %); M.p. (DSC, 5 deg min^{-1}): 209ºC (dec.). EA ($C_9H_{11}N_{11}O_6$, 369.25 g/mol); found (calc.) [%]: C: 33.90 (29.27), H: 4.18 (3.00), N: 36.53 (41.73). EA ($C_9H_{11}N_{11}O_6$*2EtOH, 369.25 g/mol); found (calc.) [%]: C: 33.90 (30.49), H: 4.18 (4.42), N: 36.53 (35.56). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3461 (vw), 3250 (w), 3142 (vw), 3087 (w), 2864 (vw), 2279 (vw), 1681 (w), 1619 (m), 1593 (m), 1572 (m), 1526 (s), 1515 (s), 1470 (w), 1443 (w), 1405 (w), 1350 (s), 1305 (s), 1235 (s), 1190 (s), 1164 (m), 1128 (m), 1099 (m), 1068 (m), 980 (s), 922 (m), 912 (m), 870 (m), 811 (w), 767 (w), 736 (s), 718 (s), 690 (m). Raman (200 mW, 25 Scans): $\tilde{\nu}$ [cm^{-1}] = 3423 (4), 3336 (4), 3292 (4), 3073 (5), 2820 (4), 1604 (30), 1553 (42), 1513 (16), 1477(21), 1362 (20), 1345 (21), 1326 (24), 1301 (58), 1196 (100), 1179 (54), 1068 (15), 922 (16), 851 (8), 814 (41), 720 (19), 507 (7), 387 (8), 360 (8), 305 (7), 237 (26), 92 (33). MS (FAB$^+$, m/z): 75.0 $[CH_7N_4^+]$ (12); (FAB$^-$, m/z): 294.0 $[C_8H_4N_7O_6^-]$ (8) , 228.0 $[C_8H_4N_7O_6^- - C_2H_2N_3]$ (6), 122 $[C_8H_4N_7O_6^- - C_2H_2N_6O_4]$ (10), 46 $[C_8H_4N_7O_6^- - C_8H_4N_6O_4]$ (25). MS (ESI, m/z): 294.0 $[C_8H_4N_7O_6^-]$ (100), 226.9 $[C_8H_4N_7O_6^- - C_2H_3N_3]$. ^{1}H NMR (400 MHz, DMSO-d$_6$, 25 °C, ppm): δ = 13.88 (s, br, 1H, NH), 9.34 (s, 2H, CH), 8.93 (s, br, 2H, NH_2), 8.66 (s, 1H, CH), 8.42 (s, br, 1H, NH), 7.35 (s, br, 4H, NH_2). ^{13}C NMR (101 MHz, DMSO-d$_6$, 25 °C, ppm): δ = 159.2 (1C, C-NH_2), 157.1 (1C, C-N) 155.2 (1C, C-H), 144.6 (2C, C-NO_2), 140.7 (1C, C-NO_2), 135.8 (1C, C-N), 125.7 (2C, C-H). ^{14}N NMR (29 MHz, DMSO-d$_6$, 25 °C, ppm): δ = −15 (3N, NO_2), −193 (1N, NH), −342 (1N, NH_2). BAM Impact sensitivity test: 40 J; Friction sensitivity test: 360 N.

Synthesis of triethylammonium salt of 3-(Picrylamino)-1,2,4-triazole (10) 3-(Picrylamino)-1,2,4-triazole (**3**) (500 mg, 1.69 mmol) was dissolved in 10 ml ethanol and triethylamine (1.00 ml, 7.17 mmol) was added. The mixture was heated to 100 °C for

2 h. The hot mixture was filtered, the solvent evaporated and the product was obtained as a brown solid. Yield: 390.0 mg (0.98 mmol; 58 %); M.p. (DSC, 5 deg min^{-1}): 263ºC (dec.). EA ($C_{14}H_{20}N_8O_6$, 396.36 g/mol), found (cal.) [%]: C: 41.68 (42.42), H: 4.97 (5.09), N: 27.72 (28.27). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3417 (vw), 3329 (vw), 3272 (vw), 3091 (vw), 3004 (w), 2800 (w), 2737 (w), 2689 (w), 2496 (w), 1631 (m), 1613 (m), 1554 (s), 1506 (m), 1494 (m), 1471 (m), 1435 (m), 1392 (w), 1364 (m), 1345 (m), 1314 (vs), 1294 (s), 1268 (vs), 1208 (m), 1162 (s), 1091 (m), 1075 (m), 1041 (m), 1012 (m), 977 (w), 943 (m), 911 (m), 870 (w), 840 (m), 810 (w), 784 (m), 743 (m), 721 (m), 707 (s), 674 (m). Raman (300 mW, 25 scans): $\tilde{\nu}$ [cm^{-1}] = 3128 (6), 2989 (13), 2946 (12), 2203 (6), 2146 (7), 1576 (33), 1530 (25), 1498 (23), 1364 (48), 1350 (68), 1312 (69), 1298 (100), 1268 (100), 1165 (10), 1076 (14), 981 (7), 944 (11), 822 (61), 651 (21), 334 (40), 97 (64). MS (FAB$^+$, m/z): 102.2 [TEA$^+$] (100); (FAB$^-$, m/z): 294.3 [M$^-$] (91), 278 [M$^-$−O] (43), 247 [M$^-$−NO_2] (23), 228 [M$^-$−$C_2H_2N_3$] (25), 212 [M$^-$−$C_2H_2N_4$] (8), 46.1 [M$^-$−$C_8H_4N_6O_4$] (24). ^{1}H-NMR (400 MHz, DMSO-d$_6$, 25 °C, ppm): δ = 8.59 (s, 2H, CH), 8.49 (s, 1H, CH), 7.64 (s, 1H, NH), 3.09 (q, 6H, J = 7.3 Hz, CH_2), 1.17 (t, 9H, J = 7.2 Hz, CH_3). ^{13}C-NMR (101 MHz, DMSO-d$_6$- 25 °C, ppm): δ = 161.3 (1C, C-N), 158.7 (1C, C-H), 142.3 (2C, C-NO_2), 141.3 (1C, C-NO_2), 125.7 (2C, C-N), 124.7 (1C, C-H), 46.3 (3C, C-H_2), 9.1 (3C, C-H_3). ^{14}N NMR (29 MHz, DMSO-d$_6$, 25 °C, ppm): δ = −11 (N, NO_2), −264 (N, NH), −322 (N, NH). BAM Impact sensitivity test: 40 J; Friction sensitivity test: 360 N.

Synthesis of hydrazinium salt of 3-(Picrylamino)-1,2,4-triazole (11) 3-(Picrylamino)-1,2,4-triazole (**3**) (451.2 mg, 1.53 mmol) was dissolved in 10 ml ethanol and hydrazinium hydrate solution (1ml) was added. The mixture was stirred for 3 hours at room temperature. After the mixture was filtered and the solvent removed. A dark brown solid was obtained as product. Yield: 376.7 mg (1.15 mmol; 75 %); M.p. (DSC, 5 deg min^{-1}): 143ºC (dec.). EA ($C_8H_9N_9O_6$, 327.21 g/mol); exp. (calc.) [%]: C: 27.49 (29.36), H: 4.37 (2.77), N: 44.65 (38.53). EA ($C_8H_9N_9O_6$*H_4N_2); exp. (calc.) [%]: C: 26.28 (26.75), H: 4.18 (3.65), N: 42.67 (42.89). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3403 (m), 3352 (m), 3075 (s), 2934 (m), 1686 (w), 1627 (s), 1590 (s), 1556 (vs), 1527 (vs), 1476 (vs), 1427 (s), 1366 (s), 1321 (vs), 1264 (vs), 1210 (s), 1157 (m), 1079 (s), 1044 (s), 967 (s), 925 (m), 907 (s), 874 (m), 817 (m), 785 (m), 742 (m), 710 (s). Raman (300 mW, 25 scans): $\tilde{\nu}$ [cm^{-1}] = 3129 (6), 3082 (6), 2186 (12), 2147 (13), 2060 (9), 1985 (8), 1594 (13), 1559 (31), 1489 (15), 1366 (60), 1343 (100), 1316 (90), 1164 (12), 1046 (11), 945 (16), 823 (47), 711 (10), 337 (27), 104 (74). MS (FAB$^+$, m/z): 33.1 [M$^+$] (10); (FAB$^-$, m/z): 294.0 [M$^-$] (100), 266.0 [M$^-$−CN] (10), 247 [M$^-$−NO_2] (10), 228.1 [M$^-$−$C_2H_2N_3$] (60), 212 [M$^-$−$C_2H_2N_4$] (15), 151.1 [M$^-$−$C_2H_2N_5O_3$] (55), 83.0 [$C_2H_3N_4$] (15) 46.1 [M$^-$−$C_8H_4N_6O_4$] (15). ^{1}H-NMR (400

MHz, DMSO-d_6, 25 °C, ppm): δ = 12.42 (s, 1H, NH), 8.60 (s, 2H, CH), 8.56 (s, 1H, CH), 7.45 (br, s, 2H, NH_2), 5.78 (br, s, 3H, NH_3). ^{13}C-NMR (101 MHz, DMSO-d_6- 25 °C, ppm): δ = 161.3 (1C, C-N), 158.3 (1C, C-H), 148.8 (2C, C-NO_2), 142.3 (1C, C-NO_2), 132.8 (1C,C-N), 125.7 (2C, C-H). ^{14}N NMR (29 MHz, DMSO-d_6, 25 °C, ppm): δ = −6 (3N, NO_2), −166 (1N, NH), −328 (5N, NH_2/NH_3). BAM Impact sensitivity test: 7 J; Friction sensitivity test: 288N.

Synthesis of triaminoguanidinium salt of 3-(Picrylamino)-1,2,4-triazole (12) The sodium salt of 3-(Picrylamino)-1,2,4-triazole (**6**) (396.5 mg, 1.25 mmol) or the potassium salt (**5**) (417.0 mg, 1.25 mmol) was dissolved in 10 ml ethanol and triaminoguanidinium chloride (176.0 mg, 1.25 mmol) was added. The mixture was stirred for 3 hours at reflux. After cooling, the mixture was filtered. A dark red solid was obtained as product. Yield: 388.5 mg (0.97 mmol; 77 %); M.p. (DSC, 5 deg min^{-1}): 195ºC (dec.). EA ($C_9H_{13}N_{13}O_6$, 399.28 g/mol); exp. (calc.) [%]: C: 26.95 (27.07), H: 3.62 (3.28), N: 44.55 (45.60). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3308 (w), 3194 (m), 1680 (s), 1646 (s), 1617 (s), 1552 (s), 1485 (m), 1432 (m), 1326 (vs), 1271 (vs), 1164 (m), 1129 (s), 1082 (m), 953 (vs), 913 (s), 789 (s), 744 (s), 712 (s), 676 (w). MS (FAB$^+$, m/z): 105.2 [M$^+$] (30); (FAB$^-$, m/z): 294.3 [M$^-$] (100), 278 [M$^-$−O] (30), 247 [M$^-$−NO_2] (25), 228.1 [M$^-$−$C_2H_2N_3$] (30), 151.1 [M$^-$−$C_2H_2N_5O_3$] (29), 46.1 [M$^-$−$C_8H_4N_6O_4$] (15). ^{1}H-NMR (400 MHz, DMSO-d_6, 25 °C, ppm): δ = 12.79 (s, br, 1H, NH), 8.59 (s, 2H, CH), 8.39 (s, 1H, CH), 7.43 (s, br, 3H, NH), 4.50 (s, br, 6H, NH_2). ^{13}C-NMR (101 MHz, DMSO-d_6- 25 °C, ppm): δ = 161.3 (1C, C-NH), 159.5 (1C, C-N) 148.2 (1C, C-H), 144.4 (2C, C-NO_2), 141.3 (1C, C-NO_2), 126.8 (1C, C-N), 124.4 (2C, C-H). ^{14}N NMR (29 MHz, DMSO-d_6, 25 °C, ppm): δ = −7 (3N, NO_2), −158 (4N, NH), −368 (3N, NH_2). BAM Impact sensitivity test: 40 J; Friction sensitivity test: 360 N.

Synthesis of potassium salt of 3-Amino-5-picrylamino-1,2,4-triazole (15) 3-Amino-5-picrylamino-1,2,4-triazole (**13**) (500 mg, 1.61 mmol) was dissolved in 10 ml ethanol and potassium hydroxide (90.0 mg, 1.61 mmol) was added. The mixture was stirred for 3 h at 100 °C. After cooling, filtering and evaporating the solvent, the product (8) could be obtained as a red-brown solid. Yield: 307 mg (0.88 mmol, 55 %); M.p. (DSC, 5 deg min^{-1}): 208ºC (dec.). EA ($C_8H_5KN_8O_6$, 348.28 g/mol), found (cal.) [%]: C: 27.06 (27.59) H: 1.87 (1.45), N: 31.60 (32.17). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3604 (vw), 3363 (vw), 3088 (vw), 1605 (m), 1537 (m), 1493 (m), 1437 (m), 1341 (m), 1273 (vs), 1167 (m), 1081 (w), 924 (w), 876 (w), 803 (w), 740 (m), 721 (m), 674 (w). MS (FAB$^+$, m/z): 39.0 [K$^+$] (20); (FAB$^-$, m/z): 309.1 [M$^-$] (25), 228.0 [M$^-$−$C_2H_3N_4$] (11), 199.3 [M$^-$−$C_2H_3N_5O$] (43), 153.2 [M$^-$−$C_2HN_6O_3$] (48), 122 [M$^-$−$C_2H_3N_7O_4$] (36), 46 [M$^-$−$C_8H_5N_7O_4$] (52). ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, ppm): δ = 8.72 (br, s, 1H, NH), 8.30 (s, 2H, CH), 4.60

(br, s, 2H, NH_2). ^{13}C NMR (101 MHz, DMSO-d_6, 25 °C, ppm): δ = 159.6 (1C, C-NH_2), 148.2 (1C, C-N), 142.6 (2C,C-NO_2), 141.9 (1C, C-N), 139.3 (1C, C-NO_2), 123.7 (1C, C-H). ^{14}N NMR (29 MHz, DMSO-d_6, 25 °C, ppm): δ = −17 (3N, NO_2), −115 (1N, NH), −370 (1N, NH_2). BAM Impact sensitivity test: 3 J; Friction sensitivity test: 360 N.

Synthesis of aminoguanidinium salt of 3-Amino-5-picrylamino-1,2,4-triazole (17) 3-Amino-5-picrylamino-1,2,4-triazole (**13**) (160 mg, 0.52 mmol) was dissolved in 10 ml methanol and aminoguanidinium bicarbonate (70.8 mg, 0.52 mmol) was added. The mixture was stirred for 3 h at 100 °C. After cooling, filtering and evaporating the solvent, the product (7) could be obtained as a dark red to black solid. Yield: 147.0 mg (0.32 mmol, 59 %); M.p. (DSC, 5 deg min^{-1}): 145ºC (dec.). EA ($C_{10}H_{18}N_{16}O_6$, 458.36 g/mol); found (calc.) [%]: C: 27.76 (26.20), H: 3.25 (3.96), N: 37.80 (48.89). EA ($C_{10}H_{18}N_{16}O_6$*MeOH); found (calc.) [%]:C: 27.76 (27.65), H: 3.25 (4.18), N: 37.80 (38.70). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3389 (w), 3089 (w), 1667 (m), 1620 (m), 1598 (m), 1569 (m), 1528 (m), 1516 (m), 1433 (m), 1344 (s), 1285 (s), 1205 (s), 1126 (s), 1082 (vs), 924 (s), 870 (m), 816 (m), 731 (s), 718 (vs), 664 (m). Raman (300 mW, 25 Scans): $\tilde{\nu}$ [cm^{-1}] = 3191 (6), 3092 (5), 2195 (6), 2060 (6), 1556 (74), 1350 (100), 1299 (89), 1175 (50), 946 (15), 929 (12), 822 (39), 719 (20), 337 (27), 92 (107). MS (FAB$^+$, m/z): 75.1 $[AG^+]$ (60); (FAB$^-$, m/z): 309.1 $[M^-]$ (54), 228.0 $[M^- - C_2H_3N_4]$ (13), 168.2 $[M^- - C_2HN_5O_3]$ (49), 153.2 $[M^- - C_2HN_6O_3]$ (56), 46 $[M^- - C_8H_5N_7O_4]$ (43). ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, ppm): δ = 8.74 (br, s, 1H, NH), 8.70 (s, 2H, CH), 5.56 (br, s, 7H, NH, NH_2), 5.11 (br, s, 2H, NH_2). ^{13}C NMR (101 MHz, DMSO-d_6, 25 °C, ppm): δ = 162.9 (1C, C-NH_2), 159.3 (1C, C-N), 155.1 (1C, C-NH_2), 141.9 (2C,C-NO_2), 140.9 (1C, C-N), 135.5 (1C, C-NO_2), 125.1 (1C, C-H). ^{14}N NMR (29 MHz, DMSO-d_6, 25 °C, ppm): δ = −18 (3N, NO_2), −226 (2N, NH), −307 (4N, NH_2). BAM Impact sensitivity test: 40 J; Friction sensitivity test: 360 N.

Synthesis of triethylammonium salt of 3-Amino-5-picrylamino-1,2,4-triazole (18) 3-Amino-5-picrylamino-1,2,4-triazole (**13**) (500 mg, 1.61 mmol) was dissolved in 10 ml ethanol and TEA (1.00 ml, 7.17 mmol) was added carefully. The mixture is stirred for 3 h at 100 °C or for 5h at room temperature. After filtering and evaporating the solvent, the product (9) could be obtained as dark brown solid. Yield: 205 mg (0.50 mmol, 31%); M.p. (DSC, 5 deg min^{-1}): 266ºC (dec.). EA ($C_{14}H_{21}N_9O_6$, 411.38 g/mol), found (cal.) [%]: C: 38.71 (40.88), H: 4.67 (5.15), N: 27.49 (30.64). EA ($C_{14}H_{21}N_9O_6$*H_2O), found (cal.) [%]: C: 38.71 (39.16), H: 4.67 (5.40), N: 27.49 (29.36). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3468 (vw), 3389 (vw), 3088 (w), 2988 (w), 2800 (w), 2737 (w), 2689 (w), 2490 (w), 1677 (w), 1613 (m), 1598 (m), 1557 (s), 1528 (s), 1514 (s), 1496 (s), 1438 (m), 1392 (m), 1338 (s), 1310 (s), 1291 (vs), 1252 (vs), 1163 (s), 1076 (m), 1034 (m), 1013 (m), 943 (m), 927 (m), 912 (m), 839 (m), 806 (m), 783 (m), 750 (m), 720 (s), 708 (s). Raman (300 mW, 25 Scans): $\tilde{\nu}$ [cm^{-1}] = 2991 (17), 2949 (18), 1561 (56), 1350 (90), 1313 (90), 1297 (100), 1165 (21), 944 (16), 822 (60), 328 (81), 97 (118). MS (FAB$^+$, m/z): 102.1 [TEA$^+$] (100); (FAB$^-$, m/z): 309.1 [M$^-$] (24), 228.0 [M$^-$−$C_2H_3N_4$] (23), 199.3 [M$^-$−$C_2H_3N_5O$] (38), 168.2 [M$^-$−$C_2HN_5O_3$] (27), 153.2 [M$^-$−$C_2HN_6O_3$] (47), 122 [M$^-$−$C_2H_3N_7O_4$] (11), 46 [M$^-$−$C_8H_5N_7O_4$] (42). ^{1}H NMR (400 MHz, DMSO-d$_6$, 25 °C, ppm): δ = 8.64 (br, s, 1H, NH), 8.59 (s, 2H, CH), 5.96 (br, s, 2H, NH_2), 3.08 (q, 6H, J = 7.3 Hz, CH_2), 1.17 (t, 9H, J = 7.2 Hz, CH_3). ^{13}C NMR (101 MHz, DMSO-d$_6$, 25 °C, ppm): δ = 160.8 (1C, C-NH_2), 155.6 (1C, C-N), 141.9 (2C,C-NO_2), 140.2 (1C, C-N), 131.0 (1C, C-NO_2), 125.2 (1C, C-H), 45.7 (3C, CH_2), 8.6 (3C, CH_3). ^{14}N NMR (29 MHz, DMSO-d$_6$, 25 °C, ppm): δ = −12 (3N, NO_2), −269 (2N, NH), −310 (1N, NH_2). BAM Impact sensitivity test: 40 J; Friction sensitivity test: 360 N.

10.4 References

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11 Supplementary Information for Chapter 6

11.1 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]. DIAMOND2 plots are shown with thermal ellipsoids at the 50% probability level.

Table S1. X-ray data and parameters for 4-7.

	4	**5·EtOH**	**6**	**7**
CCDC	1429068	1429069	1429067	1429066
Formula	$C_7H_7N_7O_9$	$C_{13}H_9N_9O_{13}$	$C_7H_7N_7O_{10}Cl$	$C_7H_7N_7O_6Cl$
FW / g mol^{-1}	333.20	545.36	370.64	306.64
Crystal system	orthorhombic	triclinic	orthorhombic	orthorhombic
Space Group	*Pbca* (No. 61)	*P-1* (No. 2)	*Pbca* (No. 61)	*Pbca* (No. 61)
Color / Habit	colorless rod	Orange block	colorless block	pale yellow block
Size [mm]	0.02 x 0.15 x 0.35	0.10 x 0.23 x 0.33	0.14 x 0.29 x 0.31	0.05 x 0.15 x 0.20
a [pm]	1213.4(6)	811.3(5)	1207.1(2)	1159.9(4)
b [pm]	1258.4(5)	1140.3(8)	1235.3(2)	1257.1(3)
c [pm]	1593.5(7)	1237.4(9)	1780.9(3)	1555.2(4)
α [°]	90	83.316(6)	90	90
β [°]	90	75.757(6)	90	90
γ [°]	90	79.733(6)	90	90
V [pm^3]	$2.4332*10^9(2)$	$1.0886*10^9$ (1)	$2.6554*10^9$ (8)	$2.2678*10^9$ (1)
Z	8	2	8	8
$\rho_{calc.}$ [g cm^{-3}]	1.819	1.664	1.854	1.796
μ [mm^{-1}]	0.169	0.149	0.363	0.379
F(000)	1360	560	1504	1248
T [K]	173	173	173	173
Θ Min-Max [°]	4.1-26.0	4.1-26.4	4.2-26.0	4.1-26.0
Dataset [h; k; l]	−14:14;−14:15;−19:19	−7:10;−14:14;−15:15	−14:14;−15:15;−21:21	−14:14;−15:15;−19:18
Reflection collected	17898	8359	36198	17183
Independent reflection	2377	4421	2598	2224
R_{int}	0.049	0.021	0.031	0.036
Observed reflection	1898	3339	2342	1934
No. parameters	236	438	245	209
R_1 (obs)[a]	0.0311	0.0525	0.0341	0.0273
wR_2 (all data)[b]	0.0722	0.1373	0.0899	0.0696
S [c]	1.02	1.04	1.07	1.05
Min./Max. Resd. [e nm^{-3}]	−200 / 260	−390 / 450	−430 / 760	−280 / 240
Device type	Oxford Xcalibur3	Oxford Xcalibur3	Oxford Xcalibur3	Oxford Xcalibur3
$\lambda_{MoK\alpha}$ [pm]	71.073	71.073	71.073	71.073
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

[a] $R_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. [b] $wR_2 = [\Sigma[w(Fo^2 - Fc^2)^2]/\Sigma[w(Fo)^2]]^{1/2}$; $w = [\sigma c^2(Fo^2) + (xP)^2 + yP]^{-1}$ and $P = (Fo^2 + 2Fc^2)/3$. [c] $S = [\Sigma\{w(Fo^2 - Fc^2)^2\}/(n - p)]^{1/2}$ (n = number of reflections; p = total number of parameters).

Table S2. torsion angles for compounds 4-7

Compound	**4**	**5**	**6**	**7**
angle of torsion / ° [a]	42.4 (2)	42.5 (3)	38.4 (3)	−51.4 (2)

[a] distortion angle between nitro C–N bond towards benzene ring plane.

11.2 Computation

All calculations were carried out using the Gaussian G09W (revision A.02) program package. 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 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).

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

Table S3. CBS-4M results and calculated gas-phase enthalpies

	M	$-H^{298}$ / a.u.	$\Delta_f H^\circ$(g,M) / kcal mol^{-1}
(3)$^+$	$C_7H_7N_6O_6^+$	1048.963685	169.9
NO_3^-	NO_3^-	280.080446	−74.9
$C_6H_2O_7^-$	$C_6H_2O_7^-$	919.37707	−89.9
ClO_4^-	ClO_4^-	760.171182	−66.3
Cl^-	Cl^-	459.809901	−55.9

Table S4. CBS-4M values and literature values for atomic $\Delta H^{\circ}{}_{f}^{298}$ / kcal mol^{-1}

	$-H^{298}$ / a.u.	NIST [S8]
H	0.500991	52.1
C	37.786156	171.3
N	54.522462	113.0
O	74.991202	59.6

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*.* With the calculated lattice enthalpy (Table 8) the gas-phase enthalpy of formation (Table 7) was converted into the solid state (standard conditions) enthalpy of formation (Table 8). 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 S5. Calculated gas phase heat of formation, molecular volumes, lattice energies and lattice enthalpies of 4-7.

	$\Delta_f H^{\circ}$(g,M) / kcal mol^{-1}	V_M / nm^3	U_L / kJ mol^{-1}	ΔH_L / kJ mol^{-1}
4	94.9	0.304	452.6	456.1
5	79.9	0.401	421.9	425.5
6	103.6	0.332	442.6	446.1
7	113.9	0.283	460.9	464.4

Table S6. Solid state energies of formation ($\Delta_f U^{\circ}$)

	$\Delta_f H^{\circ}$(s) / kcal mol^{-1}	$\Delta_f H^{\circ}$(s) / kJ mol^{-1}	Δn	$\Delta_f U^{\circ}$(s) / kJ mol^{-1}	M / g mol^{-1}	$\Delta_f U^{\circ}$(s) / kJ kg^{-1}
4	–13.9	–58.4	11.5	–29.9	333.1	–89.7
5	–21.6	–90.7	15.5	–52.2	499.3	–104.6
6	–2.9	–12.9	11.5	16.1	370.7	43.4
7	3.1	12.8	9.5	36.3	306.7	118.5

Notes: Δn being the change of moles of gaseous components when formed.

11.3 Experimental Part

General Procedures

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, all samples were measured at 25 °C. Mass spectrometric data were 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 4489modified 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". Additionally all compounds were tested for sensitivity towards electrical discharge using an Electric Spark Tester ESD 2010 EN. Energetic properties have been calculated with the EXPLO5.05 as well as the EXPLO5.601 computer code using the 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 suite] using the CBS-4M method.

Synthesis of (2,4,6-Trinitrophenyl)guanidinium nitrate (4)

(2,4,6-Trinitrophenyl)guanidine (**3**) (405 mg, 1.5 mmol) was dissolved in 10 ml H_2O and 1 ml HNO_3 (2M) was added drop wise at room temperature. The mixture then was heated to 70 °C for 3 h. After cooling and filtering the product could be obtained as orange - yellow solid. Yield: 470 mg (1.41 mmol, 94%), yellow solid; M.p. (DSC, 5 deg min^{-1}): 212ºC (dec.); EA ($C_7H_7N_7O_9$, 333.17 g/mol); found (calc.) [%]: C: 26.11 (25.23), H: 2.75 (2.12), N: 30.24 (29.43). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3406 (w), 3256 (w), 1688 (m), 1650 (m), 1606 (s), 1539 (vs), 1479 (m), 1428 (m), 1391 (m), 1318 (vs), 1264 (vs), 1160 (m), 1078 (m), 917 (m), 824 (w), 789 (m), 741 (m), 723 (s), 712 (s). MS (FAB$^+$, m/z): 271.3 [M+H$^+$] (15), 213.3 [$M^+{-}C_3H_9N_7O_2$] (8), 154.2 [$M^+{-}C_2H_5N_4O_2$] (100); (FAB$^-$, m/ z): 62.0 [NO_3^-] (10). ^{1}H-NMR (400 MHz, DMSO-d$_6$, 25 °C, ppm): δ = 8.87 (s, 2H, CH), 7.37 (br, s, 5H, NH_2, NH). ^{13}C-NMR (101 MHz, DMSO-d$_6$- 25 °C, ppm): δ = 161.2 (1C, C-$(NH_2)_2$) 158.3 (2C, C-NO_2), 144.8 (1C, C-NO_2), 142.2 (1C, CN), 125.7 (2C, C-H). ^{14}N NMR (29 MHz, DMSO-d$_6$, 25 °C, ppm): δ = −1 (1N, NO_3), −6 (3N, NO_2), −295 (3N, NH, NH_2). BAM Impact sensitivity test: 15 J; Friction sensitivity test: 360 N.

Synthesis of (2,4,6-Trinitrophenyl)guanidinium picrate (5)

(2,4,6-Trinitrophenyl)guanidine (**3**) (270.6 mg, 1.00 mmol) and picric acid (229.4 mg, 1.00 mmol) were dissolved in 10 ml ethanol and were heated for 3 hours to reflux. After cooling and evaporating the solvent the product (**5**) was obtained as orange solid. Yield : 357.2 mg (0.72 mmol, 72%), orange solid; M.p. (DSC, 5 deg min^{-1}): 293ºC (dec.); EA ($C_{13}H_9N_9O_{13}$*EtOH, 270.17 g/mol); found (calc.) [%]: C: 32.40 (33.04), H: 2.75 (2.77), N: 23.99 (23.12). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3473 (vw), 3409 (w), 2356 (w), 3204 (w), 3084 (vw), 2360 (w), 2341 (w), 1734 (vw), 1651 (m), 1606 (m), 1559 (s), 1540 (s), 1477 (m), 1427 (m), 1364 (m), 1318 (s), 1264 (s), 1160 (m), 1078 (m), 1044 (w), 931(w), 912 (m), 839 (vw), 824 (vw), 790 (m), 744 (m), 712 (s), 668 (m). Raman (300 mW, 25 Scans): $\tilde{\nu}$ [cm^{-1}] = 3088 (1), 2925 (1), 1624 (6), 1552 (14), 1500 (5), 13600 (26), 1344 (66); 1320 (58), 1309 (67), 1172 (10), 1085 (6), 1010 (2), 944 (10), 825 (28), 779 (1), 708 (2), 630 (2), 552 (2), 376 (4), 337 (9), 287 (4), 204 (10), 88 (28). MS (FAB$^+$, m/z): 271.3 [$C_7H_7N_6O_6^+$] (32), 255.3 [$C_7H_7N_6O_6^+{-}NH_2$] (5), 213 [$C_7H_7N_6O_6^+{-}CN_3H_6$] (3); (FAB$^-$, m/ z): 228.2 [$C_6H_2N_3O_7^-$] (100), 212 [$M^-{-}O$], 46.1 [$C_6H_2N_3O_7^-{-}C_6H_2N_2O_5$] (9). ^{1}H NMR (400 MHz, DMSO-d$_6$, 25 °C, ppm): δ = 8.83 (s, 2H, CH), 8.59 (s, 2H, CH), 7.15 (s, br, 5H, NH, NH_2). ^{13}C NMR (101 MHz, DMSO-d$_6$, 25 °C, ppm): δ = 161.2 (1C, C-$(NH_2)_2$), 158.4 (2C, C-NO_2), 156.9 (2C, C-NO_2), 146.5 (1C, C-NO_2), 143.6 (1C, C-O), 142.1 (1C, C-NO_2), 131.8 (1C, C-N), 125.8 (2C, C-H), 124.8 (2C, C-H). ^{14}N NMR (29 MHz, DMSO-d$_6$, 25 °C, ppm): δ = −4 (6N, NO_2), −315 (3N, NH, NH_2). BAM Impact sensitivity test: 15 J; Friction sensitivity test: 360 N.

Synthesis of (2,4,6-Trinitrophenyl)guanidinium perchlorate (6)

(2,4,6-Trinitrophenyl)guanidine (**3**) (364.5 mg , 1.35 mmol) was dissolved in 10 ml water and perchloric acid (0.12 ml, 1.35 mmol) was dropped slowly to the solution. After heating 3 hours at 80 °C the mixture is cooled to room temperature and the solvent is evaporated. The product (**6**) could be obtained as orange solid. Yield : 326 mg (0.88 mmol, 65%), orange solid; M.p. (DSC, 5 deg min^{-1}): 279ºC (dec.); EA ($C_7H_7N_6O_{10}Cl$, 370.62 g/mol); found (calc.) [%]: C: 22.28 (22.69), H: 1.98 (1.90), N: 22.11 (22.68). IR

(ATR): $\tilde{\nu}$ [cm^{-1}] = 3418 (m), 3356 (m), 3305 (m), 3269 (m), 3103 (m), 2360 (w), 2341 (w), 1838 (vw), 1690(m), 1640 (w), 1621 (w), 1607 (m); 1584 (w), 1535 (vs), 1482 (m), 1435 (w), 1392 (vw), 1341 (vs), 1307 (m), 1190 (w), 1140 (m), 1128 (m), 1061 (vs), 941 (vw), 926 (m),920 (m), 851 (w), 826 (w), 776 (w), 760 (w), 728 (m), 669 (m). Raman (300 mW, 25 Scans): $\tilde{\nu}$ [cm^{-1}] = 3096 (3), 1622 (18), 1552 (24), 1498 (5), 1392 (7), 1351 (100), 1313 (55), 1271 (21), 1178 (9), 1165 (7), 1095 (5), 1017 (2), 943 (12), 929 (9), 825 (22), 762 (3), 722 (3), 540 (3), 436 (3), 377 (5), 208 (7), 162 (10), 113 (30), 91 (32). MS (FAB$^+$, m/z): 271.3 [$C_7H_7N_6O_6^+$] (100), 255.3 [$C_7H_7N_6O_6^+{-}NH_2$] (50); (FAB$^-$, m/ z): 99.1 [ClO_4^-] (100), 83 [$ClO_4^-{-}O$] (12). ^{1}H NMR (400 MHz, DMSO-d$_6$, 25 °C, ppm): δ = 8.96 (s, 2H, CH), 7.54 (s, br, 5H, NH, NH$_2$). ^{13}C NMR (101 MHz, DMSO-d$_6$, 25 °C, ppm): δ = 161.1 (1C, C-(NH$_2$)$_2$), 158.0 (2C, C-NO$_2$), 146.8 (1C, C-NO$_2$), 130.6 (1C, C-N), 125.4 (2C, C-H). ^{14}N NMR (29 MHz, DMSO-d$_6$, 25 °C, ppm): δ = −17 (3N, NO$_2$), −335 (3N, NH, NH$_2$). BAM Impact sensitivity test: 10 J; Friction sensitivity test: 360 N; ESD: 0.7 J.

Synthesis of (2,4,6-Trinitrophenyl)guanidinium chloride (7)

(2,4,6-Trinitrophenyl)guanidine (**3**) (440.5 mg, 1.63 mmol) was dissolved in 10 ml water and hydrochloric acid (2M, 0.82 ml, 1.63 mmol) was added. After stirring for 3 hours at 80 °C the solution was cooled to room temperature and the solvent was evaporated. The product (**7**) was obtained as brown - orange solid. Yield : 298.3 mg (0.97 mmol, 60%), brown to ornage solid; M.p. (DSC, 5 deg min^{-1}): 290ºC (dec.); EA ($C_7H_7N_6O_6Cl$, 306.62 g/mol); found (calc.) [%]: C: 27.25 (27.42), H: 2.66 (2.30), N: 27.00 (27.41). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3472 (w), 3407 (w), 3204 (w), 3084 (w), 2782 (w), 2360 (m), 2341 (m), 2168 (vw), 1636 (m), 1648 (m), 1608 (s), 1538 (s), 1475 (m), 1456 (m), 1427 (m), 1335 (s), 1318 (s), 1264 (s), 1159 (m), 1094 (w), 1078 (m), 1018 (w), 937 (m), 914 (s), 860 (vw), 826 (vw), 789(w), 773 (vw), 744 (m), 715 (s), 696 (m), 668 (m). Raman (300 mW, 25 Scans): $\tilde{\nu}$ [cm^{-1}] = 3112 (4), 3025 (2), 1618 (28), 1564 (24), 1544 (20), 1484 (6), 1366 (65), 1349 (100), 1310 (38), 1296 (44), 1202 (2), 1179 (9), 1163 (5), 1095 (8), 1076 (7), 1019 (8), 1009 (14), 943 (14), 862 (4), 826 (35), 775 (2), 690 (5), 633 (6), 551 (5), 425 (3), 373 (4), 347 (10), 330 (15), 195 (20), 183 (13), 157 (13), 102 (50), 75 (47). MS (FAB$^+$, m/z): 271.3 [$C_7H_7N_6O_6^+$] (75), 255.3 [$C_7H_7N_6O_6^+{-}NH_2$] (11), 213 [$C_7H_7N_6O_6^+{-}CN_3H_6$] (10); (FAB$^-$, m/ z): 35.0 [Cl^-] (4). ^{1}H NMR (400 MHz, DMSO-d$_6$, 25 °C, ppm): δ = 8.82 (s, 2H, CH), 7.23 (s, br, 5H, NH, NH2). ^{13}C NMR (101 MHz, DMSO-d$_6$, 25 °C, ppm): δ = 161.1 (1C, C-(NH$_2$)$_2$), 158.6 (2C, C-NO$_2$), 145.5 (1C, C-NO$_2$), 142.3 (1C, C-NH), 125.7 (2C, C-H). ^{14}N NMR (29 MHz, DMSO-d$_6$, 25 °C, ppm): δ = −5 (3N, NO$_2$), −351 (3N, NH, NH$_2$). BAM Impact sensitivity test: 40 J; Friction sensitivity test: 360 N.

11.4 References

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Appendix

12 List of Abbreviations

Å	angstrom (10^{-10} m)
AD	anno Domini (after Christ)
AG	aminoguanidinium
APATO	3-Amino-5-picrylamino-1,2,4-triazole
ASTM	American Society for Testing and Materials
a.u.	atomic units
BAM	*Bundesanstalt für Materialforschung und –prüfung*
BC	before Christ
br	broad (IR and NMR)
°C	degree Celsius
calc.	calculated
CBS-4M	complete basis set, 4 parameter, minimal population localization
CE	tetryl
conc.	concentrated
d	doublet (NMR)
dd	doublet of doublet (NMR)
D	detonation velocity
DAT	1,5-diaminotetrazole
DMF	dimethylformamide
DMSO	dimethylsulfoxide
DSC	differential scanning calorimetry

Appendix

EA	elemental analysis
e. g.	exempli gratia (for example)
endo	endothermic
exo	exothermic
ESD	electrostatic discharge
et al.	*et alii* (and others)
F	specific energy
FS	friction sensitivity
FW	formula weight
G	guanidinium
h	hour
HEDM	high energetic density materials
HF	Hartree-Fock
HMX	octogen (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine)
HNAB	hexanitroazobenzene
HNS	hexanitrostilbene
Hx	hydroxylammonium
Hy	hydrazinium
Hz	hertz
IR	infrared spectroscopy
IS	impact sensitivity
J	Joule
J	coupling constant (NMR)

Appendix

K	kelvin
LA	lead acid
lit.	literature
LMU	Ludwig-Maximilians-Universität
$[M]^+$	molecule peak (MS)
M	molar
m	medium (IR), multiplet (NMR)
MF	mercury fulminate
MHz	mega Herz
min.	minutes
m.p.	melting point
MS	mass spectrometry
m/z	mass per charge (mass spectrometry)
N	Newton
NC	nitrocellulose
n.d.	no data
NG	nitroglycerin
NIMAG	number of imaginary frequencies
NMR	nuclear magnetic resonance
NQ	nitroguanidine
$p_{C\text{-}J}$ (p_{CJ})	detonation pressure
PA	picric acid
PATO	3-picrylamino-1,2,4-triazole

Appendix

PCG	picrylguanidine ((2,4,6-Trinitrophenyl)guanidine)
PETN	pentaerythritol tetranitrate
ppm	parts per million
Ω	oxygen balance
ρ	density
Q	detonation heat
RDX	royal demolitions explosive (1,3,5-trinitro-1,3,5-triazinane)
rt	roomtemperature
s	strong (IR), singlet (NMR)
SSRT	small scale reactivity test
t	triplet (NMR)
T_{dec}	decomposition temperature
T_{det} (T_E)	detonation temperature
TAG	triaminoguanidinium
TATB	triaminotrinitrobenzene
TGA	thermal gravimetric analysis
THF	tetrahydrofuran
TNT	trinitrotoluene (2-methyl-1,3,5-trinitrobenzene)
UN	United Nations
V_0	volume of detonation
VOD (V_{det})	velocity of detonation
vs	very strong (IR)
w	weak (IR)

13 Curriculum vitae

Personal data

Name	Michael Weyrauther
Titel	Master of Science
Birth date	29 Juli 1983
Birth place	Karlsruhe (Germany)
Family status	single
Nationality	German

Education

1987 - 1990	Caritas Kindergarten St. Quirin, Fürstätt, Germany
1990 - 1994	Primary School: Rosenheim-Westerndorf St. Peter, Germany
1994 - 2004	Secondary School: Finsterwalder-Gymnasium Rosenheim, Germany
2004 - 2005	Civilian Service at the Caritas Kindergarten und Hort St. Quirin, Fürstätt, Germany

Academic studies

10/2005 - 09/2008	B. Sc. Degree in Chemistry and Biochemistry, Ludwig-Maximilian-University, Munich, Germany
10/2008 - 09/2011	M. Sc. Degree in Chemistry, Ludwig-Maximilian- University, Munich, Germany
11/2011	Ph. D. (of Prof. KLAPÖTKE) at the Ludwig-Maximilian University, Munich, Germany

Appendix

Internships

05.09. - 23.09.2005	SALUS Haus GmbH & Co. KG, Bruckmühl, Germany
28.07. - 31.10.2009	University of Southern California, internship (of Prof. CHRISTE), Los Angeles, California, USA
2005 - 2011	Different subject-specific internships at the Ludwig-Maximilian University, Munich, Germany

Activities during the studies

10/2008 – 09/2011	Tutor-activities at the Ludwig-Maximilian University, Munich, Germany
05/2012	Lecture: „Innovation management and globale challanges“
04/2013	Poster presentation: NTREM 2013, Pardubice, Czech Republic
09/2014	Seminar: „Basic methods for good meetings and efficient conflict management“

Knowledge

Analytic methods	NMR, IR, Raman, MS, DSC, Pycnometric
EDV-Knowledge	Windows 95/98/XP/7, Excel, Word, Diamond, Gaussian, WinGX
Knowledge of language	German: native speaker
	English: fluent

Voluntary service

10/2013 – 2015	Cooperative member of the JCF (Jungchemiker Forum) München,

Publications

[1] T. M. Klapötke, N. Mayr, J. Stierstorfer, M. Weyrauther, Energetic ionic derivatives of 5,5'-dinitromethyl-3,3'-bis(1,2,4-oxadiazole), **2013**, University of Pardubice, Institute of Energetic Materials.

[2] T. M. Klapötke, N. Mayr, J. Stierstorfer, M. Weyrauther, Maximum Compaction of Ionic Organic Explosives: Bis(hydroxylammonium) 5,5'-Dinitromethyl-3,3'-bis(1,2,4-oxadiazolate) and its Derivatives, *Chem.- Eur. J.*, **2014**. 20(5): p. 1410-1417.

[3] T. M. Klapötke, D. Piercey, J. Stierstorfer, M. Weyrauther, The Synthesis and Energetic Properties of 5,7-Dinitrobenzo-1,2,3,4-tetrazine-1,3-dioxide (DNBTDO). *Propellants, Explos., Pyrotech.*, **2012**. 37(5): p. 527-535.

[4] Zoe L. Chioato, Thomas M. Klapötke, Frank Mieskes, Jörg Stiersdorfer and Michael Weyrauther, Studies on explosives with high thermal stabilities: 2,6-bis(picrylamino)-3,5-dinitropyridine (PYX) and its salts, Submitted to *Chem.- Eur. J.*

[5] Thomas M. Klapötke, Frank Mieskes, Jörg Stiersdorfer and Michael Weyrauther, Studies on energetic salts based on (2,4,6-Trinitrophenyl)guanidine, Submitted to *Propellants, Explos., Pyrotech.*

[6] Zoe L. Chioato, Thomas M. Klapötke, Frank Mieskes, Jörg Stiersdorfer and Michael Weyrauther, (Picrylamino)-1,2,4-triazole derivatives: High thermal stable explosives, Submitted to *Chem.- Eur. J.*