Dissertation zur Erlangung des Doktorgrades
der Fakultät für Chemie und Pharmazie
der Ludwig-Maximilians-Universität München

Investigation of Nitrogen-Rich Polymers Based on Tetrazoles and Triazoles

vorgelegt von
Stefan M. Sproll
aus
Tübingen

München 2009

Erklärung

Diese Dissertation wurde im Sinne von § 13 Abs. 3 der Promotionsordung vom 29. Januar 1998 von Herrn Prof. Dr. Thomas M. Klapötke betreut.

Ehrenwörtliche Versicherung

Diese Dissertation wurde selbstständig, ohne unerlaubte Hilfe erarbeitet.

München, den 24.11.2009

Stefan Sproll

Dissertation eingereicht am 26.11.2009

1. Berichtserstatter: Prof. Dr. Thomas M. Klapötke

2. Berichtserstatter: Prof. Dr. Konstantin Karaghiosoff

Mündliche Prüfung 12. Januar 2010

Die vorliegende Arbeit wurde in der Zeit von Januar 2007 bis November 2009 am Department Chemie und Biochemie der Ludwig-Maximilians-Universität München unter der Anleitung von

Prof. Dr. Thomas M. Klapötke

angefertig.

Danksagung

Ich danke ganz besonders Herrn Prof. Dr. Klapötke für die freundliche Aufnahme in den Arbeitskreis, sowie für die interessante Themenstellung dieser Dissertation, des Weiteren für die gute Betreuung, die es mir ermöglichte mich jederzeit mit Fragestellungen an ihn zu wenden, welche dann sofort erörtert und gelöst wurden und für die Freiheiten die es mir gestatteten kreative Antworten zu suchen und manchmal zu finden.

Herrn Prof. Dr. Konstantin Karaghiosoff möchte ich für zahlreiche NMR-Messungen danken (inklusive Hilfe bei besonders schweren Fällen), sowie für anregende Diskussionen und für die Übernahme des Zweitgutachtens.

Herrn Akad. ORat Dr. Burkhard Krumm möchte ich für seine Offenheit danken, die es mir ermöglichte mich jederzeit mit chemischen und sicherheitstechnischen Fragen an ihn zu wenden.

Frau Irene S. Scheckenbach möchte ich für ihre Freundlichkeit, die organisatorische Betreuung sowie die regelmäßige Unterhaltung mit Prüfungsbeisitzen danken.

Natürlich danke ich meinen Laborkollegen Jörg Stierstorfer, Hendrik Radies, Michael Göbel, Niko Fischer und Franziska Betzler für viele hilfreiche chemischen Diskussionen (JST, MIG) sowie das teilen des täglichen Fußballleids (HRA) und für die kreative und stets fröhliche Stimmung im Labor D3.110.

Ganz besonders danke ich auch dem Nachbarlabor für das Bereitstellen zusätzlicher Stellfläche. Franz Martin möchte ich für seine Freundschaft und die treue Begleitung durch das Chemiestudium danken. Anian Nieder danke ich für viele kulinarische Diskussionen und Ausflüge.

Alexander Penger und Karin Lux danke ich für die Ablenkungen von dem mit unter frustrierenden Laboralltag und diverse Kartenspiele.

Ganz besonders möchte ich Franz Xaver Steemann dafür danken, meine Dissertation korrigiert und für die sportliche Ertüchtigung des Arbeitskreises gesorgt zu haben. `

Stefan Huber danke ich für das unermüdliche Bestellen meiner Chemikalien und das darauffolgende Messen von Schlag- und Reibeempfindlichkeiten sowie die verlässliche Bestimmung zahlreicher Bombenwerte.

Karina Tarantik, Norbert Mayer, Richard Moll, Sebastian Rest, Chrissi Rotter und den restlichen Arbeitskreismitglieder danke ich für eine schöne produktive Zeit.

Darüber hinaus danke ich meinen Praktikanten Marcos Kettner, Luka Kovacevic, Johannes Heppekausen, Vera Hartdegen, Fabian Hanusch, Manuel Joas und Gina Friedrichs für ihre tatkräftige Unterstützung dieser Dissertation.

Außerdem danke ich natürlich meinen Eltern für die jahrelange Unterstützung, sowie Veronique Paulus für die ständige Bereitschaft sich mein Gejammer anzuhören und sich um mein leibliches Wohl zu kümmern.

Abstract

The aim of this thesis was the development of new nitrogen-rich, energetic polymers based on tetrazoles and triazoles, along with the development of energetic materials related with the polymers. The demand to the polymers was the suitability as energetic binders. Therefore, the polymers should possess high thermal and physical stabilities, in order to stabilize the energetic filler, along with moderate to good explosive characteristics. Moreover, a high stability towards chemical reactions is mandatory to prevent reactions between the polymer and the energetic filler.

The thesis can be divided into six parts. The first chapter deals with energetic materials based on tetrazolyl hydrazines. Besides nitrogen-rich polymers, obtained either by radical polymerization (poly(methyl-1-(1-vinyl-1*H*-tetrazol-5-yl)hydrazine)) or polycondensation reactions, 5-azido-1*H*-tetrazoles and functionalized tetrazenes were synthesized. The nitrogen-rich polymers prepared by polycondensation reactions of the 1,1-methyl-1*H*-tetrazolylhydrazine possess a high thermal stability (>240 °C) and are insensitive towards impact and friction. The advantage of these polymers is that the functional groups are stabilized by the formed carbamates, reducing the chemical reactivity. Nevertheless, the NH-proton of the carbamate structure is able to form hydrogen bridges, leading to increased adhesion forces between the energetic filler and the polymer. The energetic polymers formed by radical polymerization bear hydrazine moieties that increase the solubility in acids, along with possible adhesion forces with energetic fillers. The 5-azido-1*H*-tetrazoles were prepared by diazotation of tetrazolyl hydrazines. The performance of the ethyl bridged 5-azido-1*H*-tetrazoles reached the values of RDX but the compound proved to be much too sensitive towards impact and friction to find any application. The tetrazenes instead possess suitable thermal and physical stabilities along with good to moderate energetic properties. They were prepared by oxidation of tetrazolyl hydrazines, leading to the corresponding “dimer".

The second and third part of the thesis deals with complexes, either of the 5-carboxylic-1*H*-tetrazolate (part two) or bidented and tridented tetrazole ligands. The aim of the preparation of complexes was the synthesis of new coloring agents for pyrotechnical formulations. Therefore, the barium, strontium and copper 5-carboxylic-1*H*-tetrazolate were investigated. The complexes showed a high thermal and physical stability. In contrast to the 5-carboxylic-1*H*-tetrazolates, the

copper complexes of (2-(1*H*-tetrazol-1-yl)ethyl)amine and 1,2-bis(5-monomethylhydrazinyl-1*H*-tetrazolyl)ethane were very sensitive towards impact and friction. Moreover, the decomposition points of the complexes were lower than the decomposition points of the ligands themselves. An explanation could be the close arrangement of the ligand and the oxidising nitrate anion next to each other.

Besides tetrazoles, polymers based on triazoles were synthesized. The triazoles containing polymers were prepared by the reaction of acetylene derivatives with azide containing polymers (polyvinylazide and glycidyl azide polymer). The energetic polymers obtained can be divided in three classes: polymers containing nitrate esters, azide groups and nitramines. The nitrate esters were sensitive towards impact and possess a low thermal stability. The azide polymers were more sensitive towards physical stimuli than the nitrate esters, but possessed higher decomposition points. The nitramine containing polymer possessed the highest thermal stability, but proved to have only low energetic properties.

Another chapter of this thesis deals with the investigation of thiatriazoles. This strictly academic topic resulted of fruitless trials of another synthetic pathway for tetrazolyl hydrazines. Nevertheless, the several thiatriazoles were synthesized and investigated.

The last topic of this thesis are alkylated *N*,*N*-dinitramines. These compounds are known for a long time, but were not characterized properly. Therefore, we investigated two different synthetic pathways and determined the physical and thermal stabilities along with the explosive properties. The first preparation was published by Russian chemists and deals with alkylation reactions of silver dinitramide salts. Despite our efforts, we were not able to isolate any alkyl *N*,*N*-dinitramine using this route. The *N*,*N*-dinitramines were prepared according to patents by the nitration of alkyl nitramines using nitronium tetrafluoroborate. The nitramines proved to be moderate explosives, whereas the corresponding *N*,*N*-dinitramines can be classified as high explosives. The low decomposition points of the *N*,*N*-dinitramine at about 80 °C prevents these compounds from being used as explosives.

Table of Contents

1. Introduction

1.1 Chemical, Physical and Nuclear Explosions

Explosions can be caused by different sources. Thereby, three types of explosions can be distinguished: the physical, nuclear and chemical explosion.[1]

The physical explosion is a result of a formed pressure within a container or vessel, often by compressed or heated liquids or gases, leading to a sudden expansion of the gases when the container or vessel fails.[2] The compressed gases, along with fragments of the burst container, can lead to severe, damaging effects. One example for the force of a physical explosion is given by 4 kg of helium, being compressed with 600 bar in a spherical vessel with a volume of 48 L. If the vessel fails suddenly, the resulting physical detonation possesses equal blast effects as a detonation of 550 g of TNT.[2] As a summary, a physical explosion is understood, when the energy of the explosion is supported from outside the system that fails (heating of liquids, compression of gases as examples) and not by the decomposition of the "explosive material".[2]

The nuclear explosion can, as well, be understood as a physical explosion, due to the radioactive elements, which are driven together by common explosives (energy supplied from outside the system). Nevertheless, the explosive energy of a nuclear explosion is derived from the transmutation of the radioactive substance into different elements and tremendous amounts of energy. However, a thermonuclear bomb, e.g. 6-3 Li, 2-1D -> 2 4-2-He would also be a "nuclear" explosion, but not caused by radioactive elements. The power obtained by nuclear explosion exceeds the energies of chemical or physical explosions.[3] The disadvantage of nuclear explosions compared to chemical and physical explosions, regarding an application in civil or military devices, is the contamination of the environment by radioactive waste.

The chemical explosion is a result of the decomposition of molecules evolving gases and heat.

The burning rate of the chemical compound determines whether the decomposition is just a burning, a deflagration or a detonation.[2] The formation of the explosion can be caused either by direct initiation or by a deflagration to a detonation process (*DDT*).[4]

The *DDT* takes place, when a weak ignition source is applied. The deflagration of the energetic material accelerates the burning rate itself to supersonic velocities by the release of a huge amount of energy and a high rate of gas generation. Beside the properties of the material (oxygen balance, energetic groups…) the confinement of the material could be important for the formation of the *DDT* process. The confinement of the material prevents the gases formed by the burning reaction from being released into the environment. As a result, pressure is built up and a detonation takes place (unconfined TNT for example just burns, whereas confined TNT detonates).[5] This finding can be explained by the equation of the burning velocity r (*Equation 1*).

$$r = \beta p^{\alpha} \qquad (1)$$

Equation 1. Burning velocity r with β: temperature dependent coefficient, α: index which determines the pressure dependency of the burning velocity, p: pressure.

The burning velocity r depends on the pressure with $\alpha < 0$ for the deflagration and $\alpha > 0$ for the detonation. If the pressure rises due to the confinement of the energetic material and the formed gases, r rises and could reach supersonic velocities resulting in a detonation.[6]

The direct initiation or shock to detonation transition takes place if a sufficiently strong shockwave is applied for the initiation causing the reaction to couple with the shockwave. The detonation is initiated immediately.[4] The shockwave hitting the explosive material leads to a compression of the material that is heated by the resulting adiabatic heat evolution and the temperature rises above the decomposition point. Due to the decomposition of the explosive material, the shockwave is accelerated by the decomposition of the explosive material up to a certain velocity resulting in the detonation.[6] This effect is mainly used for the initiation of secondary explosives by primary explosives (*paragraph 1.2*).

1.2 Classification of Energetic Materials

Energetic materials can be roughly classified as primary and secondary explosives, propellants and pyrotechnics (*Figure 1*). The secondary explosives can be divided into explosives used in civil and in military applications, the propellants into propelling charges for ammunition and into rocket propellants.[7]

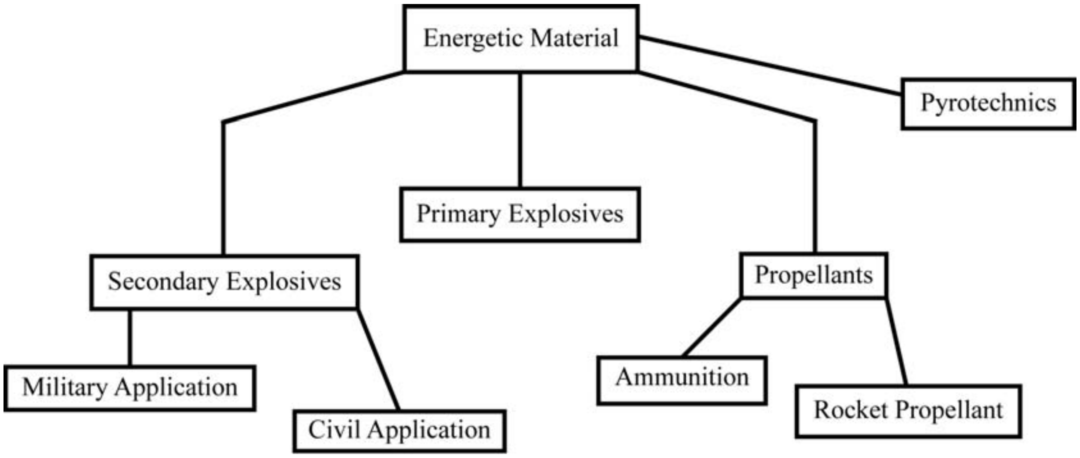
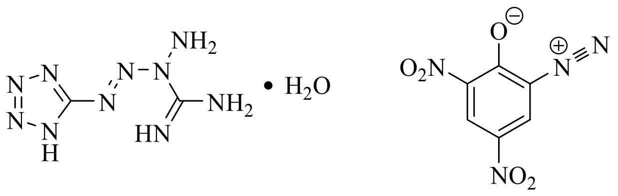


Figure 1. Classification of energetic materials.

1.2.1 Primary Explosives

Primary explosives are very sensitive explosives, which can be easily initiated by friction, impact, spark or heat. The initiation of primary explosives leads to a fast deflagration to detonation process with a shock wave formed, which is able to initiate secondary explosives. Their detonation velocities ranging between 3500 m s^{-1} and 5500 m s^{-1} are much slower than the detonation velocities of secondary explosives. Common primary explosives are lead(II)azide and lead(II)styphnate, cadmium(II)azide or mercury fulminate. The obvious disadvantage of these compounds is the toxicity of the heavy metal cations lead,[8] cadmium[9] and mercury.[10] Therefore, new less toxic primary explosives based on organic, metal free compounds were investigated and developed, as tetracene **1** and 2-diazo-4,6-dinitrophenole **2** (*Figure 2*).



1 **2**

Figure 2. Primary explosives.

Besides the development of metal free organic primaries, the replacement of the toxic cations with less toxic metals like silver[11], iron[12] or copper[13] is another topic of current interest.

1.2.2 Secondary Explosives

The second subgroup of explosives is formed by the secondary explosives. The main differences between the secondary explosives and the primary explosives are the high thermal and physical stability of the secondary explosives along with higher detonation velocities (5500 m s^{-1} to 9000 m s^{-1}). In contrast to primary explosives, it is difficult to initiate secondary explosives by friction, impact, spark or heat, due to their high stability towards thermal and physical stimuli. They are initiated by the shockwave of primary explosives instead, as already discussed in *paragraph 1.1*. Common secondary explosives are TNT, RDX, HMX, NQ und TATB (*Figure 3*).[7]

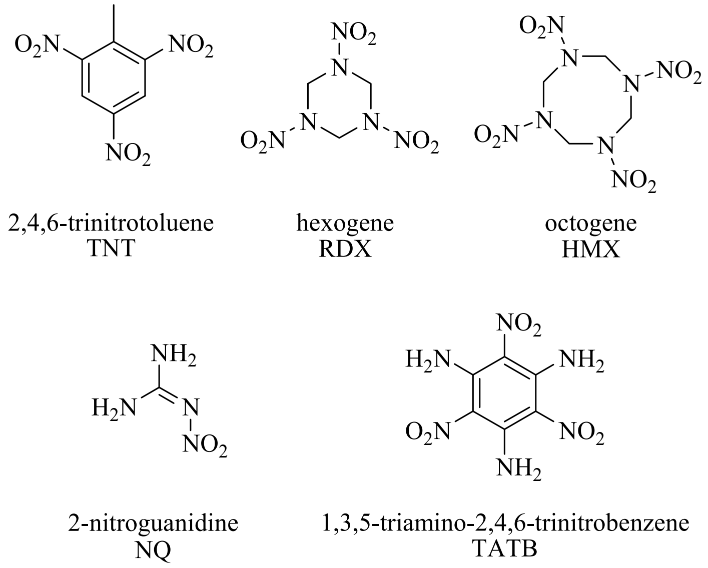


Figure 3. Common secondary explosives.

Whereas RDX and HMX are mainly used in military explosives, cheaper formulations possessing less power like ANFO (ammonium nitrate fuel oil) are used in civil applications (mining, tunnel construction…).

Important values for the characterization of a secondary explosive are the detonation pressure and velocity. Both values depend on the density and the heat of explosion (*Equation 2 and 3*).[14]

$$p_{C-J} = K\rho_0^2\Phi \qquad (2)$$

$$D = A\Phi^2(1+B\rho_0) \qquad (3)$$

$$\Phi = N\sqrt{M}\sqrt{Q}$$

Equation 2 and 3. $p_{C\text{-}J}$ is given in [kbar] and D in [mm μs^{-1}]. K, A and B are constants with the values of 15.88, 1.01 and 1.30. N is the molar quantity of released gases per gram explosive, M the mass of gases [g] per mol gas and Q is the heat of explosion.

Therefore, compounds possessing a high heat of explosion along with a high density are sought. The density can be influenced by pressing the explosive material (limited by the physical stability of the compound) or by the functional groups of the explosive compound. Nitro groups and large planar aromatic structures, for example, are known to increase the density.

1.2.3 Propellants

In contrast to primary and secondary explosives, propellants are not meant to detonate, but to deflagrate. The different fields of application demand different properties of the propellants.

Propellants used in propelling charges for ammunition need low burning temperatures and the decomposition products should not contain corrosive gases. High burning temperatures lead to severe erosion of the gun barrel (formation of iron carbide from the reaction of iron with carbon). The desired low burning temperatures complicate the development of propellants with good performance, because the specific impulse of the compound depends on the burning temperature (*Equation 4*).

$$I_{sp} = \sqrt{\frac{2\gamma R T_c}{(\gamma - 1)M}} \qquad (4)$$

Equation 4. Specific impulse I_{sp}. γ: ration of the specific heat capacity of the gas-mixture, R: ideal gas constant, T_c: temperature in the burning chamber [K], M: average molecular weight [mol kg^{-1}].

Thus, the development of propelling charges for ammunition is a challenging field of research. The first propellant used for ammunition was black powder (75 % KNO_3, 10 % sulfur and 15 % charcoal). Due to the huge amount of corrosive gases evolved during its decomposition (NO_x and SO_x), black powder is not in use in contemporary ammunition or propellant charges any more. A common propellant used in ammunition is nitrocellulose (single-based propellant), because the advantageous ratio of oxygen to carbon leads to a residue-free burning of the compound. In order to improve the specific impulse, double-based and triple-based propellants were developed based on nitrocellulose. Double based propellants like nitrocellulose and nitro glycerine compositions possess an enhanced performance unfortunately accompanied by a higher erosion of the gun barrel. In order to decrease the erosion, triple-based propellants, consisting of nitrocellulose, nitro glycerine and nitro guanidine, were developed. Whereas the single-based propellant nitrocellulose is sufficient for ammunition of guns and pistols, the double and triple-based propellants are used in tank and naval artillery ammunition.[15]

The required properties of rocket propellants differ from that of propellants for ammunition. In contrast to guns or cannons, rockets are fired usually only once (fire- and forget weapon systems). Therefore, the erosion of the rocket engine is of less importance, compared with the barrel of a gun or cannon. Instead, compounds with a high specific impulse are desired materials. If the specific impulse is raised by 20 s, the cargo carried by the rocket can be doubled.[16] Rocket propellants can be divided into solid and liquid propellants. Solid propellants contain double-based propellants (nitrocellulose and nitro glycerine) or ammonium perchlorate/aluminum, stabilized by a binder (composite propellants). Liquid propellants are hydrazine or mixtures of an oxidizer and fuel (HNO_3 and hydrazine/methyl hydrazine). The propelling charges burn much faster than rocket propellants. As a result, the pressure formed during the decomposition of the rocket propellant (70 bar) is much lower than the pressure formed by the propelling charges (up to 4000 bar).[16]

1.2.4 Pyrotechnics

Pyrotechnics can be divided into three fields, the heat generating, the smoke generating and the light emitting pyrotechnics. Heat generating pyrotechnics are used for priming charges, detonators, incendiary compositions or matches. Smoke generating pyrotechnics are used for camouflage and signalling purposes. The light emitting pyrotechnics are used either for illumination (visible and infrared), fireworks or decoy flares. Whereas heat generating and smoke generating pyrotechnics were not a topic of this dissertation, colorant agents for pyrotechnical applications were one research topic (*paragraphs 3* and *4*). Common colorant agents are metal cations like sodium (yellow), strontium or lithium (both red), barium (green) and copper (green or blue). The colorant species are formed during the decomposition of the pyrotechnical mixture. In case of the sodium and lithium salts, the elemental sodium or lithium are responsible for the yellow flame color, whereas in case of the barium, strontium and copper compounds, the flame color is caused by monovalent cations in ionic species (SrOH, SrCl, BaOH, BaCl or to a smaller extent CuCl).[17] The disadvantage of common pyrotechnical compositions is the formation of a huge amount of smoke during the decomposition. Therefore, the development of pyrotechnics based on nitrogen-rich compounds with a minimum of smoke generation is of great interest. In the past years, several attempts were started using tetrazole complexes of the colorant cations. Potential nitrogen-rich colorant agents are based either on 5,5'-hydrazine-1,2-diylbis(1*H*-tetrazole),[18] bistetrazoles and bis(tetrazol-5-yl)amines,[19] or nitriminotetrazoles and salts thereof.[20]

1.3 Explosive Devices

In general, explosive compositions always consist of an oxidizer, a fuel and a binder. The constitution of the different kinds of explosive devices differs significantly.

Ammunition of guns for example is built up by the projectile bullet, a propelling charge and a primer (*Figure 4*)

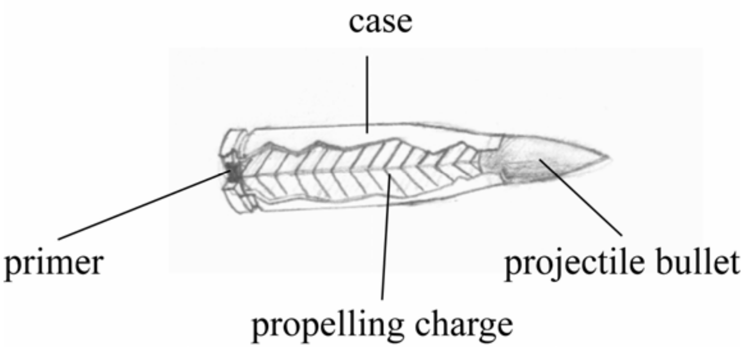


Figure 4. Constitution of gun ammunition; drawing supported by Dr. Franz Xaver Steemann.

The primer is triggered by the fireingpin of the gun and ignites the propelling charge. As already mentioned in the previous paragraphs, the primer contains lead azide or styphnate, the propelling charge black powder (out of use) or nitrocellulose. The bullet itself is meant to perform the desired destruction. The whole setup is surrounded by the casing. However, several attempts are made today to produce case-free ammunitions, as for example the case-free ammunition of the assault rifle G11 of Heckler & Koch.[21] The second option for the preparation of ammunition are the separated charges, in contrast to the fixed ammunition. The separated charges are used if the projectile is too large to be incorporated in a fixed charge. The propelling charge contains a triple-based propellant, e. g. naval artillery ammunition.

To date, the propulsion system of many military missiles and civil rockets is based on liquids or gases (for example methyl hydrazine and nitrogen tetroxide for the third stage, or liquid hydrogen and liquid oxygen for the main stage of the Ariane 5 rocket). Regarding the fact that liquids do not need any binder systems for stabilization, only propulsion systems based on solids are of interest for this dissertation.

The setup of a military missile, e. g. the TRIDENT II missile and a common skyrocket, is discussed roughly in the following paragraph. The propulsion system of both devices is based on solid propellants. The TRIDENT II missile is an intercontinental missile fired from submarines. Its precursor, the TRIDENT I missile, was first used in 1979. Since 2008, only TRIDENT II missiles are in use, in particular with nuclear warheads.[22] The setup of a rocket differs significantly from ballistic ammunition. The rocket is built up by several propulsion stages (first stage, inter stage, second stage, and third stage). The warhead or payload is carried in the top sector of the rocket *(Figure 5*).

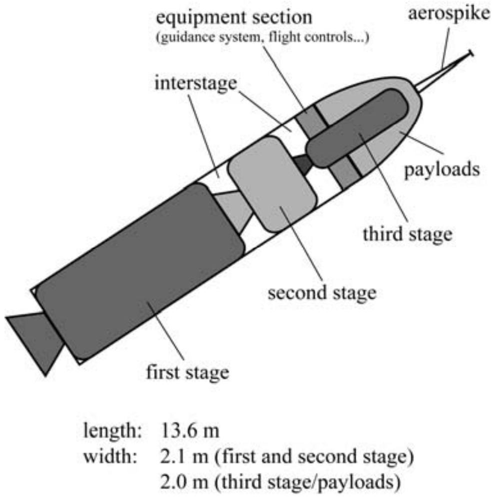


Figure 5. The TRIDENT II missile as example for a missile using a solid propellant system.[23]

A skyrocket, however, consists of a propelling charge, carrying the effect charge through the air. The effect charge is then ejected by the ejection charge. In order to assure a stable flight path, the rocket possesses a guide rod and a cap (*Figure 6*). Due to the much shorter time of flight, along with the small amount of cargo, the skyrocket possesses only one propelling charge, instead of several stages.

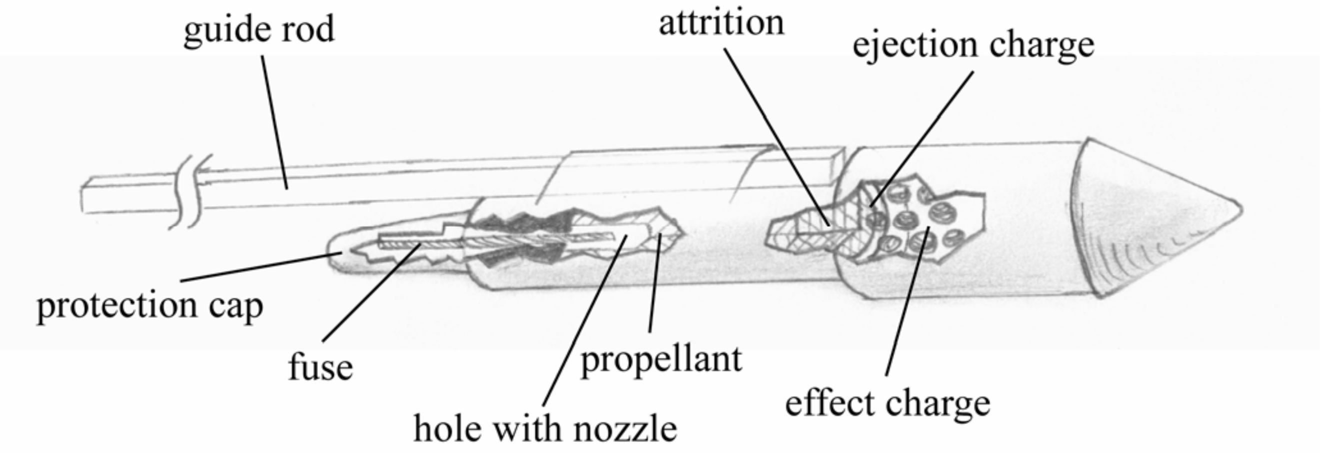


Figure 6. Skyrocket; drawing supported by Dr. Franz Xaver Steemann.

1.4 Composition of Explosive Mixtures

Common explosive compositions contain an oxidizer, a fuel and a binder. In case of smokeless powder in ammunition (*paragraph 1.3*), a binder is unnecessary, because nitrocellulose itself is an energetic binder. In the case of the TRIDENT I and II missile, the propelling composition contains HMX (explosive), aluminum (fuel) and ammonium perchlorate (oxidizer). As binder, a mixture of several polymers is applied. This mixture contains polyglycol adipate (PGA), nitrocellulose (NC), nitro glycerine (NG), and hexadiisocryanate (HDI). In order to improve the composition for the TRIDENT II missile, PGA was replaced by polyethylene glycol (PEG) to achieve a more flexible composition.[22] The solid booster of the Ariane 5 rocket contains 18 % aluminum and 68 % ammonium perchlorate. As binder, polybutadiene was used (14 %).[24]

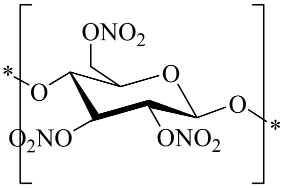
One of the most famous explosive mixtures was invented by Alfred Nobel in 1866. In order to stabilize nitro glycerine, Nobel developed the composition of 75 % nitro glycerine, 24.5 % silica and 0.5 % sodium carbonate – dynamite. In this case, silica can be seen as inorganic binder.[25] Another common explosive composition is semtex or C-4. These composition contains PETN or/and RDX and a styrene-butadiene copolymer as binder.[26]

Another large number of explosive compositions are called PBX (plastic bonded explosives). Common PBX compositions are PBX-9010 (90 % RDX, 10 % Kel F, a fluorinated polymer), PBXN-1 (68 % RDX, 20 % Al, 12 % nylon), PBXN-2 (95 % HMX, 5 % nylon), PBXN-5 (95 % HMX, 5 % viton A, a fluorinated polymer) and PBXN-201 (83 % RDX, 12 % viton A, 5 % Teflon).[27]

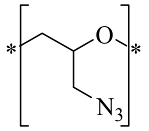
A close investigation of the explosive mixtures discussed, reveals that in all cases binders without any energetic moieties were applied. Therefore, the performance of the explosive is reduced by the amount of non-energetic material. As a consequence, several energetic polymers were developed. One example for the investigation of energetic polymers (GAP) as energetic binder is the mixture of GAP and HMX.[28]

1.5 Energetic Polymers

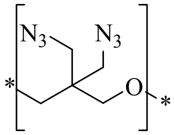
Common energetic polymers contain either nitro groups, nitric esters or azide groups (*Figure 7*).



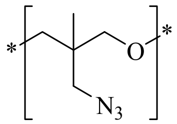
nitrocellulose **1**
NC



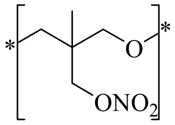
glycidyl azide polymer **2**
GAP



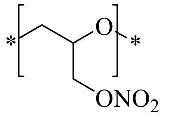
poly[3,3-bis(azidomethyl)oxetane] **3**
polyBAMO



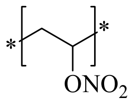
poly(azido methyl methyl oxetane) **4**
polyAMMO



poly(nitrato methyl methyl oxetane) **5**
polyNMMO/polyNIMMO



polyglycidyl nitrate **6**
polyGLYN



polyvinyl nitrate **7**
PVN

Figure 7. Selected energetic polymers.

1.5.1 Energetic Polymers Based on Cellulose

Nitrocellulose (**1**) was first described in 1846 and turned out to be a versatile polymer for different fields of application. It was used as celluloid to produce the early movies or table tennis balls, as membranes, varnish or in pyrotechnical compositions. Another application for nitrocellulose is as a binder in explosive compositions. Even after more than 150 years since its discovery, it was not substituted by new high energetic polymers, due to the low costs of production. Another important field of application is the smokeless powder, rendering **1** an indispensable material (*paragraph 1.3*). Different kinds of **1** can be obtained by different methods of nitration. The different degrees of nitration are distinguished by the nitrogen content (14.14 % empirical unattainable nitrogen content, 13.4 % practical maximum). The physical stability with an impact sensitivity larger than 3 J and a friction sensitivity larger than 353 N along with a thermal stability of only 160 °C is compensated by the extreme low costs of production and the easy application.[27]

To date, only few efforts were made to develop new energetic materials based on cellulose. Some of the best investigated energetic compounds are azidocellulose or azido cellulosenitrate.[29] Thereby it is possible to substitute either only the primary hydroxyl group[30] or the primary and secondary hydroxyl groups[31] (*Figure 8*).

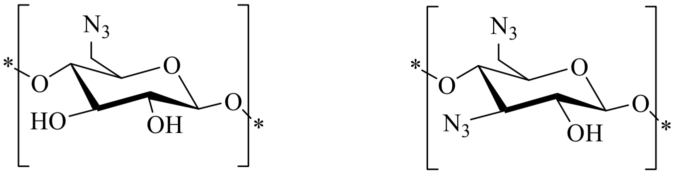
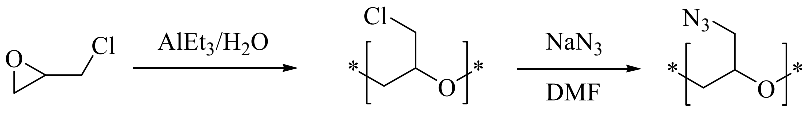


Figure 8. Possible derivatives of azido cellulose.

Azidocellulose is synthesized by first converting nitrocellulose into iodocellulose by heating it with sodium iodide. The iodine atoms are then substituted by sodium azide, yielding the azidocellulose.[32] A second method to prepare azidocellulose uses the tosylated compound instead of iodocellulose.[33] The resulting energetic polymer can be used as propellant.[31]

1.5.2 Energetic Polymers Based on Azides

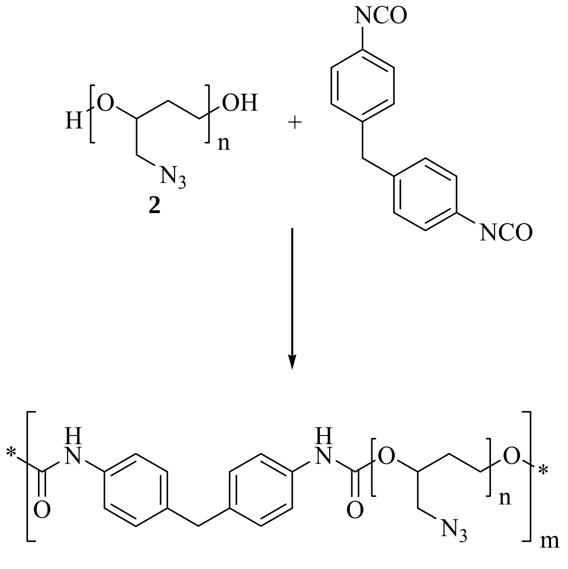
Besides nitrocellulose, GAP is a common energetic binder. The synthesis of GAP is carried out by a polymerization of epichlorhydrin with a subsequent substitution of the chlorine atom with sodium azide (*Scheme 1*).[34]



8 **9** GAP **2**

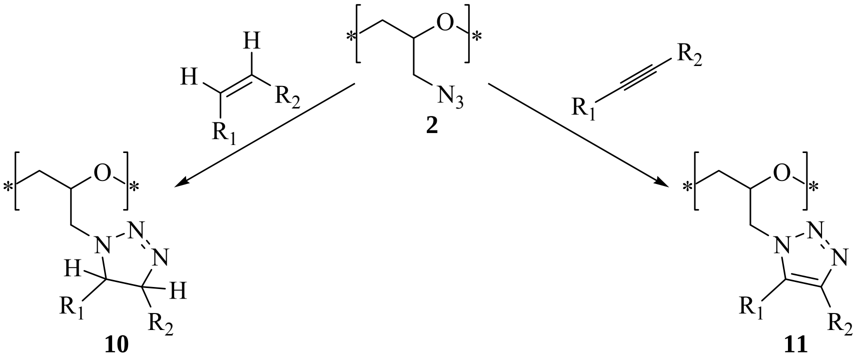
Scheme 1. Synthesis of GAP.

Despite the obviously facile chemistry, the first synthesis of GAP was reported in 1972 with a molecular weight of the starting material **9** of 25000 g mol^{-1}.[35] In order to simplify the application of GAP as energetic binder, the molecular weight was reduced to 1000 g mol^{-1}-3000 g mol^{-1}.[36] To date, several derivatives of GAP are known. The most important derivatives are common hydroxyl terminated GAP and azide terminated GAP.[37] The consistency of GAP is honey-like. Therefore, the explosive composition is mixed with GAP and a curing agent, which cross-links the different chains of GAP. Common methods use the hydroxyl groups of the hydroxyl terminated GAP for the linking-reactions with diisocyanates (*Scheme 2*).[38]



Scheme 2. Curing of GAP using a diisocyanate (starting material: GAP 1000; resulting polymer: M_n = 25000 g mol^{-1}).

Besides cross-linking using the hydroxyl groups, other cross-linking agents are known. Two examples are vinyl groups forming triazoles or imines, or derivatives of acetylene forming triazoles (*Scheme 3*).[39]

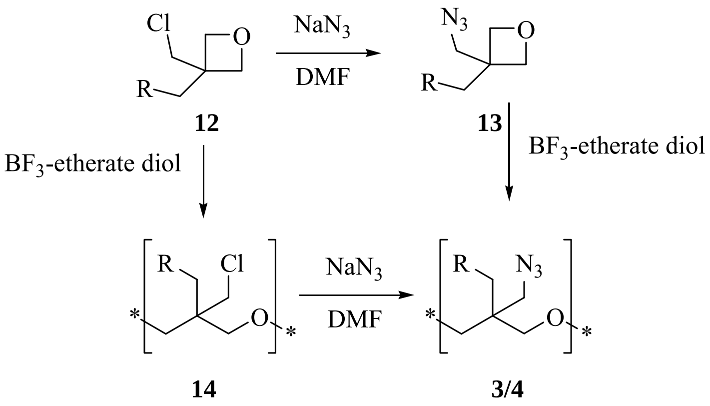


Scheme 3. Possible cross-linking reactions to cure GAP.

Besides the common curing methods, other polymers based on GAP, like the copolymers GAP/PEG (polyethylene glycol) or GAP/PCL (polycaprolactone) were investigated.[40]

The determination of the physico chemical properties of GAP is not as simple as for other common explosives. The properties depend on the degree of polymerization, the method of preparation and the structure of the polymer.[41] The friction and impact sensitivity of GAP (M_n = 2000 g mol^{-1}) are determined to be >360 N and >7 J. The high stability against friction can be explained with the oily consistency of the polymer, reducing friction forces. The limit of thermal stability was found to be 216 °C.[42]

Beside GAP, two other azide containing polymers are investigated currently as potential binders, polyBAMO and polyAMMO (*Figure 7*). Both polymers are obtained by the polymerization of the corresponding oxetanes (*Scheme 4*).[43]



R = H (**4**), CH_2Cl/CH_2N_3 (**3**)

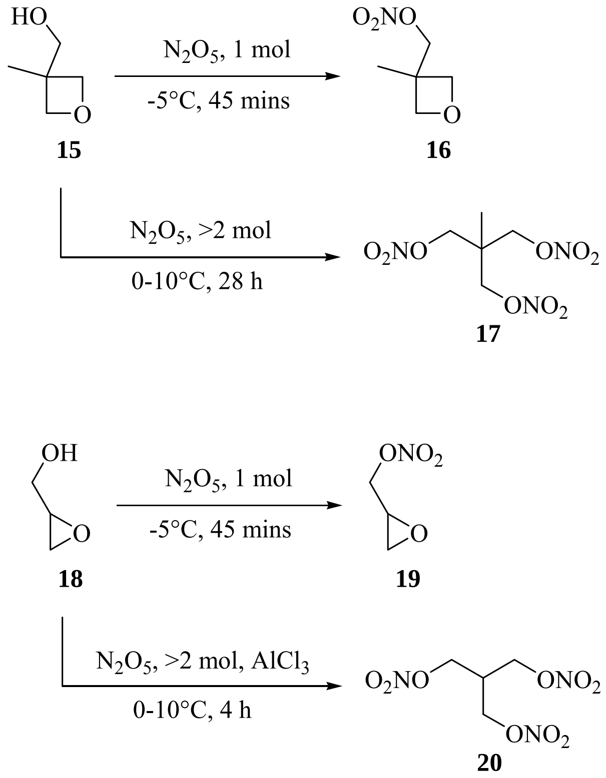
Scheme 4. Synthesis of polyAMMO (**3**) and polyBAMO (**4**).

In contrast to GAP, polyBAMO and polyAMMO are solids at ambient temperature. The molecular weights of the polymers can be controlled by the reaction conditions, an important requirement for industrial application.[44] In case of polyAMMO, a quasi-living cationic polymerization of AMMO is possible (in methylene chloride and *p*-bis(α,α-dimethyl-chloromethyl)benzene (*p*-DCC)/silver hexafluoroantimonate as initiator at -78 °C).[45] The solid character of the thermoplastic elastomer is a great advantage compared to GAP, because here no curing agent is needed.[46] A comparison of the friction and impact sensitivity of polyBAMO (>288 N and >5 J) with GAP (>360 N and >7 J) reveals the higher stability of GAP.[47] The higher sensitivity against friction of polyBAMO can be explained with the solid character of polyBAMO compared to the oily consistency of GAP. The thermal stabilities of both polymers are in a comparable range (203 °C polyBAMO, 216 °C GAP).[48]

1.5.3 Energetic Polymers Based on Nitric Esters

Common energetic binders based on nitric esters are polyNMMO (**5**), polyGLYN (**6**) or PVN (**7**). The disadvantage of these polymers compared to the energetic binders based on azides is their lower thermal stability. In case of polyvinyl nitrate, the decomposition point of 175 °C is about 40 °C lower than that of GAP. The physical stability (friction sensitivity >196 N, impact sensitivity >10 J) is similar to that of polyBAMO.[49] The advantage of PVN compared to GAP is its higher density, resulting in a better performance as explosive (1.6 g cm^{-3} and 1.3 g cm^{-3}; *paragraph 1.2.2*). As for PVN and other common nitric esters, the decomposition points of polyGLYN and polyNMMO are found at 170 °C.[50] Like GAP, polyNMMO and polyGLYN are both viscous liquids, which need to be cured for a hardening of the explosive composition.

The synthesis of polyNMMO and polyGLYN is carried out differently compared to the synthesis of the corresponding azide polymers. Whereas the azide moiety is introduced after the formation of the polymer, the monomers are nitrated with a subsequent polymerization. Otherwise, it would not be possible to obtain the hydroxyl terminated polymers, because the hydroxyl groups would be nitrated during the nitration of the polymers. Without these hydroxyl endings, it would not be possible to cross-link the polymer chains and an application as energetic binder would be impossible, as well. The nitration of the monomer is carried out using N_2O_5. Special care has to be taken regarding the stoichiometry of the monomer and N_2O_5. An excess of the nitrating agent results in a ring-opening reaction with derivatives of nitro glycerine as products (*Scheme 5*). The molecular weights of polyNMMO are in the range between 2000 and 15000 g mol^{-1}, the commonly used polyNMMO binder possesses an average molecular weight of 5500 g mol^{-1}.[50] A disadvantage of polyNMMO is its instability towards energetic radiation. Experiments showed, that gamma radiation (750 kGy) results in a change of the structure.[51]



Scheme 5. Nitration of the monomers of polyNMMO (**15**) and polyGLYN (**18**).

1.6 Adhesion and Dewetting of Polymers and Explosive Compounds

The main task of energetic binders in explosive compositions is to keep the different components of the mixture (often powders) together. The stabilization can be achieved by melting the binder with the explosive compounds and subsequent hardening of the mixture by cooling or by adding curing agents for a cross-linking of the polymer chains. Moreover, a stabilization of the explosive compound against physical stimuli like friction and impact is desired. Therefore, the adhesion between the binder and the explosive compound is another important property, besides the physical and thermal stabilities of the binder. One example for a failure of the binder would be a crack-formation in the explosive composition. The increased surface influences the burning rate of the charge, which is accelerated. The increased burning rate leads to a rising of the pressure within the device, leading to new cracks until the device is destroyed in an uncontrolled manner (worst case). The formation of cracks due to a weak binder especially in case of fast pressure, which rises after the ignition (rocket propellants, gun powders), can be very dangerous.[52]

Beside crack formation, the detachment of the polymeric matrix can lead to failures of the system. The detachment of the matrix occurs in two steps. The first step is the stress concentration at filler particles producing high local stress values. The values can reach up to the double of the applied stress. If the stress level reaches a critical value, a cavity is formed. The cavity propagates if the stress is increased until it reaches the polymer matrix. In the second step, the stress field at the filler binder interface is modified, leading to “peeling”.[53] The voids resulting from a detachment of the polymer increase the impact sensitivity, due to a heating up of the gases inside the voids in case of rapid compression (impact). Therefore, not only cracks but also detachment or dewetting of the polymeric matrix from the explosive can lead to unexpected accidents.[55,54] In order to prevent the cavities to be formed, three possibilities were reported by Oberth and Bruenner.[53] The first possibility is the formation of chemical bonds between the filler and the binder. Owing the fact, that most explosive compounds do not bear any functional groups capable to form chemical bonds, this method is limited. The second possibility is to increase the adhesive force by crystallization of the binder on the filler surface. The third and most common method is the formation of a tough membrane around the filler particles that can form chemical bonds to the binders. The compounds, being able to form those membranes are called bonding agents.[53]

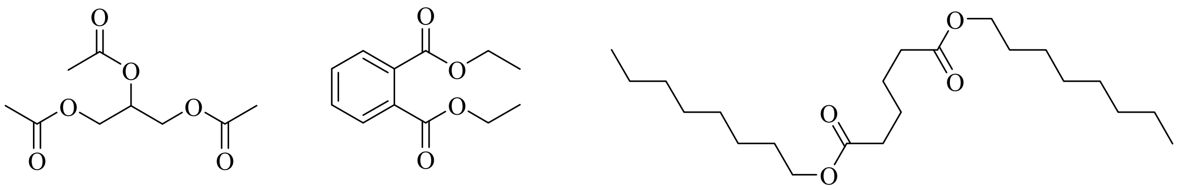
Besides the dewetting caused by the filler, a “failure” of the polymer itself is also possible. Rotations around C-C axes or the sliding of the polymer chains along each other can lead to a rearrangement of the polymeric chains, resulting in a weakening of the composition. This behavior can be reduced by introduction of bulky or rotationally stiff substituents.[52] In order to improve the adhesion of the polymer and the explosive, several binder systems were investigated.[55]

A special challenge is the development of energetic binders for nitramine-containing explosives like RDX or HMX. The weak interactions of the nitramine groups with other functionalities lead to a weak adhesion between the explosive and the polymer resulting in a dewetting of the polymer from the nitramine. Therefore, several adhesion promoters have been developed. One group of adhesion promoters are substituted amides, due to the observation, that amides are able to interact with nitro groups. If the amides bear hydroxyl groups, the hydroxyl groups can be incorporated in the polyurethane cure. Despite not being fully understood, the interactions of triethanolamine with RDX prove this aminoalcohol to be a suitable adhesion promoter, if hydroxyl-terminated polybutadiene is used as binder. Further possible promoters are polymethyl methacrylate, collagene or polymers containing hydroxyl groups or aminosilanes.[56]

1.7 Plasticizer

Besides the dewetting or detachment of the polymer, the low-temperature behavior is another important property, regarding an application as binder. Despite of being thought to stabilize and keep an explosive composition together, the polymer should not be too stiff. A certain degree of elasticity is important to absorb impact energies instead of a shattering, as would be the case for a too brittle polymer. Regarding a stable composition in the range of possible temperature exposures, the glass transition temperature (T_g) is an important value. T_g indicates the temperature, at which a liquid undergoes a glass formation. Usually T_g is below the melting point of the liquid. If the energetic binder is cooled below the T_g, it looses its elasticity and changes of the volume occur. Thus, it is indispensable to make sure that T_g is not reached by the binder. The T_g for polyNMMO for example is found to be at roughly -30 °C. The curing of the binder raises T_g by another 10 °C. In order to achieve the stability of the binder even at the minimum service temperature (-40 to -55 °C), plasticizers are used.[57]

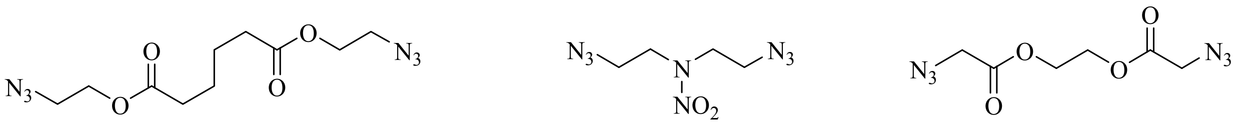
In general, two different groups of plasticizers can be distinguished: the non-energetic and the energetic plasticizers. Non-energetic plasticizers are used to modify - beside T_g - the strength, elongation toughness and the softening point of the binder. The disadvantage of the non-energetic plasticizers is their non-energetic character, which reduces the performance of the composition. Examples for non-energetic plasticizers used in rocket propellants are triacetin, diethyl phthalate and dioctyl adipate (*Figure 9*).[58]



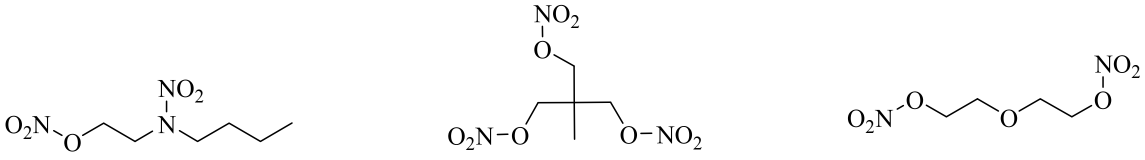
triacetin diethyl phtalate dioctyl adipate

Figure 9. Examples for non-energetic plasticizers.

The energetic plasticizers are used to improve T_g, flexibility, elasticity, and spontaneous ignition properties. The advantage of the energetic character is that the performance of the energetic composition is not reduced and even can be enhanced by the energetic plasticizers.[57] Examples for energetic plasticizers for the use in solid gun propellants are GAP, 1,5-diazido-3-nitrazapentane,[59] ethylene glycol-bis-azido acetate or *N*-*n*-butyl-*N*-(2-nitroxyethyl)nitramine (*Figure 10*).[60]



bis(2-azido ethyl) adipate 1,5-diazido-3-nitrazapentane ethylene glycol bis(azido acetate)



N-*n*-butyl-*N*-(2-nitroxyethyl)nitramine trimethylol ethane trinitrate diethylene glycol dinitrate

Figure 10. Examples for energetic plasticizers.

1.8 Concepts and Aim

Despite the existence of several energetic polymers suitable or in use as energetic binders, new polymers are desired. The low thermal stability of polymers bearing nitric esters along with the low adhesive properties of the thermal stable azide polymers justifies the development of new energetic polymers. Therefore, the aim of this dissertation was the investigation of polymers bearing new energetic groups with enhanced properties.

Polymers based on azide groups or nitric acids are well investigated (*paragraph 1.5*). To date, polymers based on tetrazoles or triazoles play an inferior role. The high thermal stability of triazoles and tetrazoles along with their energetic character renders these moieties promising candidates. Moreover, the introduction of amine or hydroxyl functionalities could lead to new possibilities to improve the adhesive forces between the binder and the explosive compound.

Another important point of view is the environmental compatibility of the energetic material. Despite the detonation of the explosive composition, a certain amount of unreacted material will be left and widespread in the surrounding area. Owing to our responsibility to protect the environment to our best, the remaining particles after an explosion (the direct damage to nature when performing an explosion is inevitable, except the explosion is not initiated) should not be toxic or at least less toxic. In the case of nitric esters and azides, highly toxic moieties are present. Besides the toxicity of the compound itself, the decomposition products of nitric esters (NO_x) are also toxic. Therefore, tetrazoles and triazoles represent a “green” alternative, because the decomposition products are only molecular nitrogen and CO/CO_2.

Taking all this into account, we decided to focus on the preparation of nitrogen-rich energetic polymers based on tetrazoles and triazoles. Special interest was laid on the thermal and physical stability of the polymers (>200 °C, impact sensitivity >15 J and friction sensitivity >100 N), along with its energetic properties (should exceed or being at least equal to those of common explosives).

References

(1) J. A. Zukas, W. P. Walters, *Explosive Effects and Applications*, Springer-Verlag New York, Inc., **1998**, 23-45.

(2) P. R. Lee, *Explosive Effects and Applications*, Springer-Verlag New York, Inc., **1998**, 23.

(3) P. R. Lee, *Explosive Effects and Applications*, Springer-Verlag New York, Inc., **1998**, 24.

(4) F. Zhang, P. A. Thibault, S. B. Murray, *Combust. Flame* **1998**, *114*, 13-25.

(5) E. Anderson, *Prog. Astronaut. Aeronaut.* **1993**, *155*, 81.

(6) T. M. Klapötke, *Chemie der hochenergetischen Materialien*, 1. Edition, Walter de Gruyter GmbH & Co. KG, Berlin, **2009**, 63-64.

(7) T. M. Klapötke, *Chemie der hochenergetischen Materialien*, 1. Edition, Walter de Gruyter GmbH & Co. KG, Berlin, **2009**, 23.

(8) a) S. H. DeMent, J. J. Chisolm, M. A. Eckhaus, J. D. Strandberg, *Journal of wildlife diseases*, **1987**, *23*, 273-278; b) S. J. Kopp, J. T. Barron, J. P. Tow, *Environmental health perspectives* **1988**, *78*, 91-99; c) N. A. Ankrah, Y. Kamiya, R. Appiah-Opong, Y. A. Akyeampon, M. M. Addae, *East African medical journal* **1996**, *73*, 375-379.

(9) a) G. G. Yannarelli, A. J. Fernandez-Alvarez, D. M. Santa-Cruz, M. L. Tomaro, *Phytochemistry* **2007**, *68*, 505-512; b) D. K. Gupta, U. N. Rai, A. Singh, M. Inouhe, *Pollution Research* **2003**, *22*, 457-463.

(10) a) S. P. Nechiporenko, M. B. Sobolev, S. E. Kolbasov, G. N. Il'icheva, *Russ. Pat.* RU2179317, **2002**; b) D. V. Roy, N. Chandrasekar, S. Kumaresan, *Pollution Research* **2004**, *23*, 251-258.

(11) T. M. Klapötke, J. Stierstorfer, A. U. Wallek, *Chem. Mater.* **2008**, *20*, 4519-4530.

(12) a) M. H. V. Huynh, M. D. Coburn, T. J. Meyer, M. Wetzler, *Proceedings of the National Academy of Sciences of the United States of America* **2006**, *103*, 10322-10327; b) M. H. V. Huynh, *Int. Pat.* WO2008143724, **2008**.

(13) a) J. W. Fronabarger, M. D. Williams, W. B. Sanborn, *Int. Pat.* WO2008048351, **2008**; b) G. Geisberger, T. M. Klapötke, J. Stierstorfer, *Eur. J. Org. Chem.* **2007**, *30*, 4743-4750.

(14) a) M. J. Kamlet, S. J. Jacobs, *J. Chem. Phys*. **1968**, *48*, 23; b) M. J. Kamlet, J. E. Ablard, *J. Chem. Phys.* **1968**, *48*, 36; c) M. J. Kamlet, C. Dickinson, *J. Chem. Phys*. **1968**, *48*, 43.

(15) T. M. Klapötke, *Chemie der hochenergetischen Materialien*, 1. Edition, Walter de Gruyter GmbH & Co. KG, Berlin, **2009**, 32-33.

(16) T. M. Klapötke, *Chemie der hochenergetischen Materialien*, 1. Edition, Walter de Gruyter GmbH & Co. KG, Berlin, **2009**, 35-43.

(17) T. M. Klapötke, S. Steinhauser, *Angew. Chem. Int. Ed.* **2008**, *47*, 3330–3347

(18) K. Karaghiosoff, T. M. Klapötke, C. M. Sabate, *Eur. J. Inorg. Chem.* **2009**, *2*, 238-250.

(19) M. A. Hiskey, D. E. Chavez, D. L. Naud, *US. Pat.* US6214139, **2001**.

(20) a) J.Stierstorfer, K. R. Tarantik, T. M. Klapötke, *Chem. Eur. J.* **2009**, *15*, 5775-5792; b) T. M. Klapötke, J. Stierstorfer, B. Weber, *Inorg. Chim. Acta* **2009**, *362*, 2311-2320; c) T. M. Klapötke, J. Stierstorfer, K. R. Tarantik, I. D. Thoma, *Z. Anorg. Allg. Chem.* **2008**, *634*, 2777-2784; d) T. M. Klapötke, H. Radies, J. Stierstorfer, *Z. Naturforsch., B: Chem. Sci.* **2007**, *62*, 1343-1352.

(21) J. Fibranz, K. Redecker, R. Fritz, *Ger. Patent*, DE4207629, **1993**.

(22) http://thebulletin.metapress.com/content/f64x2k3716wq9613/fulltext.pdf, **02.11.2009**.

(23) http://www.failureanalysisco.com/missile_telemetry_prognostics, **02.11.2009**.

(24) http://de.wikipedia.org/wiki/Ariane_5#Entwicklung_und_Vertrieb, **02.11.2009**.

(25) http://de.wikipedia.org/wiki/Dynamit, **02.11.2009**.

(26) R. Meyer, J. Köhler, A. Homburg, *Explosives*, 5. Edition, Wiley-VCH Verlag GmbH, Weinheim, **2002**, 282.

(27) R. Meyer, J. Köhler, A. Homburg, *Explosives*, 5. Edition, Wiley-VCH Verlag GmbH,

Weinheim, **2002**, 224.

(28) N. Kubota, *Propellants, Explos., Pyrotech.* **2000**, *25*, 168-171.

(29) a) Y. P. Garignan, E. E. Gilbert, *US Pat.* US87247091, **1988**; b) E. E. Gilbert, *J. Energ. Mat.* **1985**, *3*, 319-333.

(30) a) Y. Matsui, J. Ishikawa, H. Kamitakahara, T. Takano, F. Nakatsubo, *Carbohydr. Res.* **2005**, *340*, 1403-1406; b) M. Pohl, J. Schaller, F. Meister, T. Heinze, *Macromol. Rapid Commun.* **2008**, *29*, 142-148; c) B. R. Griffith, C. Krepel, X. Fu, S. Blanchard, A. Ahmed, C. E. Edmiston, J. S. Thorson, *J. Am. Chem. Soc.* **2007**, *129*, 8150-8155; d) S. Zhang, T.-T. Ong, S-C. Ng, H. S. O. Chan, *Tetrhedron Lett.* **2007**, *48*, 5487-5490; e) C. Liu, H. Baumann, *Carbohydr. Res.* **2002**, *337*, 1297-1307; f) T. Liebert, C. Hänsch, T. Heinze, *Macromol. Rapid. Commun.* **2006**, *27*, 208-213; g) T. Takano, J. Ishikawa, H. Kamitakahara, F. Nakatubo, *Carbohydr. Res.* **2007**, *342*, 2456-2480; h) T. Heinze, M. Schöbitz, M. Pohl, F. Meister, *J. Pol. Sci. A: Polym. Chem.* **2008**, *46*, 3853–3859.

(31) R. D. Guthrie, D. Murphy, *J. Chem. Soc.* **1965**, 6956-6960.

(32) E. E. Gilbert, *US Pat.*US4849514, **1989**.

(33) Azow et al. *Chem. Abstracts* **1973**, *79*, 93618.

(34) S. Brochu, G. Ampleman, *Macromolecules* **1996,** *29,* 5539-5545.

(35) E. J. Vandenberg, *U.S. Pat.* US3645917, **1972**.

(36) a) M. B. Frankel, J. E. Flanagan, *U.S. Pat.* US4268450, **1981**; b) M. B. Frankel, E. F. Witucki, D. O. Woolery, *U.S. Pat.* US4379894, **1983**.

(37) G. Ampleman, *U.S. Pat.* US5124463, **1992**.

(38) H. R. Blomquist, *US Pat.* US6802533, **2004**.

(39) C. E. Shanholtz, S. J. Riley, *US Pat.* US2005/0281968, **2004**.

(40) B. Sun. Min, *Propellants, Explos., Pyrotech.* **2008**, *33*, 131-138.

(41) A. N. Nazare, S. N. Asthana, H. Singh, *J. Energ. Mater.* **1992**, *10*, 43-63.

(42) R. Meyer, J. Köhler, A. Homburg, *Explosives*, 5. Edition, Wiley-VCH Verlag GmbH, Weinheim, **2002**, 154-155.

(43) Y. M. Mohan, Y. Mani, K. M. Raju, *Des. Monomers Polym.* **2006**, *9*, 201–236.

(44) B. Gaur, B. Lochab, V. Choudhary, I. K. Varma, *J. Macromol. Sci. Polym. Rev.* **2003**, *43*, 505.

(45) a) M. A. H. Talukder, *Makromol. Chem. Macromol. Symp.* **1991**, *42*, 501; b) M. A. H. Talukder, *ACS Polym. Prepr.* **1990**, *31*, 93.

(46) a) R. B. Wardle, P. C. Braithwaite, A. C. Haaland, J. A. Hatwell, R. R. Hendrickson, V. Lot, I. A. Wallace, C. B. Zisette, *High Energy Oxetane/HNIW Gun Propellants, 27th Int. Annual Conference of ICT*, Karlsruhe, Germany, June 25 - 28, **1996**, p. 52/1; b) Y. Oyumi, T. B. Brill, *Combust. Flame* **1986**, *65*, 127; c) N. Kubota, *22nd Int. Annual Conference of ICT*, Karlsruhe, Germany, July 2 - 5, **1991**, p. 40/1.

(47) R. Meyer, J. Köhler, A. Homburg, *Explosives*, 6. Edition, Wiley-VCH Verlag GmbH, Weinheim, **2007**, 257.

(48) J. K. Nair, R. S. Satpute, B. G. Polke, T. Mukundan, S. N. Asthana, H. Singh, *Defence Science Journal*, **2002**, *52*, 147-156.

(49) R. Meyer, J. Köhler, A. Homburg, *Explosives*, 6. Edition, Wiley-VCH Verlag GmbH, Weinheim, **2007**, 249.

(50) M. E. Colclough, H. Desai, R. W. Millar, N. C. Paul, M. J. Stewart, P. Golding, *Polym. Adv. Technol.* **2003**, *5*, 554-560.

(51) J. Akhavan, E. Kronfli, S. C. Waring, *Polymer* **2004**, *45*, 2119-2126.

(52) C. Hübner, E. Geißler, P. Elsner, P. Eyerer, *Propellants, Explos., Pyrotech.* **1999**, *24*, 119-125.

(53) A. E. Oberth, R. S. Bruenner, *Trans. SOC. Rheol.* **1965**, *9*, 165-185.

(54) L. E. Nielsen, *"Mechanical Properties of Polymers and Composites"*, Vol. 2, Marcel Dekker, New York, **1974**.

(55) a) Y. Oyumi, E. Kimura, K. Nagayama, *Propellants, Explos., Pyrotech.* **1998**, *23*, 123-127; b) Y.-C. Jeng, H.-C. Perng, H.-C. Yeh, M.-J. Chang, *Propellants, Explos., Pyrotech.* **1992**, *17*, 292-294.

(56) J. M. Bellerby, C. Kiriratnikom, *Propellants, Explos., Pyrotech.* **1989**, *14*, 82-85.

(57) N. Wingborg, C. Eldsäter, *Propellants, Explos., Pyrotech.* **2002**, *27*, 314-319.

(58) J. P. Agrawal, R. K. Bhongle, F. M. David, J. K. Nair, *J. Energ. Mater.* **1993**, *11*, 67-83.

(59) J. E. Flanagan, E. R. Wilson, M. B. Frankel, *US Pat.* US5013856, **1981**.

(60) R. S. Damse, A. Singh, *Def. Sci. J.* **2008**, *58*, 86-93.

2. Tetrazolyl Hydrazines as Precursors for Explosives and Energetic Polymers

Abstract: The class of tetrazolyl hydrazines proved to be suitable for the preparation of high explosives and energetic polymers. Based on the tetrazolyl hydrazine, 5-azidotetrazoles and tetrazenes were synthesized. Energetic polymers formed either by a polycondensation reaction or radical polymerization could also be prepared from tetrazolyl hydrazines. The advantages of the tetrazolyl hydrazines are their sufficiently high thermal stability along with their steadiness against physical stimuli. The synthesis of these compounds could be improved by using the substitution reaction of the bromine atom of 5-bromotetrazoles with hydrazine derivatives for the preparation instead of the extensive synthetic pathway starting from thiosemicarbazides. The purification of tetrazolyl hydrazines could be reduced from column chromatography to extraction methods, facilitating an industrial application of these compounds.

2.1 Introduction

To date, tetrazolyl hydrazines are a rather unknown class of tetrazoles. The first tetrazolyl hydrazine was published by Thiele in 1895[1] and was stabilized by an aromatic moiety. In order to reduce the content of carbon in the molecules, only alkylated tetrazoles were synthesized. For the preparation of polymers, two methods are generally known – the polycondensation and the radical polymerization. Both methods own their special advantages.

The polycondensation is a very gentle way to form polymers and can be carried out at rather low temperatures (especially suitable for highly energetic monomers). The disadvantage of this method is that two different molecules have to be reacted with each other, a diole or diamine and a diole- or diamineophil like a diisocyanate (hexamethylene diisocyanate) or a dicarboxylic acid chloride (oxalyl chloride or succinyl chloride). In both cases the diisocyanate or dicarboxylic acid chloride are non-energetic compounds that introduce a huge amount of carbon in the polymer, resulting in low energetic properties.

The advantage of the radical polymerization is that only a vinyl-monomer is needed. Therefore, the carbon content of the polymer can be reduced to a minimum. The disadvantages of this method are the radicals needed for the radical polymerization. Common polymer chemistry uses reactive non-energetic monomers. In case of energetic monomers, the exothermic decomposition of the molecules can be triggered by the radicals, leading to a deflagration or detonation of the monomer mixture.

Taking these advantages and disadvantages into account, polymers were synthesized by polycondensation and radical polymerization to investigate the possibilities of this chemistry. Especially the tetrazolyl hydrazines proved to be suitable monomers because of their thermal stability even under presence of radicals. Moreover the hydrazine moiety can be used as functional group for polycondensation reactions.

In order to show the huge versatility of tetrazolyl hydrazines, further non-polymeric energetic compounds were synthesized: the highly sensitive 5-azidotetrazoles and the thermal stable tetrazenes. The 5-azidotetrazoles were obtained by the reaction of sodium nitrite on the tetrazolyl

---

(1) J. Thiele, H. Ingle*, Liebigs Ann. Chem.* **1895**, *287*, 233-265.

hydrazine in hydrochloric acid and the tetrazenes were obtained as dimers by oxidation of the hydrazine moiety with elemental bromine.

2.2.1 Polymers Formed by Polycondensation Reactions

2.2.1.1 Polymer Based on 1-(2-Hydroxyethyl)-1*H*-tetrazolyl)methyl hydrazine

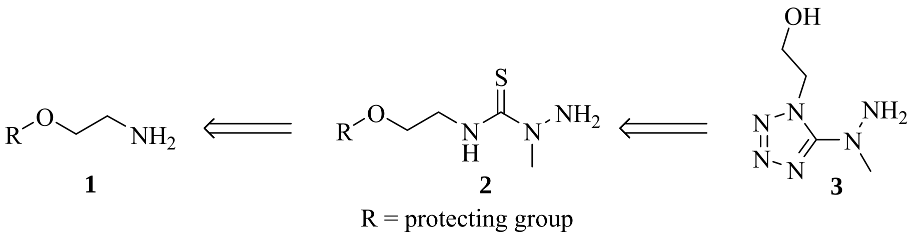
I want to thank Prof. Dr. K. Banert for this advice and help to find the way out of the gloom of ignorance.

In this paragraph, the synthetic pathway using thiosemicarbazides as starting material for the preparation of tetrazolyl hydrazines is presented. The special appreciation of this obsolescent method is justified by the months of exhausting search for potential thiosemicarbazides, always accompanied by the smell of mercaptanes. The improved synthesis of tetrazolyl hydrazines is presented in the following paragraphs.

2.2.1.1.1 Synthesis of the 1-(2-Hydroxyethyl)-1*H*-tetrazolyl)methyl hydrazine

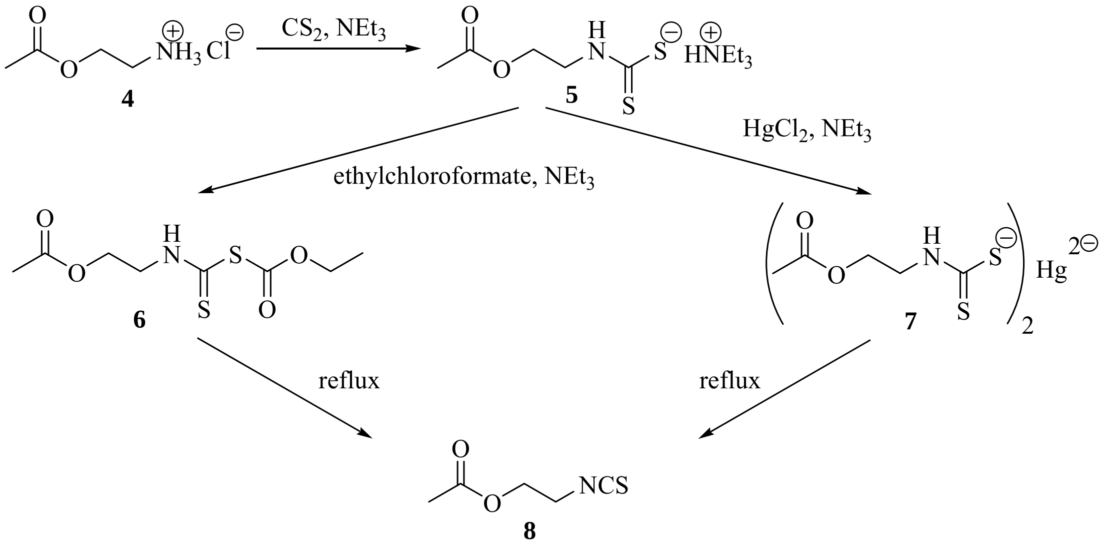
In order to gain a high nitrogen content, the 1-(2-hydroxyethyl)-1*H*-tetrazolyl)methyl hydrazine was synthesized. N1-substituted tetrazolyl hydrazines were reported in literature by F. R. Atherton and R. W. Lambert.[1] In contrast to the well known derivatives of 5-aminotetrazole,[2] alkylated derivatives of tetrazolyl hydrazines are rarely known.[3] The experiments during my master thesis showed, that an alkylation of the tetrazole moiety via alkyl halogenides analogue to known alkylations of aminotetrazole[2] are not possible, due to the reactivity of the hydrazine moiety. In this work we present a five-step synthesis starting with ethanolamine leading to the 1-(2-hydroxyethyl)-1*H*-tetrazolyl)methyl hydrazine.

To obtain (1-(2-hydroxyethyl)-1*H*-tetrazolyl)methyl hydrazine (**3**), an improved synthetic pathway (by J. J. Weigand[4]) similar to the synthesis F. R. Atherton and R. W. Lambert developed[1] was applied (*Scheme 1*).



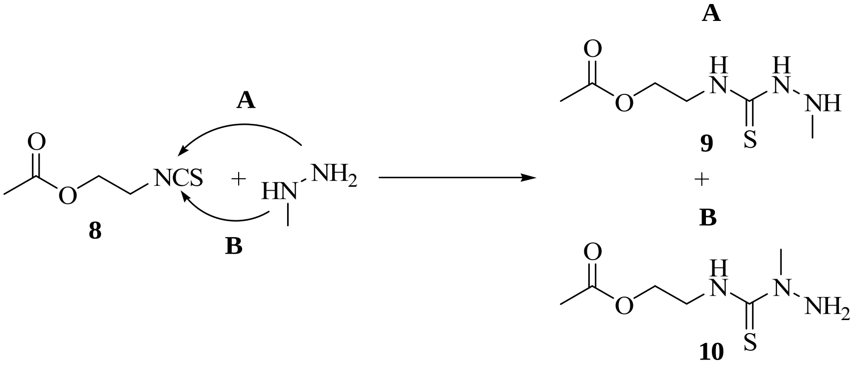
Scheme 1. Retrosynthetic pathway to (1-(2-hydroxyethyl)-1*H*-tetrazolyl)methyl hydrazine.

In the first step towards the synthesis of **3**, it turned out to be necessary to protect ethanolamine to avoid a cyclisation reaction due to a possible intramolecular attack of the hydroxyl group at the electrophilic isothiocyanate of **8**. On applying different protecting groups, only the acetyl group proved to be suitable. Based on 2-aminoethyl acetate, which was required to form the thiosemicarbazide (**2**), several different ways yielding **8** have been published.[5] Compound **8** was obtained by desulfuration of the carbamodithioic acid **5** using either mercury(II)chloride[6] or ethyl chloroformate[7] (*Scheme 2*).



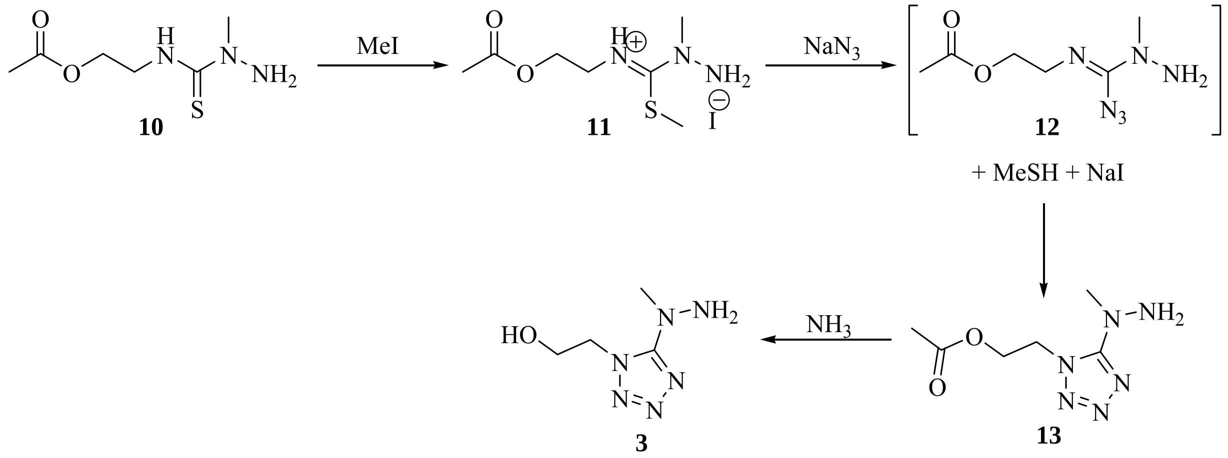
Scheme 2. Synthesis of 2-isothiocyanatoethyl acetate **8**.

Compound **8** was purified by distillation. A common way to synthesize thiosemicarbazides is the reaction between derivatives of hydrazine and isothiocyanates.[8] The 4-(2-(acetyloxy)ethyl)-2-methylthiosemicarbazide (**10**) was obtained from the reaction of methyl hydrazine at the isothiocyanate moiety of **8**. Using kinetic control, it was possible to selectively obtain **10** at 0 °C whereas carrying out the reaction at elevated temperatures yielded a mixture of both isomers **9** and **10** (*Scheme 3*), shown by ^{1}H NMR studies.



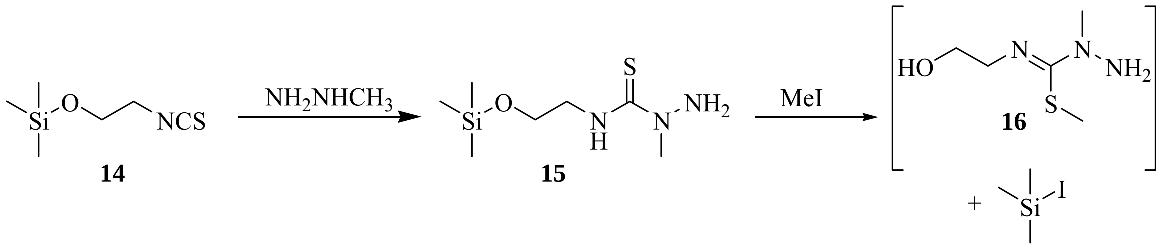
Scheme 3. Synthesis of 4-(2-(acetyloxy)ethyl)-2-methylthiosemicarbazide **10**.

In order to obtain tetrazole **13** it was necessary to methylate the sulfur atom of **10** converting it into a leaving group. The resulting methylmercaptane was substituted by azide, using a suspension of sodium azide in ethanol. The resulting azidoamine **12** underwent an electrocyclic ring closure to form the tetrazole **13**. Compound **13** had to be purified using column chromatography, before it was deprotected on treatment with concentrated ammonia for one hour at ambient temperature (*Scheme 4*).



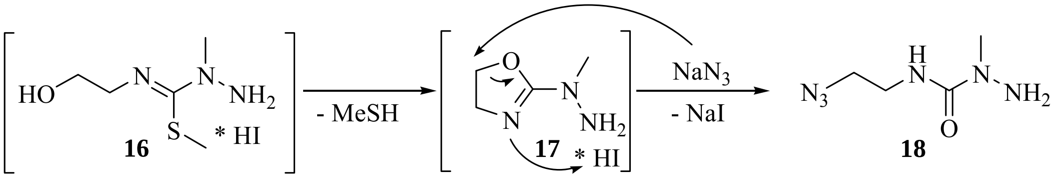
Scheme 4. Synthesis of (1-(2-hydroxyethyl)-1H-tetrazolyl)methyl hydrazine 3.

In order to point out the importance of the protecting group, a more labile protecting group was chosen to obtain the free hydroxyl group during the methylation step. We applied the trimethylsilyl group, due to its increased lability towards acidic conditions and temperature.[9] The corresponding (2-isothiocyanatoethoxy)trimethylsilane (**14**) was prepared according to *Kricheldorf* et al.[10] Adding methyl hydrazine in etheric solution yielded 2-methyl-4-(2-(trimethylsilyloxy)ethyl)thiosemicarbazide (**15**). The formation of hydrogen iodide together with a temperature of 80 °C (four hours) during the methylation step of the thiosemicarbazide **15** was sufficient for the deprotection of **15** (*Scheme 5*).



Scheme 5. Synthesis of (Z)-1-amino-3-(2-hydroxyethyl)-1,2-dimethylisothiourea **16**.

In the following step, the methylmercaptane was substituted by an intramolecular nucleophilic attack of the hydroxyl group to form the intermediate five-membered ring **17**. Sodium azide was added to the reaction mixture and the azide anion caused a ring opening by a nucleophilic attack at the oxygen-bearing CH_2-group leading to the 4-(2-azidoethyl)-2-methylsemicarbazide **18** (*Scheme 6*). Compound **18** was purified by column chromatography and a pale yellow liquid was obtained.



Scheme 6. Formation of 4-(2-azidoethyl)-2-methylsemicarbazide **18**.

2.2.1.1.2 Vibrational and NMR Spectroscopy

The analysis of compound **3** and **18** was performed by vibrational (IR) and NMR spectroscopy. The analysis of **18** (IR, NMR) showed no evidence for a tetrazole, however an azide group could unambiguously be detected, together with small signals of decomposition products. In contrast to the analytical data of the previously mentioned tetrazole **3**, the IR-spectrum showed synthesized **18** using a different way and provided us with spectra for comparison.[12]

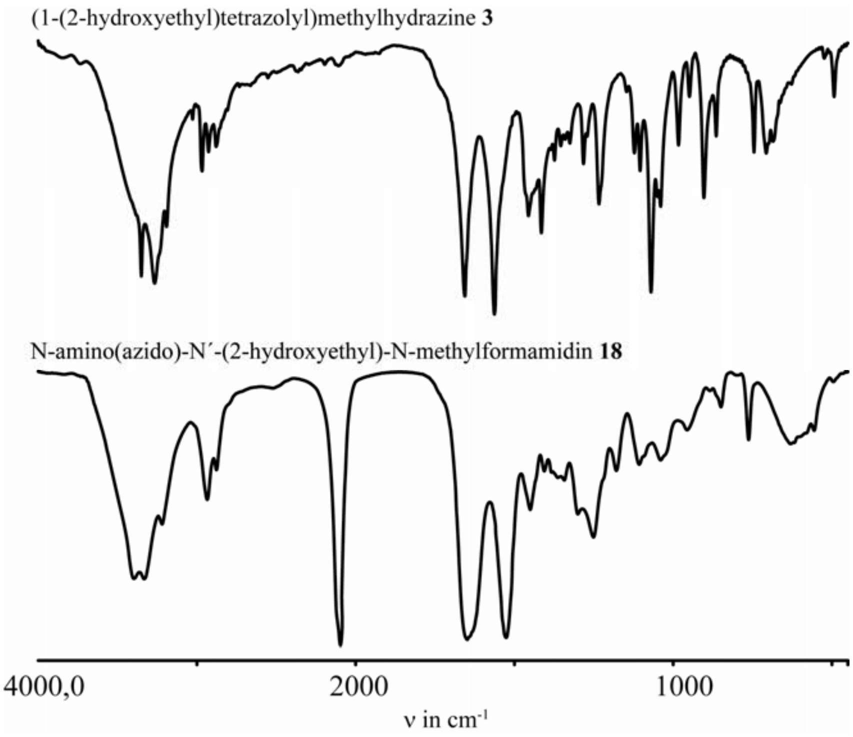


Figure 1. IR spectra of **18** and **3**, the signal appearing at 2253 cm^{-1} indicates the azide group.

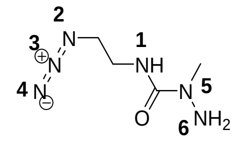
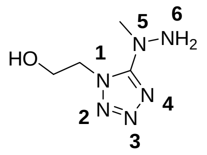
A comparison of the ^{1}H and ^{13}C NMR-data is given in *Table 1*.

Table 1. ^{1}H and ^{13}C NMR data of compound **18** and **3** in [*d6*]-DMSO.

	18			**3**		
	^{1}H		^{13}C	^{1}H		^{13}C
CH_3	singlet	2.91	38.2	singlet	3.09	44.4
OCH_2	multiplet	3.18	51.3	triplet	3.72	50.8
NCH_2	multiplet	3.28	60.3	triplet	4.49	59.5
NH_2	singlet	4.41	-	singlet	4.82	-
OH	br. triplet	6.89	-	br.singlet	4.96	-
C_q	-	-	159.7	-	-	159.2

In *Table 2*, the ^{15}N NMR data are shown. The shifts are consistent with common values for tetrazoles, in case of **3**[13] and azides, in case of **18**.[14]

Table 2. ^{15}N NMR data of **18** and **3** data in [*d6*]-DMSO.

compound	**18**	**3**
		
N1	-312.8	-174.5
N2	-286.7	-21.9
N3	-133.7	-11.0
N4	-172.8	-100.1
N5	-304.8	-313.3
N6	-307.1	-301.6

2.2.1.1.3 Crystal Structures of 3, 10 and 13

Structures **3**, **10**, and **13** were characterized by single crystal X-ray diffraction. Compound **10** crystallizes in the monoclinic space group $P2_1$/n with four molecular formulas per unit cell (*Figure 2*). The bond lengths and angles are in accordance with values observed for thiosemicarbazides in the literature.[15] The crystal structure reveals intermolecular interactions between each of the thiosemicarbazide moieties and the acetyl groups. The structure is stabilized by four hydrogen bridges. Three intermolecular hydrogen bridges exist between three different N3-donoratoms to the sulfur-acceptor atom, forming a two dimensional layer. The fourth hydrogen bridge between the donor atom N1 to the acceptor O2 connects the layers along the c-axis.

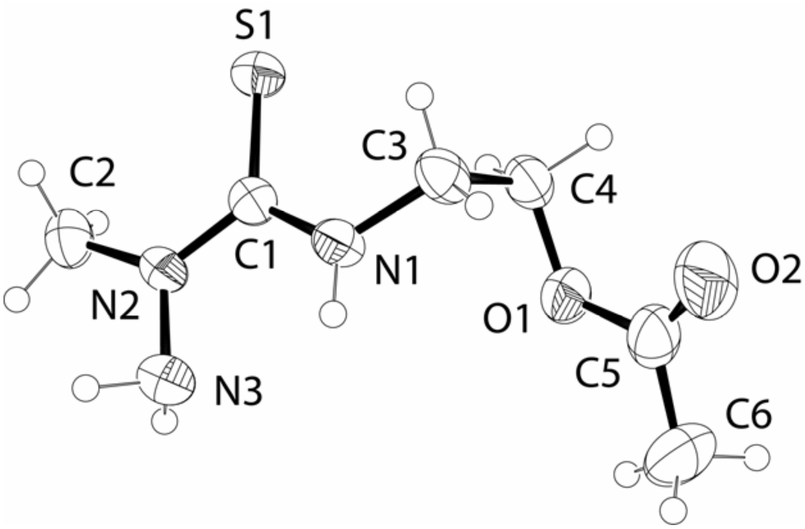


Figure 2. Molecular structure of **10**. Thermal ellipsoids are drawn at the 50% probability level.

Compound **13** crystallizes in the monoclinic space group $P2_1/n$ having four molecular formulas per unit cell (*Figure 3*). As mentioned before, the bond lengths and angles are consistent with comparable values of tetrazoles in the literature.[15] Again the acetyl groups and tetrazole moieties are each heading towards each other. Thereby the acetyl moieties are situated between two layers of tetrazoles. The structure is stabilized by two different hydrogen bonds: one between the donor atom N6 and the acceptor atom N4, connecting the tetrazole moieties, the other between the donor atom N6 and the acceptor atom O2 of the opposing molecule.

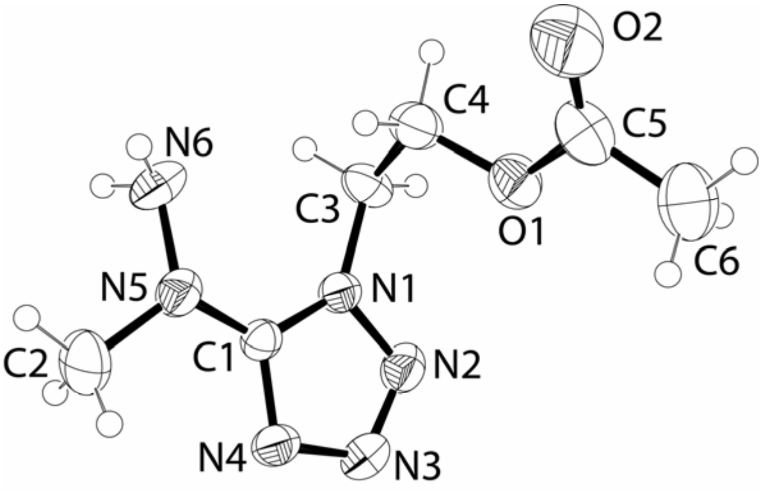


Figure 3. Molecular structure of **13**. Thermal ellipsoids are drawn at the 50% probability level.

Compound **3** crystallizes in the monoclinic space group $P2_1/c$ having four molecular formulas per unit cell (*Figure 4*). Compared to compound **13**, the N4—N3—N2 angle is about 5.5° smaller than the corresponding angle of **13**. The other angles and bond lengths show no difference compared to values from the literature.[16] In the solid state, the molecules form dimers by an intermolecular hydrogen bridge between N4 as acceptor- and O1 as donor atom. The dimers are connected by a hydrogen bridge between the donor atom N6 and the acceptor atom N2 along the b-axis. These tubular-like structures are connected by a hydrogen bond between the donor atom N6 and the acceptor atom O1.

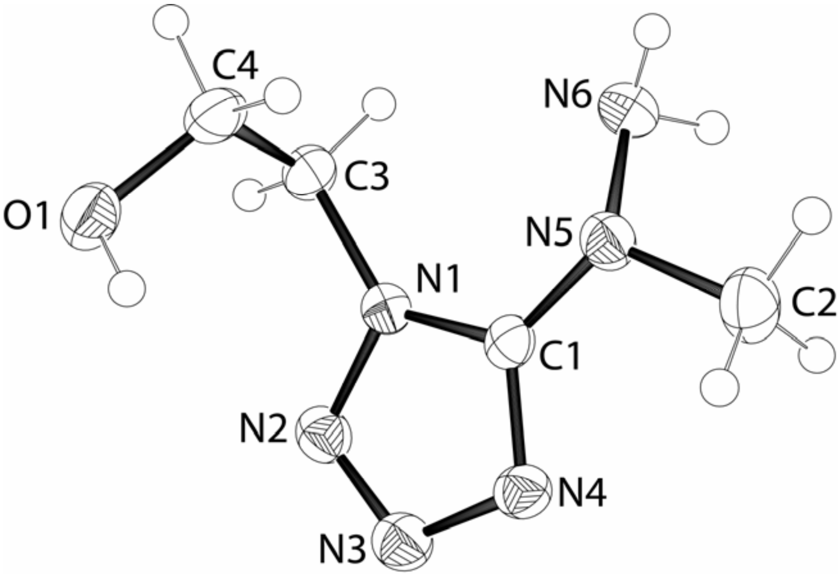
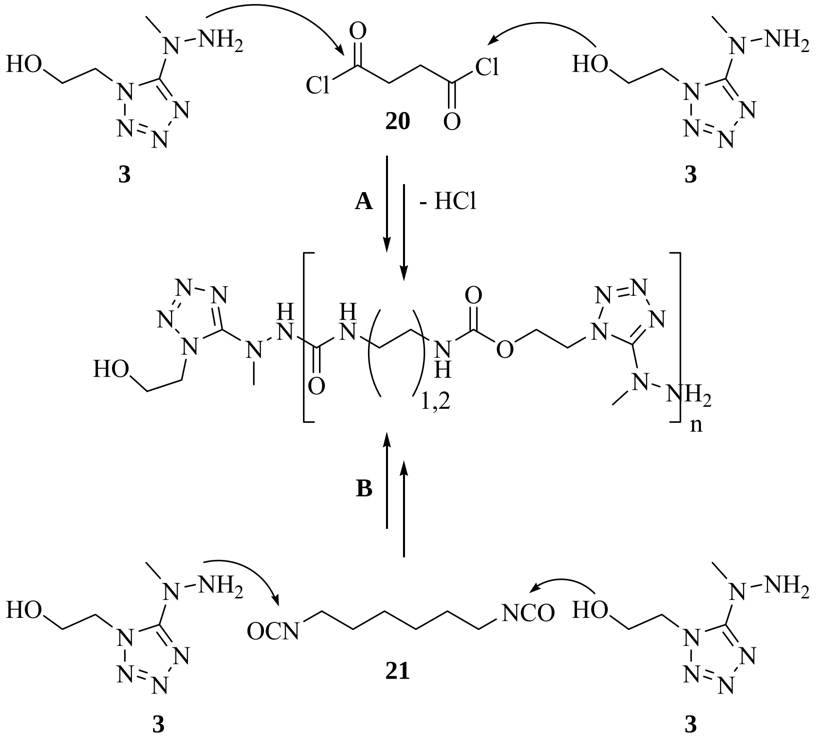


Figure 4. Molecular structure of **3**. Thermal ellipsoids are drawn at the 50% probability level.

2.2.1.1.4 Polycondensation Reactions of 1-(2-Hydroxyethyl)-1*H*-tetrazolyl)methyl hydrazine

With **3** being a bifunctional tetrazole containing a hydroxyl group and a hydrazine moiety, there are different possibilities for a polycondensation to occur. Dichlorosuccinate (**20**) and hexamethylene diisocyanate (**21**) were chosen to study the reaction with **3** (*Scheme 7*).



Scheme 7. Polycondensation and polyaddition of **3**. The attack of two hydrazine or two hydroxyl moieties at **20** or **21** are also possible.

Two different methods of polymerisation were investigated: polycondensation in solution and bulk. The experiments revealed, that the polycondensation in solution was not suitable, because either low molecular weight fragments or starting material were detected. In turn, the polymers were synthesized by melting the monomers and annealing them for several hours.

Using dichlorosuccinate as a monomer (**method A**, *Scheme 6*), only polymer chains with low molecular weights could be obtained. The average molecular weight M_n was found to be 996 g/mol. The measurement was carried out using a DMSO-solution containing 5 g/L LiBr as eluent. The elemental analysis of the polymer showed significant differences to the calculated data (found: N 28 %, C 27 %, H 5 %; calculated: N 41.37 %, C 35.42 %, H 5.57 %). These differences are expected to be a result of the high chlorine content of the polymer since the hydrogen chloride formed during the polycondensation can undergo an acid-base reaction with the hydrazine moiety of the tetrazole. Hence, the deactivated amino group does not participate in any esterfication-reactions necessary for the formation of long polymers any longer.

To avoid the formation of hydrogen chloride and the resulting deactivation of the hydrazine moiety, hexamethylene diisocyanate was chosen as monomer for a polyaddition reaction (**method B**, *Scheme 6*). The polymerization was carried out in bulk, by melting **3** at 100 °C and subsequent addition of **21**. The melt was kept at 120 °C for one hour and the polymer was obtained as prudish foam. The molecular weights of the polymer were determined by a GPC-measurement. As eluent, dimethylformamide containing 0.01 M lithium nitrate was used. With a molecular weight distribution M_w of 5850 g/mol the obtained polymer was much longer than the corresponding polymer using **20** as monomer. The polydispersity was determined to be 3.21. The softening point of the polymer was found at 55 °C, the melting area between 190 °C and 245 °C, yielding a clear and colorless liquid. Above 260 °C the polymer underwent decomposition. The elemental analysis was in agreement with the calculated values (found: N 32.81 %, C 43.26 %, H 6.82 %; calculated: N 34.33 %, C 44.16 %, H 6.79 %). Taking these results into account, the formed hydrogen chloride during the synthesis of **method A** can be determined being responsible for the partial decomposition of the polymer during the polycondensation process.

2.2.1.1.5 Conclusions

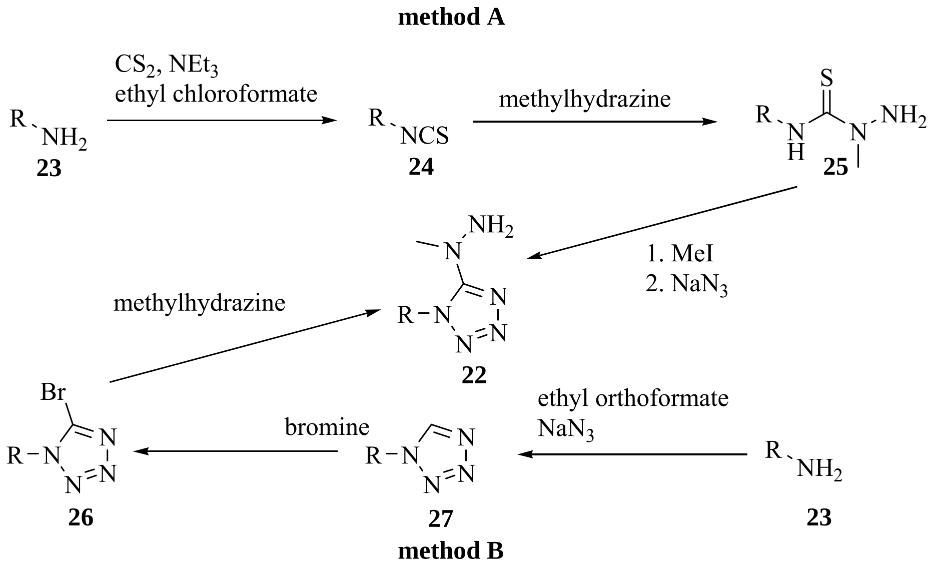
The polymer of 1-(2-hydroxyethyl)-1*H*-tetrazolyl)methyl-hydrazine **(3)** and hexamethylene diisocyanate **(21)** was readily prepared in high yields. The nitrogen rich polymer possesses a nitrogen content of 33 %, accompanied by a high thermal stability (260 °C). Moreover no sensitivity towards friction or impact can be observed. The investigated polymer can easily be converted into several derivatives using different diisocyanates as monomers. Thereby the formed polymers can be adjusted to the desired application. A probable mechanism for the formation of **3** has been suggested and furthermore the isomer 4-(2-azidoethyl)-2-methylsemicarbazide **18** was synthesized.

2.2.1.2 Nitrogen-rich Energetic Polymers Based on Alkylene Bridged Bis-(1-methyl-tetrazolylhydrazines)

The advantage of alkylene bridged tetrazolyl hydrazines is the formation of a bifunctional monomer with a small content of carbon. In order to obtain a monomer with a sufficient stability for the polycondensation, the 1-methyl-tetrazolylhydrazines were prepared. In contrast to the hydrazine derivatives (*paragraph 2.3.2*) the methyl derivatives possess an enhanced stability against physical and thermal stress, along with an improved stability towards oxidation of the hydrazine moiety. Another advantage of the methylated alkylene bridged bistetrazolylhydrazines is the purity. In contrast to the hydrazine derivatives, always containing traces of hydrogen bromide and hydrazine, the methylated compounds can be prepared with high purity. Moreover, the 1,2-bis(5-hydrazinyl-1*H*-tetrazolyl)ethane only crystallizes with one molecule of crystal water preventing it from being a suitable monomer for a polycondensation reaction. The hygroscopic tendency of the hydrazine derivatives allows the polycondensation only after drying. Due to slight decomposition of the hydrazine moiety during the drying process at elevated temperature and under high vacuum, the preparation of polymers containing the corresponding hydrazine derivatives proved to be inefficient and was not further investigated.

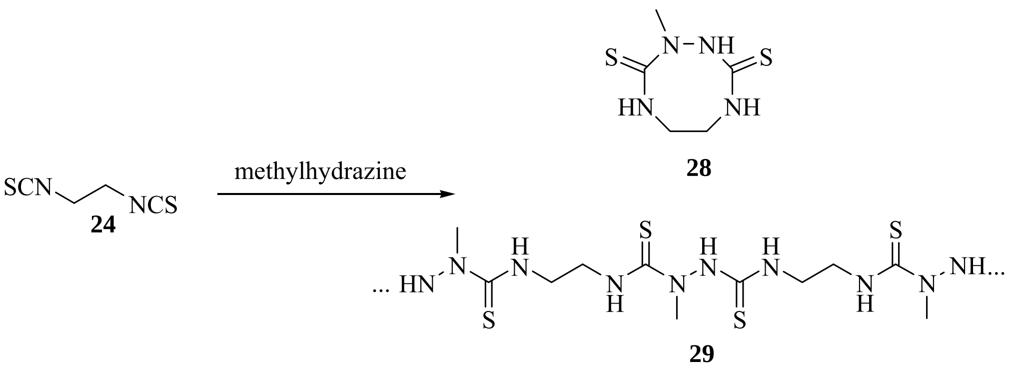
2.2.1.2.1 Synthesis of Alkylene Bridged Bis-(1-methyl-tetrazolylhydrazines)

As starting materials for the synthesis of the 1,1-methyl-tetrazolylhydrazine containing polymers the corresponding derivatives of 1,1-methyl-tetrazolylhydrazine had to be synthesized. In order to obtain polymers, possessing a satisfactory amount of nitrogen, the choice fell on the 1,2-bis(5-(1-methylhydrazinyl)-1*H*-tetrazol-1-yl)ethane (**22a**), 1,2-bis(5-(1-methylhydrazinyl)-1*H*-tetrazolyl)-1-methylethane (**22b**) and 1,2-bis(5-(1-methylhydrazinyl)-1*H*-tetrazol-1-yl)butane (**22c**). Preliminary studies concerning the *N*-[1-(2-hydroxyethyl)-1*H*-tetrazol-5-yl]-*N*-methyl hydrazine as polymeric precursor proved derivatives of tetrazolyl hydrazine suitable as monomers.[17] To date, two synthetic pathways leading to tetrazolyl hydrazines are known (*Scheme 1*).



Scheme 1. Method A and **B** for the synthesis of tetrazolyl hydrazines **22**.

The close investigation of **method A** resulted in the finding, that this method was not suitable for the preparation of **1**. The synthesis of the ethyl diisothiocyanate (**24**) was carried out as described in literature[18] but the following conversion of **24** into the corresponding dithiosemicarbazide (**25**) only resulted in an oily mixture of several polymeric products (**28** and **29**) (*Scheme 2*).



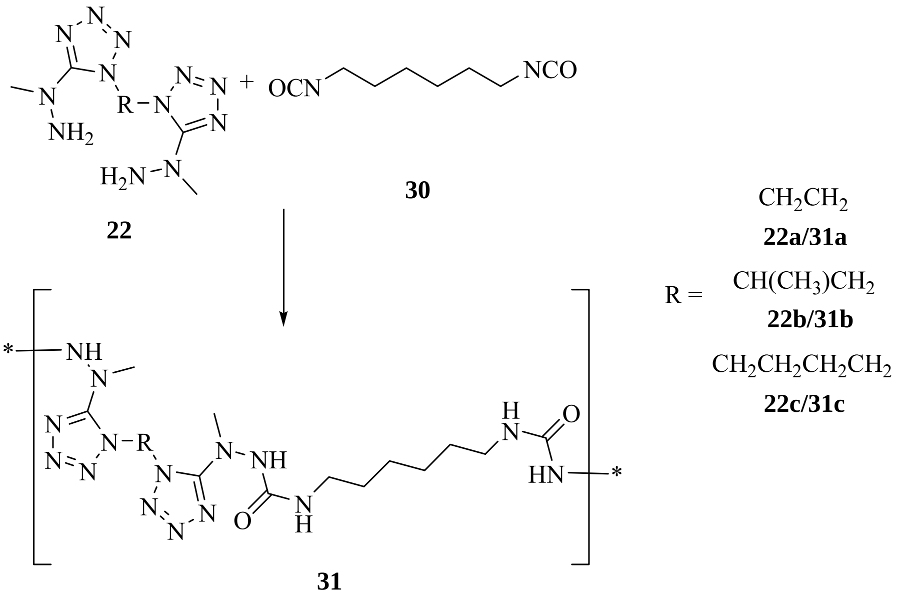
Scheme 2. Formation of possible compounds by the reaction of **3** with methyl hydrazine.

Further investigation of the formed compounds was not carried out. Several attempts were undertaken to obtain **4** by the variation of the sequence of addition and concentrations of the starting materials along with the reaction temperature and solvents, but we were not able to isolate **25**.

Method B uses 5-bromo-1*H*-tetrazoles (**26**) as intermediates for the synthesis of **22**. The corresponding 5-bromo-1*H*-tetrazoles were prepared in moderate yields as described in a previous publication[19] and in analogy to a patent.[20] The following conversion of **6** into the corresponding methylhydrazinyl derivatives **22** was carried out by the reaction of two equivalents of methyl hydrazine with **26** in 2-propanol. The yields range between 45 % and 75 % after refluxing the reaction mixture for 12 h.

2.2.1.2.2 Polycondensation of Alkylene Bridged Bis-(1-methyl-tetrazolylhydrazines) and Hexamethylene Diisocyanate

The polymerization of **22** was carried out by using hexamethylene diisocyanate (**30**) as second monomer for the polyaddition reaction (*Scheme 3*).



Scheme 3. Polymerization of **22**.

The polyaddition reaction of **30** and *N*-[1-(2-hydroxyethyl)-1*H*-tetrazol-5-yl]-*N*-methyl hydrazine was investigated previously and proved to be an efficient pathway for the preparation of polymers from suitable derivatives of tetrazolyl hydrazines[19] (*paragraph 2.2.1.1.4*). The polyaddition reaction was carried out in bulk by melting the *N*-[1-(2-hydroxyethyl)-1*H*-tetrazol-5-yl]-*N*-methyl hydrazine and a following addition of **30**. This method of preparation was also tried to be used for the preparation of polymers from **22**. Carrying out the reaction, only compound **22b** proved to be suitable. In case of **22c** a strong decomposition took place during the polyaddition reaction, due to the high melting point of **22c** (135 °C). In case of **22a**, the exothermic polyaddition reaction of the isocyanate and the hydrazine moiety reached the point of decomposition of the polymer (melting point of **22a**: 220 °C; decomposition point of **31a**: 240 °C), resulting in a sudden exothermic decomposition. These experiences showed, that a method had to be developed that allows a polymerization at rather low temperatures (lower than 170 °C), especially when working with energetic compounds. Efforts trying to perform a polymerization in solution only yielded starting materials, no matter which solvent or conditions were chosen. The limiting factor for the choice of solvent is the solubility of **22**. The bridged tetrazolyl hydrazines **22** were only soluble under acidic conditions in water, in alcohols, DMSO or DMF. Taking these results into account, a new method for the polymerization of **22** was developed by dissolving **22** in boiling DMF and adding **30** to this solution. The solvent was removed by slow evaporation at ambient pressure by heating the reaction mixture to 135 °C. After the reaction mixture was concentrated, the polymerization took place and a colorless glasslike solid was formed. The remaining DMF was removed at 140 °C under high vacuum. After drying for 8 h, an amount of DMF ranging between 7 % and 17 % was still present in the brittle polymer. The dried polymers **31a-c** could not be dissolved in DMF, even by refluxing them in an excess of DMF (200 mg polymer in 30 mL of DMF). The treatment only resulted in a swelling of the polymer. As only solvent being capable of dissolving the polymer, the highly toxic hexamethylphosphoramide (HMPT) was found. The solubility of the polymer in this solvent was rather high (120 mg in 2 mL of HMPT).

2.2.1.2.3 Analytical Data of the Polymers

Due to its insolubility in any common solvent, the polymers were investigated by vibrational spectroscopy and elemental analysis. The elemental analysis reveals the contamination of the polymer by DMF and water (*Table 1*). The amount of DMF varies between 7.5 % (**31b**) and 17.3 % (**31c**). The water content ranging between 1.8 % and 2.7 % is due to absorption of water of the polymer. Possible side products during the polycondensation reaction are ureas. The reaction of isocyanates and water to form ureas are commonly known decomposition pathways of isocyanates. Since commercially available DMF was used instead of dried DMF, a certain amount of water should be present during the polycondensation reaction. The close agreement of the elemental analysis allows the assumption, that the decomposition of the isocyanates to amines forming ureas can be neglected. A closer investigation of the content of urea moieties in the polymer was not carried out, due to limited analytical methods (insolubility in any common solvents).

Table 1. Elemental analysis of **31a-c**.

	calculated [%]			found [%]			content of DMF / water [%]
	N	C	H	N	C	H	
31a	46.42	39.80	6.20	42.27	40.16	6.17	11.2 / 1.8
containing DMF/H_2O	42.49	40.14	6.68				$C_{65}H_{129}N_{59}O_{13}$
31b	44.93	41.28	6.47	41.78	40.83	6.62	7.5 / 2.7
containing DMF/H_2O	41.74	40.73	6.84				$C_{66}H_{132}N_{58}O_{13}$
31c	43.53	42.66	6.71	38.61	43.03	6.74	17.3 / 2.1
containing DMF/H_2O	38.35	42.90	7.32				$C_{60}H_{122}N_{46}O_{12}$

The ability of swelling in DMF at 100 °C was investigated (*Table 2*). The experiments show the differences between **31a-c**. The absorption of DMF of **31b** compared to **31c** is about a third. An explanation could be the influence of the bridging alkyl group. In case of **31c**, the butyl group should lead to chains with the lowest intermolecular interactions of the polymers. The tetrazolyl hydrazine moieties of polymer **31a** are connected by an ethyl moiety. Compared to **31c** the possible intermolecular interactions of the tetrazole moieties of **31a** are higher because of the smaller alkyl bridge, leading to a lower absorbance of DMF. In case of **31b**, the methyl group of the alkyl bridge could increase the friction between the polymer chains, leading to higher intermolecular interactions. As a result, the absorbance of DMF is only a third, compared to **31c**. The amount of absorbed DMF was measured once after refluxing the polymer in DMF for one hour and once after cooling the swollen polymer to room temperature in the DMF solution and keeping it for an additional hour at 20 °C. The comparison of the absorbed DMF at 100 °C and at 20 °C points out the connection of the absorbance and the temperature. In all three cases (**31a**-**c**), the amount of absorbed DMF at 20 °C is only half of the amount at 100 °C.

Table 2. Ability of swelling of **31a**-**c** using DMF as solvent.

	weight (polymer) 0 min, 20 °C [mg]	weight (swollen polymer) 60 min, 100 °C [mg]	weight (g DMF per g polymer) 60 min, 100 °C [mg]	weight (swollen polymer) 120 min, 20 °C [mg]	weight (g DMF per g polymer) 120 min, 20 °C
31a	153	415	1712	324	1118
31b	89	184	1067	140	593
31c	113	443	2920	314	1779

For us, a determination of the average molecular weight (M_n) was not possible, because the polymers were only soluble in the highly toxic hexamethylphosphoramide. Thus, a determination of the molecular weight by common methods like GPC or viscosity without an application of the hexamethylphosphoramide was not possible.

2.2.1.2.4 Energetic Properties of the Polymers

Beside the ability of absorbing DMF, the energetic characteristics were investigated. The determination of the sensitivity against friction and impact was carried out according to BAM standards.[21] Compounds **22a-c** possess a sensitivity against impact of > 10 J but show no sensitivity against friction (> 360 N). The polymers **31a-c** are neither sensitive towards impact (> 100 J) or friction (> 360 N).

The values given in *Table 3* were calculated by using experimental values obtained by bomb calorimetric measurements. Using these values, the enthalpy of formation was calculated by applying the Hess Thermochemical Cycle, as reported in literature[22]. The heats of formation of H_2O (l) and CO_2 (g) -286 kJ mol^{-1} and -394 kJ mol^{-1} were obtained from literature[23]. The comparison of the energetic data of **31a** to **c** points out the outstanding position of **31a**. The value of $\Delta_E U_m°$ of **31a** is about 1000 kJ mol^{-1} higher than that of **31b** and **c**. The detonation velocity D(m s^{-1}) is about 500 m s^{-1} faster and the detonation pressure by 30 kbar higher. The comparison of **31b** and **31c** does not show significant differences. A comparison of **31** with energetic polymers (glycidyl azido polymer GAP, nitrocellulose) relativizes the energetic character. In contrast to common explosives, the value of $\Delta_E U_m°$ (an indication of the work performed by the explosive) is much lower. Considering the high amount of carbon of the polymer, due to the hexamethylene diisocyanate, along with the amount of DMF, the lower energetic character is not astonishing. Nevertheless, the polymers **31a-c** are nitrogen rich polymers (N: 40 %) with moderate energetic characters.

Table 3. Energetic properties of **31a**, **31b** and **31c**.

	31a	**31b**	**31c**	glycidyl azide polymer[k]
formula	$C_{65}H_{129}N_{59}O_{13}$	$C_{66}H_{132}N_{58}O_{13}$	$C_{60}H_{122}N_{46}O_{12}$	$C_3H_5N_3O$
molecular mass (g mol^{-1})	1945	1946	1680	99.1
point of decomposition (°C)	243	244	241	216
impact sensitivity (J)	> 100	> 100	> 100	> 7
friction sensitivity (N)	> 360	> 360	> 360	> 360
density (g cm^{-3})[a]	1.4	1.4	1.4	1.3
$-\Delta U_{\text{comb.}}$ (cal g^{-1})[b]	5346	5319	5573	-
ΔH_{comb} (kJ mol^{-1})[c]	235	-1471	-1823	-
$-\Delta_f H_m$ (kJ mol^{-1})[d]	14	885	2046	-
Values calculated by EXPLO5 V5.02				
$-\Delta_E U_m°$ (kJ kg^{-1})[e]	2524	1682	1532	4444
T_E (K)[f]	1847	1438	1350	2860
$p_{C\text{-}J}$ (kbar)[g]	139	109	108	135
D(m s^{-1})[h]	6887	6286	6303	6629
Gas vol. (L kg^{-1})[i]	773	777	783	738
I_s (s)[l]	157	-	-	195
I_s (s)[m] (80 % ADN)	244	241	241	247

[a] estimated from structure determination; [b] experimental (constant volume) combustion energy; [c] experimental molar enthalpy of combustion; [d] molar enthalpy of formation; [e] energy of explosion; [f] explosion temperature; [g] detonation pressure; [h] detonation velocity; [i] assuming only gaseous products; [k] obtained from the database of EXPLO5 (V5.02); [l] specific impulse (isobaric combustion, chamber pressure 60 bar, frozen expansion); [m] specific impulse of a mixture containing 75 % ammonium dinitramide as oxidizer.

The thermal behavior of **31** was investigated by DSC measurements. Despite the high content of DMF (7 % - 17 %) the evaporation of the DMF could not be assigned without a doubt to a temperature area. Instead, the DSC plot shows an endothermic reaction ranging from the starting point of the measurement (25 °C) to the point of decomposition. The endothermic behavior can be explained by the softening of the polymer along with a slow evaporation of DMF. The points of decomposition of the polymers **31a-c** are all in the same range from 241 °C to 244 °C. Compared to the points of decomposition of the tetrazolyl hydrazines **22a-c** (272 °C to 279 °C), the lower thermal stability of the polymers can be explained by the substituted hydrazine moiety, causing a destabilization of the tetrazolyl hydrazine.

2.2.1.2.5 Energetic Properties of the Bis-tetrazolylalkanes and Bis-(1-methyl-tetrazolylhydrazin)alkanes

The energetic properties were investigated to evaluate the suitability of the starting material as energetic compounds. The thermal stability of the tetrazoles **27a-c** with about 200 °C is sufficiently high. The melting point of **27a** is 134 °C and the melting points of **27b** and **27c** are 105 °C and 120 °C. The difference of the melting point to the decomposition point is in all cases larger then 70 °C. This finding renders the compounds **27a-c** suitable for melt-castable explosives. The determination of the sensitivity towards friction and impact of compounds **27a-c** gave an impact sensitivity >360 N and an impact sensitivity >40 J. As a result, the tetrazoles **27a-c** are insensitive towards friction and impact.

The decomposition points of compounds **22a-c** is with 270 °C much higher than the decomposition points of compounds **27a-c**. The melting points of **22a**, **22b** and **22c** are 220 °C, 90 °C-125 °C and 135 °C. The melting point can easily adjusted by an appropriate choice of the alkyl bridge. The impact and friction sensitivity of compounds **22a-c** is lower than that of compounds **27a-c**. The impact sensitivity was determined to be >10 J, whereas the friction sensitivity was >360 N. These results turn both compounds (**22** and **27**) into promising nitrogen rich energetic properties with a high thermal and physical stability.

Table 4. Energetic properties of **22a**, **22b** and **22c**.

	22a	**22b**	**22c**
formula	$C_6H_{14}N_{12}$	$C_7H_{16}N_{12}$	$C_8H_{18}N_{12}$
molecular mass (g mol^{-1})	254.2	268.2	282.2
point of decomposition (°C)	270	270	270
impact sensitivity (J)	> 10	> 10	> 10
friction sensitivity (N)	> 360	> 360	> 360
density (g cm^{-3})[a]	1.607	1.45	1.45
$-\Delta U_{comb.}$ (cal g^{-1})[b]	5077	4708	4898
ΔH_{comb} (kJ mol^{-1})[c]	711	243	65
$\Delta_f H_m$ (kJ mol^{-1})[d]	679	208	28
Values calculated by EXPLO5 V5.02			
$-\Delta_E U_m°$ (kJ kg^{-1})[e]	3615	1820	1225
T_E (K)[f]	2415	1584	1262
p_{C-J} (kbar)[g]	262	138	116
D(m s^{-1})[h]	8775	6932	6517
Gas vol. (L kg^{-1})[i]	813	818	819
I_s (s)[l]	195	149	132
I_s (s)[m] (80 % ADN)	247	242	241

[a] estimated from structure determination; [b] experimental (constant volume) combustion energy; [c] experimental molar enthalpy of combustion; [d] molar enthalpy of formation; [e] energy of explosion; [f] explosion temperature; [g] detonation pressure; [h] detonation velocity; [i] assuming only gaseous products; [k] obtained from the database of EXPLO5 (V5.02); [l] specific impulse (isobaric combustion, chamber pressure 60 bar, frozen expansion); [m] specific impulse of a mixture containing 75 % ammonium dinitramide as oxidizer.

Table 5. Energetic properties of **27a**, **27b** and **27c**.

	27a	**27b**	**27c**
formula	$C_4H_6N_8$	$C_5H_8N_8$	$C_6H_{10}N_8$
molecular mass (g mol^{-1})	166.1	180.1	194.1
point of decomposition (°C)	200	200	200
impact sensitivity (J)	> 40	> 40	> 40
friction sensitivity (N)	> 360	> 360	> 360
density (g cm^{-1})[a]	1.515	1.4	1.4
$-\Delta U_{\text{comb.}}$ (cal g^{-1})[b]	4115	4555	4860
ΔH_{comb} (kJ mol^{-1})[c]	418	321	158
$-\Delta_f H_m$ (kJ mol^{-1})[d]	401	301	136
Values calculated by EXPLO5 V5.02			
$-\Delta_E U_m°$ (kJ kg^{-1})[e]	3025	2437	1601
T_E (K)[f]	2368	1977	1501
$p_{C\text{-}J}$ (kbar)[g]	170	127	106
D(m s^{-1})[h]	7219	6545	6161
Gas vol. (L kg^{-1})[i]	728	733	737
I_s (s)[l]	181	162	139
I_s (s)[m] (80 % ADN)	242	241	240

[a] estimated from structure determination; [b] experimental (constant volume) combustion energy; [c] experimental molar enthalpy of combustion; [d] molar enthalpy of formation; [e] energy of explosion; [f] explosion temperature; [g] detonation pressure; [h] detonation velocity; [i] assuming only gaseous products; [k] obtained from the database of EXPLO5 (V5.02); [l] specific impulse (isobaric combustion, chamber pressure 60 bar, frozen expansion); [m] specific impulse of a mixture containing 75 % ammonium dinitramide as oxidizer.

2.2.1.2.6 Crystal Structures of 22a, 26a and 27a

Compound **22a** crystallizes in the monoclinic space group $P2_1/n$ with two molecular formulas per unit cell (*Figure 5*). The molecules are stacked along the y-axis as shown in *Figure 6*. There are no inter- or intramolecular interactions like hydrogen bridges or π-interactions between the molecules.

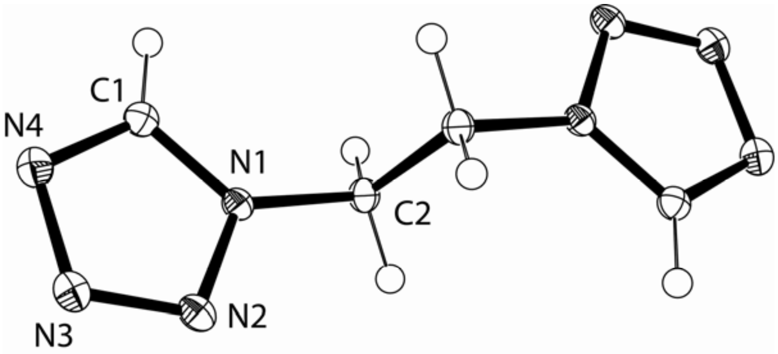


Figure 5. Molecular structure of **22a**. Thermal ellipsoids are drawn at the 50% probability level.

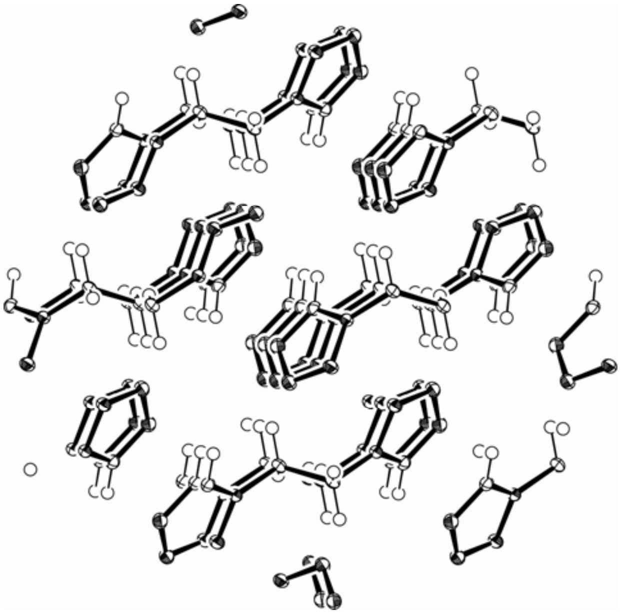


Figure 6. Arrangement of compound **22a** in the crystal along the y-axis. Thermal ellipsoids are drawn at the 50% probability level.

Compound **26a** crystallizes in the orthorhombic space group *Pbcn* with twelve molecular formulas per unit cell (*Figure 7*). In contrast to compound **22a**, **26a** forms a ball-like conformation instead of the spread conformation in the crystal. The conformation can be explained by intermolecular interactions of the bromine atom and N3 of the tetrazole moiety (*Figure 8*). The distance of a bromine atom and a nitrogen atom without interactions is reported with 3.40 Å.[24] The intermolecular distance between Br1 and N3 is found with 3.005(4) Å, the distance between Br2 and N7 with 2.949(4) Å, allowing the assumption of an intermolecular interaction of Br1 and N3. These intermolecular interactions lead to a chain-like arrangement of the molecules along the z-axis (*Figure 8*). Thereby, one molecule forms two Br-N-bridges to two other different molecules as donor and acts at the same time as acceptor of two additional Br-N-bridges.

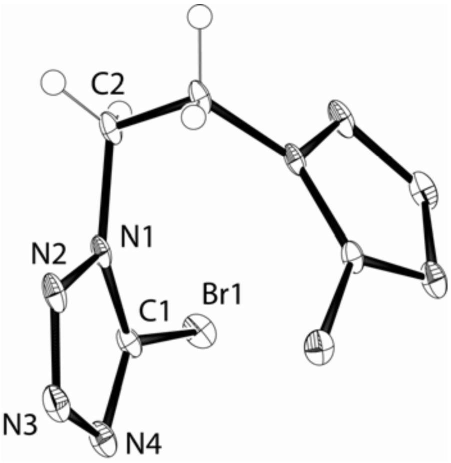


Figure 7. Molecular structure of **26a**. Thermal ellipsoids are drawn at the 50% probability level.

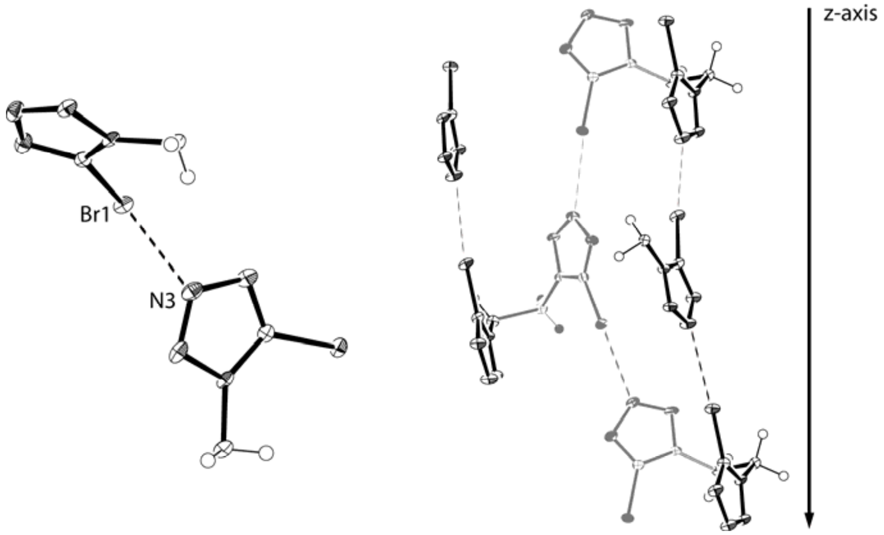


Figure 8. Intermolecular interaction of the bromine atom and the tetrazole moiety of **26a**. Thermal ellipsoids are drawn at the 50% probability level.

Compound **27a** crystallizes in the monoclinic space group *C*2/*c* with four molecules per unit cell (*Figure 9*). The structure is stabilized by three hydrogen bridges formed by the hydrazine moiety. The first two hydrogen bridges are formed by one proton to two different N3-atoms (D•••H: 3.193(3) Å, 3.299(3) Å; <(DHA): 134(2)°, 127(2)°). The third hydrogen bridge is formed between the other proton of the hydrazine moiety and N4 (D•••H: 3.158(3) Å, <(DHA): 169(2)°) (*Figure 10*).

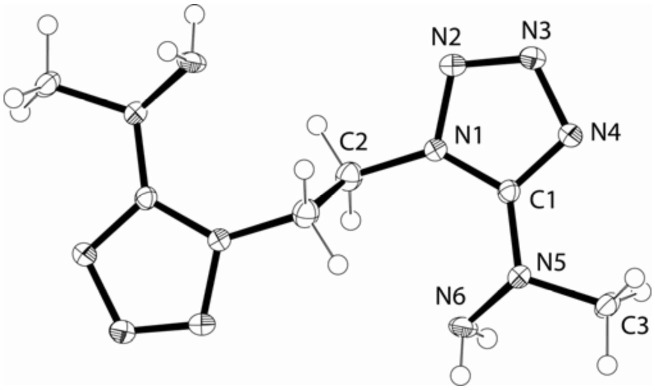


Figure 9. Molecular structure of **27a**. Thermal ellipsoids are drawn at the 50% probability level.

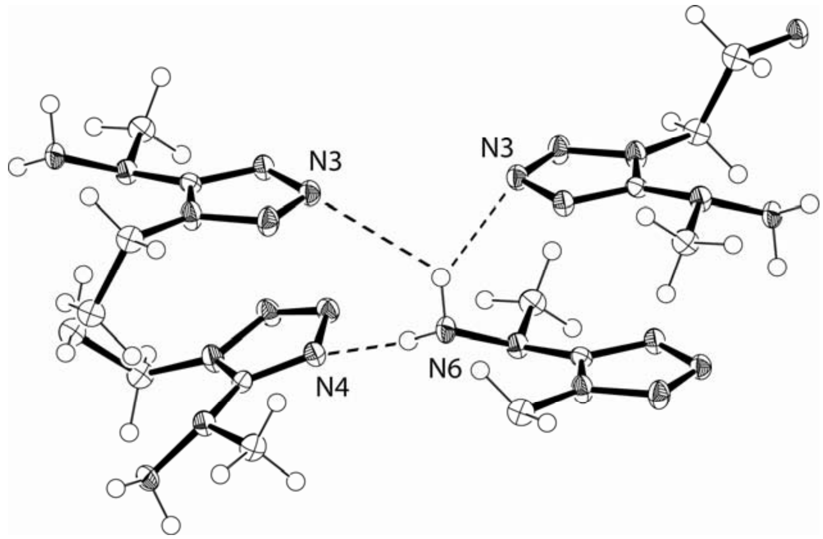


Figure 9. Hydrogen bridges formed by the hydrazine moiety of **27a**. Thermal ellipsoids are drawn at the 50% probability level.

2.2.1.2.7 Conclusions

Several polymers containing bis(5-methylhydrazinyl-1*H*-tetrazolyl)alkanes were synthesized by the reaction of the corresponding tetrazolyl hydrazines **22** with hexamethylene diisocyanate. In order to carry out the polyaddition reaction, a new method had to be developed, allowing the polymerization of tetrazolyl hydrazines with high melting points. The formed polymers **31** possess a content of nitrogen of 40 % and are insensitive towards impact and friction. The investigation of the energetic properties proved the polymers to be moderate explosives. Along with the thermal stability up to 240 °C the nitrogen rich energetic polymers **31** are promising compounds for an application as energetic binders. The ability of absorbance of DMF could be used to transfer the explosive into the polymer.

2.2.1.3 References

(1) F. R. Atherton, R. W. Lambert, *Tetrahedron* **1983**, *39*, 2599-2608.

(2) a) R. M. Herbst, C. W. Roberts, E. J. Harvill, *J. Org. Chem.* **1951**, *16*, 139-149; b) R. A. Henry, W. G. Finnegan, E. Lieber, *J. Am. Chem. Soc.* **1954**, *76*, 2894-2898; c) M. I. Barmin, S. A. Gromova, V. V. Mel'nikov, *Russ. J. Appl. Chem.* **2001**, *74*, 1156-1163.

(3) a) F. L. Scott, R. N. Butler, *J. Chem. Soc. C* **1966**, *13*, 1202-1206; b) K. Yamazaki, H. Hasegawe, K. Umekawa, Y. Ueki, N. Ohashi, M. Kanaoka, *Bioorg. Med. Chem. Lett.* **2002**, *12*, 1275-1278.

(4) J. J. Weigand, *Dissertation*, University of Munich (LMU), **2005**.

(5) Huoben-Weyl, *Methoden der organischen Chemie*, 4. Auflage, E. Müller (Hrsg.), Georg Thieme Verlag, Stuttgart, **1955**, S. 867-879.

(6) R. S. McElhinney*, J. Chem. Soc. (C)* **1966**, 950-955.

(7) a) R. Herges, A. Dikmans, U. Jana, F. Köhler, P. G. Jones, I. Dix, T. Fricke, B. König, *Eur. J. Org. Chem.* **2002**, *17*, 3004-3014; b) A. Donetti, E. Cereda, A. Ezhaya, R. Micheletti, *J. Med. Chem.* **1989**, *32*, 957-961; c) G. L. Garmaise, R. Schwartz, A. F. McKay, *J. Am. Chem. Soc.* **1958**, *80*, 3332-3334.

(8) a) B. Holmberg, B. Psilanderhielm, *J. Prakt. Chem.* **1911**, *82*, 440-450; b) J. P. Scovill, *Phosphorus, Sulfur, and Silicon* **1991**, *60*, 15-19.

(9) K. Jarowicki, P. Kocienski, *J. Chem. Soc., Perkin Trans. 1* **2000**, *16*, 2495-2527.

(10) H. R. Kricheldorf, *Angew. Chem.* **1968**, *24*, 1028; H. R. Kricheldorf, *Synthesis* **1970**, 539-560.

(11) a) C. N. Ramachandra Rao, T. S. Chao, C. W. W. Hoffman, *Anal. Chem.* **1957**, *29*, 916-918; b) S. Hirota, H. Matsumoto, H.-W. Huang, T. Sakurai, T. Kitagawa, O. Yamauchi, *Biochem. Biophys. Res. Commun.* **1998**, *243*, 435-437.

(12) K. Banert, *unpublished results*.

(13) T. M. Klapötke, J. Stierstorfer, *Helv. Chim. Acta* **2007**, *90*, 2132-2150.

(14) a) H. Quast, M. Ach, J. Balthasar, T. Hergenröther, D. Regnat, J. Lehmann, K. Banert *Helv. Chim. Acta* **2005**, *88*, 1589-1609; b) P. Cmoch, J. W. Wiench, L. Stefaniak, G. A. Webb, *J. Mol. Struc.* **1999**, *510*, 165-178; c) J. Müller, *Z. Naturforsch.* **1979**, *34b*, 536-540.

(15) a) D. Chattopadhyay, T. Banerjee, S. K. Mazumdar, *Acta Cryst.* **1991,** *C47*, 112-115; b) S. Seth, A. Biswas, A. Banerjee, S. K. Chatopadhyay, S. Ghosh, *Acta Cryst.* **1996**, *C52*, 2377-2379.

(16) a) A. S. Lyakhov, S. V. Voitekhovich, P. N. Gaponik, L. S. Ivashkevich, *Acta Cryst.* **2004**, *C60*, o293-o294; b) T. M. Klapötke, C. Kuffer, P. Mayer, K. Polborn, A. Schulz, J. J. Weigand, *Inorg. Chem.* **2005**, *44*, 5949-5958.

(17) K. Banert, T. M. Klapötke, S. M. Sproll, *Eur. J. Org. Chem.* **2009**, 275–281.

(18) Huoben-Weyl, *Methoden der organischen Chemie*, 4th edition, E. Müller (editor), Georg Thieme Verlag, Stuttgart, **1955**, 867-879.

(19) T. M. Klapötke, S. M. Sproll, *Eur. J. Org. Chem.* **2009**, *in press.*

(20) G. M. F. Lim, M. Endo, *US Pat.* US4374994, **1983**; b) D. E. Bayes, *Eu.Pat.* EP0117368A1, **1982**.

(21). a) M. Suceska, *Test Methods for Explosives*, Springer, New York, **1995**, p. 21 (impact), p. 27 (friction); b) http://www.bam.de/; c) Impact: insensitive > 40 J, less sensitive > 35 J, sensitive > 4, very sensitive > 3 J; friction: insensitive > 360 N, less sensitive = 360 N, sensitive < 360 N > 80 N, very sensitive < 80 N, extreme sensitive < 10 N; According to the UN Recommendations on the Transport of Dangerous Goods (+) indicates: not safe for transport.

(22). T. M. Klapötke, M. Stein, J. Stierstorfer, *Z. Anorg. Allg. Chem.* **2008**, *634*, 1711-1723.

(23) a) N. Wiberg, *Lehrbuch der Anorganischen Chemie / Holleman-Wiberg*, 101. Ed., de Gruyter, Berlin, **1995**, 141; b) N. Wiberg, *Lehrbuch der Anorganischen Chemie / Holleman-Wiberg*, 101. Ed., de Gruyter, Berlin, **1995**, pp 250, 859 and 1176; c) http://webbook.nist.gov/chemistry/

(24) A.Bondi, *J. Phys. Chem.* **1964**, *68*, 441.

2.2.2 Polymers Formed by Radical Polymerization

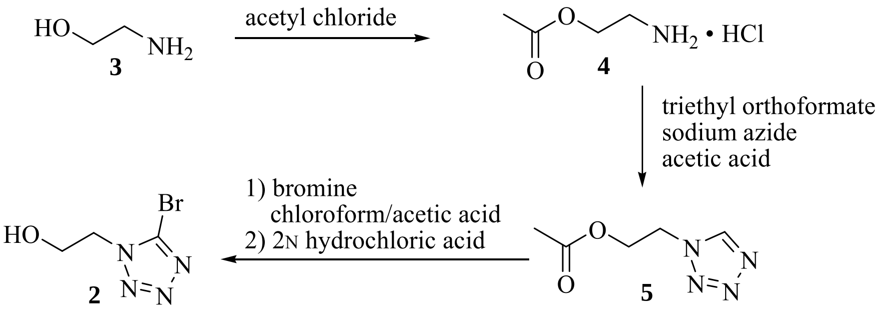
Although tetrazoles are a well-investigated group of heterocycles, the number of polymers containing these heterocycles is small. The first polymer based on tetrazoles was 1-poly(vinyltetrazole) and 1-poly(vinyl-5-amino-1*H*-tetrazole).[1] Today, several approaches to synthesize 1-poly(vinyl-1*H*-tetrazole) are known, either by radical polymerization of 1-(vinyl-1*H*-tetrazole)[1] or by the conversion of polyvinylnitrile into the tetrazole moiety by a [2+3] cycloaddition reaction with hydrazoic acid.[2] The disadvantage of these polymers is their extremely low solubility in common solvents, preventing them from any application. Therefore, they are used as copolymers with polystyrene.[3]

In order to improve their solubility and thus the applicability of these polymers, the introduction of hydrazine moieties was investigated. 5-Bromo-1-vinyl-1*H*-tetrazole (**1**) proved to be a versatile starting material. Since the intention of this work was the synthesis of nitrogen rich polymers, only hydrazine and monomethyl hydrazine were used.

To further improve the energetic characteristics, the conversion of polyvinyl tetrazolylhydrazine to the corresponding 5-azido-1*H*-tetrazole containing polymer was investigated. The investigation of the physical stabilities of the small number of known alkylated 5-azido-1*H*-tetrazoles proves this class of energetic materials as very dangerous compounds (sensitivity towards friction: > 5 N, sensitivity towards impact: > 0.15 J).[4] Despite their high sensitivity towards physical stress, their thermal stability (up to 170 °C) turns these compounds into interesting building blocks for nitrogen-rich polymers. In the case of poly-1-vinyl(5-azido)-1*H*-tetrazole, the long carbon chains of the polyvinyl moiety could work as a protection against physical stress, turning this polymer into a very interesting energetic, nitrogen containing polymer.

2.2.2.1 Synthesis of Energetic Monomers Based on 5-Bromo-1-vinyl-1*H*-tetrazole

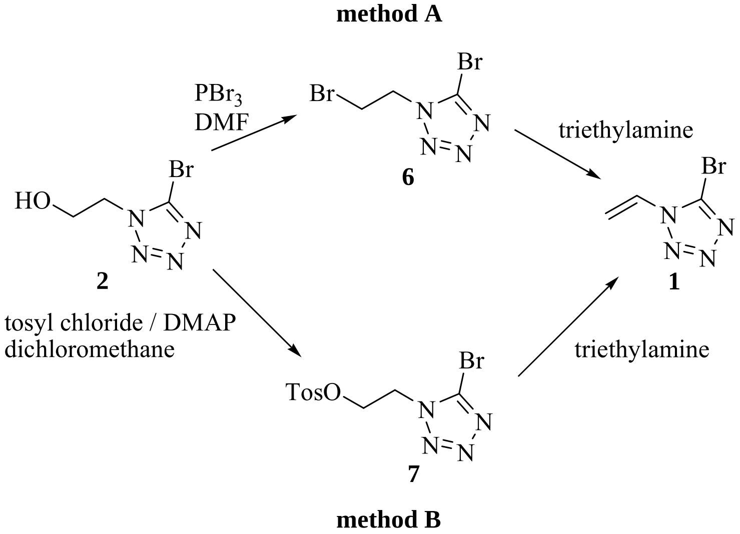
For the synthesis of 5-bromo-1-vinyl-1*H*-tetrazole (**1**), the corresponding 5-bromo-1-(2-hydroxyethyl) tetrazole (**2**), reported by Bayes,[5] proved to be a suitable starting material (*Scheme 1*).



Scheme 1. Synthesis of **2**.

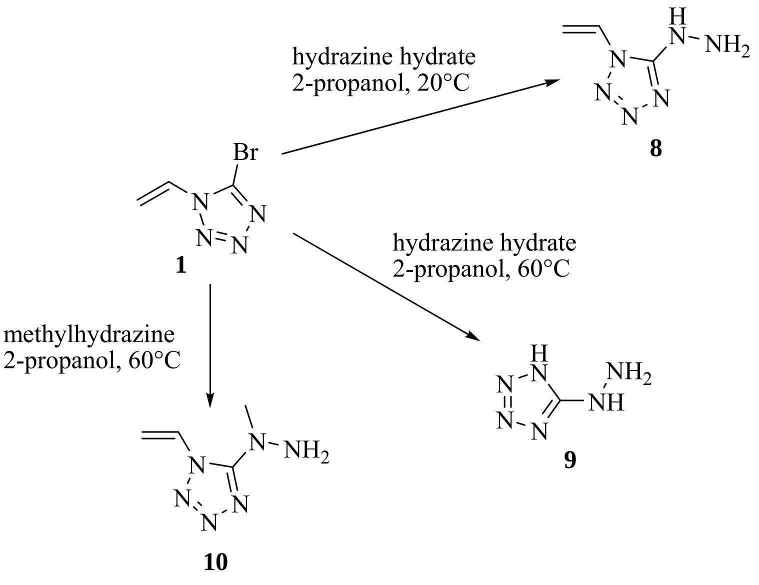
In order to convert the hydroxyethyl group into the desired vinyl group, several approaches were investigated. The idea was the elimination of the hydroxyl group, leading to the formation of the desired vinyl group. A conversion of the hydroxyl group into the corresponding chlorinated compound, as reported in literature for 1-(2-hydroxyethyl)-5-amino-1*H*-tetrazole by Finnegan,[1] and a subsequent elimination by potassium hydroxide proved not to be efficient, due to a partial halogen exchange at the 5-position of **2** along with side products, resulting in alkaline hydrolysis of the bromine atom. Taking these results into account, two methods for the preparation of **1** were developed. **Method A** (*Scheme 2*) avoids the halogen exchange at the 5-position by a bromination instead of the chlorination of the hydroxyl group by using PBr_3 in dimethylformamide.[6] The following elimination of the bromine atom was undertaken by triethylamine with a yield of 50 %. In order to improve the resulting over-all-yield of 21 %, the hydroxyl group was converted into the corresponding tosylate by the reaction of tosylchloride with **2** in dichloromethane[7] (**method B**, *Scheme 2*). The yield of the tosylation (80 %) exceeded the yield of the bromination of the hydroxyl group by 40 %. The elimination of the tosyl group of **7** by triethylamine at 100 °C gave higher yields (57 %) than the elimination of the bromine (*Scheme 2*). The over-all-yield of **method A** (21 %) could be improved to 46 % by using

method B.



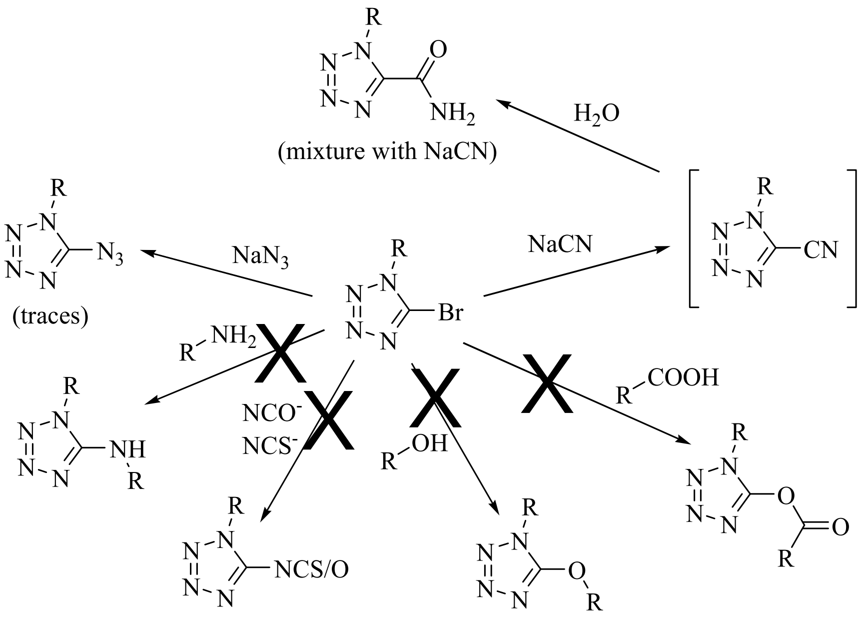
Scheme 2. Synthesis of 5-bromo-1-vinyl-1*H*-tetrazole (**1**).

In order to increase the nitrogen content of the monomer, the bromine atom was substituted by hydrazine and methyl hydrazine. The experiments showed that the formation of the products **8** and **10** is dependent on the reaction conditions. In contrast to the formation of **10**, which was performed at 60 °C, the formation of **8** was only possible at ambient temperature. Applying the same conditions as for the synthesis of **10** resulted in a loss of the vinyl group and only yielded 5-tetrazolylhydrazine **9**. Moreover, the purification of **8** was difficult, because of its high solubility in water, along with a hygroscopic character. Beside the impurities of water and hydrazine, **8** was more likely to form the corresponding bromide by the reaction of **8** with hydrobromic acid emerging from the substitution reaction, than compound **10** (*Scheme 3*).



Scheme 3. Synthesis of the nitrogen rich monomers **8** and **10**.

Beside the hydrazine derivatives, other compounds based on the 5-bromo-1*H*-tetrazole seem to possess suitable properties as energetic compounds. Therefore, further substitution reactions were carried out (*Scheme 4*). In case of alcohols, carbon acids and amines, the nucleophilicity of the oxygen atom or the nitrogen atom was not high enough to substitute the bromine atom. In case of anionic nucleophiles like cyanide, cyanate, thiocyanate and azide, the reactivity was higher compared to the organic nucleophiles and substitution products could be detected. In case of the azide anion, traces of the corresponding 5-azido-1*H*-tetrazole could be observed in the reaction mixture by mass spectrometry. The main percentage of the 5-bromo-1*H*-tetrazole was decomposed during the reaction and the yield of the 5-azido-1*H*-tetrazole was not high enough to obtain any pure product. The substitution of the bromine atom by the cyanide anion did not result in the corresponding 5-cyano-1*H*-tetrazole, but in the 1*H*-tetrazole-5-carboxamide, the hydrolysis product of 5-cyano-1*H*-tetrazole. The purification of the compound was difficult, because of the solubility of the 1*H*-tetrazole-5-carboxamide. It was only soluble in water and for us it was not possible to separate it from the excess of cyanide applied. The reactions with cyanate and thiocyanate only yielded decomposition products. The substitution reactions were not only carried out using the vinyl compounds, but also with other 5-bromo-1*H*-tetrazoles, reported in *paragraph 2.2*.

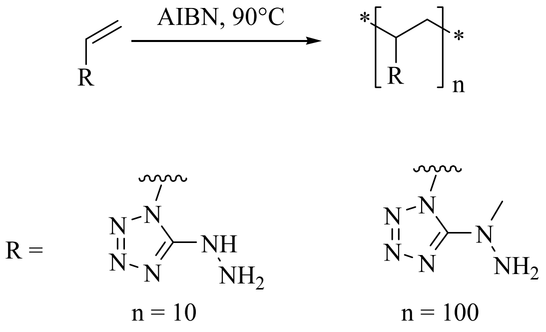


Scheme 4. Substitution reactions based on 5-bromo-1*H*-tetrazole.

2.2.2.2 Synthesis of the Polymers by Radical Polymerization

A possible pathway for the synthesis of nitrogen rich energetic polymers based on **1** would be a polymerization of **1** and a subsequent substitution of the bromine atom by a polymer analogue reaction. Trials to polymerize **1** by using AIBN in bulk at 80 °C resulted in three of four experiments in a deflagration of **1** after 5 to 10 minutes. Beside the radical polymerization in bulk, a radical polymerization in different solvents and anionic and cationic polymerizations in solution were carried out, but only yielded starting the material.

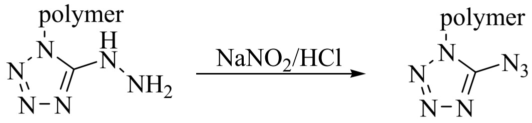
The polymerization of **8** and **10** was carried out in bulk by using AIBN. A polymerization in solution only yielded starting materials, as was observed in the experiments of the polymerization of **1** in solution. Therefore, the polymerization had to be performed in bulk at 90 °C. The AIBN had to be added carefully in several steps over 15 minutes, because an addition of more than 60 mg of AIBN resulted in a deflagration of **8** or **10**. One problem of the polymerization turned out to be the hydrazine moiety. The hydrogen atoms act as radical interceptor, leading to short chains along with starting material. To obtain a complete conversion, several portions of AIBN had to be added over 15 minutes (*Scheme 5*). Nevertheless, the yield of the polymerization of **8** (25 %-30 %) was much lower than the yield of the polymerization of **10** (85 %). An explanation could be the loss of the vinyl moiety at elevated temperatures along with a decomposition initiated by the AIBN (*paragraph 2.2.2.1*).



11 **12**

Scheme 5. Polymerization of **8** and **10**.

In order to further increase the nitrogen content of the polymer and its energetic character, the hydrazine moiety was converted into an azide group. The conversion of **11** to the corresponding 5-azido-1*H*-tetrazole containing polymer (**13**) was carried out by the reaction of sodium nitrite and the hydrazine moiety in 2 N HCl. Being not soluble in aqueous media, a suspension of **11** in hydrochloric acid was used. To ensure a complete conversion, an excess of sodium nitrite was applied (*Scheme 6*).



11 **13**

Scheme 6. Synthesis of **13**.

2.2.2.3 Analytical Data of the Polymers

The investigation of the average molecular masses (M_n) of **11** and **12** showed the expected difference. Whereas the polymer formed by the polymerization of **8** possessed a value for M_n corresponding to ten molecular units in one chain, the polymer of **10** was much longer (about 100 molecular formulas per chain). This effect can be explained by the acidic NH-proton of **8** acting more efficient as a radical interceptor of the NH_2-protons. Moreover, the shorter chains can also be explained by impurities of water or hydrazine, being always present in the samples of **8** along with the slow decomposition of **8** at increased temperature.

The analysis of **13** showed a partial decomposition of the tetrazolyl hydrazine moieties. The determination of the average molecular weight M_n was undertaken by GPC. One problem was the insolubility even in DMF. The determination of M_n was carried out with the soluble parts of the polymer whereas the insoluble parts were dismissed (insoluble parts: ~15 %). Using an IR and UV 275 nm detector the average M_n was determined to be 1400 g/mol, corresponding to ten monomers in a chain. The elemental analysis, along with the average molecular weight, allowed an estimated formula of $C_{37}H_{56}N_{51}O_{10}$. The calculated formula for a chain of ten monomers ($C_{30}H_{30}N_{70}$) differs significantly from the experimentally obtained one. The main differences are the reduced content of nitrogen and the increased content of oxygen. The reduced content of nitrogen can be explained with a partial decomposition of the hydrazine and the tetrazole moiety yielding amine-containing parts. Taking this assumption into account, the oxygen content can be explained by a nitration of the formed amines, yielding a small content of primary or secondary nitramines. The nitro groups can be detected in the IR-spectra of **13**. Beside the strong vibration of the azide group around 2100 cm^{-1}, the commonly known vibrations of the nitro group around 1600 cm^{-1}-1500 cm^{-1} and at 800 cm^{-1} can be inevitably assigned.[8]

2.2.2.4 Energetic Properties of the Polymers

Comparing the values of $\Delta_E U_m°$ (an indication of the work performed by the explosive) of the polymers, **13** shows the highest energetic properties, due to the 5-azidotetrazole moieties (**11**: -2621 kJ kg^{-1}, **12**: -1160 kJ kg^{-1} and **13**: -4324 kJ kg^{-1}; *Table 1*). As expected, polymer **12** possesses the lowest energetic properties, due to the methyl moiety stabilizing the tetrazolyl hydrazine and increasing the carbon content ($\Delta_E U_m°$ only 25 % of $\Delta_E U_m°$ of **13**). The energetic character of polymer **11** lies between the $\Delta_E U_m°$ values of **12** and **13**. The value of $\Delta_E U_m°$ is in case of **13** equal to that of GAP. Another important value for the evaluation of energetic characteristics is the detonation velocity *D*. A comparison of these values of polymers **11** to **13** shows, that polymer **11** and **13** exceed the detonation velocity of GAP by 400 m s^{-1} in case of **11** and 600 m s^{-1} in the case of **13**. The specific impulse, an indication of the qualification as propellant, is only in case of **13** comparable with the value of GAP.

The thermal stability was determined by DSC measurements. Polymer **12** possesses the highest thermal stability showing exothermic decomposition above 276 °C. The decomposition temperatures of polymers **11** and **13** are in the range of GAP (203 °C and 174 °C).

Polymers **11** and **12** proved to be insensitive towards friction and less sensitive towards impact.[10,11] Polymer **13** was sensitive towards friction and sensitive towards impact.[9,10] The physical stability of polymers **11** and **12** is much higher than that of GAP, whereas the values of **13** are in the same range. The difference of the sensitivity towards friction of **13** and GAP can be explained by the consistency of the polymers (solid in case of **13**, viscous oil in case of GAP).

The advantage of polymer **13** is its value of $\Delta_E U_m°$ comparable with the value of GAP, along with a much higher detonation velocity. Moreover, **13** is a solid, in contrast to GAP, which has to be cured in order to be applied as binder.

Table 1. Energetic properties of **11**, **12** and **13**.

	11	**12**	**13**	**GAP**[k]
molecular formula	$C_{31}N_{56}H_{65}O_2$	$C_{413}N_{575}H_{760}O_{14}$	$C_{37}N_{51}H_{56}O_{10}$	$(C_3N_3H_5O)_{20}$
T_{dec} (°C)	203	276	174	216
M_n (g mol^{-1})	1254	13990	1375	2000
density (g cm^{-3})[a]	1.45	1.45	1.45	1.3
sensitivity towards friction (N)	360	360	160	360
sensitivity towards impact (J)	35	45	7	7
$-\Delta U_{comb.}$ (cal g^{-1})[b]	4460	4650	4464	-
$-\Delta H_{comb}$ (kJ mol^{-1})[c]	23384	272630	25656	-
$\Delta_f H_m$ (kJ mol^{-1})[d]	1754	-30	2962	-
Values calculated by EXPLO5 V5.02				
$-\Delta_E U_m$° (kJ kg^{-1})[e]	2621	1160	4324	4444
T_E (K)[f]	2015	1249	2957	2860
$p_{C\text{-}J}$ (kbar)[g]	154	100	173	135
D(m s^{-1})[h]	7074	6005	7205	6629
Gas vol. (L kg^{-1})[i]	792	764	721	738
I_s (s)[l]	166	126	200	195
I_s (s)[m]	243	234	247	248

[a] estimated from structure determination; [b] experimental (constant volume) combustion energy; [c] experimental molar enthalpy of combustion; [d] molar enthalpy of formation; [e] energy of explosion; [f] explosion temperature; [g] detonation pressure; [h] detonation velocity; [i] assuming only gaseous products; [k] obtained from the database of EXPLO5 (V5.02); [l] specific impulse (isobaric combustion, chamber pressure 60 bar, frozen expansion); [m] specific impulse of a mixture containing 75 % ammonium dinitramide as oxidizer.

2.2.2.5 Crystal Structures of Compounds 1, 7 and 10

Compound **7** crystallizes in the monoclinic space group $P2_1/c$ with four molecular formulas per unit cell (*Figure 1*). The arrangement of the molecules in the crystal structure is zig-zag-like along the y-axis. The structure is stabilized by an intermolecular interaction of the bromine atom with one oxygen atom of the tosyl moiety (*Figure 2*). The distance between the bromine atom and the oxygen atom O2 is found to be 3.0006(14) Å. The distance between a bromine atom and an oxygen atom without any interactions is reported as 3.37 Å.[11] The distance found in the crystal structure is by 12 % shorter than the distance without interaction, allowing the assumption of an intermolecular bromine-oxygen interaction.

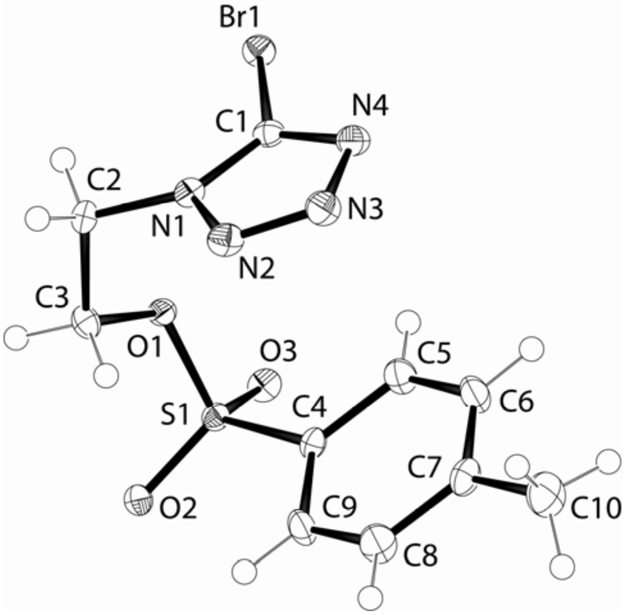


Figure 1. Molecular structure of **7**. Thermal ellipsoids are drawn at the 50% probability level.

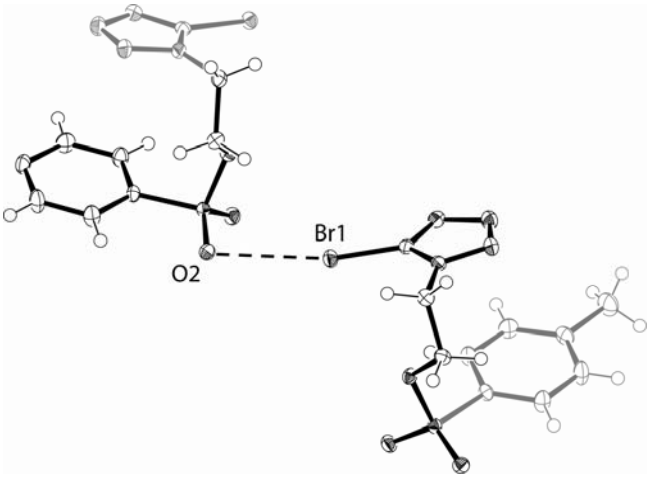


Figure 2. Intermolecular interaction of the bromine atom with the oxygen atom O2.

Compound **1** crystallizes in the orthorhombic space group *Pnma* with four molecular formulas per unit cell (*Figure 3*). The geometry of the molecule is planar, allowing the assumption, that the π-system is delocalized over the whole molecule. The molecules form zig-zag chains along the x-axis, caused by intermolecular interactions of the bromine atom and N4 of the tetrazole moiety (*Figure 4*). The distance between Br1 and N4 in the crystal structure is found to be 2.999(2) Å. The distance between a bromine atom and a nitrogen atom without interactions is reported to be 3.4 Å.[11] Due to the planar geometry of **1**, the chains form layers. Between these layers, no intermolecular interactions can be observed.

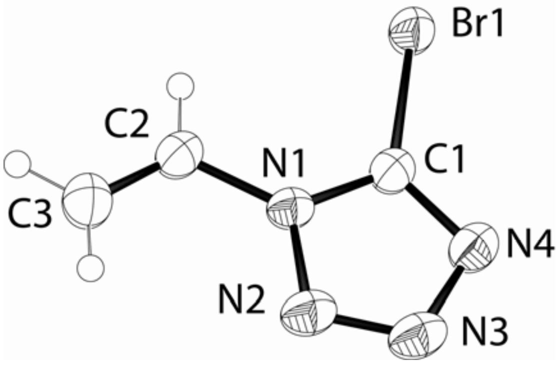


Figure 3. Molecular structure of **1**. Thermal ellipsoids are drawn at the 50% probability level.

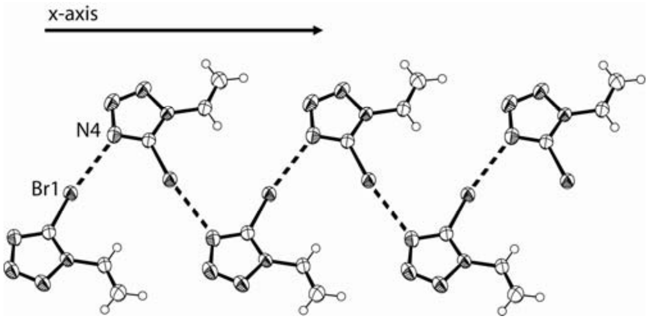


Figure 4. Intermolecular interactions of the bromine with N4 along the x-axis.

Compound **10** crystallizes in the monoclinic space group $P2_1/n$ with four molecular formulas per unit cell (*Figure 5*). The planar coordination geometry of N5 (the three angles are 120° and the N6-N5-C1-N4 torsion angle is found to be 177°) showing the sp^2-hybridisation of the N5 nitrogen, with the free electron pair being part of the delocalized π-electron system of the molecule. The free electron pair of N6 directly points towards the proton at C3 of the vinyl groups. This finding leads to the assumption that N6 forms an intramolecular hydrogen bridge to the proton at C3 (D•••A: 2.957(3) Å; <DHA: 124.9(17)°). Beside of the intramolecular hydrogen bridge, two other hydrogen bridges are found. The first is formed by the first proton of N6 to N4 and the second by the second proton of N6 to N2 (D•••A: 3.070(2) Å, 3.270(3) Å; <DHA: 158(2)°, 150(2)°; *Figure 6*). The arrangement of the molecules leads to a zig-zag pattern along the y-axis (*Figure 7*).

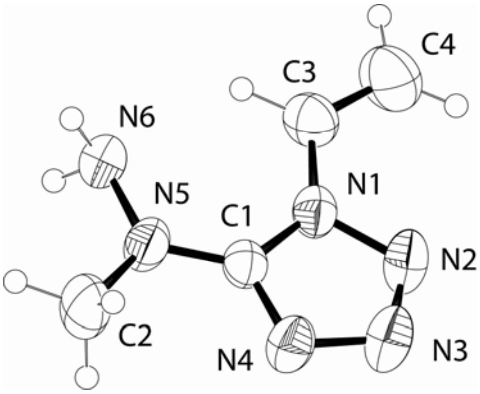


Figure 5. Molecular structure of **7**. Thermal ellipsoids are drawn at the 50% probability level.

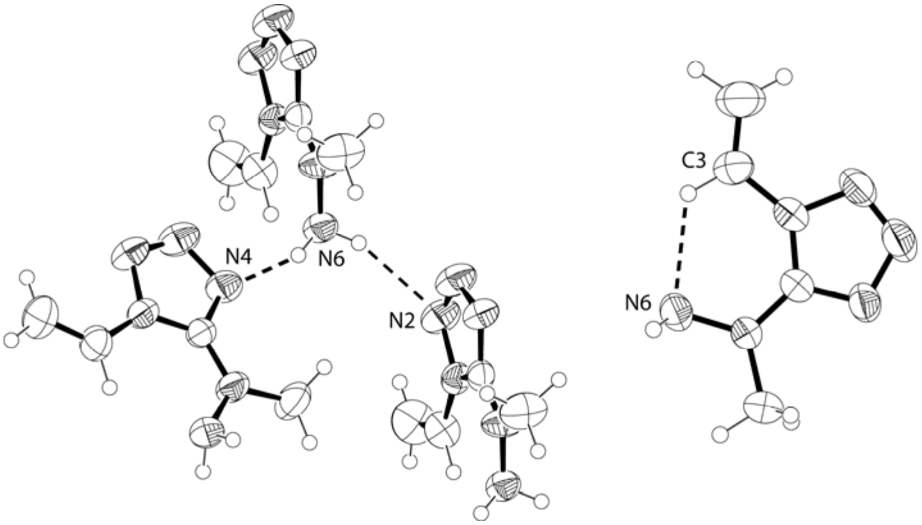


Figure 6. Inter- and intramolecular hydrogen bridges of **7**. Thermal ellipsoids are drawn at the 50% probability level.

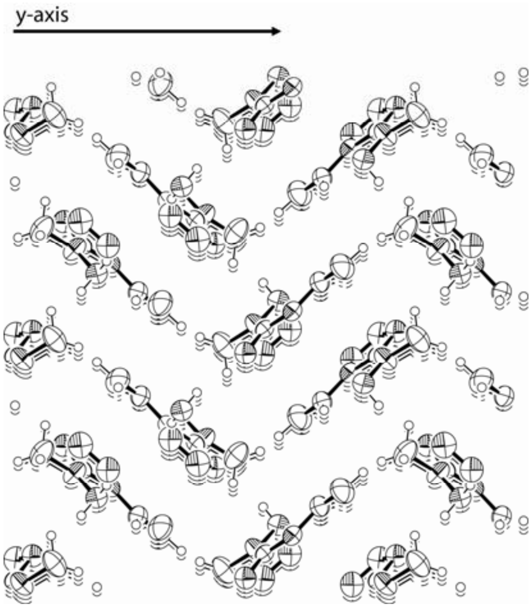


Figure 7. Zig-zag pattern of **7** along the y-axis. Thermal ellipsoids are drawn at the 50% probability level.

2.2.2.6 Conclusions

Three nitrogen-rich energetic polymers were synthesized and characterized. Poly-1-vinyl(5-hydrazinyl)-1*H*-tetrazole (**11**), poly-1-vinyl(5-1-methylhydrazinyl)-1*H*-tetrazole (**12**) and the 5-azido-1*H*-tetrazole containing polymer (**13**) proved to be moderate to good explosives along with sufficient thermal and physical stabilities. The nitrogen content is located between 50 % and 60 %, turning them into promising materials for the development of new gas generating compositions. The synthesis of **11**, **12** and **13** was carried out using 5-bromo-1-vinyl-1*H*-tetrazole (**1**) as starting material. The polymers were investigated by vibrational spectroscopy (IR) and the energetic properties were determined by bomb calorimetric measurements.

2.2.2.7 References

(1) a) W. G. Finnegan, R. A. Henry, S. Skolnik, *US Patent 3004959*, **1961**; b) W. G. Finnegan, R. A. Henry, S. Skolnik, S. *US Patent 3055911,* **1962**.

(2) C. G. Miller, G. K. Williams, *U.S. Patents. 264982*, **2007**.

(3). N. V. Tsarevsky, K. V. Bernaerts, B. Dufour, F. E. Du Prez, K. Matyjaszewski, *Macromolecules,* **2004**, *37,* 9308-9313.

(4) T. M. Klapötke, S. M. Sproll, *Eur. J. Org. Chem.* **2009**, *25*, 4284-4289.

(5) D. E. Bayes, *Eu. Patent EP0117368A1*, **1982**.

(6) R. M. Coates, P. D. Senter, W. R. Baker, *J. Org. Chem.* **1982**, *47*, 3597-3607.

(7) E. Pinot, A. Guy, A. Fournial, L. Balas, J.-C. Rossi, T. Durand, *J. Org. Chem.* **2008**, *73*, 3063-3069.

(8) M. Hesse, H. Meier, B. Zeeh, *Spektroskopische Methoden in der organischen Chemie,* 6th edition, Thieme, Stuttgart; New York, **2002**, p. 48 and p. 55.

(9) a) M. Suceska, *Test Methods for Explosives*, Springer, New York, **1995**, p. 21 (impact), p. 27 (friction); b) http://www.bam.de/.

(10) Impact: insensitive > 40 J, less sensitive > 35 J, sensitive > 4 J, very sensitive < 4 J; friction: insensitive > 360 N, less sensitive = 360 N, sensitive < 360 N > 80 N, very sensitive < 80 N, extreme sensitive < 10 N; According to the UN Recommendations on the Transport of Dangerous Goods (+) indicates: not safe for transport.

(11) A.Bondi, *J.Phys.Chem.* **1964**, *68*, 441.

2.3 Energetic Compounds Based on Tetrazolyl Hydrazines

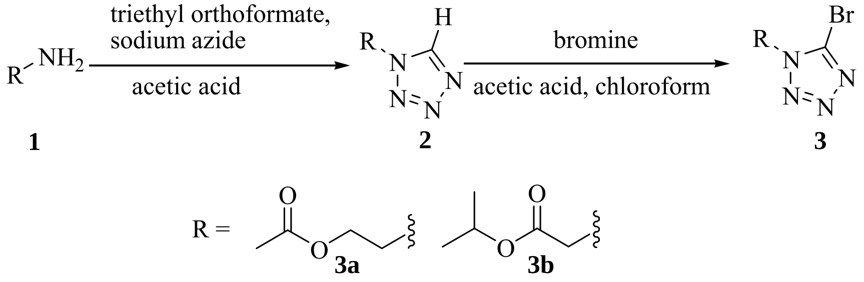
2.3.1 Synthesis of Functionalized Tetrazenes as Energetic Compounds

A suitable class of nitrogen rich compounds are 1,4-bis(1*H*-tetrazolyl)tetrazenes. 1,4-bis(1-methyl-1*H*-tetrazol-5-yl)-1,4-dimethyl-2-tetrazene was first prepared in 2004 by nitrosylation of *N*,1-dimethyl-1*H*-tetrazol-5-amine and reduction to the corresponding 1-methyl-1-(1-methyl-1*H*-tetrazol-5-yl)hydrazine. The tetrazolylhydrazine was then oxidized to form the 1,4-bis(1-methyl-1*H*-tetrazol-5-yl)-1,4-dimethyl-2-tetrazene using bromine.[1] The synthesis of bromo-1*H*-tetrazoles[2] was generalized and used to establish a new route to form the corresponding methyltetrazolylhydrazines in high yields.

2.3.1.1 Synthesis of Tetrazenes

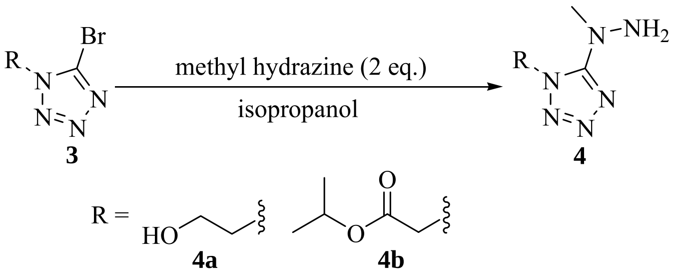
Tetrazenes can be prepared by oxidation of hydrazines.[1,3] As a consequence, the tetrazolyltetrazenes presented in this work were obtained via the corresponding tetrazolyl hydrazines. Therefore, efficient routes for the synthesis of tetrazolyl hydrazines were necessary. A possible pathway reported in literature starts from thiosemicarbazides, which were converted into the corresponding *S*-methylthiosemicarbazides with a subsequent substitution of the methyl mercaptane with azide (*paragraph 2.2.1.1*). Taking into account, that a purification of the resulting tetrazolyl hydrazine (**3**, *paragraph 2.2.1.1*, *Scheme 4*) by column chromatography was necessary, the reaction proved not to be suitable for up scaling.

In order to improve the synthesis, a new route using 5-bromo-1*H*-tetrazoles as intermediates has been developed (*paragraph 2.2.1.2*). Despite being useful starting materials for 5-substituted tetrazoles, only a small number of 5-bromo-1*H*-tetrazoles have been reported in literature.[4] The synthesis of 2-(5-bromo-tetrazol-1-yl)-ethanol (**3a**) reported in a patent by Bayes[4b] was generalized and used to prepare the (5-bromo-1*H*-tetrazol-1-yl)-acetic acid isopropyl ester (**3b**), with 2-aminoethyl acetate and isopropyl 2-aminoacetate as suitable starting materials. The experiments showed, that in case of the amino acetate derivative (to form **3b**), only the isopropyl ester proved to be a stable protecting group against an intramolecular attack of the methyl hydrazine moiety later inserted, in contrast to the ethyl or methyl ester. To form the tetrazoles, the amine group was converted into the 5*H*-tetrazole using standard reactions of triethyl orthoformate and sodium azide in acetic acid.[5] In the following step, the 5-position of the tetrazole was brominated using elemental bromine (*Scheme 1*).



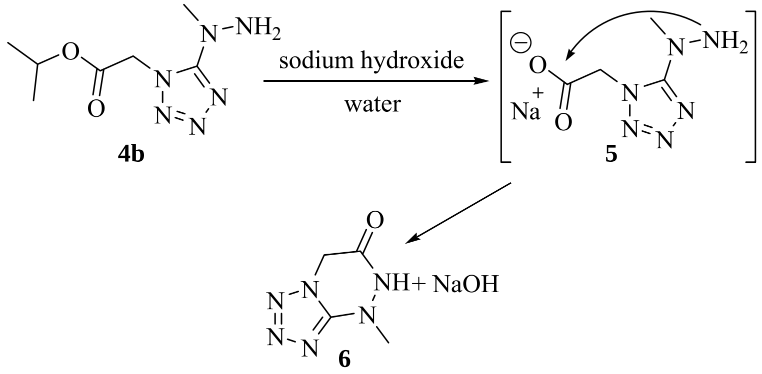
Scheme 1. Synthesis of 5-bromotetrazoles **3**.

In the case of **3a**, the resulting 5-bromotetrazole was deprotected by hydrochloric acid.[5] Purification by column chromatography was not possible, due to decomposition observed during the process. Crude **3a** and **3b** were converted into the corresponding tetrazolyl hydrazines **4** by substitution of the bromine atom by methyl hydrazine. The experiments showed, that isopropanol was a suitable solvent. The yields dropped when other alcohols, acetonitrile or other organic solvents were used. Carrying out the reaction, neither the 2-methyl isomer nor side products arising from the hydrolysis of the bromotetrazole were observed (*Scheme 2*). The tetrazolyl hydrazines were obtained as slightly impure oil. The crude products were used for further reactions.



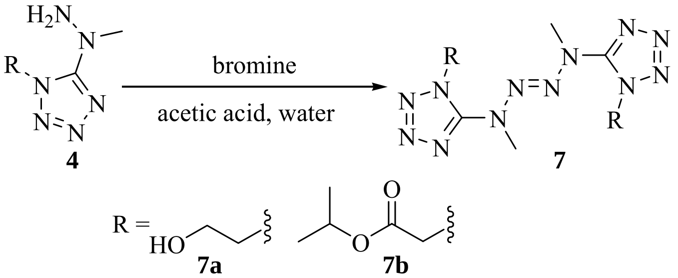
Scheme 2. Synthesis of the tetrazolyl hydrazines **4**.

A deprotection of **4b** using potassium hydroxide in water yielded the polycycle **6** as crystalline solid along with several other compounds, which were not identified. The formed carbon acid undergoes immediately an intra- and intermolecular condensation with the hydrazine moiety, even in alkaline medium yielding either **6** or polymeric side products (*Scheme 3*).



Scheme 3. Formation of **11**.

The tetrazolyl hydrazines **4a** and **4b** were converted into the corresponding tetrazenes using saturated bromine water at 0 °C. The product precipitated from the clear reaction mixture and was filtered off. The yields varied between 50 % and 60 % (*Scheme 4*).



Scheme 4. Synthesis of the tetrazolyl tetrazenes **7**.

Compound **7b** was deprotected using boiling, concentrated sodium hydroxide solution. The corresponding carbon acid **8** was recovered by neutralizing the alkaline solution with hydrochloric acid.

2.3.1.2 Vibrational and NMR Spectroscopic Data of 7a, 7b and 8

Compounds **7a**, **7b** and **8** were identified using vibrational IR spectroscopy. Selected values are given in *Table 1*. The calculated values given in *Table 1* were used to assign the observed vibrations.

Table 1. Comparison between selected vibrations of **7a**, **7b** and **8** with the calculated values of **8** using DFT BLYP/6-31G*.

7a	**7b**	**8**			vibration
exp.	exp.	exp.	theory * 0.9940	theory	
3347		3436	3502	3524	$\nu_s/\nu_{as}(OH)$
2972	2999	3012	3036	3055	$\nu_{as}(CH_3)$
2944	2984	2972	3007	3026	$\nu_s(CH_2)$
2885	2944	2945	2977	2995	$\nu_s(CH_3)$
	1754	1747	1778	1789	$\nu_{as}(COOH)$
		1738	1777	1788	$\nu_{as}(COOH)$
1572	1569	1565	1527	1537	ν_{as}(tetrazol)
1470	1470	1478	1479	1488	$\delta_s(CH_3)$
1444	1450	1447	1436	1445	ν_s(tetrazene)/$\delta_s(CH_3)$
1417		1433	1421	1430	$\delta_s(CH_3)/\delta_s(CH_2)$
		1423	1417	1426	ν_s(tetrazene)/$\delta_s(CH_3)$
	1414	1413	1416	1425	$\delta_s(CH_3)/\delta_s(CH_2)$
	1394	1400	1397	1406	ν_s(tetrazole)/$\delta_s(CH_3)/\delta_s(CH_2)$
1360	1348	1351	1360	1369	$\nu_s(CH_2COOH)$
1337		1332	1312	1320	ν_s(tetrazene)/$\delta_{as}(CH_2)$
1295	1278	1295	1282	1290	$\nu_s(CH_2COOH)$
1261		1262	1250	1258	ν_s(tetrazol)
1224	1218	1207	1190	1198	ν_s(tetrazole)/δ_{as}(tetrazole)/$\delta_{as}(CH_2)$

1106	1106	1100	1100	1107	ν_{as}(COOH)/ν_{as}(tetrazole)/ ν_{as}(tetrazene)/ν_{s}(N-CH$_3$)
1098	1083	1075	1060	1067	ν_{as}(tetrazole)/δ_{as}(tetrazole)/ ν_{as}(tetrazene)
1015	1007	1020	1023	1030	ν_{as}(CH$_2$COOH)/ν_{as}(tetrazole)/$_{as}$(tetrazene)/δ_{s}(N-CH$_3$)
978		993	980	986	ν_{s}(tetrazole)/δ_{s}(N-CH$_3$)/ ν_{as}(tetrazene)
	959	965	972	978	ν_{as}(tetrazole)/δ_{s}(N-CH$_3$)/ ν_{as}(tetrazene)/γ(COCH$_2$)
857	848	854	866	872	ν_{as}(tetrazole)/γ(COCH$_2$)
		798	778	783	ν_{s}(CH$_2$COOH)/ν_{as}(tetrazole)/ ν_{as}(tetrazene)/δ_{s}(N-CH$_3$)
	658	656	654	658	γ_{s}(COOH)

Beside the analysis of the tetrazenes by means of vibrational spectroscopy, the compounds were characterized by NMR spectroscopy. A comparison between the ^{15}N NMR spectra of **8** and **7a** is given in *Figure 1*. The assignment of the nitrogen atoms was carried out in analogy to values reported in literature.[6] In case of **7a**, N2 shows a clear triplet, a result of the $^{3}J_{NH}$-coupling ($^{3}J_{NH}$ = 2.0 Hz) with the CH$_2$-group. N1 forms a multiplet by the ^{2}J- and ^{3}J-coupling with the hydroxyethyl group. However, **8** only shows the triplet of N2 ($^{3}J_{NH}$ = 1.7 Hz). N1 forms a broad signal without showing any clear $^{2}J_{NH}$-coupling with the CH$_2$-group. An explanation for the missing $^{2}J_{NH}$-coupling could be the much lower concentration, due to the low solubility of **8** in DMSO. In both cases neither the $^{2}J_{NH}$- nor the $^{3}J_{NH}$-coupling with the methyl moiety was observed.

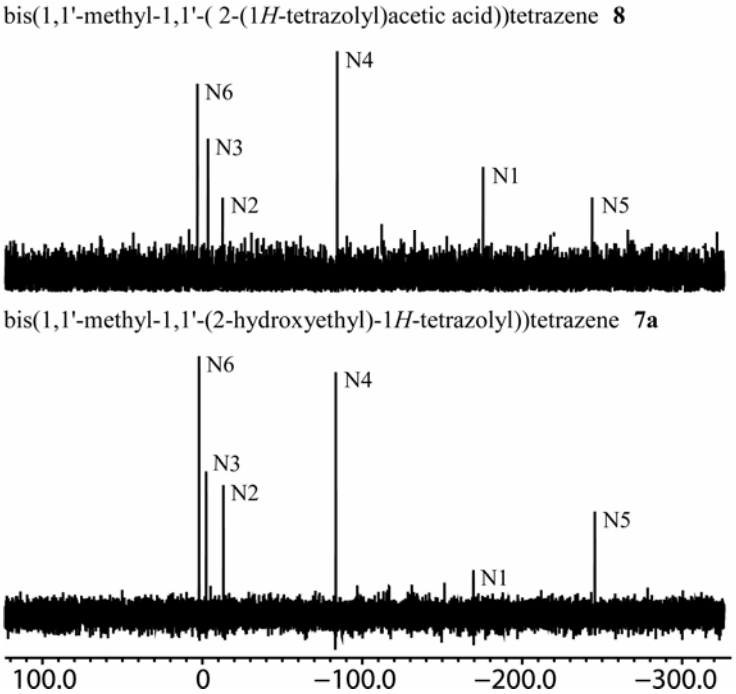


Figure 1. ^{15}N spectra of **8** and **7a** in *d6*-DMSO.

2.3.1.3 Energetic Properties of 7a, 7b and 8

Since **7a**, **7b** and **8** are energetic materials, determination of the energetic properties was of interest. Therefore, the thermal behavior was investigated by DSC-measurements, the heats of combustion by bomb calorimetric measurements and the sensitivity towards impact and friction by BAM methods.[7,8]

The tetrazenes show no melting points, but sharp decomposition points. Comparing the DSC data of the tetrazenes, compounds **7a** and **7b** possess similar decomposition points of 167 °C and 160 °C. In contrast, the point of decomposition of **8** (207 °C) is about 40 °C higher than those of **7a** and **7b**. This effect can be rationalized by strong intermolecular interactions of the molecules in the crystal structure, as shown in *paragraph 2.3.1.4*, resulting in a stabilization of the molecule. Taking the crystallographic data of **7a**, **7b** and **8** into account, the points of decomposition can be correlated with the amount of intermolecular interactions in the crystal structure. Compound **7b** shows no intermolecular interactions at all and possesses a decomposition point of 160 °C. Compound **7b** forms four hydrogen bridges between a hydroxyl group and the tetrazole moiety connecting three molecules (decomposition point: 167 °C). The structure of **8**, stabilized the most by four hydrogen bridges between the carboxylic acid and the tetrazole moiety, shows the highest decomposition point (207 °C). Electronic effects of the different moieties of the tetrazoles **7b** and **8** as explanation for the higher thermal stability can be neglected. The difference between **7b** and **8** is the esterfication of the carbon acid. The isopropyl ester should lead to a reduction of the electron withdrawing effect of the carbon acid. Electron rich tetrazole moieties are known to be much more stable than tetrazoles bearing electron withdrawing groups.[9] As a result, compound **7b** should be more stable than **8**. Since the experimental data proves **8** being more stable than **7b**, this effect can be explained by the crystal structure with its intermolecular interactions, and not to electronic effects of the substituents.

To analyze the energetic properties of the compounds, the energies of combustion ($\Delta_c U$) were measured using bomb calorimetry. Using these values, the enthalpy of formation was calculated by applying the Hess Thermochemical Cycle, as reported in literature.[10] The heats of formation of H_2O (l) and CO_2 (g) -286 kJ mol^{-1} and -394 kJ mol^{-1} were obtained from literature[11] and the combustion reactions of **7a**, **7b** and **8** are given in *equation 1*.

$$\textbf{7 a:}\quad C_8H_{16}N_{12}O_2\,(s) + 11\ O_2\,(g) \longrightarrow 8\ CO_2\,(g) + 8\ H_2O\,(l) + 6\ N_2\,(g)$$

$$\textbf{7 b:}\quad C_{14}H_{24}N_{12}O_4\,(s) + 18\ O_2\,(g) \longrightarrow 14\ CO_2\,(g) + 12\ H_2O\,(l) + 6\ N_2\,(g)$$

$$\textbf{8:}\quad C_8H_{12}N_{12}O_4\,(s) + 9\ O_2\,(g) \longrightarrow 8\ CO_2\,(g) + 6\ H_2O\,(l) + 6\ N_2\,(g)$$

Equation 1. Combustion reactions of **7a**, **7b** and **8**.

The values of the energy of explosion, the explosion temperature, the detonation pressure, the detonation velocity and the gas volume have been calculated using the enthalpies of formation and the EXPLO5 program[12] (*Table 2*).

Table 2. Energetic properties of **7a, 7b** and **8.**

	7a	**7b**	**8**	TNT[k]	RDX[k]
formula	$C_8H_{16}N_{12}O_2$	$C_{14}H_{24}N_{12}O_4$	$C_8H_{12}N_{12}O_4$	$C_3H_6N_6O_6$	$C_3H_6N_6O_6$
molecular mass	312.33	424.45	340.26	227.1	222.1
density (g cm^{-3})[a]	1.539	1.401	1.614	1.65	1.82
-$\Delta U_{\mathrm{comb.}}$ (cal g^{-1})[b]	4528	4976	3528		
-ΔH_{comb} (kJ mol^{-1})[c]	473	-101	153		
$\Delta_f H_m$ (kJ mol^{-1})[d]	435	-151	119		
Values calculated by EXPLO5 V5.02					
-$\Delta_E U_m°$ (kJ kg^{-1})[e]	3586	2560	3363	5099	6052
T_E (K)[f]	2441	1914	2588	3737	4358
$p_{C\text{-}J}$ (kbar)[g]	197	121	179	205	356
D(m s^{-1})[h]	7662	6355	7073	7176	9055
Gas vol. (L kg^{-1})[i]	773	730	721	620	793
$\mathrm{I_s}$ (s)[l]	160	-	163	200	252
$\mathrm{I_s}$ (s)[m] (70 % ADN)	238	216	240	240	232

[a] estimated from structure determination; [b] experimental (constant volume) combustion energy; [c] experimental molar enthalpy of combustion; [d] molar enthalpy of formation; [e] energy of explosion; [f] explosion temperature; [g] detonation pressure; [h] detonation velocity; [i] assuming only gaseous products; [k] obtained from the database of EXPLO5 (V5.02); [l] specific impulse (isobaric combustion, chamber pressure 60 bar, frozen expansion); [m] specific impulse of a mixture containing 75 % ammonium dinitramide as oxidizer.

Compared to RDX (a common high explosive) and nitrocellulose (a common propellant) the values of **7a** and **8** lie between those of RDX and nitrocellulose. The temperature of explosion is by 1300 K (nitrocellulose) respectively 2000 K (RDX) lower. Compared to nitrocellulose the detonation pressure is comparable, whereas the temperature of explosion is significantly lower.

The sensitivity towards impact and friction was determined according to BAM standard. The sensitivity towards friction of **7a** and **8** is lower than 240 N. The sensitivity towards impact is lower than 5 J. In case of **7b**, the sensitivity towards friction is lower than 160 N and the sensitivity towards impact lower than 7 J. The lower sensitivity towards friction of **7b** compared to **7a** and **8** can be rationalized by the lack of intermolecular interactions and the resulting lower stabilization in the crystal structure.

2.3.1.4 Crystal Structures of 6, 7a, 7b and 8

Compound **6** crystallizes in the orthorhombic space group *Pcnn* with eight molecular formulas per unit cell (*Figure 2*). Two hydrogen bridges are present in the crystal structure. The donor atom N6 forms one intermolecular hydrogen bridge to O1, leading to dimerization (*Figure 3*).

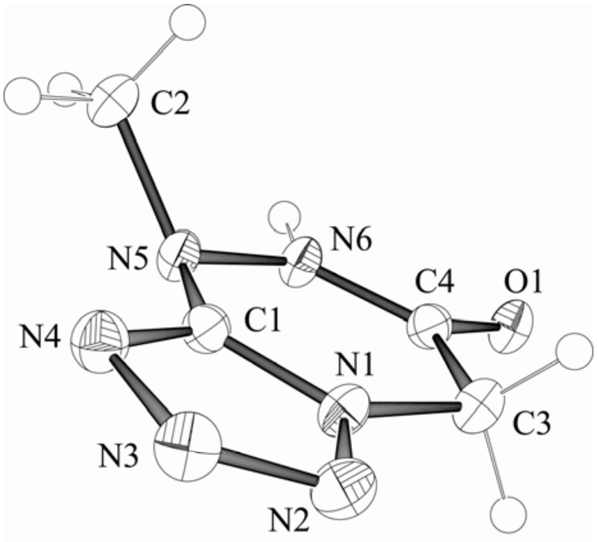


Figure 2. Molecular structure of **6**. Thermal ellipsoids are drawn at the 50% probability level.

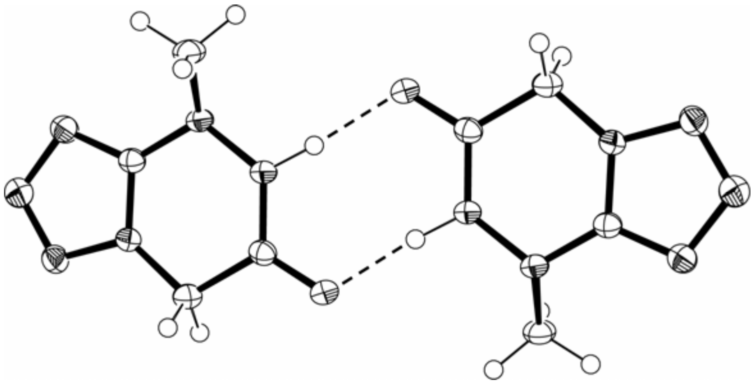


Figure 3. Intermolecular hydrogen bridges of **6**. Thermal ellipsoids are drawn at the 50% probability level

Compound **7a** crystallizes in the orthorhombic space group *Pbca* with four molecular formulas per unit cell (*Figure 4*). The bond distances and angles of the tetrazole moiety and the alkyl substituent are in accordance with values reported in literature.[13] The bond distance between N6 and N7 (1.255 Å) equates to common values of double bonds (1.25 Å).[15] The bond distance of N5–N6 (1.366 Å) lies between a N-N single bond (1.46 Å) and a double bond (1.25 Å). Furthermore, the C1–N5 bond (1.366 Å) is shortened by 1.26 Å, compared to C–N single bonds (1.47 Å) commonly observed. The crystal structure is stabilized by an intermolecular hydrogen bridge between the donor atom O1 and the acceptor atom N4. Thereby, the tetrazole moieties are connected by two hydrogen bridges between each other. As a result, three molecules are connected by four hydrogen bridges (*Figure 5*).

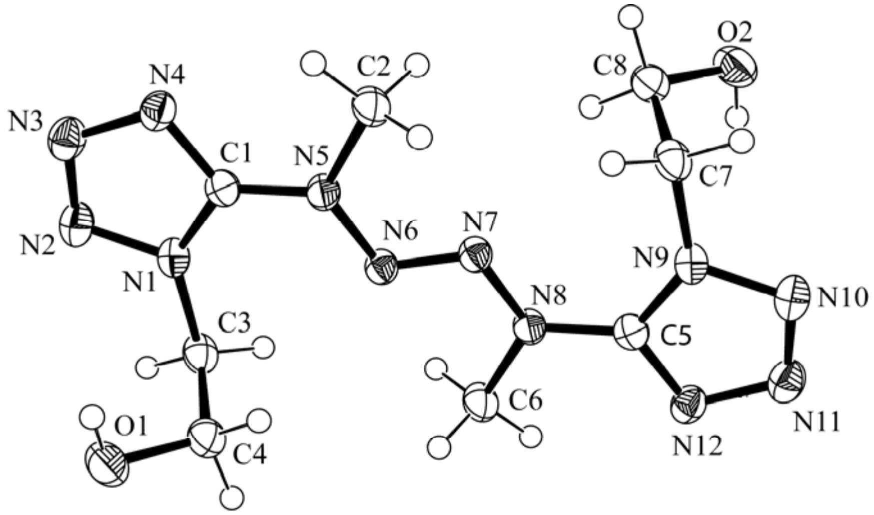


Figure 4. Molecular structure of **7a**. Thermal ellipsoids are drawn at the 50% probability level.

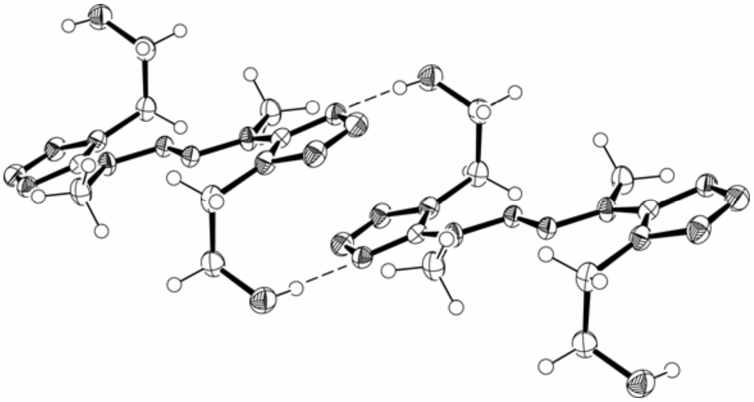


Figure 5. Intermolecular hydrogen bridges of **7a**. Thermal ellipsoids are drawn at the 50% probability level.

Compound **7b** crystallizes in the triclinic space group *P*-1 with one molecular formula per unit cell (*Figure 6*). The bond distances and angles are in accordance with **7a**. Due to the protected carbon acid no inter- or intramolecular interactions are observed.

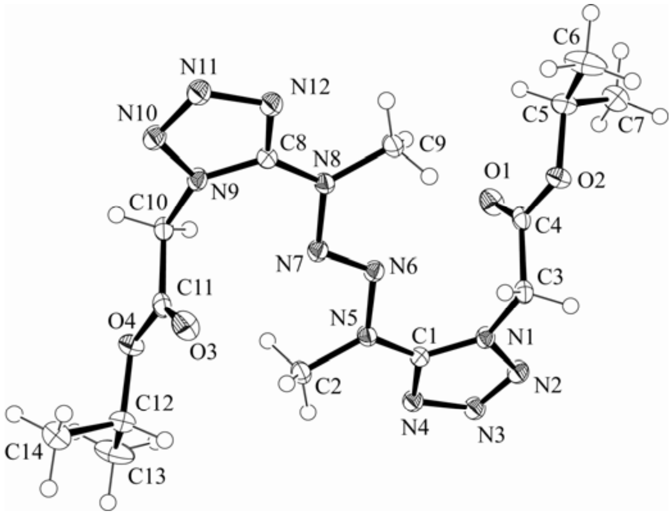


Figure 6. Molecular structure of **7b**. Thermal ellipsoids are drawn at the 50% probability level.

Compound **8** crystallizes in the monoclinic space group $P2_1/c$ with four molecular formulas per unit cell (*Figure 7*). The bond distances and angles are in accordance with these of compounds **7a** and **7b**. The crystal structure is stabilized by four intermolecular hydrogen bridges, one between the donor atom O2 and the acceptor atom N4 and the other one between the donor atom O4 and the acceptor atom N12. In contrast to the structure of **7a**, five molecules are connected to each other by the four hydrogen bridges (*Figure 8*).

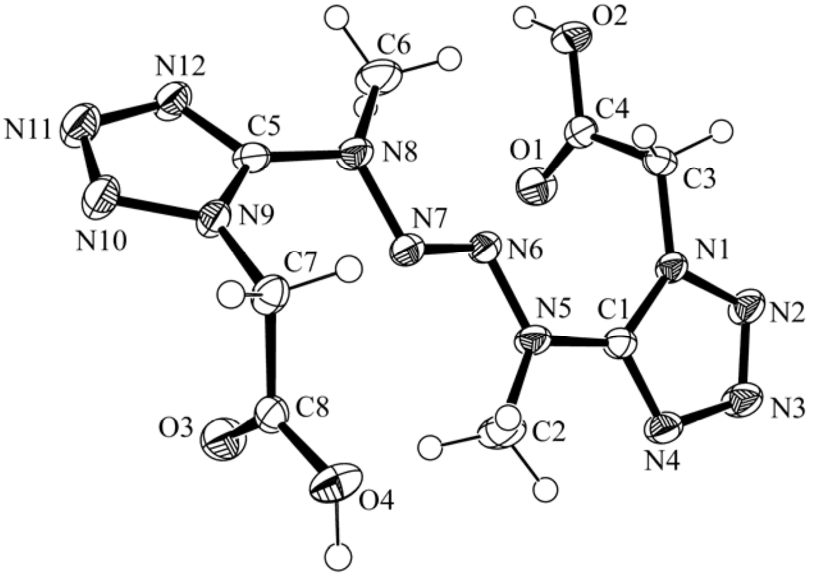


Figure 7. Molecular structure of **8**. Thermal ellipsoids are drawn at the 50% probability level.

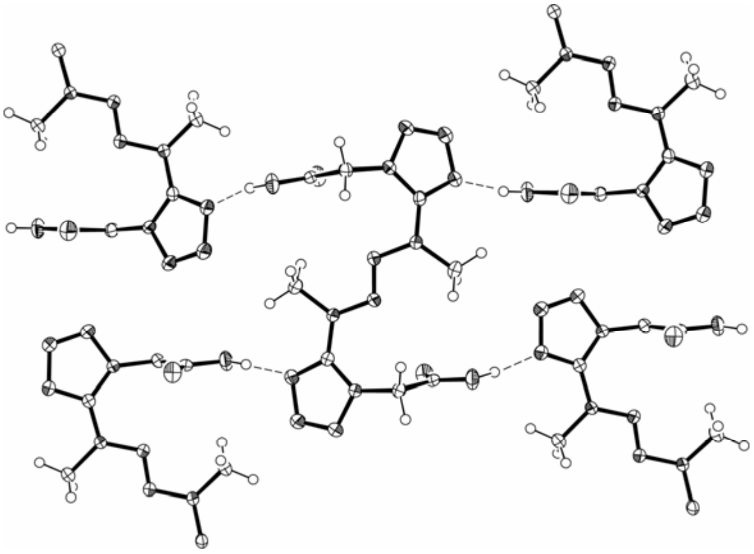


Figure 8. Molecular structure and intermolecular hydrogen bridges of **8**. Thermal ellipsoids are drawn at the 50% probability level.

A comparison between the hydrogen bridges of **7a** and **8** is given in *Table 3*.

Table 3. Hydrogen bridges of **7a** and **8**.

	donor atom	acceptor atom	D–H [Å]	H•••A [Å]	D•••A [Å]	(D–H•••A)
7a	O1	N4	0.888	2.010	2.895	173.8
8	O2	N4	0.941	1.810	2.737	167.8
	O4	N12	0.939	1.791	2.714	166.8

2.3.1.5 Conclusions

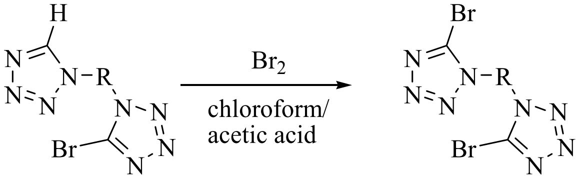
1,4-Bis[1-(2-hydroxyethyl)-1*H*-tetrazol-5-yl]-1,4-dimethyl-2-tetrazene (**7a**), 1,4-bis[1-(isopropoxy-carbonylmethyl)-1*H*-tetrazol-5-yl]-1,4-dimethyl-2-tetrazene **7b**) and 1,4-bis[1-)carboxymethyl)-1*H*-tetrazol-5-yl]-1,4-dimethyl-2-tetrazene (**8**) were prepared as nitrogen-rich compounds. The evaluation of the energetic properties points out, that these compounds are suitable as propellants or gas generating agents. The advantage lies in the high thermal stability and the low temperature of explosion, along with average detonation velocities and pressures. Moreover, a new high yield synthesis of tetrazolyl hydrazines *via* bromotetrazoles has been developed.

2.3.2 Alkylene Bridged 5-Azido-1*H*-tetrazoles

Among nitrogen rich compounds, the 5-azido-1*H*-tetrazolate anion possesses one of the highest contents of nitrogen. For this reason, the tetrazole moiety was applied to generate new nitrogen rich compounds like the hydrazinium 5-azido-1*H*-tetrazolate, nearly reaching a nitrogen content of 90 %.[15] Whereas 5-azido-1*H*-tetrazole and its salts were thoroughly investigated,[16] organic 5-azido-1*H*-tetrazoles are rarely known.[17] The 5-azido-1*H*-tetrazoles known in literature have in common, that they are stabilized by an aromatic substituent, like phenyl and its derivatives.[18] Therefore, the investigation of alkylated 5-azido-1*H*-tetrazoles could lead to valuable new nitrogen-rich building blocks. The problem when working with 5-azido-1*H*-tetrazoles is their high sensitivity towards friction or impact. Some alkali salts of 5-azido-1*H*-tetrazole even detonate spontaneously out of solution.[16] As a consequence, an alkylation of ionic 5-azidotetrazolate, analogue to known alkylations of 5-amino- or 5-nitrotetrazolates,[19] was avoided. Taking these risks into account, it was necessary to develop a secure route for the preparation of alkylated bis-5-azidotetrazoles. Common syntheses for 1H-5-azidotetrazole use either diaminoguanidine[17b] or the reaction of sodium nitrite in hydrochloric acid with tetrazolyl hydrazine.[20] In order to introduce the hydrazine-moiety into alkylated tetrazoles, 5-bromo-1*H*-tetrazoles proved to be suitable starting materials, as already demonstrated in *paragraphs 2.2.1.2* and *2.3.1*. The advantage of this synthesis is that the first hazardous compounds appear in the last step as the desired bis-5-azido-1*H*-tetrazoles and can thereby be performed with a minimum of risk for the operating chemist.

2.3.2.1 Synthesis of 5-Azido-1*H*-tetrazoles

Due to the high physical sensitivities, a secure high-yield synthesis for alkyl bridged bis-5-azido-1*H*-tetrazoles was developed. The synthesis starts with bistetrazolyl alkanes that are converted into the corresponding di(5-bromo-1*H*-tetrazolyl) alkanes (**10**) by bromination of the tetrazoles with elemental bromine,[4b,21] as already reported in *paragraphs 2.2.1.2* and *2.3.1* (*Scheme 6*).

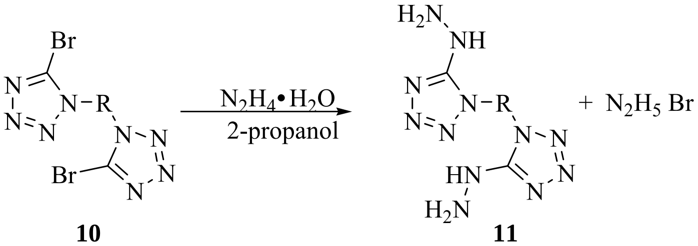


9 **10**

R = CH_2CH_2 (**9a**/**10a**), $CH(CH_3)CH_2$ (**9b**/**10b**),$CH_2CH_2CH_2CH_2$ (**9c**/**10c**)

Scheme 6. Synthesis of 5-bromo-1*H*-tetrazoles **10**.

Experiments to use other reagents, like *N*-bromosuccinimide for the bromination, yielded only mixtures of product and starting material. A complete conversion of the tetrazole into the corresponding 5-bromo-1*H*-tetrazole was not possible, even after applying a large excess of *N*-bromosuccinimide and a time of reaction of three days. Using elemental bromine for the bromination, a time of reaction of two days proved to be mandatory for a complete conversion of the starting material. The next step was the substitution of the bromine atom by hydrazine. Carrying out the reaction, only propan-2-ol turned out to be suitable as solvent. To obtain a complete conversion into the di(hydrazinyltetrazolyl) alkanes (**11**), an excess of hydrazine had to be applied (*Scheme 7*).



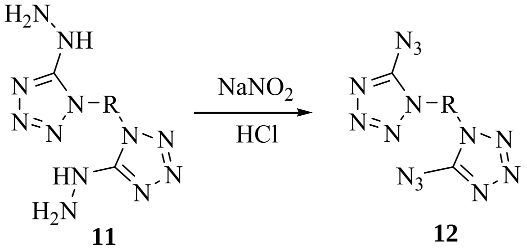
10 **11**

R = CH_2CH_2 (**10a**/**11a**), $CH(CH_3)CH_2$ (**10b**/**11b**),$CH_2CH_2CH_2CH_2$ (**10c**/**11c**)

Scheme 7. Synthesis of the di(5-hydrazinyl-1*H*-tetrazolyl) alkanes (**11**).

The formed hydrogen bromide precipitated as hydrazine hydrobromide and could be removed by hot filtration. Compound **11a** was purified by recrystallisation from water. **11a** was obtained as crystalline monohydrate, whereas recrystallized **11c** was obtained as colorless amorphous powder. Compound **11b** was used as crude material for further reactions, because a recrystallization from common solvents was not possible, probably due to a hindered crystallization. An explanation gives the asymmetric character of the 1-methylethyl bridge disturbing the packing in the crystal structure. This effect becomes obvious when comparing the melting points of **12a**, **12b** and **12c**. The impurities of **11b** contained traces of hydrazine and hydrogen bromide, coordinating as adducts to the hydrazine moieties of the tetrazole. Purification by column chromatography was not possible either (low solubility in organic solvents). The tetrazolyl hydrazines **11** were then converted into the corresponding bis-5-azido-1*H*-tetrazoles **12** by the reaction with sodium nitrite in hydrochloric acid. Therefore, the tetrazolyl hydrazines were dissolved in 2 N hydrochloric acid and an excess of sodium nitrite in water was added drop wise until gaseous nitrogen dioxide evolved (*Scheme 8*).

In case of **12a** and **12c** the product precipitated from the solution and could be obtained by filtration. Compound **12b** was recovered by extraction of the aqueous solution with dichloromethane.



R = CH_2CH_2 (**11a**/**12a**), $CH(CH_3)CH_2$ (**11b**/**12b**),$CH_2CH_2CH_2CH_2$ (**11c**/**12c**)

Scheme 8. Synthesis of 5-azido-1*H*-tetrazole **12**.

2.3.2.2 IR and NMR Spectroscopic Data of 12

The bis-5-azido-1*H*-tetrazoles can be easily analyzed by IR-spectroscopy.[22] In case of **12a**, the strong azide vibration is found at 2172 cm^{-1}, in case of **12b** and **12c** at 2168 cm^{-1} (*Figure 9*).

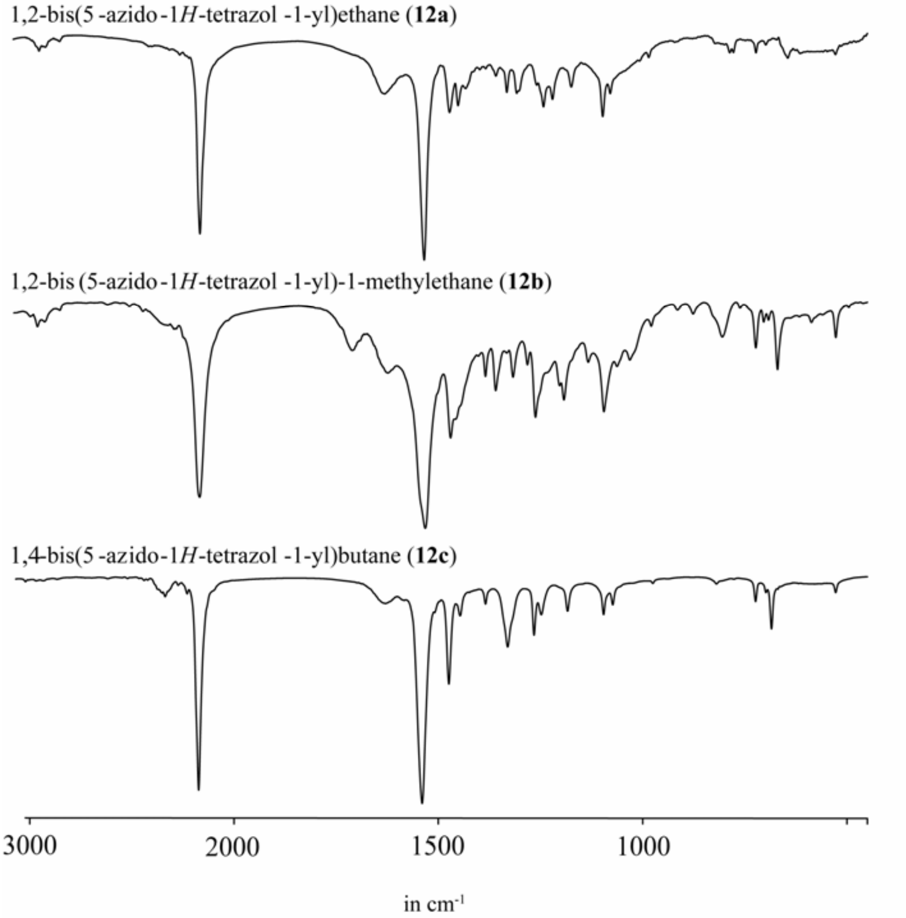


Figure 9. IR spectroscopic data of **12a**, **12b** and **12c**.

Figure 10 shows a comparison between the ^{15}N NMR data of **12a**, **12b** and **12c**. The chemical shifts are in accordance with common values reported in literature.[23] In case of **12b**, N2, N3 and N6 are split into two resonances, due to the asymmetry of the molecule. The difference between the nitrogen atoms ($N3_a/N3_b$ and $N6_a/N6_b$) of 0.2 ppm and 0.3 ppm does not allow further assignments. The difference of 3.6 ppm of $N2_a/N2_b$ offers the assumption, that $N2_b$ (-17.5 ppm) is part of the azidotetrazolyl moiety next to the methyl group.

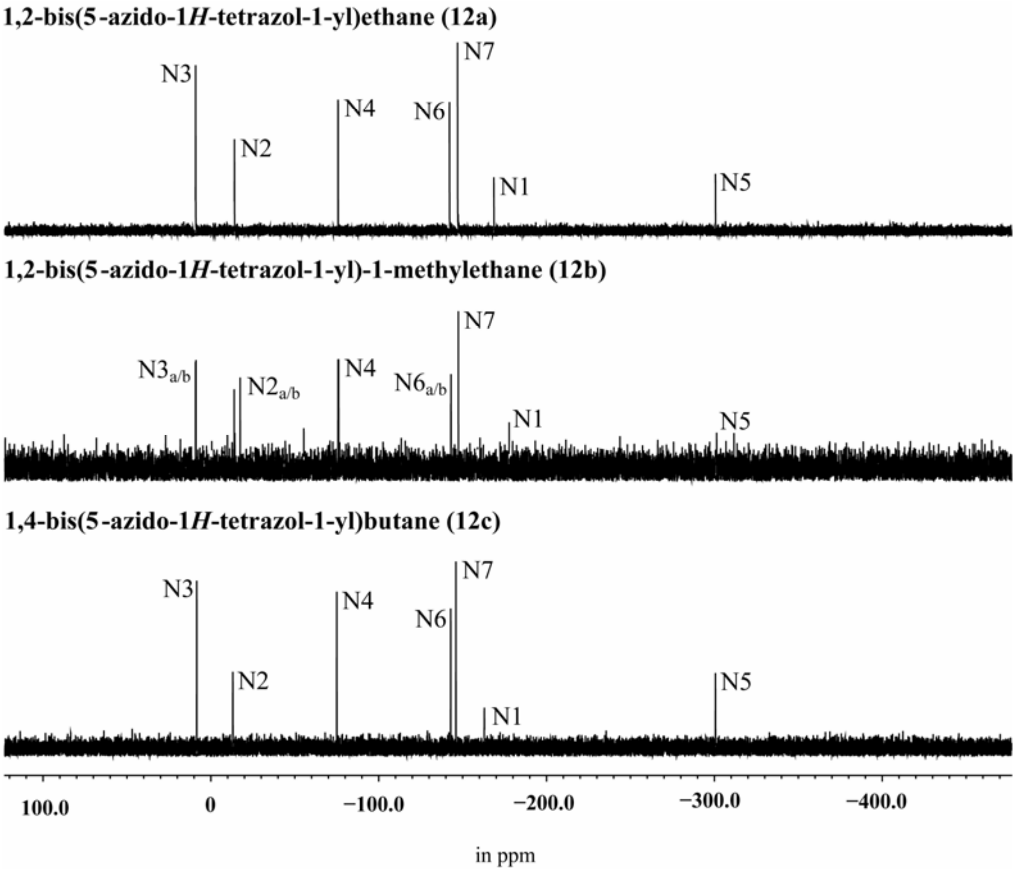


Figure 10. ^{15}N NMR spectra of **12a**, **12b** and **12c**.

2.3.2.3 Crystal Structures of 11a and 12a

Compound **11a** crystallizes as monohydrate in the triclinic space group *P*-1 with one molecular formula per unit cell (*Figure 11*). The molecular structure is stabilized by several hydrogen bridges. Thereby, the outstanding significance of the hydrate becomes obvious. The structure is stabilized by three hydrogen bridges to the water molecule, one between the proton of N5 and the oxygen atom O1 as acceptor, and two with the oxygen atom O1 as donor and N2 respectively N6 as acceptor. Another hydrogen bridge is formed between the protons of N6 and N4 of a neighboring molecule of **11a** (*Figure 12*).

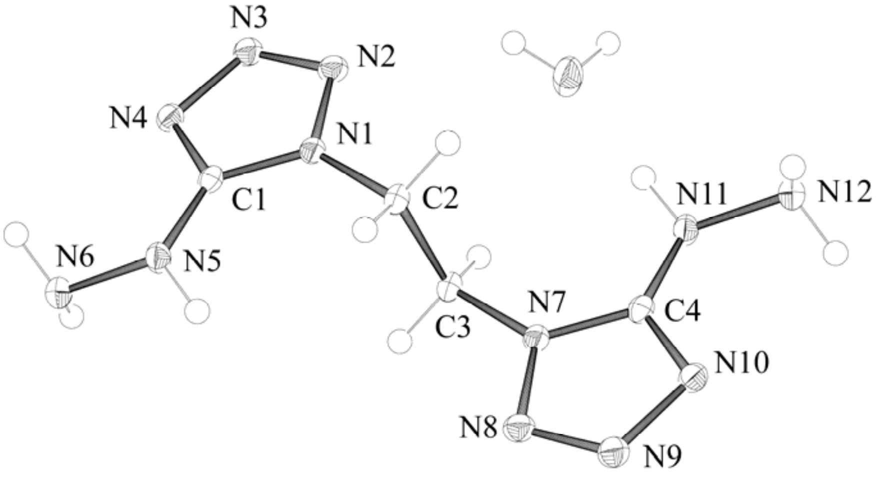


Figure 11. Molecular structure of **11a**. Thermal ellipsoids are drawn at the 50% probability level.

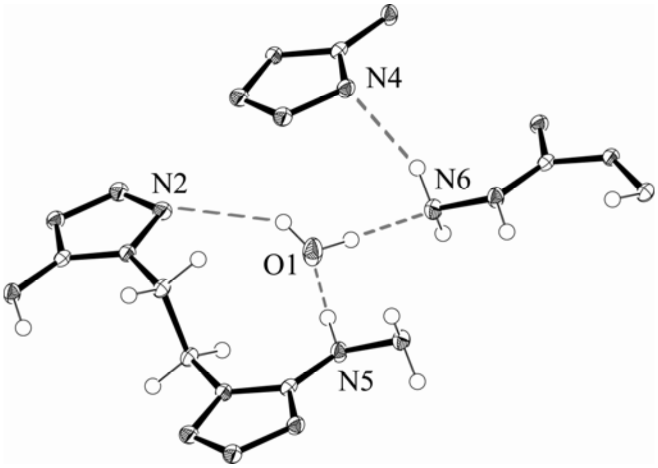


Figure 12. Hydrogen bridges formed between **11a** and the crystal water. Thermal ellipsoids are drawn at the 50% probability level.

Compound **12a** crystallizes in the triclinic space group *P*-1 with one molecular formula per unit cell (*Figure 13*). In contrast to compound **3a**, there is no crystal water present. The high density of **12a** with 1.66 g cm^{-3} is a result of the dense packing of the molecules. Thereby, the 5-azido-1*H*-tetrazole moiety of one molecule lies above the 5-azido-1*H*-tetrazole moiety of the next molecule, forming chains. The distance between two tetrazole moieties equals with 3.2 Å twice the *van der Waals* radius of a nitrogen atom (1.54 Å).

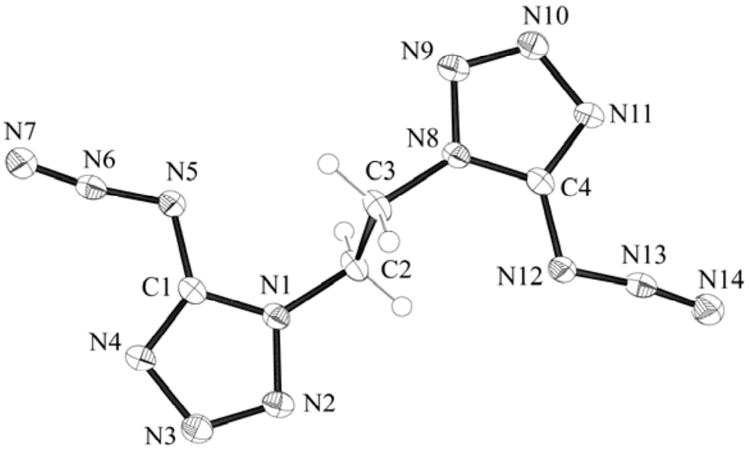


Figure 13. Molecular structure of **12a**. Thermal ellipsoids are drawn at the 50% probability level.

2.3.2.4 Energetic Properties of 12a, 12b and 12c

Despite their thermal stability up to 170 °C, the alkylated bis-5-azido-1*H*-tetrazoles presented, are highly dangerous materials, due to their high sensitivity towards friction or impact. The sensitivities of compounds **12a**, **12b** and **12c** towards impact were determined in each case to be lower than 0.15 J, the sensitivity towards friction were lower than 5 N.[9] The sensitivities of the 5-bromo-1*H*-tetrazoles **10a**, **10b** and **10c** towards friction were lower than 200 N and the sensitivity towards impact lower than 15 J. Compared to the 5-azido and 5-bromo-1*H*-tetrazoles, the hydrazine derivatives **11a** and **11c** were the most stable compounds towards impact and friction (impact > 50 J, friction > 360 N).

The investigation of the energetic properties of compounds **12a** and **12c** reveals their highly explosive characteristics. Especially compound **12a** possesses a detonation velocity of 8500 m s^{-1} along with a value of Q_v of -5500 kJ kg^{-1}. These values are close to the properties of RDX (detonation velocity of 9000 m s^{-1} and Q_v of -6000 kJ kg^{-1}). The advantage of **12a** compared to RDX is the lack of the toxic nitro groups. But in contrast to RDX, the sensitivity against impact and friction is much too low for any reasonable application.

Table 3. Energetic properties of **12a**, **12b** and **12c**.

	12a	**12b**	**12c**
formula	$C_4H_4N_{14}$	$C_5H_6N_{14}$	$C_6H_9N_{14}$
molecular mass	248.0743	262.0895	276.1056
density (g cm^{-3})	1.663	-	1.401
melting point (°C)	110	77	94
decomposition point (°C)	169	170	164
impact sensitivity (J)	> 0.15	> 0.15	> 0.15
friction sensitivity (N)	< 5	< 5	< 5
Ω (%)	-64.5	-	-92.7
$\Delta_f H°$(g,M) (kcal mol^{-1})[a]	322.0	-	302.4
Q_v (kJ kg^{-1})[b]	-5476	-	-4887
T_E (K)[c]	4127	-	3487
p(kbar)[d]	277	-	183
D(m s^{-1})[e]	8429	-	7431
Gas vol. (L kg^{-1})[f]	716	-	724

[a] calculated using CBS-4M[24]; values obtained by calculation using the EXPLO5 software[12]: [b] energy of explosion; [c] explosion temperature; [b] detonation pressure; [e] detonation velocity; [f] assuming only gaseous products.

2.3.2.5 Conclusions

A general, high yield synthesis of alkylated bis-5-azidotetrazoles was developed. In contrast to common methods, the preparation presented is safe and with minimum risk for the operating person. By optimizing the synthesis of bis-5-azido-1*H*-tetrazoles, these nitrogen rich compounds can evolve themselves into useful building blocks for nitrogen chemistry by using the azide moiety for further reactions. The tetrazoles presented were all characterized by vibrational and NMR spectroscopy, mass spectrometry and in case of 1,2-bis(5-hydrazinyl-1*H*-tetrazol-1-yl)ethane (**11a**) and 1,2-bis(5-azido-1*H*-tetrazol-1-yl)ethane (**12a**), the crystal structure was determined by single crystal X-ray diffraction.

2.3.3 References

(1) T. M. Klapötke, P. Mayer, A. Schulz, J. J. Weigand, *Propellants, Explos., Pyrotech.* **2004**, *29*, 325-332.

(2) G. M. F. Lim, M. Endo, *US Pat.* US4374994, **1983**; b) D. E. Bayes, *Eu.Pat.* EP0117368A1, **1982**.

(3) a) T. G. Back, *J. Chem. Soc., Chem. Comm.* **1981**, *11*, 530-531; b) D. H. Bae, H. J. Shine, *J. Org. Chem.* **1981**, *46*, 4700-4704.

(4) a) W. L. Collibee, M. Nakajima, J.-P. Anselme, *J. Org. Chem.* **1995**, *60*, 468-469;b) D. E. Bayes, *Eu. Pat.* EP0117368A1, **1982**; c) R. Bruns, H. Uhr, E. Vogl, *Int. Pat.* WO2006161228, **2006**.

(5) a) O. H. Justiz, R. Fernandez-Lafuente, J. M. Guisan, P. Negri, M. Pregnolato, M. Terreni, *J. Org. Chem.* **1997**, *62*, 9099-9106; b) P. J. van Köningsbruggen, Y. Garcia, G. Bravic, D. Chasseau, O. Kahn, *Inorg. Chim. Acta* **2001**, *326*, 101-105; c) T. M. Potewar, A. Shafi, R. J. Lahoti, K. V. Srinivasan, *Tetrahedron Lett.* **2007**, *48*, 1721-1724.

(6) T. M. Klapötke, N. Minar, J. Stierstorfer, *Polyhedron*, **2008**, in press.

(7) a) M. Suceska, *Test Methods for Explosives*, Springer, New York, **1995**, p. 21 (impact), p. 27 (friction); b) http://www.bam.de/.

(8) Impact: insensitive > 40 J, less sensitive > 35 J, sensitive > 4 J, very sensitive < 4 J; friction: insensitive > 360 N, less sensitive = 360 N, sensitive < 360 N > 80 N, very sensitive < 80 N, extreme sensitive < 10 N; According to the UN Recommendations on the Transport of Dangerous Goods.

(9) A. Gao, A. L. Rheingold, T. B. Brill, *Propellants, Explos., Pyrotech.* **1991**, *16*, 97-104;

(10) T. M. Klapötke, M. Stein, J. Stierstorfer, *Z. Anorg. Allg. Chem.* **2008**, *634*, 1711-1723.

(11) a) N. Wiberg, *Lehrbuch der Anorganischen Chemie / Holleman-Wiberg*, 101. Ed., de Gruyter, Berlin, **1995**, 141; b) N. Wiberg, *Lehrbuch der Anorganischen Chemie / Holleman-Wiberg*, 101. Ed., de Gruyter, Berlin, **1995**, pp 250, 859 and 1176; c) http://webbook.nist.gov/chemistry/

(12) a) M. Suceska, *Proc. of 30th Int. Annual Conference of ICT, Karlsruhe, Germany*, ed. Fraunhofer-Institut für chemische Technologie, DWS Werbeagentur und Verlag GmbH, Karlsruhe, 1999, 50/1; b) EXPLO5.V2, Computer program for calculation of detonation parameters, P, M. Suceska, *Proc. of 32nd Int. Annual Conference of ICT, Karlsruhe, Germany*, ed. Fraunhofer-Institut für chemische Technologie, DWS Werbeagentur und Verlag GmbH, Karlsruhe, 2001, pp. 110/1.

(13) a) A. S. Lyakhov, S. V. Voitekhovich, P. N. Gaponik, L. S. Ivashkevich, *Acta Cryst.* **2004**, *C60*, o293-o294; b) T. M. Klapötke, C. Kuffer, P. Mayer, K. Polborn, A. Schulz, J. J. Weigand, *Inorg. Chem.* **2005**, *44*, 5949-5958.

(14) A. F. Holleman, E. Wiberg, N. Wiberg, *Lehrbuch der Anorganischen Chemie*, 101. Auflage, Walter de Gruyter Verlag, Berlin, New York, **1995**, 1842.

(15) T. M. Klapötke, J. Stierstorfer, *J. Am. Chem. Soc.* **2009**, *131*, 1122-1134.

(16) a) F. Walter, K. Flick, *US Pat.* US2179783, **1939**; b) E. Lieber, D. R. Levering, *J. Am. Chem. Soc.* **1951**, *73*, 1313-1317; c) A. Hammerl, T. M. Klapötke, P. Mayer, J. J. Weigand, *Propellants, Explos., Pyrotech.* **2005**, *30*, 17-26.

(17) a) R. Stolle, K. Ehrmann, D. Rieder, H. Wille, H. Winter, F. Henke-Stark, *Journal fuer Praktische Chemie*, **1932**, *134*, 282-309; b) J. C. Kauer, W. A. Sheppard, *J. Org. Chem.* **1967**, *32*, 3580-3593; c) R. Weiss, R. H. Lowack, *Angew. Chem. Int. Ed.* **1991**, *103*, 1162-1163; d) S. Shuki, K. Yamamoto, M. Yagi, T. Inoue, H. Fukagawa, H. Hattori, H. Yamamura, M. Kawai, Y. Butsugan, *Eur. J. Org. Chem.* **1998**, *1*, 121-127.

(18) a) C. A. Maggiulli, R. E. Paine, *Bel. Pat.* BE671402, **1966**; b) J. C. Kauer, W. A. Sheppard, *J. Org. Chem.* **1967**, *32*, 3580-3593.

(19) a) R. A. Henry, W. G. Finnegan, *J. Am. Chem. Soc.* **1954**, *78*, 1635-1636; b) K. R. Wilson, R. M. Herbst, W. J Haak, *J. Org. Chem.* **1959**, *24*, 1046-1051; c) S. V.

Voitekhovich, P. N. Gaponik, A. S. Lyakhov, O. A. Ivashkevich, *Tetrahedron*, **2008**, *64*, 8721-8725.

(20) J. Thiele, H. Ingle, Liebigs *Ann. Chem.* **1895**, *287*, 233-265.

(21) J. Heppekausen, T. M. Klapötke, S. M. Sproll, *J. Org. Chem.*, **2009**, *74*, 2460-2466.

(22) a) C. N. R. Rao, T. S. Chao, C. W. W. Hoffman, *Anal. Chem.* **1957**, *29*, 916-918; b) S. Hirota, H. Matsumoto, H.-W. Huang, T. Sakurai, T. Kitagawa, O. Yamauchi, *Biochem. Biophys. Res. Commun.* **1998**, *243*, 435-437.

(23) J. Stierstorfer, T. M. Klapötke, A. Hammerl, R. D. Chapman, *Z. Anorg. Allg. Chem.* **2008**, *634*, 1051-1057.

(24) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., *Gaussian 03, Revision A.1*, Pittsburgh, PA, **2003**.

2.4 Experimental Section

2.4.1 Polymers Formed by Polycondensation Reactions

2.4.1.1 Polymer Based on 1-(2-hydroxyethyl)-1*H*-tetrazolyl)methyl-hydrazine

2-Aminoethyl acetate **1** was synthesized according to literature,[1] as 2-isothiocyanatoethyl acetate **8.**[2]

2.4.1.1.1 Synthesis of 4-(2-(acetyloxy)ethyl)-2-methylthiosemi- carbazide 10

2-Isothiocyanatoethyl acetate 8 (7.3 g, 50 mmol) was dissolved in 10 mL of diethyl ether and a solution of methyl hydrazine (2.3 g, 50 mmol) and 5 mL diethyl ether was added dropwise at 0 °C. After stirring for 1 h, the product separated as colorless solid. Compound 10 was purified by recrystallization from ethanol (8.6 g, 90 %).

m. p. 81 °C.

IR (KBr, cm-1): $\tilde{\nu}$ = 3323 (s), 3271 (m), 3183 (w), 2924 (w), 1736 (vs), 1634 (m), 1620 (m), 1526 (s), 1442 (m), 1384 (m), 1370 (m), 1276 (m), 1243 (s), 1144 (m), 1048 (s), 926 (w), 908 (w), 877 (w), 812 (w), 693 (w), 607 (w).

Raman (200 mW, 25° C, cm-1): $\tilde{\nu}$ = 3323 (100), 3267 (96), 3186 (89), 3000 (57), 2960 (75), 2937 (77), 1728 (26), 1626 (31), 1456 (29), 1435 (30), 1378 (23), 1294 (18), 1221 (15), 1148 (13), 1088 (10), 1069 (10), 1054 (11), 993 (11), 910 (11), 871 (13), 815 (38), 665 (54), 645 (18), 566 (12), 478 (34).

^{1}H NMR (*d6*-DMSO) δ: 2.01 (s, 3H, CCH_3), 3.44 (s, 3H, NCH_3), 3.67 (q, 2H, CH_2), 4.10 (t, 2H, CH_2), 4.88 (NH_2), 8.28 (t, 1H, N*H*).

^{13}C NMR (*d6*-DMSO) δ: 21.3 (CCH_3), 43.1 (NCH_3), 43.7 (NCH_2), 63.2 (OCH_2), 170.9 (*C*O), 181.8 (*C*S).

m/z (DEI+): 191.1 (18), 131.0 (67), 130.0 (10), 116.0 (18), 115.0 (27), 114.0 (33), 104.0 (10), 89.0 (16), 87.0 (9), 86.0 (27), 85.0 (36), 74.0 (9), 69.0 (20), 60.0 (11), 59.0 (9), 57.1 (10), 45.9 (100), 44.8 (26), 43.7 (11), 42.6 (86), 41.5 (9).

$C_6H_{13}N_3O_2S$ (191.0728 found M 191.0735).

elemental analysis: calcd (%) for $C_6H_{13}N_3O_2S$: C 37.68, H 6.85, N 21.97, S 16.77; found C 37.70, H 6.71, N 21.90, S 16.75.

2.4.1.1.2 Synthesis of 1-(2-(acetyloxyethyl)-1*H*-tetrazolyl)methyl-hydrazine 13

4-(2-(Acetyloxy)ethyl)-2-methylthiosemi-carbazide **10** (2.3 g, 12 mmol) was suspended in 40 mL ethanol and iodomethane (1.9 g, 13 mmol) was added. The mixture was stirred under reflux for 4 h. After cooling to 20 °C, sodium azide (2.6 g, 40 mmol) was added and the mixture was stirred for further 12 h under reflux. The solvent was removed and the resulting oil was extracted with dichloromethane. The organic phases were collected and the solvent removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, ethanol/diethylether 1:9, $R_f = 0.17$). The product was obtained as colorless crystals (860 mg, 36 %).

m.p. 77.9 - 79.5 °C.

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3434 (w), 3357 (m), 3263 (w), 2996 (w), 2965 (w), 2903 (w), 1732 (vs), 1645 (s), 1560 (m), 1467 (m), 1443 (m), 1409 (m), 1391 (m), 1260 (s), 1157 (w), 1126 (w), 1107 (m), 1040 (m), 994 (m), 939 (m), 909 (m), 739 (w), 697 (w), 686 (w), 635 (vs), 608 (vs), 489 (w).

Raman (200 mW, 25° C, cm^{-1}): $\tilde{\nu}$ = 3357 (25), 3263 (46), 3032 (36), 2994 (69), 2983 (62), 2961 (65), 2935 (82), 2791 (27), 1722 (76), 1643 (42), 1566 (30), 1467 (51), 1407 (54), 1338 (30), 1286 (76), 1270 (70), 1231 (43), 1155 (21), 1130 (32), 1108 (80), 1053 (28), 998 (27), 938 (33), 817 (70), 699 (100), 634 (96), 526 (45).

^{1}H NMR ($CDCl_3$) δ: 1.83 (s, 3H, CCH_3), 3.12 (s, 3H, NCH_3), 4.09 (NH_2), 4.28 (t, 2H, CH_2), 4.62 (t, 2H, CH_2).

^{13}C NMR ($CDCl_3$) δ: 20.6 (CCH_3), 44.7 (NCH_3), 47.2 (NCH_2), 61.7 (OCH_2), 158.6 (C_q), 170.7 (CO).

^{15}N NMR ($CDCl_3$) δ: -0.3 (N3), -16.8 (N2), -90.1 (N4), -175.1 (N1), -298.5 (NH_2), -312.5 (NCH_3).

m/z (DEI+): 200.2 [M] (22), 158.2 (9), 115.1 (5), 87.1 (83), 69.1 (12), 43.1 (100), 15.1 (13); $C_6H_{12}N_6O_2$ (200.1 found M 200.2).

elemental analysis: calcd (%) for $C_6H_{12}N_6O_2$: C 36.00, H 6.04, N 41.98; found C 36.00, H 5.87, N 41.36.

2.4.1.1.3 Synthesis of 1-(2-Hydroxyethyl)-1*H*-tetrazolyl)methyl-hydrazine 3

1-(2-(Acetyloxyethyl)-1*H*-tetrazolyl)methyl-hydrazine **13** (320 mg, 1.6 mmol) was dissolved in 30 mL 0.1 M aqueous potassium hydroxide solution and stirred for 1 h at ambient temperature. The solvent was removed and the obtained oil extracted with acetonitrile. After recrystallization from acetonitrile colorless crystals formed (150 mg, 59 %).

m.p. 111.0 - 117.8 °C.

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3350 (s), 3266 (s), 2967 (w), 2926 (w), 2878 (w), 1656 (vs), 1563 (vs), 1455 (m), 1415 (m), 1373 (m), 1340 (w), 1325 (w), 1282 (m), 1233 (m), 1122 (m), 1104 (m), 1069 (vs), 1039 (m), 983 (m), 948 (w), 903 (m), 864 (m), 745 (m), 707 (m), 684 (m), 493 (m).

Raman (200 mW, 25° C, cm^{-1}): $\tilde{\nu}$ = 3351 (40), 3232 (38), 3193 (34), 3028 (32), 2976 (100), 2928 (37), 2882 (38), 2809 (24), 1654 (41), 1566 (35), 1466 (56), 1418 (47), 1378 (32), 1352 (34), 1284 (66), 1268 (59), 1231 (30), 1105 (55), 1071 (29), 987 (19), 950 (23), 864 (52), 692 (91), 633 (54), 523 (28), 498 (27).

^{1}H NMR (*d6*-DMSO) δ: 3.09 (s, 3H, NCH_3), 3.72 (t, 2H, OCH_2), 4.49 (t, 2H, NCH_2), 4.82 (s, 2H, NH_2), 4.96 (br. t, 1H, O*H*).

^{13}C NMR (*d6*-DMSO) δ: 44.4 (CH_3), 50.8 (OCH_2), 59.5 (NCH_2), 159.2 (C_q).

^{15}N NMR (D_2O) δ: -11.0 (N3), -21.9 (N2), -100.1 (N4), -174.5 (N1), -301.6 (NH_2), -313.3

(NCH_3).

m/z (DEI+): 158.1 [M],143.1, 127.1, 113.1, 87.1, 69.1, 55.1, 43.1, 31.1, 28.1.

elemental analysis: calcd (%) for $C_4H_{10}N_6O$: C 30.38, H 6.37, N 53.14; found: C 30.43, H 6.46, N 52.23.

2.4.1.1.4 Synthesis of 4-(2-(Trimethylsilyloxy)ethyl)-2-methylthiosemicarbazide 15

Ethanolamine (1.2 g, 20 mmol) was dissolved in 15 mL ethyl acetate and triethylamine (4.1 g, 40 mmol) was added at 0 °C. Chlorotrimethylsilane (4.3 g, 40 mmol) was added dropwise with vigorous stirring. After stirring at ambient temperature for 30 min, the solid was filtered off and washed with 20 mL ethyl acetate. After adding carbon disulfide (1.9 g, 25 mmol) the solution was stirred at 0 °C for 1 h and an additional hour at room temperature. Then chlorotrimethylsilane (2.3 g, 21 mmol) and triethylamine (2.0 g, 20 mmol) were added dropwise. The reaction mixture was refluxed for 1 h. The solid was filtered off and washed twice with ethyl acetate. The solvent was removed under reduced pressure. A solution of methyl hydrazine (0.9 g, 20 mmol) in 3 mL diethyl ether was added dropwise at 0 °C to the resulting yellow-brownish oil, dissolved in 5 mL diethyl ether. After stirring for 30 min at 0 °C and further 1.5 h at room temperature the solvent was removed under reduced pressure and the product slowly crystallized off the dark oil. Recrystallization from diethyl ether yielded **15** as colorless solid (0.8 g, 17 %).

m. p. 84 °C - 90 °C.

IR (KBr, cm^{-1}): $\tilde{\nu}$= 3317 (s), 3249 (m), 3178 (w), 3149 (m), 2961 (w), 2873 (w), 1643 (m), 1528 (vs), 1367 (m), 1303 (s), 1262 (m), 1251 (s), 1213 (w), 1164 (s), 1081 (vs), 1049 (vs), 895 (s), 866 (s), 839 (vs), 748 (m), 707 (vw).

^{1}H NMR (*d6*-DMSO) δ: 0.08 (s, 6H, $SiCH_3$), 3.62 – 3.90 (m, 7H, CH_3, $2xCH_2$).

^{13}C NMR (*d6*-DMSO) δ: -0.53 ($SiCH_3$), 43.80 (CH_3), 47.39 (CH_2), 62.51(CH_2), 182.11 (CS).

m/z (DEI+): 221.1 [M] (8), 160.0 (21), 131.0 (29), 117.1 (8), 116.0 (36), 115.0 (12), 114.0 (83), 105.0 (12), 101.0 (12), 89.0 (20), 86.0 (15), 75.0 (12), 73.0 (74), 46.0 (100), 45.0 (9)

$C_7H_{19}N_3OSSi$ (221.1018 found M 221.1006).

elemental analysis: calcd (%) for $C_7H_{19}N_3OSSi$: C 37.97, H 8.65, N 18.98, S 14.48; found C 37.54, H 8.79, N 18.98, S 14.48.

2.4.1.1.5 Synthesis of 4-(2-Azidoethyl)-2-methylsemicarbazide 18

4-(2-(Trimethylsilyloxy)ethyl)-2-methyl-thiosemicarbazide **15** (1.0 g, 4.5 mmol) was dissolved in 15 mL ethanol and methyl iodine (0.6 g, 4.5 mmol) was added. After refluxing for 4 h, the reaction mixture was cooled down to 40 °C and sodium azide (0.4 g, 6.8 mmol) was added. The suspension was refluxed for 18 h. The solvent was removed under reduced pressure and the residue was extracted with dichloromethane. The solvent was removed under reduced pressure and the resulting oil purified by column chromatography (dichloromethane/ethyl acetate 1:1, $R_f = 0.2$) (0.4 g, 56 %).

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3400 (m), 3314 (m), 3208 (m), 2933 (m), 2874 (m), 2104 (vs), 1652 (vs), 1520 (vs), 1451 (m), 1403 (m), 1359 (m), 1300 (m), 1247 (m), 1174 (m), 1106 (m), 1053 (s), 1028 (vs), 1009 (s), 957 (m), 849 (w), 821 (w), 761 (m), 627 (m), 555 (m).

^{1}H NMR (*d6*-DMSO) δ: 2.91 (s, 3H, NCH_3), 3.18 (m, 2H, OCH_2), 3.28 (m, 2H, NCH_2), 4.41 (s, 2H, NH_2), 6.89 (br. t, 1H, O*H*).

^{13}C NMR (*d6*-DMSO) δ: 38.2 (CH_3), 51.3 (OCH_2), 60.3 (NCH_2), 159.7 (C_q)

^{15}N NMR (*d6*-DMSO) δ: -133.- (N3), -172.8 (N4), -286.7 (N2), -304.8 (N5), -307.1 (N6), -312.8 (N1).

m/z (DEI+): 158.2 [M] (8), 149.1 (6), 129.1 (40), 114.1 (41), 102.1 (12), 73.1 (14), 60.1 (39), 46.1 (100), 45.1 (48), 30.1 (75), 26.1 (30).

2.4.1.1.6 Polymerization of 3 and 21

1-(2-Hydroxyethyl)-1*H*-tetrazolyl) methyl hydrazine **3** (500 mg, 3.2 mmol) was mixed with hexamethylene diisocyanate **21** (531 mg, 3.2 mmol) and heated for 1 h to 120 °C. The polymer was obtained as hard, sproudish foam (960 mg, 93 %).

m.p. 190 – 245 °C, dec. 260 °C.

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2926 (w), 2851 (w), 1636 (vs), 1539 (m), 1454 (w), 1261 (w), 1099 (w), 1034 (w), 803 (vw), 591 (w).

elemental analysis: calcd (%) for $C_8H_{15}N_8O_3$: C 44.16, H 6.79, N 34.33; found: C 43.05, H 6.76, N 33.45;

M_w = 5850 g/mol.

2.4.1.2 Nitrogen-rich Energetic Polymers Based on Alkylbridged Bis-(1-methyl-tetrazolylhydrazines)

1,2,-bis(1-tetrazolyl)ethane,[3] 1-methyl-1,2,-bis(1-tetrazolyl) ethane[4] and 1,2,-bis(1-tetrazolyl)butane[5] were prepared after literature.

2.4.1.2.1 General Synthesis of Bis(5-bromo-1*H*-tetrazolyl)alkanes

Bis-1*H*-tetrazolylalkane (31 mmol) was dissolved in a mixture of 20 mL acetic acid and 40 mL chloroform. The mixture was heated to 60 °C and bromine (20.0 g, 124 mmol) was added. After refluxing for 48 h, the solvent was removed and the residue neutralized by a saturated sodium carbonate solution. The aqueous phase was extracted using ethyl acetate. After removing the solvent, the bromotetrazole was obtained as slightly yellow powder.

2.4.1.2.2 1,2-Bis(5-bromo-1*H*-tetrazolyl)ethane 26a

yield: 3.8 g, 11.8 mmol, 38 %.

m. p./dec. 159 °C.

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3443 (m), 3024 (w), 2974 (w), 2157 (w), 2126 (w), 1639 (w), 1571 (w), 1443 (s), 1419 (vs), 1396 (s), 1301 (w), 1290 (m), 1241 (s), 1172 (s), 1142 (s), 1098 (m), 1059 (w), 976 (m), 941 (w), 669 (m), 652 (m), 503 (m).

^{1}H NMR (*d6*-DMSO) δ: 4.95 (s, 2H, CH_2).

^{13}C NMR (*d6*-DMSO) δ: 47.46 (CH$_2$), 135.70 (C_q).

elemental analysis: calcd (%) for $C_4H_4Br_2N_8$: C 14.83, H 1.24, N 34.59; found: C 14.94, H 1.33, N 34.93.

2.4.1.2.3 1,2-Bis(5-bromo-1*H*-tetrazolyl)-1-methylethane 26b

yield: 8.6 g, 25.7 mmol, 83 %.

m. p. 92 °C, dec. 164 °C.

IR (KBr, cm-1): = 3013 (w), 2985 (w), 2924 (w), 1709 (m), 1636 (m), 1532 (w), 1454 (m), 1426 (vs), 1416 (vs), 1399 (vs), 1389 (vs), 1362 (m), 1356 (m), 1307 (w), 1297 (w), 1242 (m), 1201 (m), 1187 (m), 1157 (m), 1123 (m), 1095 (m), 1082 (w), 1058 (w), 1024 (w), 975 (w), 924 (vw), 912 (vw), 760 (w), 696 (vw), 687 (vw), 680 (vw), 644 (vw), 635 (vw), 538 (vw), 509 (vw), 485 (vw).

^{1}H NMR (*d6*-DMSO) δ: 1.75 (d, 3H, CH_3), 4.92 (m, 2H, CH_2), 5.20 (m, 1H, C*H*).

^{13}C NMR (*d6*-DMSO) δ: 17.8 (*C*H$_3$), 52.0 (*C*H$_2$), 55.3 (*C*H), 135.6 (C_q).

m/z (DEI): 339 (1 %) (M+H), 259 (17), 179 (100), 149 (10), 99 (18), 83 (8), 69 (39), 68 (30), 67 (16), 56 (21), 55 (43), 54 (18), 53 (21), 42 (39), 41 (47), 39 (13), 28 (39), 27 (12).

elemental analysis: calcd (%) for $C_5H_6Br_2N_8$: C 17.77, H 1.79, N 33.16; found: C 17.95, H 1.98, N 33.42.

2.4.1.2.4 1,4-Bis(5-bromo-1*H*-tetrazolyl)butane 26c

yield: 3.9 g, 11.2 mmol, 36 %.

m. p. 140 °C, dec. 196 °C.

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2962 (w), 2926 (w), 2855 (w), 1699 (w), 1558 (w), 1540 (w), 1465 (m), 1456 (m), 1430 (m), 1416 (m), 1395 (s), 1281 (w), 1233 (m), 1175 (s), 1100 (m), 981 (m), 790 (vs), 656 (m).

^{1}H NMR (*d6*-DMSO) δ: 1.88 (s, 1H, CH_2), 4.44 (s, 1H, CH_2)

^{13}C NMR (*d6*-DMSO) δ: 25.8 (*C*H$_2$), 47.9 (*C*H$_2$), 134.8 (C_q).

m/z (DEI): 348 (10 %) (M-H), 346 (10), 284 (19), 282 (19), 198 (6), 155 (34), 139 (4), 92

(10), 91 (100), 65 (25), 63 (6), 55 (4), 54 (4), 53 (4), 51 (4), 45 (5), 39 (8), 31 (10), 29 (5).

elemental analysis: calcd (%) for $C_6H_8Br_2N_8$: C 20.47, H 2.29, N 31.83; found: C 20.96, H 2.30, N 32.68.

2.4.1.2.5 General Synthesis of Bis(5-monomethylhydrazinyl-1*H*-tetrazolyl)alkanes 22a, 22b and 22c

A suspension of 6 mmol bis(5-brom-1*H*-tetrazolyl)alkane and 1.1 g (24 mmol) methyl hydrazine in 50 mL of 2-propanol was refluxed for 10 h. The solvent was removed and the residue was washed with water.

2.4.1.2.6 1,2-Bis(5-monomethylhydrazinyl-1*H*-tetrazolyl)ethane 22a

yield: 75 %.

m. p. 219 °C; dec**.** 278 °C.

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3433 (m), 3292 (s), 3182 (m), 2972 (w), 2917 (w), 2872 (w), 2789 (w), 1654 (vs), 1565 (s), 1449 (s), 1424 (m), 1406 (m), 1349 (w), 1333 (w), 1310 (w), 1278 (w), 1267 (m), 1255 (m), 1228 (m), 1194 (w), 1162 (w), 1123 (m), 1101 (m), 1091 (m), 1057 (m), 980 (w), 914 (m), 748 (w), 734 (w), 725 (m), 686 (w), 627 (w), 523 (w), 461 (w), 418 (w).

^{1}H NMR (*d6*-DMSO) δ: 3.14 (s, 6H, CH_3), 3.35 (s, 4H, NH_2), 4.90 (s, 4H, CH_2).

^{13}C NMR (*d6*-DMSO) δ: 44.2 (CH_3), 47.6 (CH_2), 159.1 (N=C).

elemental analysis: calcd (%) for $C_6H_{14}N_{11}$*0.14HBr: C 27.11, N 63.23, H 5.36; found C 27.41, N 63.65, H 5.03.

2.4.1.2.7 1-Methyl-1,2-bis(5-monomethylhydrazinyl-1*H*-tetrazolyl)ethane 22b

yield: 45 %.

m. p. 90 °C-125 °C; dec. 272 °C.

IR (KBr, cm^{-1}): $\widetilde{\nu}$ = 3292 (vs), 3183 (s), 2980 (m), 3932 (w), 1660 (vs), 1574 (s), 1550 (s), 1450 (s), 1428 (m), 1410 (m), 1383 (vw), 1331 (w), 1282 (w), 1261 (w), 1230 (w), 1177 (w), 1151 (vw), 1124 (w), 1101 (m), 1054 (m), 1029 (w), 989 (vw), 915 (m), 771 (vw), 749 (vw), 739 (vw), 613 (w), 554 (vw).

^{1}H NMR (*d6*-DMSO) δ: 1.47 (d, 3H, ^3J = 7.04 Hz) CCH_3), 3.02 (s, 3H, NCH_3), 3.12 (s, 3H, NCH_3), 4.74 (s, 2H, NH_2), 4.88 (s, 2H, NH_2), 4.89 (m, 2H, CH_2), 5.94 (hex, 1H, ^3J = 6.18 Hz, CH).

^{13}C NMR (*d6*-DMSO) δ: 18.2 (CCH_3), 44.2 (NCH_3), 44.5 (NCH_3), 52.4 (CH_2), 53.9 (CH), 159.1 (C_q), 159.3 (C_q).

elemental analysis: calcd (%) for $C_7H_{16}N_{12}$*0.14HBr: C 30.04, N 60.06, H 5.81; found C 29.95, N 60.02, H 5.55.

2.4.1.2.8 1,4-Bis(5-monomethylhydrazinyl-1*H*-tetrazolyl)butane 22c

yield: 54 %.

m. p. 135 °C; dec. 279 °C.

IR (KBr, cm^{-1}): $\widetilde{\nu}$ = 3348(s), 3314 (m), 3216 (w), 3173 (m), 2968 (m), 2864 (w), 2792 (vw), 1642 (vw), 1550 (vw), 1460 (m), 1423 (m), 1407 (m), 1382 (vw), 1353 (vw), 1320 (vw), 1213 (w), 1133 (vw), 1116 (vw), 1095 (w), 1020 (w), 987 (w), 889 (m), 794 (w), 740 (w), 624 (vw).

^{1}H NMR (*d6*-DMSO) δ: 1.78 (s, 2H, CCH_2), 3.14 (s, 6H, CH_3), 4.51 (s, 2H, CH_2), 4.86 (s, 2H, NH_2);

^{13}C NMR (*d6*-DMSO) δ: 26.3 (CCH_2), 44.4 (CH_3), 48.1 (CH_2), 159.1 (N=C).

elemental analysis: calcd (%) for $C_8H_{18}N_{12}$: C 34.04, N 59.54, H 6.43; found C 34.01, N

59.72, H 6.12.

2.4.1.2.9 Polymerization of Bis(5-monomethylhydrazinyl-1*H*-tetrazolyl)alkanes 22a, 22b and 22c

Compound **1** (2 mmol) was dissolved in 3 mL DMF at 135 °C. Hexamethylene diisocyanate (328 mg, 2 mmol) were added. The solvent was evaporated at ambient pressure by heating the solution at 135 °C in an open flask. After removing the solvent, a rubber-like solid was formed. The polymer was dried under high vacuum at 135 °C for 8 h. Yield: 98 %.

2.4.1.2.10 Polymer of 1,2-bis(5-monomethylhydrazinyl-1*H*-tetrazolyl) ethane 31a

dec. 243 °C.

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3431 (vs), 3282 (s), 2964 (m), 2934 (m), 2861 (w), 1990 (vw), 1734 (m), 1635 (s), 1408 (m), 1384 (m), 1262 (m), 1228 (m), 1098 (m), 1024 (m), 919 (vw), 801 (w), 735 (vw), 599 (vw).

elemental analysis: calcd (%) for $C_{65}H_{129}N_{59}O_{13}$: C 40.14, N 42.49, H 6.68; found C 40.16, N 42.27, H 6.17.

2.4.1.2.11 Polymer of 1-methyl-1,2-bis(5-monomethylhydrazinyl-1*H*-tetrazolyl)ethane 31b

dec. 244 °C.

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3444 (vs), 3296 (s), 2967 (w), 2934 (w), 2855 (w), 2277 (vw), 1724 (m), 1635 (m), 1412 (m), 1384 (m), 1261 (m), 1228 (m), 1099 (m), 1021 (m), 913 (vw), 873 (vw), 800 (w), 735 (w), 745 (w), 618 (w).

elemental analysis: calcd (%) for $C_{66}H_{132}N_{58}O_{13}$: C 40.73, N 41.74, H 6.84; found C 40.83, N 41.78, H 6.62.

2.4.1.2.12 Polymer of 1,4-bis(5-monomethylhydrazinyl-1*H*-tetrazolyl) butane 31c

dec. 241 °C.

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3423 (vs), 3256 (s), 2933 (m), 2861 (m), 2550 (vw), 1717 (m), 1636 (m), 1454 (m), 1384 (m), 1262 (m), 1192 (m), 1156 (m), 1119 (m), 1100 (m), 1051 (m), 1018 (m), 907 (vw), 798 (w), 749 (w), 615 (w).

elemental analysis: calcd (%) for $C_{60}H_{122}N_{46}O_{12}$: C 42.90, N 38.35, H 7.32; found C 43.03, N 38.61, H 6.74.

2.4.2 Polymers Formed by Radical Polymerization

2-(5-Bromo-1*H*-tetrazol-1-yl)ethanol (**2**) was prepared according to Bayes.[6]

2.4.2.1 Synthesis of 2-(5-Bromo-1*H*-tetrazol-1-yl)ethyl 4-methylbenzenesulfonate 7

p-Toluenesulfonyl chloride (18.0 g, 94 mmol), triethylamine (9.8 g, 98 mmol) and 4-dimethylaminopyridine (5.7 g, 47 mmol) were added to a solution of 2-(5-bromo-1*H*-tetrazol-1-yl)ethanol (18.0 g, 94 mmol) in dichloromethane at 0 °C. After stirring for 3 h at ambient temperature, the reaction mixture was washed three times with saturated ammonium chloride solution. The organic phase was dried over sodium sulfate and the solvent was removed under reduced pressure. The product was obtained as brownish solid (25.7 g, 74.3 mmol, 79 %).

m. p. 91 °C.

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3977 (vw), 2975 (vw), 2973 (vw), 1597 (w), 1454 (m), 1436 (m), 1412 (m), 1395 (m), 1355 (vs), 1293 (w), 1241 (w), 1190 (vs), 1177 (vs), 1135 (m), 1094 (m), 1052 (m), 1005 (s), 906 (s), 809 (m), 776 (m), 776 (s), 664 (s), 578 (m), 554 (s), 489 (w).

^{1}H NMR ($CDCl_3$) δ: 2.42 (s, 3H, CH_3), 4.46 (t, 2H, ^3J = 4.9 Hz, CH_2), 4.63 (t, 2H, ^3J = 4.9 Hz, CH_2), 7.29 (d, 2H, ^3J = 7.9 Hz, C*H*), 7.61 (d, 2H, ^3J = 8.2 Hz, C*H*).

^{13}C NMR ($CDCl_3$) δ: 21.8 (CH_3), 47.3 (CH_2), 66.1 (CH_2), 127.8 (*C*H), 130.3 (*C*H), 141.7 (C_q), 145.9 ($C_{qtetrazol}$)).

m/z (DCI+): 348.0 (10), 346.0 (10) (M), 284.1 (22), 282.1 (22), 240.1 (5), 238.1 (5), 198.1 (7), 175.2 (12), 171.1 (4), 155.1 (36), 131.2 (7), 91.1 (100), 90.2 (24), 89.2 (7), 65.2 (23), 63.2 (5), 39.1 (5).

elemental analysis: calcd (%) for ($C_{10}H_{11}BrN_4O_3S$): C 34.59, N 16.14, H 3.19; found: C 34.73, N 16.26, H 3.03,

friction sensitivity: >360 N; impact sensitivity: >100 J.

2.4.2.2 Synthesis of 5-Bromo-1-vinyl-1*H*-tetrazole 1

2-(5-Bromo-1*H*-tetrazol-1-yl)ethyl 4-methylbenzenesulfonate 7 (10.3 g, 29.3 mmol) was suspended in 20 mL of triethylamine and refluxed for 4 h. After addition of 200 mL 2N HCl, the aqueous phase was then extracted 3 times with diethylether. The combined organic phases were then extracted with 80 mL of 2N HCl, saturated sodium carbonate solution and 100 mL of brine. After removal of the solvent in slightly reduced vacuum, the product was recovered by sublimation from the dark brown residue and obtained as colorless crystals (2.9 g, 17 mmol, 57 %).

m. p. 57 °C, dec. 136 °C.

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3128 (vw), 3100 (vw), 2944 (vw), 1734 (vw), 1638 (s), 1424 (s), 1401 (s), 1373 (s), 1259 (w), 1227 (m), 1200 (w), 1108 (vs), 1053 (m), 1017 (m), 962 (w), 944 (m), 962 (m), 802 (w), 720 (vw), 669 (m), 637 (w), 550 (vw), 532 (vw).

^{1}H NMR ($CDCl_3$) δ: 5.50 (d, 1H, ^1J = 1.9 Hz, $^3J_{cis}$ = 8.8 Hz, C*H₂*), 6.19 (d, 1H, ^1J = 1.9 Hz, $^3J_{trans}$ = 15.4 Hz, C*H₂*), 7.92 (dd, 1H, $^3J_{trans}$ = 15.4 Hz, $^3J_{cis}$ = 8.8 Hz, C*H*).

^{13}C NMR ($CDCl_3$) δ: 111.8 (*C*H₂), 125.1(*C*H), 131.9 (C_q).

m/z (DCI+): 175.0 [M+H], 69.

elemental analysis: calcd (%) for ($C_3H_3BrN_4$): C 20.59, N 32.02, H 1.73; found: C 20.92, N 31.82, H 1.91.

friction sensitivity: >120 N; impact sensitivity: >35 J.

2.4.2.3 Synthesis of 1-(1-Vinyl-1*H*-tetrazol-5-yl)hydrazine 8

5-Bromo-1-vinyl-1*H*-tetrazole 1 (2.0 g, 11.6 mmol) was dissolved in 20 mL of 2-propanol. Hydrazine monohydrate (2.3 g, 46.4 mmol) was added and the reaction mixture stirred for 12 h. The formed hydrazinium hydrobromide was filtered off and the solvent removed under reduced pressure. The product was obtained as slightly impure oil, which solidified over several hours

(0.4 g, 3.2 mmol, 27 %).

m. p. 70 °C, dec. 207 °C.

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3426 (vs), 2956 (m), 2918 (m), 2853 (w), 1645 (m), 1580 (m), 1393 (w), 1312 (vw), 1260 (w), 1168 (w), 1099 (m), 1017 (w), 972 (m), 800 (m), 735 (w).

^{1}H NMR (*d6*-DMSO) δ: 4.55 (br. s, 2H, N*H*$_2$), 5.16 (d, 1H, $^3J_{cis}$ = 8.9 Hz, C*H*$_2$), 5.70 (d, 1H, $^3J_{trans}$ = 15.7 Hz, C*H*$_2$), 7.30 (dd, 1H, $^3J_{trans}$ = 15.7 Hz, $^3J_{cis}$ = 8.91 Hz, C*H*), 8.44 (s, 1H, N*H*).

^{13}C NMR (*d6*-DMSO) δ: 105.6 (*C*H$_2$), 126.6 (*C*H), 157.2 (C_q).

m/z (DEI+): 126.2 [M] (18), 99.2 (43), 91.2 (9), 84.2 (18), 82.1 (11), 80.1 (11), 69.2 (10), 68.2 (15), 57.2 (17), 44.1 (15), 43.2 (100), 42.2 (53), 41.2 (18), 39.2 (11), 30.2 (11), 29.1 (24), 28.2 (76), 27.1 (17).

elemental analysis: calcd (%) for ($C_3H_6N_6$*0.2HBr): C 25.32, N 59.06, H 4.39; found: C 24.94, N 59.37, H 4.70.

friction sensitivity: >360 N; impact sensitivity: >50 J.

2.4.2.4 Synthesis of 1-Methyl-1-(1-vinyl-1*H*-tetrazol-5-yl)hydrazine 10

5-Bromo-1-vinyl-1*H*-tetrazole 1 (2.0 g, 11.6 mmol) was dissolved in 30 mL of 2-propanol. Monomethyl hydrazine (1.1 g, 23.2 mmol) was added and the reaction mixture was refluxed for 12 h. The solvent was removed under reduced pressure and the residue was washed with methylene chloride. The residue was extracted using acetonitrile. After removal of the solvent, the product was obtained as colorless solid (1.4 g, 9.9 mmol, 85 %).

m. p. 56 °C, dec. 203 °C.

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3430 (s), 3341 (s), 300 (w), 2964 (m), 2927 (m), 2870 (w), 2801 (vw), 1646 (vs), 1554 (w), 1441 (m), 1421 (s), 1412 (s), 1323 (w), 1261 (m), 1216 (m), 1159 (m), 1099 (m), 1040 (m), 988 (w), 909 (m), 802 (m), 735 (m), 693 (vw), 661 (vw), 617 (vw).

^{1}H NMR (*d6*-DMSO) δ: 3.19 (s, 3H, CH_3), 5.03 (s, 2H, NH_2), 5.05 (d, 1H, $^3J_{cis}$ = 8.91 Hz, CH_2), 5.63 (d, 1H, $^3J_{trans}$ = 15.73 Hz, CH_2), 7.92 (dd, 1H, $^3J_{trans}$ = 15.73 Hz, $^3J_{cis}$ = 8.91 Hz, C*H*).

^{13}C NMR (*d6*-DMSO) δ: 44.3 (N*C*H$_3$), 104.9 (*C*H$_2$), 129.6 (*C*H), 157.2 (C_q).

m/z (DCI+): 141.2 [M], 87.1, 75.

elemental analysis: calcd (%) for ($C_4H_8N_6$): C 34.28, N 59.97, H 5.75; found: C 34.41, N 59.76, H 5.80.

friction sensitivity: >360 N; impact sensitivity: >100 J.

2.4.2.5 Synthesis of Poly-1-vinyl(5-hydrazinyl)-1*H*-tetrazole 11

1-(1-Vinyl-1*H*-tetrazol-5-yl)hydrazine 8 (700 mg, 5.5 mmol) was molten at 85 °C and AIBN (15 mg) was added carefully. Additional 15 mg of AIBN was added two times over 20 min. After 4 h, the polymer was cooled to ambient temperature and washed with 20 mL of water. The polymer was obtained as colorless solid after filtration (130 mg, 19 %).

dec. 203 °C.

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3431 (m), 3250 (m), 3086 (m), 2978 (m), 2926 (m), 1608 (vs), 1520 (m), 1434 (m), 1402 (m), 1374 (m), 1337 (m), 1314 (w), 1262 (w), 1082 (m), 948 (vw), 879 (vw), 821 (vw), 804 (vw), 733 (vw), 697 (vw), 660 (vw), 553 (vw).

elemental analysis: calcd (%) for ($[C_3H_6N_6]_x$): C 28.57, N 66.64, H 4.80; found: C 27.20, N 61.35, H 5.03,

friction sensitivity: >360 N; impact sensitivity: >35 J.

2.4.2.6 Synthesis of Poly-1-vinyl(5-1-methylhydrazinyl)-1*H*-tetrazole 12

1-Methyl-1-(1-vinyl-1*H*-tetrazol-5-yl)hydrazine **10** (300 mg, 2.1 mmol) was molten at 78 °C and AIBN (15 mg) was added carefully. An additional 15 mg of AIBN was added two times over 20 min. After 4 h, the polymer was cooled to ambient temperature and washed with hot dichloromethane and 20 mL of water. The polymer was obtained as colorless solid (260 mg, 87 %).

dec. 276 °C.

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3430 (vs), 3341 (vs), 3225 (m), 3010 (m), 2964 (m), 2927 (m), 2873 (w), 2801 (vw), 1646 (vw), 1554 (vw), 1412 (m), 1382 (m), 1323 (w), 1261 (m), 1216 (m), 1099 (m), 1040 (m), 987 (w), 909 (m), 802 (w), 735 (w), 693 (vw), 658 (vw), 617 (vw).

elemental analysis: calcd (%) for ($[C_4H_8N_6]_x$): C 34.28, N 59.97, H 5.75; found: C 35.44, N 57.49, H 5.45.

friction sensitivity: >360 N; impact sensitivity: >45 J.

2.4.2.7 Synthesis of the 5-azido-1*H*-tetrazole Containing Polymer 13

Poly-1-vinyl(5-hydrazinyl)-1*H*-tetrazole 11 (200 mg) was suspended in 15 mL of 2N HCl. Saturated sodium nitrite solution was added drop wise at 0 °C over 10 min, until the formation of NO_2 was observed. After 10 min, the solid was filtered off and washed with 200 mL of water. The polymer was obtained as a brown solid (120 mg, 60 %).

dec. 174 °C.

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3432 (vs), 2963 (w), 2929 (w), 2851 (vw), 2164 (m), 1697 (w), 1625 (m), 1531 (s), 1442 (w), 1384 (w), 1261 (w), 1177 (w), 1093 (m), 1020 (w), 803(w), 721 (vw), 581 (vw), 523 (vw).

elemental analysis: calcd (%) for ($C_{37}H_{56}N_{51}O_{10}$): C 32.32, N 51.95, H 4.10; found: C 31.46, N 50.53, H 3.99.

friction sensitivity: >160 N; impact sensitivity: >7 J.

2.4.3 Tetrazenes

Iso-propyl-2-aminoacetate hydrochlorid was synthesized according to the literature,[7] 2-(5-bromo-1*H*-tetrazol-1-yl)ethanol (**4a**) according to Bayes,[6] isopropyl 2-(1*H*-tetrazol-1-yl)acetate (**2b**) was prepared according to the literature.[8]

2.4.3.1 Synthesis of (5-Bromo-1*H*-tetrazol-1-yl)-acetic acid isopropyl ester 3b

Crude 1*H*-tetrazol-1-yl-acetic acid isopropyl ester (**2b**) (33.4 g, 214 mmol) and bromine (81.1 g, 508 mmol) were dissolved in a mixture of 350 mL chloroform and 175 mL acetic acid. The solution was stirred at 80 °C under reflux for 48 h. Afterwards the bromine and the acetic acid were removed under reduced pressure. The residue was neutralized with saturated sodium carbonate solution, extracted with ethyl acetate, washed with 2M HCl and saturated sodium carbonate solution. The organic phase was dried over $MgSO_4$ and solvent was removed under reduced pressure. The product was obtained as slightly impure orange oil (26.3 g, 106 mmol, yield 50 %).

IR (KBr) (cm^{-1}): $\tilde{\nu}$ = 3390 (w), 3141 (w), 2986 (m), 2941 (w), 2881 (w), 2160 (w), 1749 (vs),1630 (w), 1542 (w), 1455 (m), 1419 (m), 1377 (s), 1344 (w), 1300 (w), 1272 (m), 1233 (vs),1184 (m), 1147 (w), 1058 (w), 1021 (w), 978 (w), 957 (w), 901 (w), 843 (w), 776 (w), 702(w), 584 (w).

^{1}H NMR ($CDCl_3$): δ = 1.20 (d, 6H, ^3J = 6.3 Hz, CH_3), 5.03 (sept, 1H, ^3J = 6.2 Hz, C*H*), 5.08 (s, 2H, CH_2).

^{13}C NMR ($CDCl_3$, 100 MHz, 25°C): δ = 14.0 (CH_3), 21.3 (CH_3), 48.9 (*C*H), 70.3 (CH_2),135.6 (C_q), 165.0 (*C*O).

m/z (DEI+): 249.0 [M+H] (8), 248.0 [M] (2), 235.0 (11), 233.0 (9), 191.0 (42), 189.0 (43), 164.0 (45), 163.0 (8), 162.0 (43), 134.9 (42), 132.9 (43), 107.9 (22), 105.9 (22), 92.9 (10), 90.9 (10), 55.0 (47), 54.0 (20), 53.0 (23), 43.0 (100), 42.0 (11), 41.0 (31).

$C_6H_9BrN_4O_2$ (247.9909 found M 247.9890).

2.4.3.2 Synthesis of *N*-[5-(*N*-Methyl-hydrazino)-1*H*-tetrazol-1-yl]-acetic Acid Isopropyl Ester 4b

Crude (5-bromo-1*H*-tetrazol-1-yl)-acetic acid isopropyl ester (**3b**) (6.50 g, 26.1 mmol) and of methyl hydrazine (2.40 g, 52.0 mmol) were dissolved in 50 mL propan-2-ol and heated under reflux for 6 h. Afterwards the solution was evaporated to dryness and 50 mL dichloromethane were added. The precipitate was filtered off and the filtrate was concentrated under reduced pressure. The product was obtained as slightly impure orange oil (5.30 g, 24.7 mmol, yield 95 %).

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3337 (m), 3202 (w), 2982 (m), 2938 (m), 2879 (w), 1747 (vs), 1661 (s), 1574 (s), 1450 (m), 1412 (m), 1379 (m), 1281 (m), 1223 (vs), 1147 (m), 1103 (s), 1047 (m), 958 (m), 915 (m), 903 (m), 845 (w), 779 (w), 737 (w), 627 (vw), 589 (vw).

^{1}H NMR (*d6*-DMSO): δ = 1.13 (d, 6H, ^3J = 6.3 Hz, CH_3), 3.09 (s, 3H, NCH_3), 4.90 (sept, 1H, ^3J = 6.2 Hz, CH), 4.73 (s, 2H, NH_2), 5.18 (s, 2H, CH_2).

^{13}C NMR (*d6*-DMSO): δ = 21.4 (CH_3), 29.5 (CH_3), 43.1 (NCH_3), 49.8 (CH_2), 68.8 (CH), 158.3 (C_q), 166.9 (CO).

^{15}N-NMR (*d6*-DMSO) δ: 1.6 (N3), -18.0 (N2), -91.3 (N4), -180.9 (N1), -300.4 (N6), -309.7 (N5).

m/z (DEI+): 214.1 (5) [M], 172.1 (7), 156.1 (10), 155.1 (16), 141.1 (10), 127.1 (5), 101.0 (32), 85.1 (6), 73.1 (26), 56.0 (12), 55.0 (48), 46.0 (6), 45.0 (29), 44.0 (11), 43.0 (100), 42.0 (8), 41.0 (20).

$C_7H_{14}N_6O_2$ (214.1178 found M 214.1166).

2.4.3.3 Synthesis of *N*-[1-(2-Hydroxyethyl)-1*H*-tetrazol-5-yl]-*N*-methyl hydrazine 4a

2-(5-2-(5-Bromo-1*H*-tetrazol-1-yl)-ethanol (**8a**) (4.70 g, 20.0 mmol) and methyl hydrazine (1.90 g, 41.2 mmol) were dissolved in 50 mL propan-2-ol and heated under reflux for 6 h. Afterwards the solution was evaporated to dryness and 50 mL DCM were added. The precipitate was filtered off and the filtrate was concentrated under reduced pressure. The product was obtained as colorless solid (5.30 g, 24.7 mmol, yield 95 %).

m.p. 111.0 - 117.8 °C.

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3350 (s), 3266 (s), 2967 (w), 2926 (w), 2878 (w), 1656 (vs), 1563 (vs), 1455 (m), 1415 (m), 1373 (m), 1340 (w), 1325 (w), 1282 (m), 1233 (m), 1122 (m), 1104 (m), 1069 (vs), 1039 (m), 983 (m), 948 (w), 903 (m), 864 (m), 745 (m), 707 (m), 684 (m), 493 (m).

Raman (200 mW, 25° C, cm^{-1}): $\tilde{\nu}$ = 3351 (40), 3232 (38), 3193 (34), 3028 (32), 2976 (100), 2928 (37), 2882 (38), 2809 (24), 1654 (41), 1566 (35), 1466 (56), 1418 (47), 1378 (32), 1352 (34), 1284 (66), 1268 (59), 1231 (30), 1105 (55), 1071 (29), 987 (19), 950 (23), 864 (52), 692 (91), 633 (54), 523 (28), 498 (27).

^{1}H NMR (*d6*-DMSO) δ: 3.09 (s, 3H, NCH_3), 3.72 (t, 2H, OCH_2), 4.49 (t, 2H, NCH_2), 4.82 (s, 2H, NH_2), 4.96 (br. t, 1H, OH).

^{13}C NMR (*d6*-DMSO) δ: 44.4 (CH_3), 50.8 (OCH_2), 59.5 (NCH_2), 159.2 (C_q).

^{15}N NMR (*d6*-DMSO) δ: -11.0 (N3), -21.9 (N2), -100.1 (N4), -174.5 (N1), -301.6 (N6), 313.3 (N5).

m/z (DEI+): 158.1 [M], 143.1, 127.1, 113.1, 87.1, 69.1, 55.1, 43.1, 31.1, 28.1.

elemental analysis: calcd (%) for $C_4H_{10}N_6O$: C 30.77, H 5.16, N 53.82; found: C 30.63, H 5.13, N 53.29.

2.4.3.4 Synthesis of 1,4-bis[1-(2-Hydroxyethyl)-1*H*-tetrazol-5-yl]-1,4-dimethyl-2-tetrazene 7a

To a solution of *N*-[1-(2-hydroxyethyl)-1*H*-tetrazol-5-yl]-*N*-methylhydrazine (**9a**) (0.25 g, 1.70 mmol) in a mixture of 2 mL water and 0.5 mL acetic acid 25 mL of a saturated solution of bromine in water was added dropwise at 0 °C. The precipitate was filtered off and evaporated to dryness. The product was obtained as colorless solid (0.13 g, 0.45 mmol, yield 53 %).

IR (KBr) (cm^{-1}): $\tilde{\nu}$ = 3347 (m), 2972 (w), 2944 (w), 2885 (w), 1717 (w), 1636 (w), 1572 (vs), 1470 (m), 1444 (m), 1417 (m), 1381 (w), 1360 (w), 1337 (w), 1295 (w), 1274 (w), 1261 (w), 1224 (m), 1149 (m), 1106 (m), 1098 (m), 1059 (m), 1036 (w), 1015 (m), 978 (w), 945 (w), 857 (w), 802 (w), 728 (m), 696 (m), 668 (m), 639 (w), 551 (w); 497 (w), 459 (w).

Raman (200 mW, 25° C, cm^{-1}): $\tilde{\nu}$ = 3022 (3), 2973 (5), 2944 (5), 1611 (23), 1502 (100), 1463 (21), 1447 (18), 1410 (32), 1382 (9), 1360 (7), 1308 (4), 1278 (4), 1240 (15), 1125 (5), 1105 (10), 1057 (3), 973 (3), 856 (6), 672 (9), 537 (4), 362 (5), 331 (7), 257 (3).

^{1}H NMR (*d6*-DMSO): δ = 3.61 (s, 3H, CH_3), 3.76 (t, 2H, ^{3}J = 5.82 Hz, OCH_2), 4.58 (t, 2H, ^{3}J = 5.82 Hz, CH_2), 5.14 (broad s, 1H, O*H*).

^{13}C NMR (*d6*-DMSO): δ = 35.5 (N*C*H$_3$), 51.3 (OCH_2), 59.1 (NCH_2), 154.2 (C_q).

^{15}N-NMR (*d6*-DMSO) δ: 2.0 (N6), -2.4 (N3), -13.2 (N2), -83.5 (N4), -169.5 (N1), -245.4 (N5).

m/z (DEI+): 312.3 [M] (7.6), 284.3 (8.5), 225.3 (1.7), 198.3 (3.8), 172.3 (16.9), 142.3 (75.1), 113.2 (90.7), 100.2 (61.6), 45.2 (100), 28.2 (59.4).

elemental analysis: calcd (%) for $C_8H_{16}N_{12}O_2$: C 30.77, H 5.16, N 53.58; found: C 30.59, H 5.40, N 53.67.

impact sensitivity: 5 J friction sensitivity: 240 N.

2.4.3.5 Synthesis of 1,4-Bis[1-isopropoxycarbonylmethyl-1*H*-tetrazol-5-yl]-1,4-dimethyl-2-tetrazene 7b

To a solution *N*-[5-(*N*-methyl-hydrazino)-1*H*-tetrazol-1-yl]-acetic acid isopropyl ester (**9b**) (6.30 g, 29.4 mmol) in a mixture of 20 mL water and 5 mL acetic acid 400 mL of a saturated solution of bromine in water was added dropwise at 0 °C. The precipitate was filtered off and evaporated to dryness. The product was obtained as colorless solid (5.65 g, 13.3 mmol, yield 60 %).

IR (KBr) (cm^{-1}): $\tilde{\nu}$ = 3487 (w), 3395 (w), 2999 (m), 2984 (m), 2965 (w), 2944 (w), 2884 (w), 1754 (s), 1627 (w), 1569 (vs), 1470 (m), 1450 (m), 1414 (m), 1383 (m), 1348 (w), 1329 (w), 1278 (w), 1218 (s), 1181 (w), 1144 (m), 1106 (s), 1083 (m), 1007 (m), 959 (m), 944 (w), 903 (w), 848 (m), 732 (w), 711 (w), 658 (m), 586 (w), 476 (w), 458 (w).

Raman (200 mW, 25° C, cm^{-1}): $\tilde{\nu}$ = 2999 (26), 2963 (32), 2945 (24), 1753 (11), 1601 (44), 1500 (100), 1471 (24), 1445 (24), 1408 (34), 1351 (17), 1328 (11), 1226 (23), 1188 (10), 1149 (8), 1104 (23), 1010 (6), 971 (6), 904 (9), 866 (20), 835 (10), 770 (7), 723 (9), 683 (7), 593 (5), 537 (7), 417 (13), 381 (19), 290 (19), 227 (13).

^{1}H NMR (*d6*-DMSO,): δ = 1.13 (d, 6H, ^{3}J = 6.32 Hz, CCH_3), 3.58 (s, 3H, NCH_3), 4.91 (sept, 1H, ^{3}J = 6.32 Hz, C*H*), 5.53 (s, 2H, CH_2).

^{13}C NMR (*d6*-DMSO): δ = 21.9 (CCH_3), 35.3 (NCH_3), 50.4 (*C*H), 70.5 (CH_2), 154.6 (C_q), 166.9 (*C*O).

m/z (DEI+): 424.3 [M] (89.1), 410.3 (6.6), 337.3 (8.7), 282.3 (1.9), 226.3 (42.0), 199.3 (47.8), 156.3 (26.3), 127.2 (25.7), 113.2 (15.9), 101.2 (6.7), 84.2 (8.4), 73.2 (13.5), 55.2 (20.1), 43.2 (17.8).

impact sensitivity: 7 J friction sensitivity: 160 N

2.4.2.6 Synthesis of 1,4-Bis[1-carboxymethyl-1*H*-tetrazol-5-yl]-1,4-dimethyl-2-tetrazene 8

A suspension of bis(1,1'-methyl-1,1'-(iso-propyl-2-(1H-tetrazolyl) acetate))tetrazene (0.10 g, 0.24 mmol) in a 10M solution of NaOH in water was heated until the solid was dissolved. Afterwards concentrated hydrochloric acid was added to the cooled solution and the precipitate was filtered off. The product was obtained as colorless solid (0.07 g, 0.19 mmol, yield 78 %).

IR (KBr) (cm^{-1}): $\tilde{\nu}$ = 3436 (m), 3012(m), 2972 (m), 2945 (w), 2718 (w), 2592 (w), 2515 (w), 1786 (w), 1747 (s), 1738 (s), 1607 (m), 1565 (vs), 1478 (m), 1433 (w), 1423 (w), 1413 (w), 1400 (m), 1351 (vw), 1332 (vw), 1262 (vw), 1207 (s), 1140 (m), 1100 (m), 1075 (m), 1020 (w), 1009 (m), 993 (m), 965 (vw), 942 (vw), 893 (vw), 854 (vw), 818 (m), 798 (m), 733 (vw), 728 (vw), 693 (w), 689 (w), 565 (m), 648 (m), 463 (w).

Raman (200 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 3044 (7), 3014 (19), 2973 (37), 2947 (16), 1739 (15), 1603 (94), 1492 (92), 1467 (100), 1446 (41), 1404 (61), 1354 (35), 1330 (18), 1312 (16), 1271 (11), 1235 (27), 1185 (16), 1117 (19), 1103 (27), 964 (9), 943 (8), 898 (14), 855 (24), 795 (12), 733 (13), 694 (9), 651 (9), 583 (13), 528 (9), 428 (26), 380 (15), 327 (20), 291 (20), 249 (15).

^{1}H NMR (*d6*-DMSO): δ = 3.62 (s, 6H, CH_3), 5.46 (s, 2H, CH_2), 13.68 (br.s, 1H, COO*H*).

^{13}C NMR (*d6*-DMSO): δ = 35.3 (*C*H$_3$), 50.8 (*C*H$_2$), 154.7 (C_q), 169.0 (*C*O).

^{15}N-NMR (*d6*-DMSO) δ: 3.1 (N6), -3.6 (N3), -12.7 (N2), -84.3 (N4), -175.6 (N1), -243.7 (N5).

m/z (DEI+): 340.4 [M] (6), 322.2 (16), 256.3 (13), 212.2 (14), 211.2 (13), 191.1 (10), 189.1 (9), 177.3 (11), 167.2 (9), 164.1 (13), 162.2 (10), 161.2 (9), 152.2 (9), 149.2 (32), 137.3 (8), 135.2 (37), 133.1 (10), 129.2 (12), 127.2 (21), 125.3 (10), 121.2 (8), 113.2 (9), 112.2 (14), 111.2 (23), 109.2 (10), 105.2 (11), 99.2 (9), 98.2 (13), 97.2 (36), 96.2 (9), 95.2 (16), 91.2 (10), 85.2 (19), 84.2 (18), 83.2 (42), 82.1 (27), 81.2 (29), 80.0 (11), 79.1 (8), 77.1 (10), 71.2 (31), 70.2 (21), 69.2 (58), 68.2 (11), 67.2 (12), 60.1 (9), 57.1 (52), 56.1 (19), 55.1 (53), 54.1 (11), 45.1 (9), 44.1 (43), 43.1 (100), 41.1 (34).

elemental analysis: calcd (%) for $C_8H_{12}N_{12}O_4$: C 28.24, H 3.55, N 49.40; found: C 28.25, H

3.95, N 49.09.

impact sensitivity: 5 J friction sensitivity: 240 N.

2.4.4 Alkylene bridged Bis-5-azidotetrazoles

1,2,-bis(1-tetrazolyl)ethane,[9] 1-methyl-1,2,-bis(1-tetrazolyl) ethane[10] and 1,2,-bis(1-tetrazolyl)butane[11] were prepared after literature. The synthesis of the bis(5-bromo-1*H*-tetrazolyl)alkanes is given in *paragraph 2.4.1.2*.

2.4.4.1 General Synthesis of Bis(5-hydrazinyl-1*H*-tetrazolyl)alkanes

To a slurry of bis(5-bromo-1*H*-tetrazolyl)alkane (2.9 mmol) in 30 mL 2-propanol, hydrazine hydrate (0.9 g, 18.0 mmol) was added and the reaction mixture was refluxed for 10 h, while the product precipitated as colorless solid. The hot suspension was filtered and the colorless product washed with 30 mL of hot 2-propanol. In case of **11a** and **11b,** the residue was recrystallized from 10 mL of hot water.

2.4.4.2 1,2-Bis(5-hydrazinyl-1*H*-tetrazol-1-yl)ethane 11a

yield: 65 %.

m. p. 155 °C, dec. 206 °C.

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3559 (m), 3306 (s), 3204 (s), 3163 (m), 3049 (m), 1639 (m), 1599 (vs), 1544 (m), 1459 (m), 1434 (w), 1331 (w), 1269 (w), 1167 (w), 1107 (m), 1078 (m), 975 (w), 843 (vw), 704 (w), 638 (w).

^{1}H NMR ($CDCl_3$) δ: 4.43 (s, 2H, NCH_2), 4.62 (s, 2H, NH_2), 8.11 (s, 1H, NH).

^{13}C NMR ($CDCl_3$) δ: 44.9 (NCH_2), 158.6 (C_q).

m/z (DEI) 226 (1 %) (M), 169 (14), 168 (6), 153 (4), 126 (4), 114 (10), 113 (8), 112 (10), 111 (37), 101 (3), 99 (3), 98 (6), 97 (5), 96 (4), 86 (23), 85 (35), 84 (13), 71 (9), 70 (14), 69 (100), 68

(8), 67 (5), 58 (8), 57 (28), 56 (25), 55 (35), 54 (8), 53 (12), 45 (4).

elemental analysis: calcd (%) for $C_4H_{10}N_{12}$*H_2O*0.2 HBr: calc. C 18.45, H 4.72, N 64.55; found: C 18.92, H 4.78, N 64.85.

2.4.4.3 1,4-Bis(5-hydrazinyl-1*H*-tetrazol-1-yl)butane 11c

yield: 82 %.

m. p. 186 °C, dec. 191 °C.

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3329 (m), 3292 (m), 3023 (w), 1588 (vs), 1559 (s), 1521 (m), 1474 (m), 1457 (m), 1410 (m), 1377 (m), 1338 (m), 1294 (m), 1252 (m), 1227 (w), 1155 (w), 1109 (s), 1082 (vs), 1020 (w), 991 (w), 924 (m), 819 (s), 740 (m).

^{1}H NMR (*d6*-DMSO) δ: 1.66 (br m, 2H, CCH_2), 4.18 (br t, 2H, NCH_2), 4.41 (s, 2H, NH_2), 8.01 (s, 1H, N*H*).

^{13}C NMR (*d6*-DMSO) δ: 26.0 (C*C*H$_2$), 45.1 (N*C*H$_2$), 158.7 (C_q).

elemental analysis: calcd (%) for $C_6H_{14}N_{12}$*0.17 HBr: calc. C 26.92, H 5.33, N 62.78; found: C 27.40, H 5.18, N 62.55.

2.4.4.4 General Synthesis of Bis(5-azido-1*H*-tetrazolyl)alkanes

Bis(5-hydrazinyl-1H-tetrazolyl)alkane (3.0 mmol) was dissolved in 30 mL of 2N hydrochloric acid. An excess of saturated sodium nitrite solution in water was added drop wise at 0 °C until the formation of gaseous NO_2 was observed. In cases of **12a** and **12c**, the product precipitated as colorless solid, was filtered off and washed with 100 mL of cold water. In case of **12b**, the clear brownish solution was extracted 3 times with dichloromethane. The organic phases were dried with sodium sulfate and the solvent was removed under reduced pressure. The product was obtained as slightly brownish oil, which solidified after two to three days.

2.4.4.5 1,2-Bis(5-azido-1*H*-tetrazol-1-yl)ethane 12a

yield: 74 %.

m. p. 110 °C, dec. 169 °C.

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3431 (w), 2172 (vs), 1629 (vw), 1539 (vs), 1474 (m), 1446 (vw), 1384 (vw), 1330 (w), 1265 (w), 1183 (w), 1095 (w), 1073 (vw), 723 (vw), 684 (w), 527 (vw).

^{1}H NMR (*d6*-DMSO) δ: 4.60 (s, 1H, CH_2).

^{13}C NMR (*d6*-DMSO) δ: 45.2 (CH_2), 153.2 (C_q).

^{15}N NMR (*d6*-DMSO) δ: 9.1 (N3), -14.1 (N2), -75.8 (N4), -142.2 (N6), -147.0 (N7), -168.6 (N1), -300.7 (N5).

m/z (DEI+): 249.0772 (M+H) (6), 248.0743 (M) (77), 138.0530 (13), 124.0378 (55), 109.0405 (11), 82.0023 (4), 80.9947 (8), 68.9947 (10), 68.0000 (22), 67.0056 (12), 56.0261 (9), 55.0197 (41), 54.0256 (13), 54.0128 (51), 54.0006 (100), 53.0059 (43), 44.0343 (15), 43.0745 (33), 42.1062 (63), 41.0973 (19).

$C_4H_4N_{14}$ (248.0743 found M 248.0743).

2.4.4.6 1,2-Bis(5-azido-1*H*-tetrazol-1-yl)-1-methylethane 12b

yield: 66 %.

m. p. 77 °C, dec. 170 °C.

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2997 (vw), 2959 (vw), 2926 (vw), 2168 (vs), 1709 (w), 1622 (w), 1530 (vs), 1467 (m), 1383 (w), 1356 (w), 1315 (w), 1280 (vw), 1261 (m), 1191 (m), 1060 (w), 1028 (w), 976 (vw), 914 (vw), 876 (vw), 802 (vw), 721 (vw), 667 (w), 585 (vw), 526 (vw).

^{1}H NMR (*d6*-DMSO) δ: 1.60 (d, 3H, ^3J = 6.83 Hz, CH_3), 4.60 (d, 2H, ^3J = 6.23 Hz, CH_2), 4.86 (sex, 1H, ^3J = 6.23 Hz, 6.83 Hz, C*H*).

^{13}C NMR (*d6*-DMSO) δ: 17.1 (CH_3), 49.7 (*C*H), 53.4 (CH_2), 152.7 (C_q), 153.2 (C_q).

^{15}N NMR (*d6*-DMSO) δ: 9.1 ($N3_a$), 8.9 ($N3_b$), -13.9 ($N2_a$), -17.5 ($N2_b$), -75.8 ($N4_a$), -76.1 ($N4_b$), -143.0 ($N6_a$), -143.1 ($N6_b$), -147.4 (N7), -177.8 (N1), -301.4 (N5).

m/z (DEI+): 232.0895 (M) (42), 138.0515 (11), 124.0372 (115), 95.0149 (9), 68.9947 (11), 68.0149 (19), 56.0472 (16), 54.0065 (100), 53.0104 (22), 43.9258 (14), 42.9305 (29), 41.9316 (19), 40.8796 (68).

$C_5H_6N_{14}$ (262.0895 found M 262.0900).

2.4.4.7 1,4-Bis(5-azido-1*H*-tetrazol-1-yl)butane 12c

yield: 79 %.

m. p. 94 °C, dec. 164 °C.

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2952 (vw), 2922 (vw), 2849 (vw), 2168 (vs), 1628 (w), 1533 (vs), 1473 (m), 1451 (m), 1482 (w), 1355 (w), 1331 (w), 1307 (w), 1258 (w), 1243 (m), 1219 (m), 1172 (w), 1097 (m), 1079 (w), 1008 (vw), 985 (vw), 787 (vw), 778 (vw), 723 (vw), 697 (vw), 643 (vw), 527 (vw).

^{1}H NMR (*d6*-DMSO) δ: 1.78 (s, 1H, CH_2), 4.16 (s, 1H, CH_2).

^{13}C NMR (*d6*-DMSO) δ: 25.6 (CCH_2), 46.0 (NCH_2), 152.7 (C_q)

^{15}N NMR (*d6*-DMSO) δ: 8.4 (N3), -13.1 (N2), -75.0 (N4), -142.9 (N6), -146.0 (N7), -163.0 (N1), -300.6 (N5).

m/z (DEI+): 277.3 (M+H) (1), 276.3 (1), 245.2 (2), 206.3 (25), 165.3 (8), 124.3 (6), 109.3 (9), 95.2 (37), 81.2 (5), 68 (15), 56.2 (22), 55.2 (100), 54.2 (18), 53.2 (10), 43.2 (7), 42.2 (25), 40.2 (10), 39.2 (17), 29.2 (18), 28.2 (28), 27.2 (18).

$C_6H_9N_{14}$ (276.1056 [M]; 277.1135 [M+H]; found 277.1134 [M+H]).

2.4.5 References

(1) J. Gonda, P. Kristian, J. Sipos, *Czech. Patent 239396*, **1986**.

(2) C. Ortiz Mellet, J. L. Jimenez Blanco, J. M. Garcia Fernandez, J. Fuentes, *J. Carbohydrate Chemistry* **1995**, *14*, 1133-1152.

(3) P. N. Gaponik, V. P. Karavai, Yu. V. Grigor'ev, *Khimiya Geterotsiklicheskikh Soedinenii* **1985**, *11*, 1521-1524.

(4) P. J. van Koningsbruggen, Y. Garcia, O. Kahn, L. Fournes, H. Kooijman, A. L. Spek, J. G. Haasnoot, J. Moscovici, K. Provost, A. Michalowicz, F. Renz, P. Guetlich, *Inorg. Chem.* **2000**, *39*, 1 891-1900.

(5) P. J. van Koningsbruggen, Y. Garcia, H. Kooijman, A. L. Spek, J. G. Haasnoot, O. Kahn, J. Linares, E. Codjovi, F. Varret, *Dalton Trans.*, **2001**, *4*, 466-471.

(6) D. E. Bayes, *Eu. Pat. EP0117368A1*, **1982**.

(7) J. Casas, R. Grigg, C. Najera, J. M. Sansano, *Eu. J. Org. Chem.* **2001**, *10*, 1971-1982.

(8) M. Konstantinov, A. Nikolov, N. Tsoneva, N. Petcov, *Appl. Biochem. Biotechnol.* **1992**, *33*, 177-182.

(9) P. N. Gaponik, V. P. Karavai, Yu. V. Grigor'ev, *Khimiya Geterotsiklicheskikh Soedinenii* **1985**, *11*, 1521-1524.

(10) P. J. van Koningsbruggen, Y. Garcia, O. Kahn, L. Fournes, H. Kooijman, A. L. Spek, J. G. Haasnoot, J. Moscovici, K. Provost, A. Michalowicz, F. Renz, P. Guetlich, *Inorg. Chem.* **2000**, *39*, 1891-1900.

(11) P. J. van Koningsbruggen, Y. Garcia, H. Kooijman, A. L. Spek, J. G. Haasnoot, O. Kahn, J. Linares, E. Codjovi, F. Varret, *Dalton Trans.*, **2001**, *4*, 466-471.

2.5 Crystallographic Data

2.5.1 Polymers Formed by Polycondensation Reactions

2.5.1.1 Polymer Based on 1-(2-hydroxyethyl)-1*H*-tetrazolyl)methyl hydrazine

CCDC-695558 (10), -695556 (13) and -695557 (3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

	10	**13**	**3**
Formula	$C_6H_{13}N_3O_2S$	$C_6H_{12}N_6O_2$	$C_4H_{10}N_6O$
M_r [g mol^{-1}]	191.25	200.22	158.18
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
a [Å]	6.8896(8)	11.808(2)	7.7148(12)
b [Å]	7.0185(7)	7.9679(16)	7.5255(10)
c [Å]	20.2201(19)	11.460(2)	12.7433(18)
α [°]	90	90	90
β [°]	89.808(8)	112.64(3)	100.655(13)
γ [°]	90	90	90
V [Å³]	977.73(18)	995.2(3)	727.09(18)
Z	4	4	4
F(000)	408	424	336
$\rho_{calc.}$ [g cm^{-3}]	1.299	1.336	1.445
μ [mm^{-1}]	0.300	0.104	0.111
2 theta [°]	53.98	49.99	51.99
Index range	$-8 \leq h \leq 8$	$-14 \leq h \leq 13$	$-9 \leq h \leq 9$
	$-8 \leq k \leq 8$	$-9 \leq k \leq 9$	$-5 \leq k \leq 9$
	$-25 \leq l \leq 25$	$-13 \leq l \leq 13$	$-13 \leq l \leq 15$
λ [Å]	0.71073	0.71073	0.71073
T [K]	200(2)	200(2)	200(2)
Reflections collected	10765	8920	3647
Unique reflections	2124	1742	1424
Parameter	138	153	141
S	1.119	1.126	1.074
R_{int}	0.0819	0.0460	0.0281
R_1/ wR_2 [$I>2\sigma(I)$]	0.0655/0.1454	0.0428/0.1030	0.0344/0.0858
R_1/ wR_2	0.0826/0.1568	0.0495/ 0.1082	0.0464/ 0.0938

2.5.1.2 Nitrogen-rich Energetic Polymers Based on Alkylene Bridged Bis-(1-methyl-tetrazolylhydrazines)

CCDC-752242 (**26a**) and 752241 (**27a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

	22a	**26a**	**27a**
Formula	$C_4H_6N_8$	$C_4H_4N_8Br_2$	$C_6H_{14}N_{12}$
M_r [g mol^{-1}]	166.17	323.97	254.29
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/n$	*Pbcn*	$C2/c$
a [Å]	7.2530(2)	15.4697(4)	10.8128(4)
b [Å]	5.3748(2)	13.4925(3)	7.5255(10)
c [Å]	9.0328(3))	13.4826(3)	10.3639(4)
α [°]	90	90	90
β [°]	102.776(3)	90	93.310(3)
γ [°]	90	90	90
V [Å³]	343.41(2)	2814.16(11)	1114.82(7)
Z	2	12	4
F(000)	172	1694	536
$\rho_{calc.}$ [g cm^{-3}]	1.607	2.309	1.515
μ [mm^{-1}]	0.120	8.616	0.112
2 theta [°]	50.00	54.99	52.47
Index range	$-8 \leq h \leq 8$ $-6 \leq k \leq 6$ $-10 \leq l \leq 10$	$-14 \leq h \leq 20$ $-17 \leq k \leq 16$ $-17 \leq l \leq 17$	$-11 \leq h \leq 12$ $-9 \leq k \leq 13$ $-12 \leq l \leq 12$
λ [Å]	0.71073	0.71073	0.71073
T [K]	200(2)	200(2)	200(2)
Reflections	3005	14768	7360
Unique reflections	609	3207	1113
Parameter	67	214	141
S	1.099	0.882	1.074
R_{int}	0.0278	0.0665	0.0281
R_1/ wR_2 [I>2σ(I)]	0.0280/0.0638	0.0356/0.0705	0.0491/0.1182
R_1/ wR_2	0.0334/0.0676	0.0717/0.0764	0.0607/0.1264

2.5.2 Polymers Formed by Radical Polymerization

CCDC-742853 (**1**), -742852 (**7**) and -742851 (**10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

	1	**7**	**10**
Formula	$C_3H_3N_4Br$	$C_{10}H_{11}BrN_4O_3S$	$C_4H_8N_6$
M_r [g mol^{-1}]	175.00	347.20	140.16
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	*Pnma*	*P*21/*c*	*P*21/*n*
a [Å]	7.4368(2)	6.9438(2)	7.1943(3)
b [Å]	6.4442(3)	26.6687(5)	12.6152(5)
c [Å]	11.8738(3)	7.6877(2)	7.8085(3)
α [°]	90	90	90
β [°]	90	113.713(3)	91.199(3)
γ [°]	90	90	90
V [Å^3]	569.04(3)	1303.43(6)	708.53(5)
Z	4	4	4
F(000)	336	696	296
$\rho_{calc.}$ [g cm^{-3}]	2.043	1.769	1.314
μ [mm^{-1}]	7.11	3.323	0.13
2 theta [°]	53.99	54.00	52.00
Index range	$-9 \leq h \leq 9$ $-8 \leq k \leq 8$ $-15 \leq l \leq 15$	$-8 \leq h \leq 8$ $-34 \leq k \leq 34$ $-9 \leq l \leq 9$	$-8 \leq h \leq 8$ $-15 \leq k \leq 15$ $-9 \leq l \leq 9$
λ [Å]	0.71073	0.71073	0.71073
T [K]	200(2)	200(2)	200(2)
Reflections	7395	14131	5187
Unique reflections	678	2829	1391
Parameter	58	216	111
S	1.154	1.054	0.978
R_{int}	0.0494	0.0312	0.0286
R_1/ wR_2 [I>2σ(I)]	0.0197/ 0.0457	0.0347/ 0.0538	0.0731 / 0.1321
R_1/ wR_2	0.0249/ 0.0516	0.0224/ 0.0496	0.0441/ 0.1160

2.5.3.1 Synthesis of Functionalized Tetrazenes as Energetic Compounds

	6	**7a**	**7b**	**8**
Formula	$C_4H_6N_6O$	$C_8H_{16}N_{12}O_2$	$C_{14}H_{24}N_{12}O_4$	$C_8H_{12}N_{12}O_4$
M_r [g mol^{-1}]	154.15	312.33	424.45	340.26
Crystal system	orthorhombic	orthorhombic	triclinic	monoclinic
Space group	*P*cnn	*P*bca	*P*bca	*P*21/c
a [Å]	12.8213(7)	8.4761(4)	6.2353(3)	11.0279(4)
b [Å]	15.9442(7)	9.8701(5)	9.1720(4)	15.4282(4)
c [Å]	6.1647(4)	16.1109(8)	9.7460(6)	8.9824(3)
α [°]	90	90	114.736(5)	90
β [°]	90	90	94.422(4)	113.594(4)
γ [°]	90	90	92.195(4)	90
V [Å³]	1260.22(12)	1347.83	503.19(5)	1400.51(8)
Z	8	4	1	4
F(000)	640	656	224	704
$\rho_{calc.}$ [g cm^{-3}]	1.625	1.539	1.401	1.614
μ [mm^{-1}]	0.13	0.12	0.108	0.13
2 theta [°]	52.98	51.99	53.00	52.00
Index range	$-16 \leq h \leq 16$	$-12 \leq h \leq 12$	$-7 \leq h \leq 7$	$-7 \leq h \leq 7$
	$-20 \leq k \leq 20$	$-10 \leq k \leq 10$	$-11 \leq k \leq 11$	$-11 \leq k \leq 11$
	$-7 \leq l \leq 7$	$-19 \leq l \leq 19$	$-12 \leq l \leq 12$	$-12 \leq l \leq 12$
λ [Å]	0.71073	0.71073	0.71073	0.71073
T [K]	200(2)	200(2)	200(2)	200(2)
Reflections	13138	19337	12103	11242
Unique reflections	1299	1319	2072	2744
Parameter	124	133	161	227
S	1.044	1.058	1.112	1.057
R_{int}	0.0299	0.0264	0.0260	0.0299
R_1/ wR_2 [I>2σ(I)]	0.0543/ 0.1145	0.0271/0.0702	0.0407/0.0858	0.0429 / 0.0799
R_1/ wR_2	0.0393/ 0.1023	0.0381/0.0782	0.0381/0.0796	0.0291 / 0.0740

2.5.3.2 Alkylene bridged Bis-5-azidotetrazoles

CCDC-724763 (**11a**) and -724764 (**12a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

	11a	**12a**
Formula	$C_4H_{14}N_{12}O_2$	$C_4H_4N_{14}$
M_r [g mol^{-1}]	262.27	248.21
Crystal system	triclinic	triclinic
Space group	*P*-1	*P*-1
a [Å]	6.536(3)	6.2749(4)
b [Å]	6.5993(18)	6.5994(5)
c [Å]	6.777(4)	6.7695(5)
α [°]	83.04(3)	108.840(6)
β [°]	72.78(4)	106.017(6)
γ [°]	84.22(3)	97.143(6)
V [Å³]	276.5(2)	247.89(3)
Z	1	1
F(000)	138	126
$\rho_{calc.}$ [g cm^{-3}]	1.575	1.663
μ [mm^{-1}]	0.128	0.130
2 theta [°]	55.99	53.97
Index range	$-8 \leq h \leq 8$	$-8 \leq h \leq 8$
	$-8 \leq k \leq 8$	$-8 \leq k \leq 8$
	$-8 \leq l \leq 8$	$-8 \leq l \leq 8$
λ [Å]	0.71073	0.71073
T [K]	200(2)	200(2)
Reflections	3162	5540
Unique reflections	1331	1078
Parameter	110	90
S	1.131	1.039
R_{int}	0.0354	0.0285
R_1/ wR_2 [I>2σ(I)]	0.0299/0.0785	0.0285/0.0778
R_1/ wR_2	0.0354/0.0809	0.0351/ 0.0806

3. Investigation of 1*H*-Tetrazole-5-carboxylic Acid as Energetic Precursor

Abstract: 1*H*-Tetrazole-5-carboxylic acid was used for the preparation of energetic salts of earth alkali and transition metal cations. Moreover, esterfication and substitution reactions were investigated to introduce energetic moieties. The preparation of alkylated derivatives of the tetrazole-5-carboxylic acid bearing functionalities like hydroxyl or amine groups to moiety could lead to a monomer suitable for polycondensation reactions.

3.1 Introduction

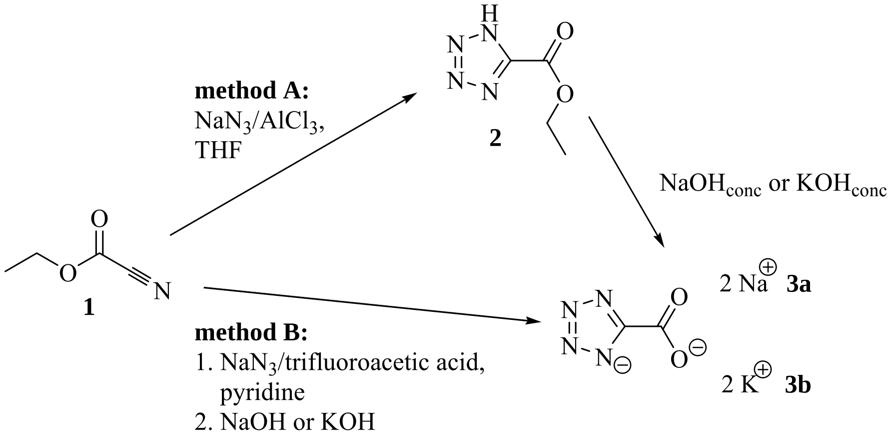
The ambition to investigate the field of tetrazole-5-carboxylic acid chemistry was the synthesis of new tetrazole-containing polymers with a low content of carbon. Therefore, the tetrazole-5-carboxylate anion appeared to be the ideal candidate, because of its neutral oxygen balance (with CO, H_2O and N_2 as decomposition products). Another advantage of the tetrazole-5-carboxylic acid is its improved thermal and physical stability, compared to 5-nitrotetrazolate (friction sensitivity in case of the potassium, rubidium and cesium salt of 5-nitrotetrazolate[1] >5 N and impact sensitivity in case of the hydrazine, diaminoguanidine and triaminoguanidine salt of 5-nitrotetrazolate[2] >4 J). The resulting polymers based on the 1*H*-tetrazole-5-carboxylic acid should possess a high decomposition point along with a low sensitivity towards physical stimuli.

3.2 Trials of Esterfication and Substitution reactions of 1*H*-Tetrazole-5-carboxylic Acid

Substitution reactions of tetrazolate anions are common methods for the synthesis of alkylated tetrazoles.[3] Another method for preparation of derivatives of tetrazole-5-carboxylic acid is the esterfication reaction of the carboxylic acid.

3.2.1 Synthesis of Sodium and Potassium 1*H*-Tetrazole-5-carboxylate and Ethyl 1*H*-Tetrazole-5-carboxylate

To synthesize complexes of 1*H*-tetrazole-5-carboxylic acid, two different preparation pathways were investigated. The first method was the synthesis of ethyl 1*H*-tetrazole-5-carboxylate (**2**) developed by Behringer.[4] The formed ethyl ester **2** was converted into the corresponding disodium salt of 1*H*-tetrazole-5-carboxylic acid (**3a**) by treatment with a concentrated solution of sodium hydroxide in hot water. In the second step, the solution was acidified to pH 1 and the desired metal nitrate was added (*Scheme 1,* **method A**). The second pathway was to generate directly the dipotassium salt of the tetrazole-5-carboxylic acid (**3b**) according to a European patent.[5] The yields of this reaction were reported with up to 99 % in case of **3a** and 90 % in case of the **3b**. A further investigation of the formed colorless powder revealed, that it contained a varying amount of the corresponding carbonates (between 10 % to 20 %), a result of the decomposition of the used ethyl cyanoformate (**1**) during the reaction. Carrying out the reaction several times, only yields of 60 % could be achieved (*Scheme 1,* **method B**). Compared with the yield of **method A** (10 % to 15 %), **method B** was more suitable to prepare large quantities of the 1*H*-tetrazole-5-carboxylate. The advantage of **method A** was the purity of the formed product. Instead of **method B**, **method A** yields pure product and the formed salt can be used stoichiometrically. Compounds **3a** and **3b** yielded by **method B** were always contaminated by carbonate and also contained a varying amount of crystal water. In this work, the 1*H*-tetrazole-5-carboxylate of **method B** was used, because a stoichiometric usage of **3** and the desired cation was not necessary.



Scheme 1. Method A and **method B** for the synthesis of **3a** or **3b**.

3.2.2 Trials of the Synthesis of 1*H*-Tetrazole-5-carboxylate Esters

In order to obtain new energetic compounds based on the 1*H*-tetrazole-5-carboxylic acid, esterfication reactions of the anion were investigated. To date, several esters based on the 1*H*-tetrazole-5-carboxylic acid are known.[6] Potential energetic compounds based on the 1*H*-tetrazole-5-carboxylic acid are given in *Figure 1.*

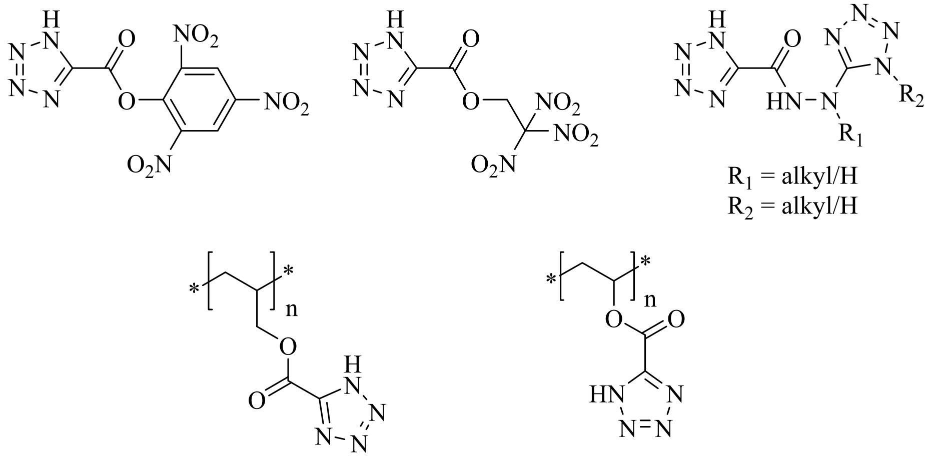
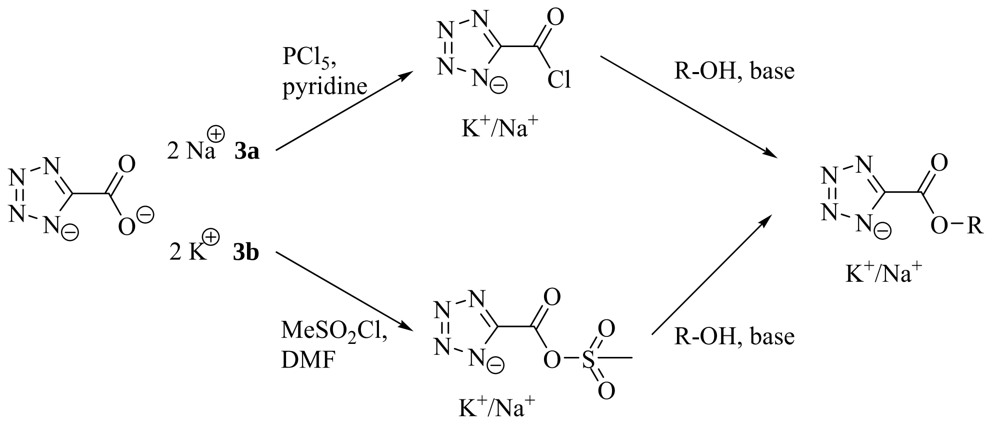


Figure 1. Potential energetic compounds based on 1*H*-tetrazole-5-carboxylic acid.

The comparison of the known esters and the potential energetic esters reveals, that the reported esterfication reactions were carried out with reactive alcohols or amines, whereas the sought energetic compounds are formed by the reaction of two deactivated reaction partners. Therefore, esterfication reactions of alkyl alcohols and aromatic alcohols were investigated to optimize the reaction.

The esterfication reactions reported are all carried out by an activation of the carboxylate moiety and a subsequent reaction with the alcohol or amine. The carboxylic acid group is either activated by a chlorination using PCl_5 and pyridine[7] or by methanesulfonyl chloride[8] (*Scheme 2*).



Scheme 2. Esterfication reactions of the 1*H*-tetrazole-5-carboxylic acid.

Carrying out the reaction with alkyl alcohols like ethanol or with aromatic alcohols like benzyl alcohol, we were not able to isolate the pure ester. The product could be detected by mass spectrometry in some cases, but purification neither by extraction nor by column chromatography was successful. Because of these drawbacks, we decided to leave the esterfication reaction of 1*H*-tetrazole-5-carboxylate, despite the reports of successful 1*H*-tetrazole-5-carboxylic esters in the literature.

Another method for the preparation of the 1*H*-tetrazole-5-carboxylic ester is the reaction of ethyl cyanoformate and alkyl azides.[9] Preliminary reactions of azido ethanol and 2-azidoethyl acetate with ethyl cyanoformate in a teflon lined bomb at 130 °C only led to a black residue which contained tetrazoles (determined by mass spectrometry). Further purification or isolation of the product was not possible.

These findings led to the decision, that the 1*H*-tetrazole-5-carboxylic acid was not suitable for the preparation of energetic compounds. Nevertheless, a closer investigation of these reactions in future could lead to promising energetic compounds.

3.2.3 Trials of Substitution Reactions Using the 1*H*-Tetrazole-5-carboxylate Anion as Nucleophile

Substitution reactions of halogenated alkanes and tetrazolate anions are common methods for the preparation of alkylated tetrazoles.[10] The substitution reactions were carried out using chloroethanol and bromo acetic acid and **3a**. For us, it was not possible to isolate any product, neither by extraction nor by column chromatography. In order to exclude interactions of the carboxyl group, the reactions were also carried out with the corresponding ethyl ester. But, in contrast to known methods,[11] we were not able to isolate any product.

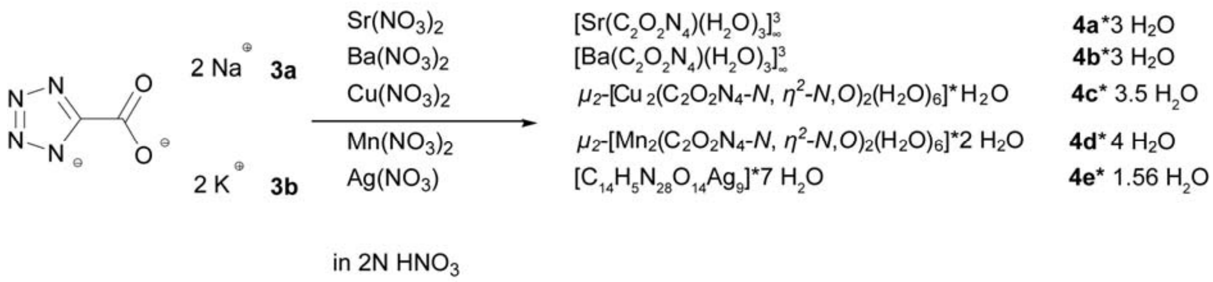
3.3 Tetrazole-5-carboxylic Acid Based Salts of Earth Alkali and Transition Metal Cations

Among the tetrazole chemistry, complexes and salts of tetrazoles and tetrazolates are common and well investigated compounds. One example for their versatility is the [µ-tris(1,2-bis(tetrazol-1-yl)propane-*N1*,*N1*‘)iron(II)] bis(perchlorate), an iron(II) chain[12] or [tris(1,4-bis(tetrazol-1-yl)butane-*N1*,*N1*)iron(II)] bis(perchlorate), a 3-D structure[13] both showing spin-crossover. Another interesting class of tetrazole-containing complexes is formed by the copper nitriminotetrazoles. These compounds show weak antiferromagnetic interactions.[14] Beyond that, the chemistry of lanthanide tetrazolates is another proof for the versatility of the tetrazolate ligand. Example are the formation of hydrogels of La(III) cations with 5-(2-pyridyl)tetrazolate[15] or potential new contrast agents based on lanthanide(III) cations and 5-(2-pyridyl)tetrazolate or 5-(2-pyridyl-1-oxide)tetrazolate.[16] Furthermore, complexes containing cations like barium, strontium or copper are sought components for pyrotechnical mixtures by the combination of the energetic nitrogen rich ligand and the colorant metal cation.[17] Especially the usage of copper(II)-compounds instead of barium in green fireworks was intensively studied.[18] The red flame colors can be obtained either by strontium, lithium or calcium.[19] In case of strontium, the red flame color is formed by the light-emitting species Sr(I)OH and Sr(I)Cl, being formed in the gas phase.[20]

With regard to an industrial application, special interest was laid on the investigation of colorant agents for pyrotechnical compositions. Particularly in case of civil applications, physical and thermal stable colorant agents are desired for a safe handling.

3.3.1 Synthesis of the Strontium, Barium, Copper(II), Manganese(II) and Silver 1*H*-Tetrazole-5-carboxylate

In order to convert **3a** or **3b** into the desired strontium, barium, copper, manganese and silver salts, **3a** or **3b** were dissolved in the corresponding 2N mineral acid to remove residues of carbonate (in case of nitrates in nitric acid or in case of the chlorides in hydrochloric acid) and a fivefold excess of the salt was added (*Scheme 2*). In case of the copper (**4c**), manganese (II) (**4d**) and silver 1*H*-tetrazol-5-carboxylate (**4e**), the product precipitated instantly, whereas the strontium (**4a**) and barium (**4b**) salts crystallized after some hours.



Scheme 2. Synthesis of the strontium, barium, copper, manganese and silver salt.

3.3.2 Vibrational and NMR Spectroscopy of the Complexes

Compounds **4a***3 H_2O, **4b***3 H_2O, **4c***3.5 H_2O, **4d***4 H_2O and **4e***1.56 H_2O were characterized by IR spectroscopy. A comparison between the different spectra shows the characteristic bands of the anion, along with the vibrations of the crystal water. The broadness of the band at about 3400 cm^{-1} (OH-stretching) depends on the number of different molecules of crystal water. Compound **4d** *4 H_2O possesses a strong band at 3440 cm^{-1} with three shoulders at 3381 cm^{-1}, 3289 cm^{-1} and 3171 cm^{-1}, similar to the pattern of **4c***3.5 H_2O (strong band at 3421 cm^{-1} with two shoulders at 3256 cm^{-1} and 3118 cm^{-1}). Surprisingly, the patterns of **4a***3 H_2O and **4b***3 H_2O are very different. Compound **4a*** H_2O only possesses a strong, sharp band at 3421 cm^{-1} with two shoulders at 3565 cm^{-1} and 3250 cm^{-1}, whereas **4b***3 H_2O shows four equivalent bands at 3539 cm^{-1}, 3453 cm^{-1}, 3368 cm^{-1} and 3230 cm^{-1}.

An investigation of the vibrations of the anion of **4a***3 H_2O, **4b***3 H_2O, **4c***3.5 H_2O, **4d***4 H_2O and **4e***1.56 H_2O reveals only small differences between the different complexes (*Table 1*). An exception is the asymmetric valence vibration of the carboxyl group. The band of the asymmetric valence vibration ranges from 1576 cm^{-1} (barium salt **4b***3 H_2O) to 1661 cm^{-1} (copper salt **4c***3.5 H_2O). For being the only compound with two cations per $C_2N_4O_2$-anion, the silver salt **4e*** 1.56 H_2O was not considered in the discussion of the IR spectra. A comparison between selected vibrations of **4a***3 H_2O, **4b***3 H_2O, **4c***3.5 H_2O, **4d***4 H_2O and **4e***1.56 H_2O and calculated values of the uncoordinated $C_2N_4O_2$-anion are given in *Table 1*.

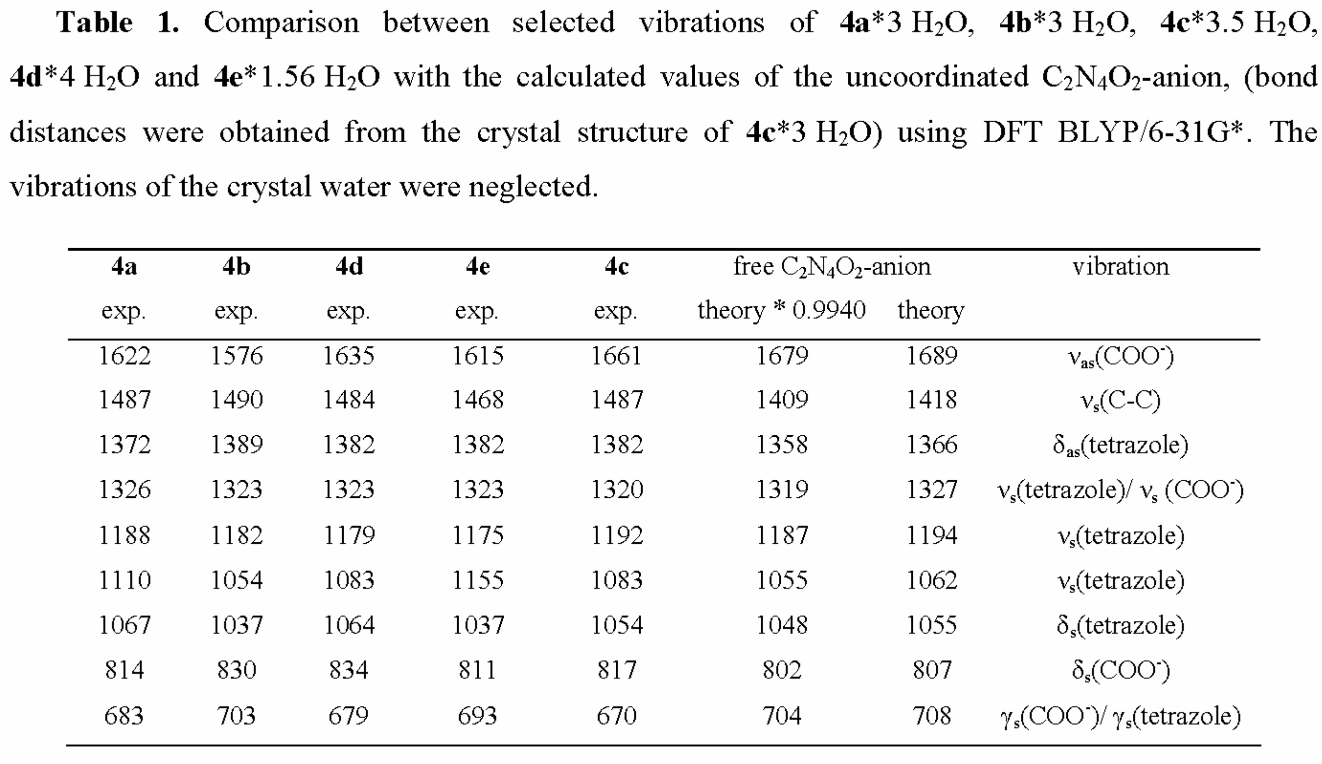


Table 1. Comparison between selected vibrations of **4a***3 H_2O, **4b***3 H_2O, **4c***3.5 H_2O, **4d***4 H_2O and **4e***1.56 H_2O with the calculated values of the uncoordinated $C_2N_4O_2$-anion, (bond distances were obtained from the crystal structure of **4c***3 H_2O) using DFT BLYP/6-31G*. The vibrations of the crystal water were neglected.

4a	**4b**	**4d**	**4e**	**4c**	free $C_2N_4O_2$-anion		vibration
exp.	exp.	exp.	exp.	exp.	theory * 0.9940	theory	
1622	1576	1635	1615	1661	1679	1689	$\nu_{as}(COO^-)$
1487	1490	1484	1468	1487	1409	1418	$\nu_s(C\text{-}C)$
1372	1389	1382	1382	1382	1358	1366	δ_{as}(tetrazole)
1326	1323	1323	1323	1320	1319	1327	ν_s(tetrazole)/ ν_s (COO^-)
1188	1182	1179	1175	1192	1187	1194	ν_s(tetrazole)
1110	1054	1083	1155	1083	1055	1062	ν_s(tetrazole)
1067	1037	1064	1037	1054	1048	1055	δ_s(tetrazole)
814	830	834	811	817	802	807	$\delta_s(COO^-)$
683	703	679	693	670	704	708	$\gamma_s(COO^-)$/ γ_s(tetrazole)

The ^{13}C and ^{15}N NMR spectrum of the 1*H*-tetrazol-5-carboxylate anion was recorded using the disodium salt, because the solubility of compounds **4a***3 H_2O, **4b***3 H_2O, **4c***3.5 H_2O, **4d***4 H_2O and **4e***1.56 H_2O in any solvents was not sufficient for a NMR spectrum. To verify the assignment, the ^{13}C and ^{15}N NMR shifts were calculated using the isotropic magnetic shieldings of the GIAO (Gauge-Independent Atomic Orbital) method implemented in G03.[21,22] The NMR shielding tensors were calculated at the MPW1PW91/aug-cc-pVDZ level of theory using the GIAO method.[22] The calculations gave a chemical shift of 165.1 ppm for the carboxyl group and 162.8 ppm for the tetrazole carbon atom. These results confirm the assignment of C5 to the signal at 160.6 ppm and C6 to the signal at 167.5 ppm. Compared to sodium 5-nitrotetrazolate (167.5 ppm, C5, *d6*-acetone),[23] ammonium 5-nitrotetrazolate (169.5 ppm, C5, *d6*-DMSO)[24] and 1*H*-imidazole-2-carboxylic acid (141.1 ppm CN_2, 157.6 COOH, *d6*-DMSO), the chemical shift of the quaternary carbon atom of the tetrazole moiety is located between these compounds. In case of the ^{15}N NMR, the experimental shifts of -3.5 ppm for N2 and N3 and -67.3 ppm for N1 and N4 are in accordance with the calculated values of +10.6 ppm for N2 and N3 and -47.5 ppm for N1 and N4.

3.3.3 Crystal Structures of the Strontium, Barium, Copper(II) and Manganese(II) 1*H*-Tetrazole-5-carboxylate

In order to investigate the different types of coordination of earth alkali salts and transition metal salts, crystals of **4a** (*2.75 H_2O, *2.5 H_2O), **4b***3 H_2O, **4c***4 H_2O and **4d***5 H_2O were synthesized. In this listing, the manganese salt **4d***5 H_2O only possesses academic character, because an application as colorant agent in pyrotechnics is not possible.

3.3.3.1 Transition Metal Complexes of 1*H*-Tetrazole-5-carboxylate

The structures of the transition metal salts of 1*H*-tetrazol-5-carboxyate, copper **4c***4 H_2O and manganese **4d***5 H_2O are similar. Compound **4c***4 H_2O crystallizes in the monoclinic space group *C*2/*c* with eight molecular formulas per unit cell and four molecules water per copper cation. The copper 1*H*-tetrazol-5-carboxylate units form dinuclear complexes, involving two copper 1*H*-tetrazol-5-carboxylate units and six molecules of water (*Figure 1*). The copper cation is coordinated equatorial to N1 and O1 of the first, N2 of the second 1*H*-tetrazol-5-carboxylate anion and to one molecule of water (O4). Two other molecules of water are coordinated axial to the copper cation (O3/O5), leading to a distorted octahedral sphere of coordination (*Figure 1*). The bond length of the equatorial water molecule (O4; 1.931 Å) is about 21 % shorter than the bond length to the axial water molecule (O3; 2.343 Å). The bond length of the other axial molecule of water (O5) with 2.523 Å is elongated, compared to O3. The remaining molecule water (O6) is connected by several hydrogen bonds to the other water molecules and to N3.

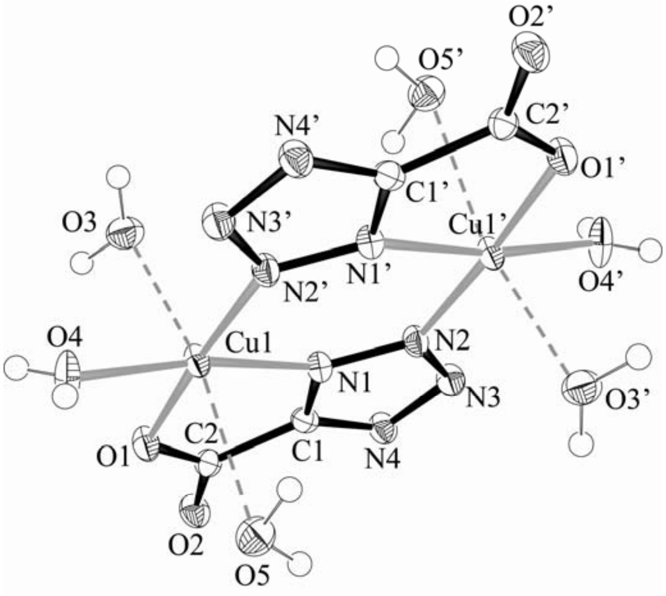


Figure 1. Molecular structure of the dinuclear complex of **4c***4 H_2O. Thermal ellipsoids are drawn at the 50% probability level.

Like **4c***4 H_2O, **4d***5 H_2O crystallizes in the monoclinic space group *C*2/*c* with eight molecular formulas per unit cell and five molecules of crystal water per manganese cation. In contrast to **4c***4 H_2O, the manganese cation is coordinated octahedral without distortion by two 1*H*-tetrazol-5-carboxylate moieties and three molecules of water (*Figure 2*). The bond distances between the cation and the water molecules vary between 2.117 Å and 2.173 Å. Like the copper cation, the manganese cation is coordinated to O1 and N1 of the first and N2 of the second 1*H*-tetrazol-5-carboxylate anion. The molecules of crystal water have a significant part in the structure by stabilizing it with several hydrogen bonds. Three molecules of water are coordinated equatorial and axial to the manganese cation (O3, O4 and O5), whereas the last two water molecules form hydrogen bonds to the water molecules and N3.

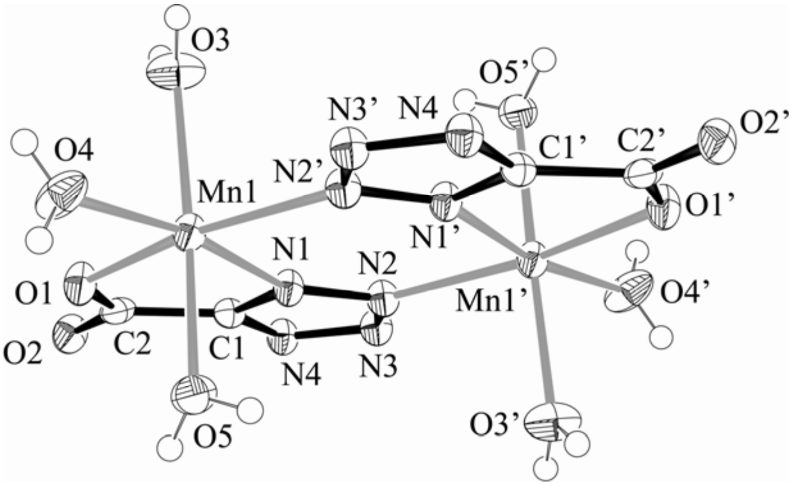


Figure 2. Molecular structure of the dinuclear complex of **4d***5 H_2O. Thermal ellipsoids are drawn at the 50% probability level.

3.3.3.2 Earth Alkali Metal Complexes of 1*H*-Tetrazole-5-carboxylate

Compound **4a** crystallizes in two modifications, the tetragonal modification **4a1** and the monoclinic modification **4a2**. The monoclinic modification was obtained of a hot saturated aqueous solution. The more symmetric tetragonal modification was obtained by a slow crystallization at room temperature.

Compound **4a2***2.5 H_2O crystallizes in the monoclinic space group *P*2(1)*c* with four molecular formulas per unit cell. The asymmetric unit contains four strontium 1*H*-tetrazol-5-carboxylate moieties with ten molecules of crystal water. The structure is built up by two different modes of coordination of the strontium cations. The first structural motif is built up by chains along the a-axis, formed by the coordination of the strontium cations to the N2, N3 and O1 and O2 of two different 1*H*-tetrazol-5-carboxylate anions (**motif A**, *Figure 3*). In addition, the chains are stabilized by the coordination of the two strontium cations to the bridging water molecules of O42/O43 or O45/O48 (**motif A**). The second motif contains the connection of two chains by three 1*H*-tetrazol-5-carboxylate moieties (**motif B**, *Figure 4*). The coordination of these 1*H*-tetrazol-5-carboxylate anions is similar to the coordination of the copper and manganese salt. One strontium cation is coordinated to O1 and N1, whereas the second cation is coordinated to N2 (**motif B**). Besides the two main motifs, several 1*H*-tetrazol-5-carboxylate anions are arranged to saturate open positions of coordination, like the 1*H*-tetrazol-5-carboxylate anion **3**, coordinated to Sr1 (O31 and N31) and Sr4 (O32). The network of hydrogen bonds stabilizing the structure consists of 19 different hydrogen bonds.

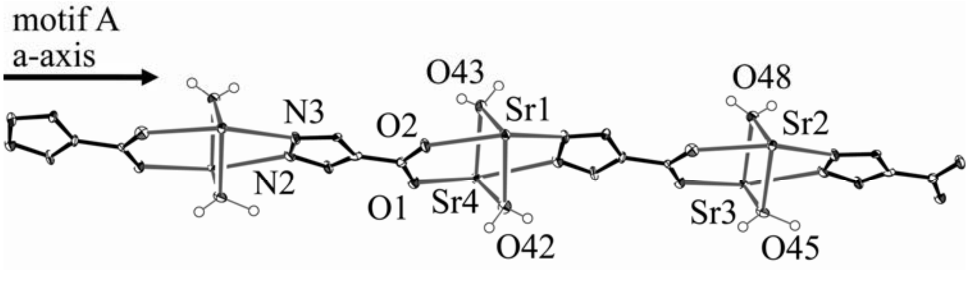


Figure 3. Motif A of the structure of **4a2***2.5 H_2O. Thermal ellipsoids are drawn at the 50% probability level.

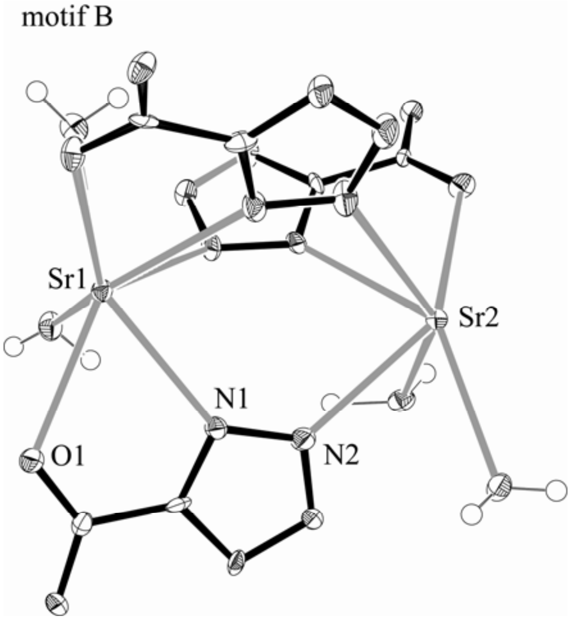


Figure 4. Motif B of the structure of **4a2***2.5 H_2O. Thermal ellipsoids are drawn at the 50% probability level.

Compound **4a1***2.75 H_2O crystallizes in the tetragonal space group *P*4/*n* with two molecular formulas per unit cell and 2.75 molecules of crystal water per 1*H*-tetrazol-5-carboxylate anion. In contrast to the monoclinic modification, the tetragonal modification does only contain two water molecules embedded in the structure. The lesser role of the crystal water compared to **4a2***2.5 H_2O is pointed out by the small number of hydrogen bonds formed, compared to **4a2***2.5 H_2O (**4a1***2.75 H_2O: 5 different hydrogen bonds, **4a2***2.5 H_2O: 19 different hydrogen bonds). The structure of **4a1***2.75 H_2O is built up by two motifs. **Motif A** (*Figure 5*) consists of chains along the c-axis. The strontium atom is coordinated to N1 and O1 of two 1*H*-tetrazol-5-carboxylate anions. The connection between the strontium cations is formed by one 1*H*-tetrazol-5-carboxylate anion that is coordinated with its oxygen atom to the first and by N2 to the second strontium cation. The remaining free positions of coordination are saturated by molecules of water (*Figure 5*). The chains are connected among each other by hydrogen bonds formed by molecules of water coordinated to the strontium atom (*Figure 5*). The combination of the chains leads to a porous structure with channels along the c-axis (*Figure 6*). A closer investigation of the channel structure reveals that two different kinds of channels are found as demonstrated in *Figure*

6. The first channel, channel I, is filled with the molecules of water attached to the strontium atom. The bigger channel II is filled with strongly distorted molecules of crystal water, which are not involved in the structure, either by coordination to a strontium cation, a 1*H*-tetrazol-5-carboxylate anion or the formation of hydrogen bonds. Comparing the dimensions of the channels, channel I has a diameter of 7.3 Å, whereas channel II has a diameter of 9.5 Å (measured from one strontium cation to the opposing strontium cation). The crystal water was neglected for the determination of the diameter. If the crystal water attached to the strontium atom is considered for the determination of the diameter, channel I achieves a diameter of 2.9 Å and channel II 5.1 Å. Taking these results into account, the structure could be able to absorb small atoms or molecules, if the distorted, unbound water molecules are removed. This effect could turn this compound into an interesting structure for further investigations in the field of porous materials.

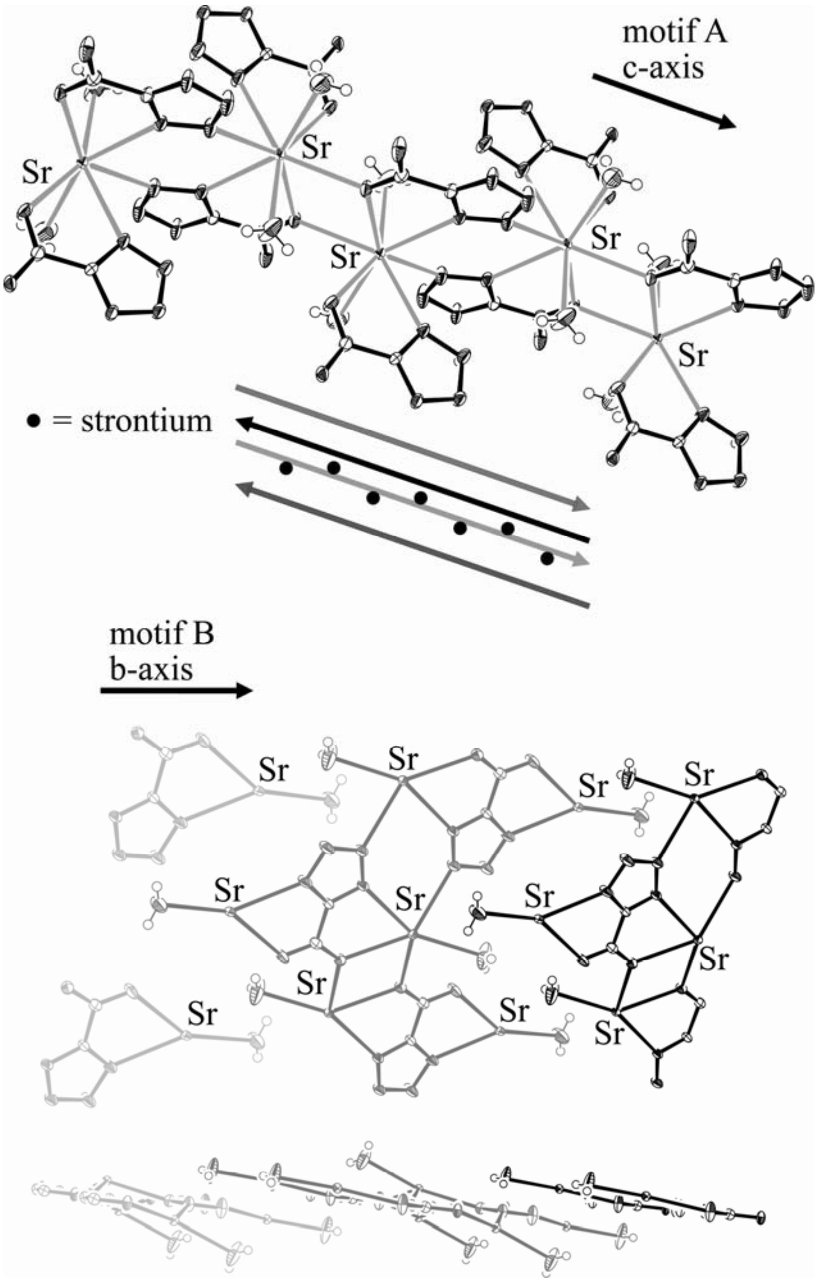


Figure 5. Motif A and **B** of the structure of **4a1***2.75 H_2O. Thermal ellipsoids are drawn at the 50% probability level.

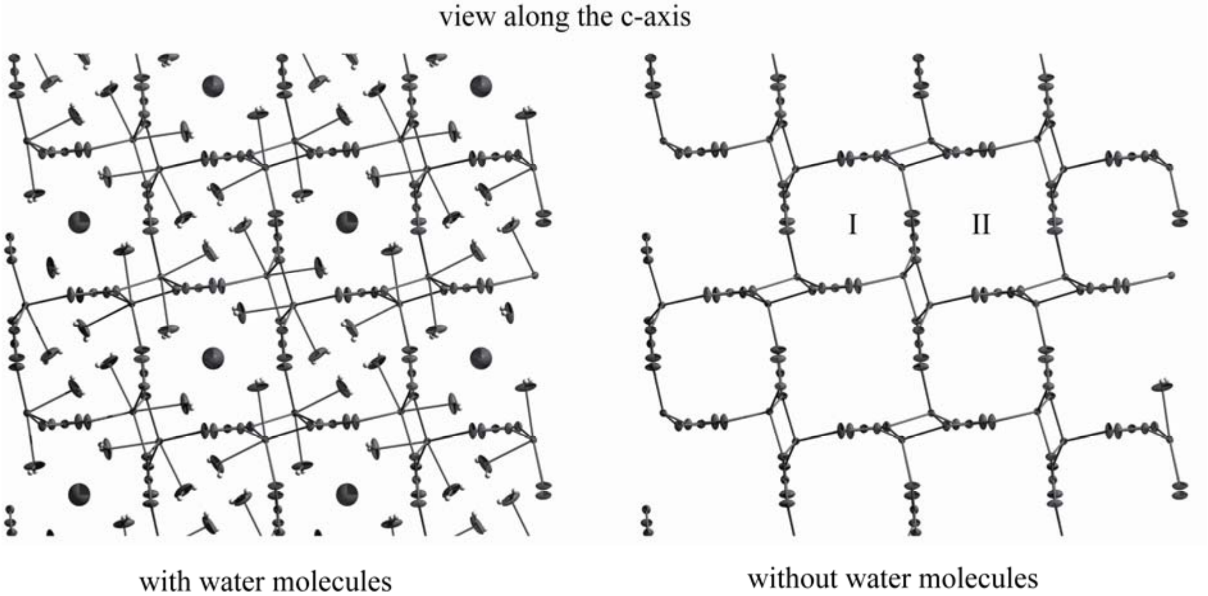


Figure 6. View along the c-axis of the structure of **4a1***2.75 H_2O. Thermal ellipsoids are drawn at the 50% probability level.

Compound **4b***3 H_2O crystallizes in the monoclinic space group *P*2(1)*c* with four molecular formulas per unit cell and three molecules of crystal water per 1*H*-tetrazol-5-carboxylate. The structure is built up by only one motif, as shown in *Figure 7*. The barium cation is coordinated to four 1*H*-tetrazol-5-carboxylate anions; two are coordinated by N1 and O1, whereas the third one is coordinated with N2/N3 and the last one with O1 and O2. Each 1*H*-tetrazol-5-carboxylate anion is bound to four barium atoms, two times by N1/N4 and O1/O2 and one time by N2/N3 and O1 and O2 (*Figure 8*). In addition, the structure is stabilized by six hydrogen bonds between the water molecules and of water molecules to N1 and N2. In contrast to structures **4a1***2.75 H_2O and **4a2***2.5 H_2O, the barium 1*H*-tetrazol-5-carboxylate forms layers in the b-c-plane. Thereby, the barium and 1*H*-tetrazol-5-carboxylate anions are situated in the layer, whereas the crystal water is arranged between these layers. The layers are connected by hydrogen bonds. The shortest distance between two layers with negligence of the water molecules is 5.4 Å between the barium cation and N1 of the opposing layer.

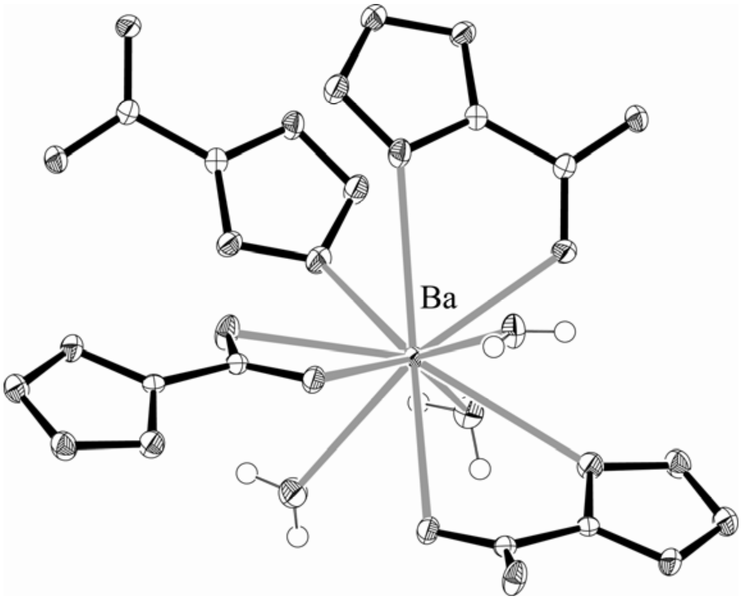


Figure 7. Coordination of the barium atom of **4b***3 H_2O. Thermal ellipsoids are drawn at the 50% probability level.

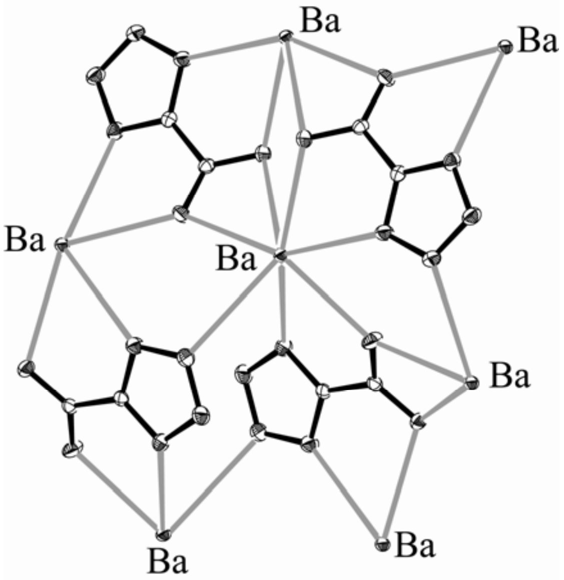


Figure 8. Interactions of the tetrazol-5-carboxylate anions with the barium cations of **4b***3 H_2O. Thermal ellipsoids are drawn at the 50% probability level.

The data of the solution and refinement of the crystal structure for the 1*H*-tetrazol-5-carboxylate complexes are given in *Table 2*. A closer investigation of the bond lengths shows only small differences between the structures. In cases of **4c***4 H_2O and **4d***5 H_2O, the bond length of the coordinated oxygen atom is slightly elongated, compared to the uncoordinated oxygen atom (3.4 % in case of **4c***4 H_2O and 1.0 % in case of **4d***5 H_2O).

3.3.4 Energetic Properties and Flame Color

The energetic properties were investigated by DSC measurements and the sensitivity towards impact and friction was determined by using BAM standards.[25,26] The DSC data were obtained by using the precipitated powder instead of the crystalline solid. The samples were dried under high vacuum to remove any moisture beside crystal water.

The analysis of the thermal stability by DSC measurements revealed significant differences between the compounds (*Figure 9*). Comparing the transition metal complexes **4c***3.5 H_2O, **4d***4 H_2O and **4e***1.56 H_2O, the silver 1*H*-tetrazol-5-carboxylate **4e***1.56 H_2O was thermally the last stable compound with a point of decomposition of 200 °C. The decomposition area of **4e***1.56 H_2O shows a broad exothermic signal, suggesting a complex mechanism of decomposition. The molecular formula obtained by elemental analysis of **4e***1.56 H_2O is $(C_{14}H_5N_{28}O_{14}Ag_9)$*7 H_2O. In contrast to the other 1*H*-tetrazol-5-carboxylate salts, the DSC data of **4e***1.56 H_2O do not show any clear point of dehydration but a broad area of dehydration ranging from 60 °C to 140 °C. Compounds **4c***3.5 H_2O and **4d***4 H_2O possess major differences concerning their thermal behavior, although having both similar crystal structures. In case of the copper 1*H*-tetrazol-5-carboxylate **4c***3.5 H_2O, an endothermic signal at 116 °C indicates the point of dehydration (powder possesses 3.5 molecules of crystal water per copper 1*H*-tetrazol-5-carboxylate). The shoulder of this signal shows that the dehydration takes place in two steps. The decomposition point at 254 °C is about 130 °C lower than that of the manganese 1*H*-tetrazol-5-carboxylate (386 °C). In contrast to the copper 1*H*-tetrazol-5-carboxylate, the dehydration points of the manganese 1*H*-tetrazol-5-carboxylate **4d***4 H_2O can be clearly distinguished (powder possesses four molecules of crystal water). The first point of dehydration is located at 81 °C, the second at 99 °C and the third and fourth is merged with an onset of 126 °C.

A comparison between the earth metal salts of 1*H*-tetrazol-5-carboxylate reveals that the thermal stability of the strontium salt **4a***3 H_2O is 30 °C lower than that of the barium salt **4b***3 H_2O. In contrast to the transition metal 1*H*-tetrazol-5-carboxylates, **4a***3 H_2O and **4b***3 H_2O possess only one point of dehydration (**4a***3 H_2O: 166 °C, **4b***3 H_2O: 124 °C). The difference of the dehydration points of 40 °C proofs the weaker bound crystal water in the barium structure **4b***3 H_2O. This finding is in accordance with the arrangement of the crystal water in the two structures. In case of the strontium 1*H*-tetrazol-5-carboxylate **4a***3 H_2O, the water molecules are involved in the structure and have significant contribution to the stability of the structure. In case of the barium 1*H*-tetrazol-5-carboxylate **4b***3 H_2O, the crystal water is embedded between the barium 1*H*-tetrazol-5-carboxylate layers.

The investigation of the sensitivity of the 1*H*-tetrazol-5-carboxylate salts towards friction and impact points the higher stability of the 1*H*-tetrazol-5-carboxylate anion out, compared to the 5-nitrotetrazolate anion.[1,2] Compounds **4a***3 H_2O, **4b***3 H_2O and **4e***1.56 H_2O do not show any sensitivity towards friction and impact. In case of the transition metal salts, the copper 1*H*-tetrazol-5-carboxylate **4c***3.5 H_2O possesses a sensitivity towards friction of >288 N, whereas the manganese 1*H*-tetrazol-5-carboxylate with a sensitivity towards friction of >324 N is slightly more stable. Both compounds are insensitive towards impact.[25,26,27] The grain sizes of the sample of **4a***3 H_2O and **4b***3 H_2O were between 500 μm and 1000 μm, the grain size of **4c***3 H_2O was 80 μm to 160 μm and the grain sizes of **4d***4 H_2O and **4e***1.56 H_2O were between 250 μm and 500 μm.

The flame color of compounds **4a***3 H_2O, **4b***3 H_2O and **4c***3.5 H_2O are in accordance with the expected colors. The strontium salt **4a***3 H_2O decomposes under emission of a slightly red flame color, whereas the barium salt **4b***3 H_2O possesses a pale greenish flame color. In both cases, the intensity of the flame color is not very high, due to the stability of the complexes. The intensity of the color could be achieved by higher temperatures of decomposition, using different oxidizers. In case of **4c***3.5 H_2O, the flame color is green with a moderate intensity. These findings turn compounds **4a***3 H_2O to **4c***3.5 H_2O into valuable components for pyrotechnic applications, due to their simple high-yield synthesis along with a high thermal stability. Moreover, their insensitivity against friction and impact are another advantage, regarding an industrial application.

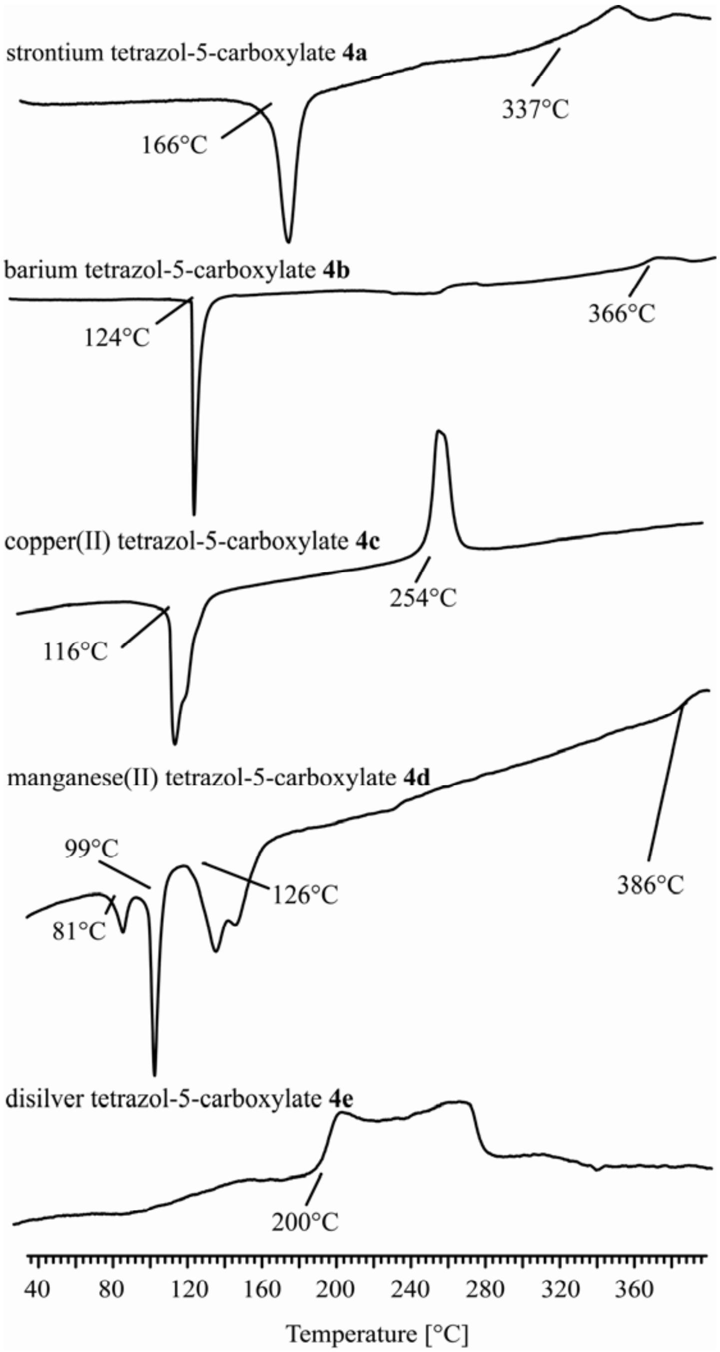


Figure 9. DSC plots of the 1*H*-tetrazol-5-carboxylate salts (exo = up).

3.3.5 Conclusions

The strontium **4a** (*3 H_2O, *2.75 H_2O, *2.5 H_2O), barium **4b** (*3 H_2O), copper **4c** (*3.5 H_2O, *4 H_2O), manganese **4d** (*4 H_2O, *5 H_2O) and silver 1*H*-tetrazol-5-carboxylate **4e** (*1.56 H_2O) were synthesized and characterized by IR and NMR spectroscopy. In cases of **4a** (*2.75 H_2O, *2.5 H_2O), **4b***3 H_2O, **4c***4 H_2O and **4d***5 H_2O, the crystal structures were determined using single crystal X-ray diffraction. The analysis of the physical and thermal stability of the compounds revealed their insensitivity towards friction and impact, along with thermal stabilities up to 380 °C. The flame coloration of the strontium 1*H*-tetrazol-5-carboxylate **4a***3 H_2O (red), barium 1*H*-tetrazol-5-carboxylate **4b***3 H_2O (pale greenish) and copper 1*H*-tetrazol-5-carboxylate **4c***3.5 H_2O (green) renders these compounds into promising components for pyrotechnic applications. Another advantage of these compounds is their low solubility in water, along with a lack of toxic moieties (nitro groups, azides) or anions (perchlorate). These properties turn the strontium, barium and copper 1*H*-tetrazol-5-carboxylates into ecologically interesting substitutes for toxic pyrotechnic compositions.

The porous structure of the tetragonal modification of the strontium 1*H*-tetrazol-5-carboxylate **4a1***2.75 H_2O contains channels along the c-axis. The bigger channel with a diameter of 9.5 Å (without crystal water) or 5.1 Å (with crystal water) should be able to absorb small molecules or atoms. This feature could be used for further investigations in the fields of catalysis or purification.

3.3.6 Experimental Section

CAUTION! Tetrazoles are highly energetic compounds with sensitivity towards heat and impact. Although we had no problems in synthesis, proper protective measures (safety glasses, face shield, leather coat, earthened equipment and shoes, Kevlar® gloves and ear plugs) should be used when undertaking work involving these compounds.

The dipotassium and disodium tetrazol-5-carboxylate were synthesized after a European patent.[28]

3.3.6.1 General Synthesis for Metal 1*H*-Tetrazol-5-carboxylates

Crude dipotassium 1*H*-tetrazol-5-carboxylate (1.0 g, 5.3 mmol), was dissolved in 6 mL 2N nitric acid to remove residues of potassium carbonate. A saturated solution of the corresponding metal nitrate (15.9 mmol) was added at room temperature under vigorous stirring.

In case of **4c***3.5 H_2O, **4d***4 H_2O and **4e***1.56 H_2O, the product instantly precipitated as turquoise (**4c***3.5 H_2O) or colorless (**4d***4 H_2O and **4e***1.56 H_2O) powder. The solvent was removed by filtration and the solid was washed with 50 mL of water and 20 mL of methanol. The product was dried under high vacuum.

In case of **4a***3 H_2O and **4b***3 H_2O, the resulting solution was kept at room temperature and the product was obtained by slow crystallization. The formed crystals were collected by filtration and were washed with 50 mL of water and 20 mL of methanol. The product was dried under high vacuum.

3.3.6.2 Strontium 1*H*-tetrazol-5-carboxylate 4a*3 H_2O

yield: 68 %.

dehydr. 166 °C, dec. 337 °C.

IR (KBr) (cm^{-1}): $\tilde{\nu}$ = 3429 (vs), 2964 (w), 2920 (vw), 2853 (vw), 2802 (vw), 2708 (vw), 2639 (vw), 2613 (vw), 2449 (vw), 2419 (vw), 1987 (vw), 1789 (w), 1678 (m), 1622 (vs), 1487 (m), 1437 (m), 1414 (m), 1372 (s), 1326 (s), 1309 (m), 1262 (m), 1230 (w), 1217 (w), 1188 (w), 1110 (w), 1093 (w), 1067 (w), 1054 (w), 1014 (w), 949 (vw), 839 (vw), 814 (m), 736 (w), 711 (w), 683 (w), 658 (w), 575 (w), 547 (w), 464 (w).

elemental analysis: calcd (%) for $Sr_2(C_6N_{12}O_6)$*6 H_2O (621.89): C 11.60, H 2.27, N 27.04; found: C 11.60, H 2.44, N 27.31.

3.3.6.3 Barium 1*H*-tetrazol-5-carboxylate 4b*3 H_2O

yield: 70 %.

dehydr. 124 °C, dec. 366 °C.

IR (KBr) (cm^{-1}): $\tilde{\nu}$ = 3541 (vs), 3458 (vs), 3377 (vs), 3229 (vs), 2547 (vw), 2457 (vw), 2289 (vw), 2213 (vw), 2196 (vw), 2182 (vw), 2120 (vw), 2106 (vw), 2091 (vw), 2075 (vw), 1945 (vw), 1857 (vw), 1667 (m), 1576 (vs), 1490 (vs), 1389 (vs), 1323 (vs), 1182 (s), 1149 (m), 1067 (w), 1054 (m), 1037 (m), 830 (vs), 770 (m), 732 (m), 703 (m), 674 (m), 543 (m), 523 (m), 454 (w).

elemental analysis: calcd (%) for $Ba(C_2N_4O_2)$*$3H_2O$: C 7.92, H 1.99, N 18.47; found: C 7.99, H 1.99, N 18.55.

3.3.6.4 Copper(II) 1*H*-tetrazol-5-carboxylate 4c*3.5 H_2O

yield: 91 %.

dehydr. 116 °C, dec. 254 °C.

IR (KBr) (cm^{-1}): $\tilde{\nu}$ = 3426 (vs), 3098 (m), 2501 (vw), 2324 (vw), 2214 (vw), 1661 (m), 1630 (m), 1487 (m), 1430 (m), 1382 (w), 1320 (m), 1262 (w), 1231 (w), 1192 (w), 1136 (w), 1083 (w), 1055 (vw), 834 (w), 817 (w), 670 (w), 627 (w), 578 (w).

elemental analysis: calcd (%) for $Cu(C_2N_4O_2)*3.5H_2O$: C 10.07, H 2.96, N 23.48; found: C 10.03, H 2.82, N 23.45.

3.3.6.5 Manganese(II) 1*H*-tetrazol-5-carboxylate 4d*4 H_2O

yield: 85 %.

dehydr. 81 °C, 99 °C, 126 °C, dec. 386 °C.

IR (KBr) (cm^{-1}): $\tilde{\nu}$ = 3440 (vs), 3381 (vs), 3289 (vs), 3177 (s), 2289 (vw), 2218 (vw), 1652 (vs), 1635(vs), 1484 (m), 1409 (m), 1382 (w), 1323 (s), 1262 (w), 1217 (w), 1179 (w), 1115 (w), 1083 (w), 1064 (w), 834 (m), 825 (w), 679 (m), 478 (w).

elemental analysis: calcd (%) for $Mn(C_2N_4O_2)*4H_2O$: C 9.34, H 3.92, N 21.80; found: C 9.20, H 3.68, N 21.69.

3.3.6.6 Disilver 1*H*-tetrazol-5-carboxylate 4e*1.56 H_2O

yield: 98 %.

dec. 200 °C.

IR (KBr) (cm^{-1}): $\tilde{\nu}$ = 3431 (m), 2962 (vw), 2924 (vw), 2101 (vw), 1615 (vs), 1468 (m), 1382 (m), 1323 (m), 1261 (w), 1175 (w), 1140 (w), 1099 (w), 1055 (w), 1037 (w), 875 (w), 833 (w), 811 (m), 693 (w), 670 (w), 576 (w).

elemental analysis: calcd (%) for $(Ag_9C_{14}H_5N_{28}O_{14})*7H_2O$: C 8.91, H 1.02, N 20.79; found: C 8.76, H 0.92, N 20.86.

3.3.7 Crystallographic Data

Further details of the crystal structure investigation(s) can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-420720 (**4a1***2.75 H_2O), 420719 (**4a2***2.5 H_2O), 420716 (**4b***3 H_2O), 420717 (**4c***4 H_2O) and 420718 (**4d***5 H_2O).

3.3.7.1 Earth Alkali Metal Tetrazol-5-carboxylate Complexes

	4a1*2.75 H_2O	**4a2***2.5 H_2O	**4b***3 H_2O
Formula	$C_8H_{16}N_{16}O_{19}Sr_4$	$C_8H_{20}N_{16}O_{18}Sr_4$	$C_2H_6BaN_4O_5$
M_r [g mol^{-1}]	990.85	978.88	303.45
Crystal system	tetragonal	monoclinic	monoclinic
Space group	P4/n	P2(1)/c	P2(1)/c
a [Å]	12.9854(2)	17.5090(6)	6.6773(2)
b [Å]	12.9854(2)	9.2732(3)	11.4639(4)
c [Å]	8.8601(3)	18.4285(7)	10.0846(3)
α [°]	90	90	90
β [°]	90	106.031(4)	90.856(3)
γ [°]	90	90	90
V [Å³]	1494.00	2875.78	771.87
Z	2	4	4
F(000)	912.0	1504.0	568.0
$\rho_{calc.}$ [g cm^{-3}]	2.096	1.845	2.611
μ [mm^{-1}]	7.19	7.44	5.14
2 theta [°]	57.68	53.00	52.99
Index range	$-16 \leq h \leq 16$	$-12 \leq h \leq 12$	$-8 \leq h \leq 8$
	$-16 \leq k \leq 14$	$-11 \leq k \leq 10$	$-14 \leq k \leq 14$
	$-10 \leq l \leq 11$	$-22 \leq l \leq 23$	$-12 \leq l \leq 12$
λ [Å]	0.71073	0.71073	0.71073
T [K]	200(2)	200(2)	200(2)
Reflections collected	11346	13962	7876
Unique reflections	1786	5845	1598
Parameter	125	415	133
S	0.840	0.920	0.981
R_{int}	0.0349	0.0642	0.0409
R_1/ wR_2 [I>2σ(I)]	0.0205/0.0346	0.0463/0.0864	0.0168/0.0387
R_1/ wR_2	0.0426/0.0358	0.1082/0.0984	0.0212/0.0396

3.3.7.2 Transition Metal Tetrazol-5-carboxylate Complexes

	4c*4 H_2O	**4d***5 H_2O
Formula	$C_2H_8CuN_4O_6$	$C_2H_{10}MnN_4O_7$
M_r [g mol^{-1}]	247.65	257.08
Crystal system	monoclinic	monoclinic
Space group	C2/c	C2/c
a [Å]	15.5106(10)	7.3516(5)
b [Å]	6.4029(4)	12.9931(9)
c [Å]	17.7351(12)	19.8142(16)
α [°]	90	90
β [°]	114.494(8)	100.351(5)
γ [°]	90	90
V [$Å^3$]	1602.8(2)	1861.85
Z	8	8
F(000)	1000.0	1048.0
$\rho_{calc.}$ [g cm^{-3}]	2.053	1.834
μ [mm^{-1}]	2.74	1.44
2 theta [°]	51.99	49.98
Index range	$-18 \leq h \leq 18$	$-8 \leq h \leq 8$
	$-6 \leq k \leq 7$	$-15 \leq k \leq 14$
	$-21 \leq l \leq 13$	$-23 \leq l \leq 18$
λ [Å]	0.71073	0.71073
T [K]	200(2)	200(2)
Reflections	3152	4348
Unique reflections	1566	1630
Parameter	150	168
S	1.030	0.909
R_{int}	0.0257	0.0359
R_1/ wR_2 [I>2σ(I)]	0.0284/0.0771	0.0276/0.0526
R_1/ wR_2	0.0369/0.0796	0.0474/0.0561

3.4 References

(1) T. M. Klapötke, C. Miro Sabate, J. M. Welch, *Dalton Trans.* **2008**, *45*, 6372-6380.

(2) T. M. Klapötke, P. Mayer, C. Miro Sabate, J. M. Welch, N. Wiegand, *Inorg. Chem.* **2008**, *13*, 6014-6027.

(3) R. A. Henry, W. G. Finnegan, *J. Am. Chem. Soc.* **1954**, *78*, 1635-1636; K. R. Wilson, R. M. Herbst, W. J Haak, *J. Org. Chem.* **1959**, *24*, 1046-1051; S. V. Voitekhovich, P. N. Gaponik, A. S. Lyakhov, O. A. Ivashkevich, *Tetrahedron* **2008**, *64*, 8721-8725.

(4) H. Behringer, K. Kohl, *Chem. Ber.* **1956**, *89*, 2648-2653.

(5) N. D. Griffiths, B. J. Hibberd, A. A. Thatcher, *Eu Patent, EU0323885*, **1989**.

(6) a) D. Moderhack, *J. Heterocycl. Chem.* **1977**, *14*, 757-763; b) R. T. Buckler, H. E. Hartzler, E. Kurchacova, G. Nichols, B. M. Phillips, *J. Med. Chem.* **1978**, *21*, 1254-1260; c) C. Csongar, P. Weinberg, M. Gessner, G. Tomaschewski, *J. Prakt. Chem.* **1987**, *329*, 1111-1115; d) J. D. Hayler, T. J. Grinter, V. Novak, N. J. Lewis, *World Patent*, *WO9532199*, **1995**.

(7) a) D. Moderhack, *J. Heterocycl. Chem.* **1977**, *14*, 757-763; b) C. Csongar, P. Weinberg, M. Gessner, G. Tomaschewski, *J. Prakt. Chem.* **1987**, *329*, 1111-1115.

(8) J. D. Hayler, T. J. Grinter, V. Novak, N. J. Lewis, *World Patent*, *WO9532199*, **1995**.

(9) a) G. Molteni, P. Del Buttero, *Tetrahedron* **2005**, *61*, 4983-4987; b) M. Cavero-Tomas, M. Gowravaram, H. Huynh, H. Ni, S. Stokes, *World Patent*, *WO2006040558*, **2006**; c) L. Bosch, J. Vilarrasa, *Angew. Chem. Int. Ed.* **2007**, *46*, 3926-3930.

(10) a) D. Moderhack, *Chem. Ber.* **1975**, *108*, 887-896; b) C. F. Purchase, A. D. White, M. K. Anderson, T. M. A. Bocan, R. F. Bousley, K. L. Mamelehle, R. Homan, B. R. Krause, P. Lee, *Bioorg. Med. Chem.* **1996**, *6*, 1753-1758; c) A. R. Katritzky, D. A. Irina, I. A. Shcherbakova, J. Chem, S. A. Belyakov, *J. Heterocycl. Chem.* **1996**, *33*, 1107-1114.

(11) M. Ito, N. Matsunaga, M. Yamada, T. Hitaka, S. Yamamoto, *World Patent, WO2007145349*, **2007**.

(12) P. J. van Koningsbruggen, Y. Garcia, O. Kahn, L. Fournes, H. Kooijman, A. L. Spek, J. G. Haasnoot, J. Moscovici, K. Provost, A. Michalowicz, F. Renz, P. Guetlich, *Inorganic Chemistry* **2000**, *39*, 1891-1900.

(13) P. J. van Koningsbruggen, Y. Garcia, H. Kooijman, A. L. Spek, J. G. Haasnoot, O. Kahn, J. Linares, E. Codjovi, F. Varret, *Dalton Trans.* **2001**, *4*, 466-471.

(14) T. M. Klapötke, J. Stierstorfer, B. Weber, *Inorg. Chim. Acta* **2009**, *362*, 2311-2320.

(15) P. C. Andrews, P. C. Junk, M. Massi, M. Silberstein, *Chem. Commun.* **2006**, 3317-3319.

(16) A. Faccetti, A. Abbotto, L. Beverina, S. Bradamante, P. Mariani, C. L. Stern, T. J. Marks, A. Vacca, G. A. Pagani, *Chem. Commun.* **2004**, 1770-1771.

(17) a) T. M. Klapötke, J. Stierstorfer, K. R. Tarantik, I. D. Thoma, *Z. Anorg. Allg. Chem.* **2008**, *634*, 2777-2784; b) T. M. Klapötke, M. Stein, J. Stierstorfer, *Z. Anorg. Allg. Chem.* **2008**, *634*, 1867-1874.

(18) a) G. Steinhauser, K. Tarantik, T. M. Klapötke, *J. Pyrotech.* **2008**, *27*, 3-13; b) A. Hammerl, G. Holl, T. M. Klapötke, P. Mayer, H. Nöth, H. Piotrowski, M. Warchhold, *Eur. J. Inorg. Chem.* **2002**, *4*, 834; c) M. Friedrich, J. C. Ga´lvez-Ruiz, T. M. Klapötke, P. Mayer, B. Weber, J. J. Weigand, *Inorg. Chem.* 2**005**, *44*, 8044; d) T. M. Klapötke, P. Mayer, K. Polborn, J. Stierstorfer, J. J. Weigand, *New Trends in Research of Energetic Materials*, Proceedings of the Seminar, *9th*, Pardubice, Czech Republic, **2006**, *Pt. 2*, 641.

(19) E.-C. Koch, *J. Pyrotech.* **2001**, *13*, 1.

(20) T. M. Klapötke, J. Stierstorfer, K. R. Tarantik, I. D. Thoma, *Z. Anorg. Allg. Chem.* **2008**, *634*, 2777-2784.

(21) M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R.

Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian, Inc., Gaussian 03, Revision A.1, Pittsburgh, PA, **2003**.

(22) a) K. Wolinski, J. F. Hilton, P. J. Pulay, *J. Am. Chem. Soc.* **1990**, *112*, 8251-8260; b) J. L. Dodds, R. McWeeny, A.J. Sadlej, *Mol. Phys.* **1980**, *41*, 1419-1430; c) R. Ditchfield, *Mol. Phys.* **1974**, *27*, 789-807; (d) R. McWeeny, *Phys. Rev.* **1962**, *126*, 1028-1034.

(23) T. M. Klapötke, P. Mayer, K. Polborn, J. M. Welch, *New Trends in Research of Energetic Materials, Proceedings of the Seminar, 9th, Pardubice*, Czech Republic, Apr. 19-21, **2006**, (Pt. 2), P631-640.

(24) T. M. Klapötke, P. Mayer, C. Miro-Sabate, J. M. Welch, N. Wiegand, *Inorg. Chem.* **2008**, *47*, 6014-6027.

(25) http://www.bam.de.

(26) 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 a.>80 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.

(27) T. M. Klapötke, C. M. Rienäcker, *Propellants Explos. Pyrotech.* **2001**, *26*, 43-47.

(28) N. D. Griffiths, B. J. W. F. Brynley, A. A. Thatcher, *Eu. Pat.* EP0323885, **1989**.

4. Coordination Polymers Based on Copper(II) Complexes with Neutral Tetrazole-Containing Ligands

Abstract: Two different copper complexes were synthesized. The first one is a three-dimensional structure based on copper(II) nitrate and the tridented tetrazole ligand tris(2-(1*H*-tetrazol-1-yl)ethyl)amine. The second coordination polymer based on copper(II) nitrate was formed by using 1,2-bis(5-monomethylhydrazinyl-1*H*-tetrazolyl)ethane as neutral ligand. Both complexes possess a green flame color and are suitable for an application as colorant agents in pyrotechnical applications.

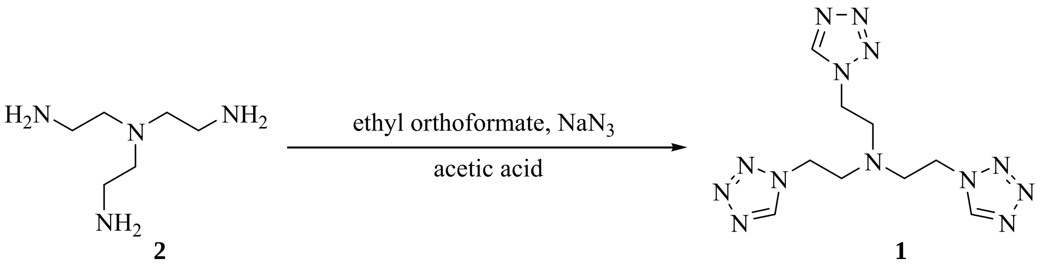
4.1 Introduction

Besides the application of tetrazoles as organic compounds in explosives or in pharmaceutical chemistry,[1] their ability to form complexes with organic and metal cations is an appreciated feature. In inorganic chemistry, tetrazoles are widely used as neutral or ionic ligands in coordination chemistry. Copper complexes of nitriminotetrazolate showing weak antiferromagnetic interactions[2] or potential new contrast agents based on lanthanide(III) cations and 5-(2-pyridyl)tetrazolate or 5-(2-pyridyl-1-oxide)tetrazolate[3] are some examples. Beside mononuclear or dinuclear complexes based on tetrazoles, coordination polymers are an interesting topic. One example of coordiation polymers containing copper and silver cations was contributed by Schmidbauer by using paracyclophane as bridging ligand.[4] Having possible industrial applications in mind, our choice fell on the copper cation, because of its green flame color (if free of chloride atoms). Especially energetic copper(II) complexes are sought compounds as promising alternative to commonly used toxic flame colorant agents.

4.2 Synthesis and Characterization of a Three-dimensional Coordination Polymer based on Copper(II)nitrate and a tridented Tetrazole Ligand

4.2.1 Synthesis of the Tris(2-(1*H*-tetrazol-1-yl)ethyl)amine and the Coordination Polymer

The synthesis of tris(2-(1*H*-tetrazol-1-yl)ethyl)amine (**1**) was carried out according to common methods. Instead of the substitution reaction of the highly toxic tris(2-chloroethyl)amine with 1*H*-tetrazolates,[5] the commercially available tris(2-aminoethyl)amine (**2**) was used. The amine groups were converted into the tetrazole moieties by ethyl orthoformate and sodium azide in acetic acid[6] (*Scheme 1*).



Scheme 1. Synthesis of **1**.

The yield of the reaction is very low (10 %), compared to common yields of the reaction (40 % - 60 %). An explanation could be intramolecular reactions of the amine groups and the ethyl orthoformate leading to polymers and ring systems. A closer investigation of the formed compounds was not carried out. The remaining amine group of **1** was tried to be used as base in acid-base reactions with energetic acids like perchloric acid and nitric acid. Despite being well soluble in acidic media, only starting materials could be isolated instead of the expected salts. An explanation for the low basicity of the amine moiety could be found in the steric hindrance of the tetrazolylethyl moieties. The copper complex **3** of **1** was synthesized by the reaction of **1** with copper(II)nitrate in 2N nitric acid. Complex **3** precipitates from the aqueous solution and was obtained by filtration. The fast precipitation, carried out by the addition of a hot saturated solution of **1** to a concentrated copper(II)nitrate solution (both in 2N nitric acid) yields a light turquoise powder. If a diluted solution of **1** and copper(II)nitrate in water is heated to 100 °C, followed by the addition of 2N nitric acid, **3** does not precipitate, but crystallizes within 12 h. The formed copper compounds are identical regarding their elemental analysis.

4.2.2 Crystal Structure of 1 and 3

Compound **1** crystallizes in the monoclinic space group $P2_1/c$ with four molecular formulas per unit cell (*Figure 1*). The tetrazole moieties are oriented in such a manner, that a ball-like conformation of **1** is achieved. The free electron pair of the amine nitrogen atom N13 points towards the centre of the sphere. This conformation explains the low basicity of the nitrogen atom, due to the high sterical hindrance of the free electron pair by the substituents. The structure is stabilized by two intramolecular hydrogen bridges. The first is formed between C1-H1 as donor and N12 as acceptor, the second between C2-H2 as donor and N4 as acceptor.[7] In contrast to the expected symmetry, **1** does not possess the three-fold rotational symmetry within the crystal structure, because of a disarrangement of the tetrazole moiety containing C3 and N9 to N12.

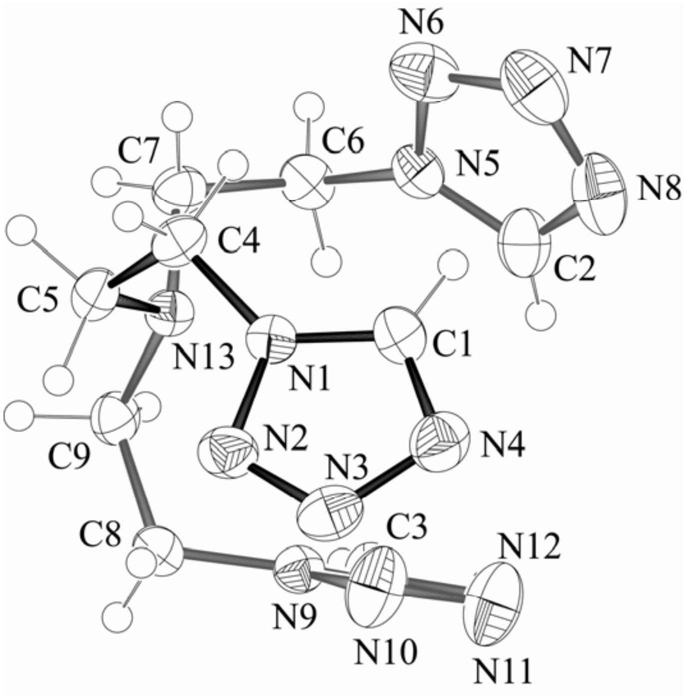


Figure 1. Molecular structure of **1**. Thermal ellipsoids are drawn at the 50% probability level.

The copper complex **3** crystallizes in the triclinic space group *P*-1 with two molecular formulas per unit cell (molecular formula: $[(C_9H_{15}N_{13})_2Cu](NO_3)_2$). The investigation of the conformation of the tristetrazole **1** and the tristetrazole moiety of **3** shows significant differences. Due to the coordination to the copper cation, the ball-like conformation of **1** is spread and the tetrazolyl ethyl substituents are oriented away from N13 (*Figure 2*). But in spite of the spread character of the amine nitrogen N13, only the complex of the neutral ligand instead of the corresponding nitrate salt was formed although 2N nitric acid was used as solvent. This behavior is another proof of the low basicity of N13. Another difference between **1** and the tristetrazole moiety of **3** is the coordination geometry of the amine nitrogen N13. In case of **1**, the three angles between the alkyl moieties are equal (111.6 °), whereas the values of the angles of **3** vary by 1.6 ° (114.9 °, 114.3 ° and 113.3 °). The sum of the angles of **1** is 334.8 °, the sum of the angles of the tristetrazole moiety of **3** is 342.5 ° (*Figure 3*).

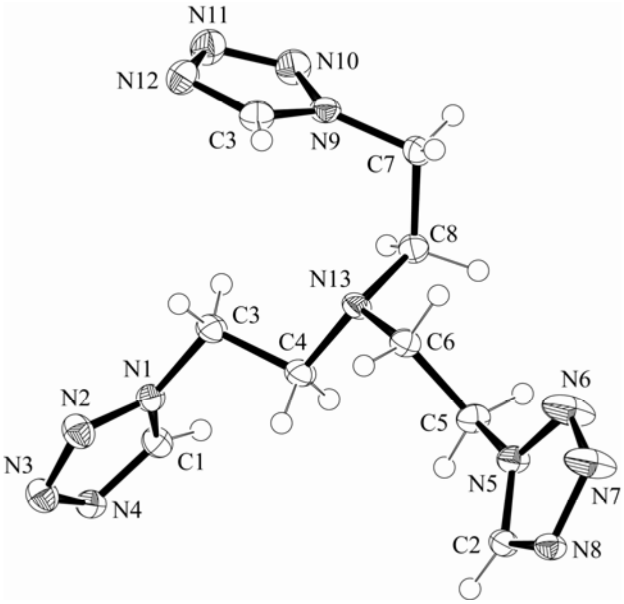


Figure 2. Molecular structure of the tristetrazole **1** of the copper complex **3**. Thermal ellipsoids are drawn at the 50% probability level.

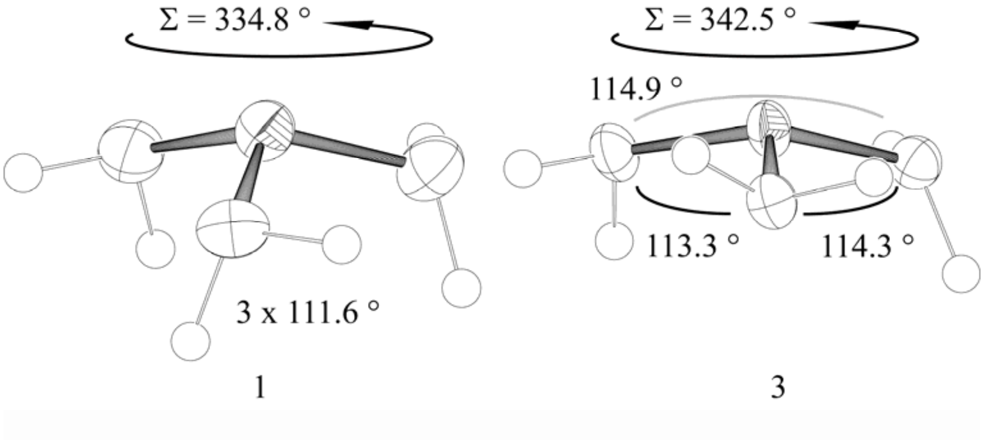


Figure 3. Planarity of the amine nitrogen atom of **1** and in the copper complex **3**.

The copper cation of **3** is coordinated distorted octahedral by six tetrazole moieties of six different tristetrazole moieties (*Figure 4*). The tetrazole moieties are all coordinated to the copper cation with the nitrogen atom next to the tetrazole carbon (N4, N8 and N12). The distances to the tetrazole moieties of the equatorial coordination are 2.02 Å, whereas the distance to the axial tetrazole moieties is significantly longer (2.44 Å). These distances lead to the expected distorted octahedral coordination. The nitrate anion is integrated into the structure by two different non-classical hydrogen bonds. The first is formed between C1-H1 as donor and O3 of the nitrate anion as acceptor (D•••A: 3.282 Å, angle: 171.2 °), the second between C2-H2 as donor and O2 of the nitrate anion as acceptor (D•••A: 3.194 Å, angle: 148.6 °). The tristetrazole moieties and the copper cation form a three dimensional network, within the porous network, the existing channels are crowed with the nitrate anion (*Figure 5*).

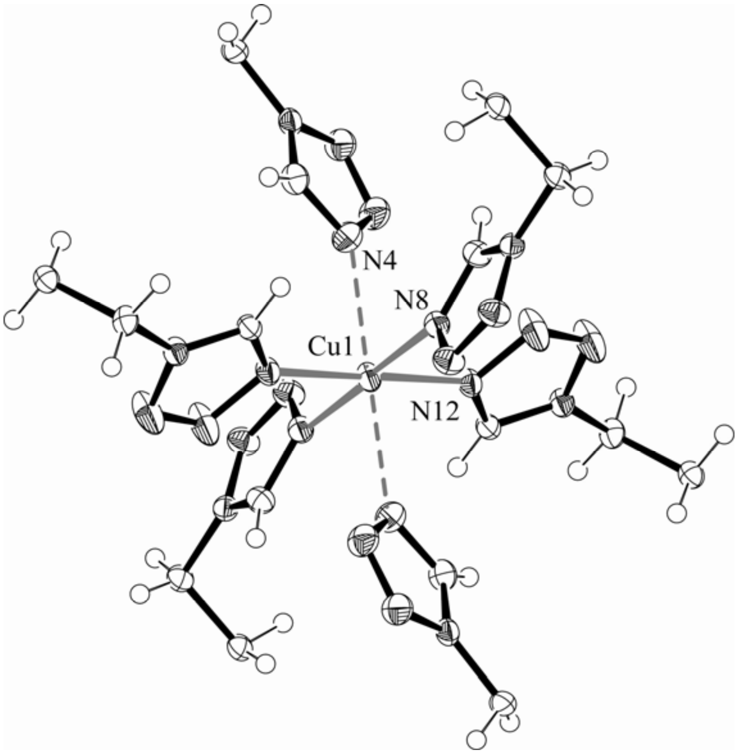


Figure 4. Coordination of the copper atom by the tetrazole moieties. Thermal ellipsoids are drawn at the 50% probability level.

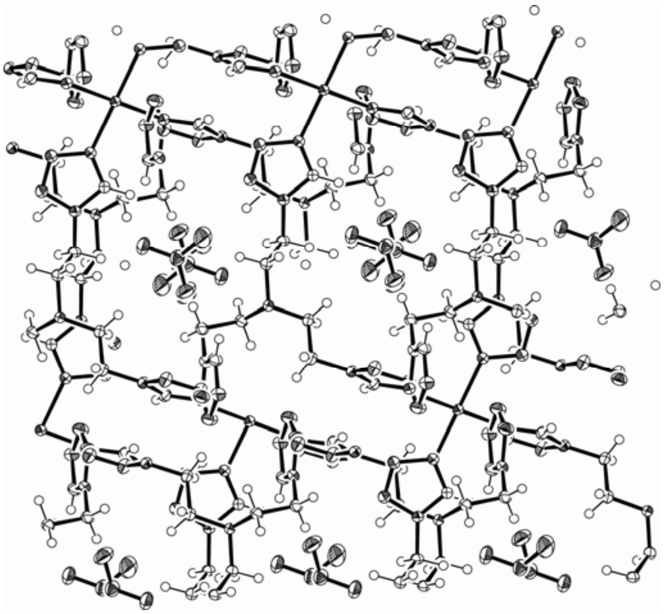


Figure 5. Arrangement of **3** in the crystal.

4.2.3 Energetic Properties of 1 and 3

In order to analyze a potential application of **1** as gas generating agent or **3** as colorant agent in pyrotechnical applications, the thermal and physical stability of **1** and **3** was determined by BAM methods.[8,9]

The sensitivity towards impact of **1** (>25 J) was slightly higher than that of **3** (>10 J). The sensitivity towards friction of both compounds was higher than 360 N. According to the UN Recommendations on the Transport of Dangerous Goods[9] both compounds are insensitive towards friction and sensitive towards impact.

The thermal stability of **1** and **3** was determined using DSC measurements (*Figure 6*). Compound **1** melts at 142 °C and possesses a point of decomposition at 199 °C. The difference of nearly 60 °C between the melting point and decomposition point allows an application as melt-castable explosive. Compound **3** does not possess any melting points. Instead, three points of decomposition can be found (135 °C, 168 °C and 190 °C). The analysis of the thermal stability of **3** reveals its disadvantage. For an application, the explosive compound should reach at least a thermal stability of 200 °C to grant a safe handling.

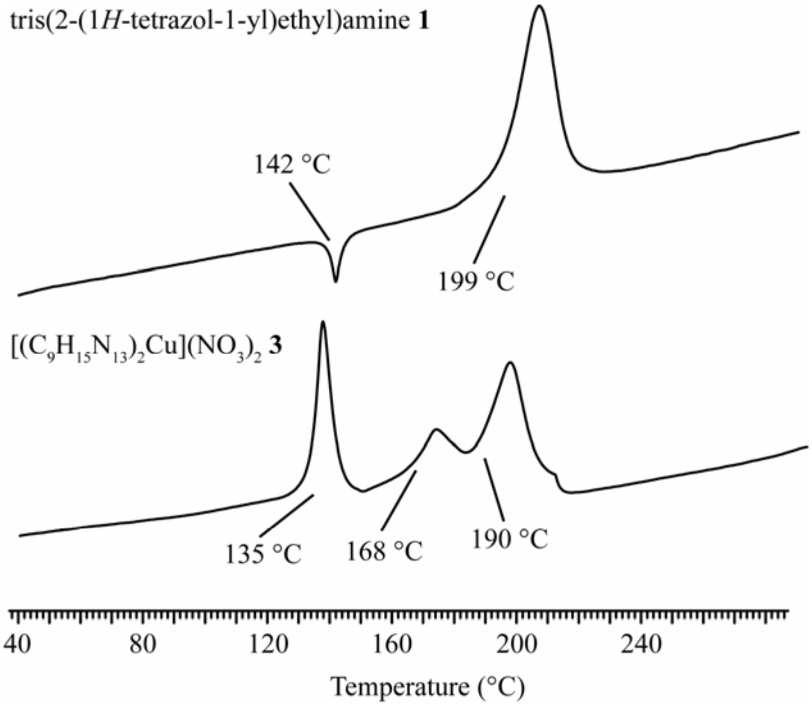


Figure 6. DSC-plot of **1** and **3** (exo = up).

The energetic properties of **1** were determined by bomb calorimetric measurements along with calculations using the EXPLO5 software.[10] The energy of combustion (ΔU_c) was determined by bomb calorimetric measurements. The enthalpy of formation was calculated using ΔU_c with the Hess thermochemical cycle as reported in literature.[11] The combustion reaction of **1** is given in *Figure 7*. The heats of formation of H_2O (l) (-286 kJ mol^{-1}) and CO_2 (g) (-394 kJ mol^{-1}) were obtained from literature.[12] The energetic properties of **3** could not be calculated by the EXPLO5 software, because copper is not implemented in the software. The energetic properties of **1** are summarized in *Table 2*.

$$C_9H_{15}N_{13} + 12.75\ O_2 \longrightarrow 9\ CO_2 + 7.5\ H_2O + 6.5\ N_2$$

Figure 7. Combustion reaction of **1**.

In order to classify the performance of **1**, a comparison of **1** and common explosives (TNT, RDX and nitrocellulose) is given in *Table 2*. In comparison with these compounds, **1** proves to be a moderate explosive. The advantage of **1** compared to TNT, RDX or nitrocellulose is its environmental compatibility. TNT, RDX as well as nitrocellulose bear nitro groups or nitric esters as energetic moieties. The toxicity of nitroaromatic compounds[13] or explosives containing nitro functions (nitrogroup, nitric ester)[14] was intensively studied and the importance of environment friendly explosives realized. Compound **1** possesses enhanced energetic properties compared with TNT, but does not contain any toxic moieties like nitro or azide groups.

Table 2. Energetic properties of **1**.

	1	TNT[k]	RDX[k]	nitrocellulose[k]
formula	$C_9H_{15}N_{13}$	$C_3H_6N_6O_6$	$C_3H_6N_6O_6$	$C_6H_{7.26}N_{2.74}O_{10.48}$
molecular mass	305.31	227.1	222.1	285
density (g cm^{-3})[a]	1.451	1.65	1.82	1.3-1.7
Impact sensitivity (J)	25	15	7.5	3
Friction sensitivity (N)	360	353	120	353
$-\Delta U_{\text{comb.}}$ (cal g^{-1})[b]	6584			
ΔH_{comb} (kJ mol^{-1})[c]	896			
$\Delta_f H_m$ (kJ mol^{-1})[d]	860			
Values calculated by EXPLO5 V5.02				
$-\Delta_E U_m°$ (kJ kg^{-1})[e]	3656	5099	6016	4479
T_E (K)[f]	2459	3737	4344	3736
$p_{C\text{-}J}$ (kbar)[g]	176	205	348	167
D (m s^{-1})[h]	7443	7176	8969	6673
Gas vol. (L kg^{-1})[i]	735	620	790	711
I_s (s)[l]	193	200	252	227
I_s (s)[m] (70 % ADN)	242	240	232	230

[a] estimated from a structure determination; [b] experimental (constant volume) combustion energy; [c] experimental molar enthalpy of combustion; [d] molar enthalpy of formation; [e] energy of explosion; [f] explosion temperature; [g] detonation pressure; [h] detonation velocity; [i] assuming only gaseous products; [k] obtained from the database of EXPLO5 V5.02; [l] specific impulse (isobaric combustion, chamber pressure 60 bar, frozen expansion); [m] specific impulse of a mixture containing 70 % ammonium dinitramide as oxidizer.

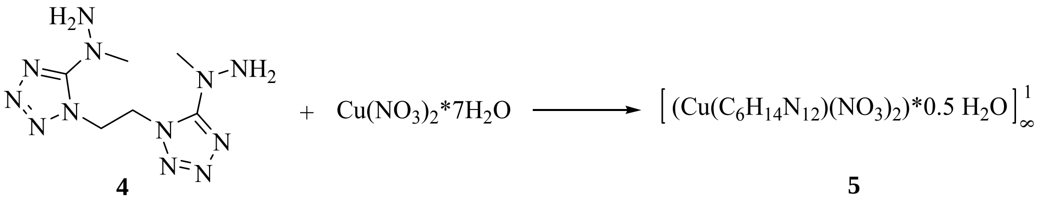
4.2.4 Conclusions

Tris(2-(1*H*-tetrazol-1-yl)ethyl)amine **1** and the corresponding complex of two tris(2-(1*H*-tetrazol-1-yl)ethyl)amine and one copper(II)nitrate **3** were synthesized. Both compounds are insensitive towards friction and sensitive towards impact. Compound **1** possesses a point of decomposition of 199 °C and a melting point of 142 °C. The difference of 60 °C between the melting point and decomposition point renders this compound into a useful melt-castable explosive. Moreover, a comparison between common explosives and **1** showed its moderate energetic properties along with its improved environmental compatibility. In case of **3**, the low thermal stability prevents this compound from being used as colorant agent in pyrotechnical applications. Both compounds were characterized by vibrational spectroscopy (IR) and the crystal structure was determined by single crystal X-ray diffraction.

4.3 Synthesis of a One-Dimensional Coordination Polymer Based on Copper(II) nitrate and 1,2-Bis(5-monomethylhydrazinyl-1*H*-tetrazolyl)ethane

4.3.1 Synthesis of the Complex of Copper(II) Nitrate and 1,2-Bis(5-monomethyl hydrazinyl-1H-tetrazolyl)ethane

The synthesis of 1,2-bis(5-monomethylhydrazinyl-1*H*-tetrazolyl)ethane (**4**) was performed after *paragraph 2.2.1.2*. The copper(II) complex (**5**) was obtained by heating a 1:1 mixture of copper(II) nitrate heptahydrate and **4** in water. The complex crystallized after some time as violet crystals from the solution (*Scheme 2*).



Scheme 2. Synthesis of the copper(II) complex **5**.

4.3.2 Crystal Structure of 5

The copper(II) complex **5** crystallizes as hemihydrate in the monoclinic space group *Pbca* with eight molecular formulas per unit cell. The 1,2-bis(5-monomethylhydrazinyl-1*H*-tetrazolyl)ethane ligand of **5** adopts a compact conformation (*Figure 8*), instead of the spread geometry of the free ligand **4** (compare *paragraph 2.2.1.2.6*, *Figure 9*). The molecule was twisted around the C2-C3 bond to create the compact structure observed. The comparison of the torsion angle of the free ligand **4** and the ligand in the complex **5** illustrates this finding. The torsion angle of **4** is found to be exactly 180.0 ° (N1-C2-C2'-N1'), whereas the torsion angle of the ligand **5** is determined to be -66.4 ° (N1-C2-C3-N7).

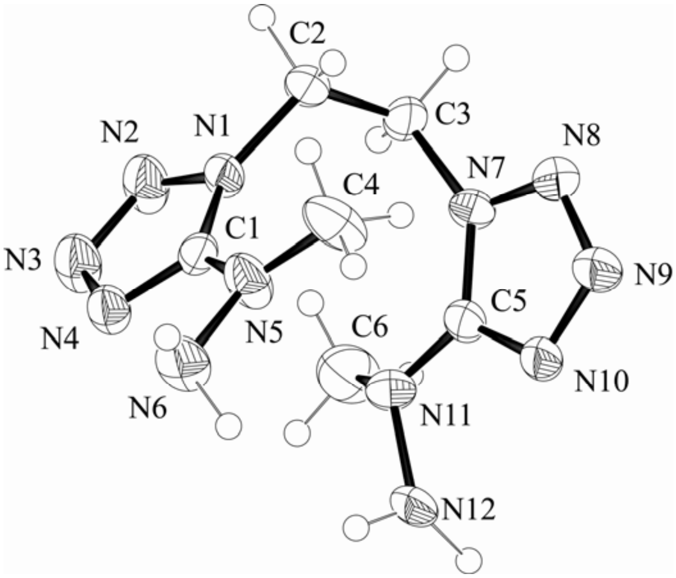


Figure 8. Molecular structure of the ligand of the complex **4**. Thermal ellipsoids are drawn at the 50% probability level.

The copper cation is coordinated distorted octahedral by two different 1,2-bis(5-monomethylhydrazinyl-1*H*-tetrazolyl)ethane moieties and two nitrate anions (*Figure 9*). The bond lengths of the equatorial coordinated nitrogen atoms to the copper cation are all found in the range of 1.948 Å to 2.019 Å. The axial bond distances to the nitrate oxygen atoms O1 and O4 are longer, as expected for the distorted octahedral coordination geometry. The bond length of Cu1-O1 is found to be 2.807 Å, whereas the bond length of Cu1-O4 is by 15 % shorter (2.395 Å).

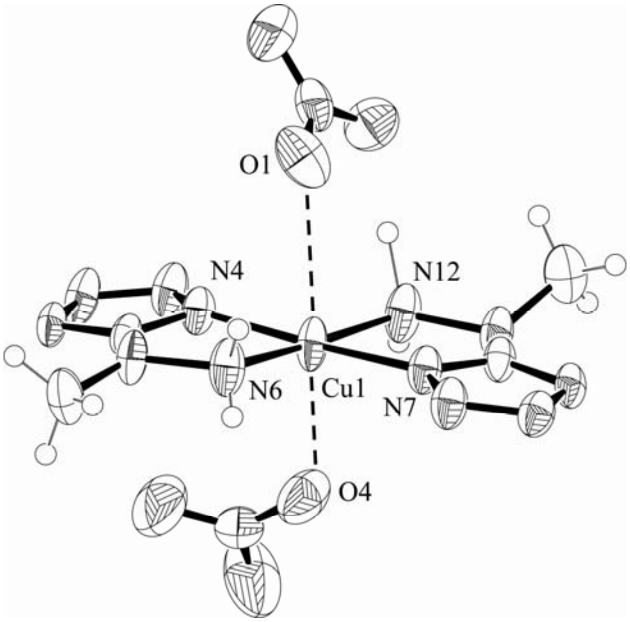


Figure 9. Coordination of the copper cation in the complex **5**. Thermal ellipsoids are drawn at the 50% probability level.

The connection of two copper cations by one ligand leads to the formation of a one-dimensional coordination polymer. The twisted conformation at the C2-C3 bond of the ligand results in zig-zag chains along the x-axis (*Figure 10*). The arrangement of the chains along the x-axis in the crystal structure is shown in *Figure 11*. The chains are arranged next to each other, forming layers. Between these layers, the highly distorted molecule of water is embedded.

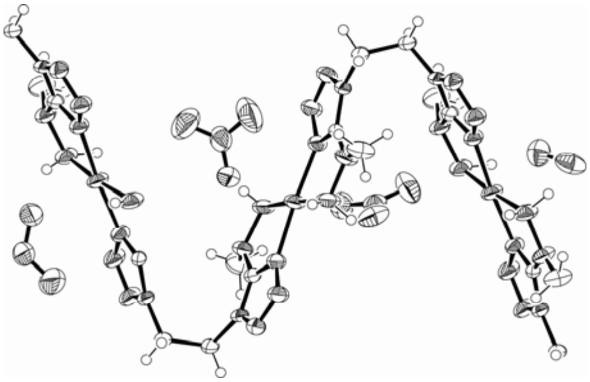


Figure 10. Zig-zag chain of the coordination polymer. Thermal ellipsoids are drawn at the 50% probability level.

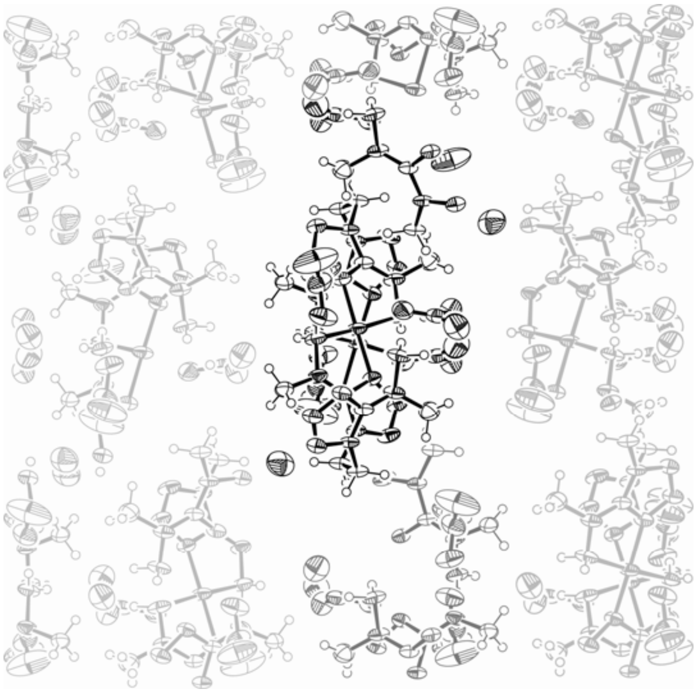


Figure 11. Arrangement of the chains along the x-axis. Thermal ellipsoids are drawn at the 50% probability level.

The crystal structure is stabilized by several hydrogen bridges. Due to the fact, that the hydrogen atoms of the highly disordered water molecule could not be found, only hydrogen bridges formed by the hydrazine moiety are discussed. The nitrogen atom N6 of the hydrazine moiety forms two hydrogen bridges to two nitrate anions (*Figure 12*). Each proton of N6 is connected with two oxygen atoms of the nitrate anions. Both nitrate anions are coordinated to different copper cations than N6. The nitrogen atom N12 of the other hydrazine moiety forms two hydrogen bridges to one nitrate anion, in analogy to N6 (*Figure 12*). But in contrast to N6, the second proton forms a hydrogen bridge to the oxygen atom of the nitrate anion, coordinated to the copper cation N12 is coordinated to. The bond distances and angles of the hydrogen bridges are given in *Table 3*.

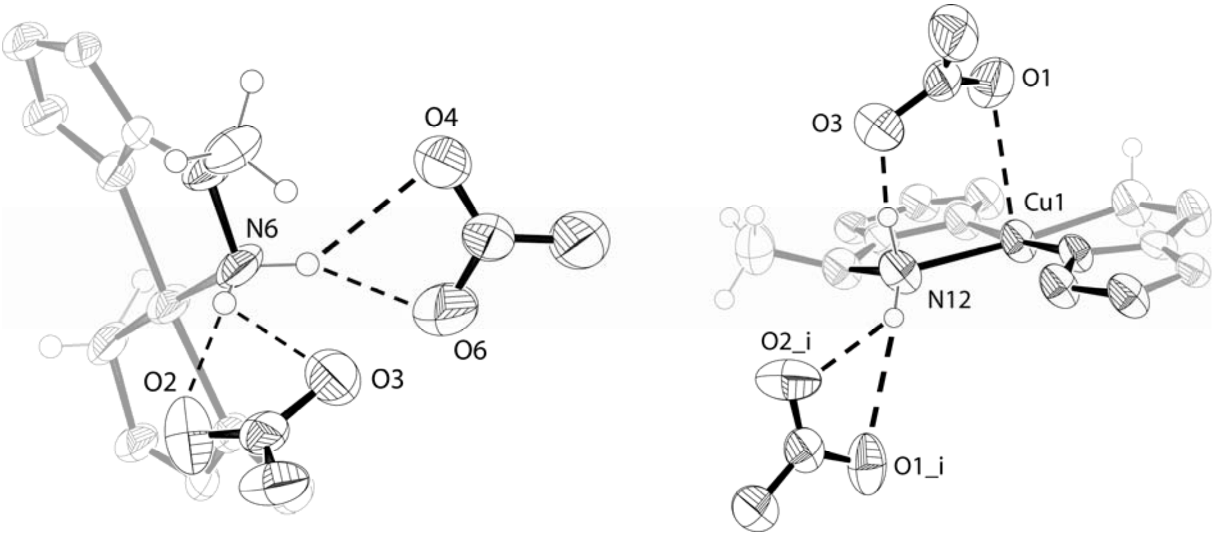


Figure 12. Hydrogen bridges formed by N6 and N12. Thermal ellipsoids are drawn at the 50% probability level.

Table 3. Hydrogen bonds of the hydrazine moiety of the ligand of **5**.

donor atom	acceptor atom	D–H [pm]	H•••A [pm]	D•••A [pm]	< (D–H•••A)
N6	O2	0.755	2.376	3.126	172.04
N6	O3	0.755	2.517	3.033	127.18
N6	O4	0.928	2.297	2.956	143.69
N6	O6	0.928	2.078	2.956	157.43
N12	O1_i	0.782	2.417	3.192	171.50
N12	O2_i	0.782	2.489	3.061	131.13
N12	O3	1.202	1.637	2.814	164.50

4.3.3 Energetic Properties of 5

In order to investigate the suitability of **5** as green colorant agent in pyrotechnical applications, its thermal and physical stability was determined. The friction and impact sensitivity was determined by BAM methods.[8,9] In case of **5**, the determination of the energetic characteristics was not possible, because copper containing compounds are not included in the

EXPLO5 software.

The analysis of the thermal stability of **4** and **5** reveals significant differences (*Figure 13*). The thermal stability of **5** is by 90 °C lower than that of the free ligand (**5**: 180 °C; **4**: 270 °C, *paragraph 2.2.1.2.4*, *Table 4*). In search for an explanation of the reduced thermal stability, two possible options can be found. One explanation would be a destabilization of the ligand by the copper cation. However, a large number of copper(II)-tetrazole complexes are reported in literature with a higher point of decomposition, compared to **5**.[15] A more convincing explanation would be that the nitrate anions next to the hydrazine moiety simplify an oxidation of the hydrazine moiety, leading to the decomposition of the ligand.

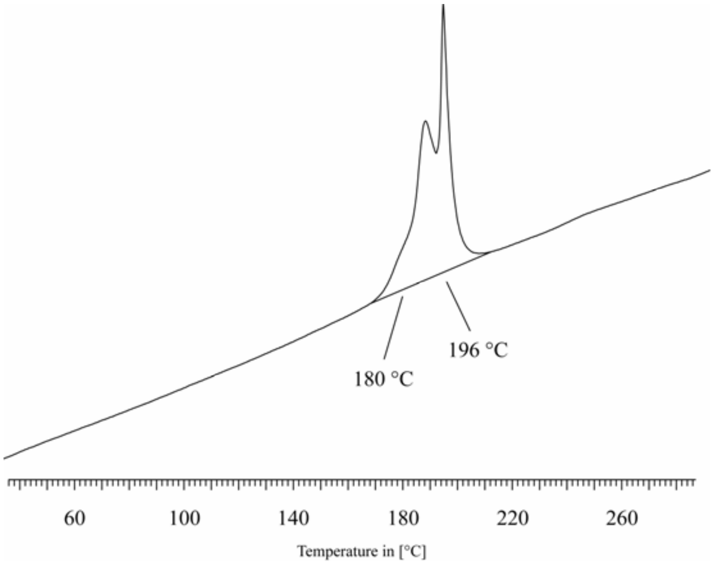


Figure 13. DSC-plot of complex **5** (exo = up).

The comparison of the impact and friction sensitivities of **4** and **5** prove the decreased sensitivity of **5** compared to the tetrazole **4**. Compound **4** is insensitive towards friction (>360 N, *paragraph 2.2.1.2.4*), whereas **5** is sensitive towards friction (>120 N).

Regarding the sensitivity towards impact, compound **4** is sensitive towards impact (>10 J, *paragraph 2.2.1.2.4*), whereas the impact sensitivity of **5** was determined to be >1 J, proving the destabilization of the ligand by either the copper cation or the nitrate anions.

4.3.4 Conclusions

A one-dimensional coordination polymer based on copper(II) nitrate and 1,2-bis(5-monomethylhydrazinyl-1*H*-tetrazolyl)ethane was prepared. The thermal and physical stability was investigated and the complex proved not to be suitable as green colorant agent for pyrotechnical applications. The energetic characteristics of the ligand itself and the starting material 1,2-bis(1*H*-tetrazolyl)ethane were determined by bomb calorimetric measurements and calculations using the EXPLO5 software. Both compounds proved to be moderate energetic materials with high thermal and physical stabilities. Due to a lack of toxic nitro or azide groups both compounds are potential environment friendly gas generating agents.

4.4 Experimental Section

CAUTION! Tetrazoles, bromotetrazoles, tetrazolylhydrazines and azidotetrazoles are highly energetic compounds with sensitivity towards heat and impact. Although we had no problems in synthesis, proper protective measures (safety glasses, face shield, leather coat, earthened equipment and shoes, Kevlar® gloves and ear plugs) should be used when undertaking work involving these compounds.

The preparation of 1,2-bis(5-monomethylhydrazinyl-1*H*-tetrazolyl)ethane **1,** 1,2-bis(5-bromo-1*H*-tetrazolyl)ethane **2** and 1,2-bis(1*H*-tetrazolyl)ethane **3** is reported in the experimental section of *paragraph 2.2.1.*

4.4.1 Synthesis of Tris(2-(1*H*-tetrazol-1-yl)ethyl)amine 1

Tris(2-aminoethyl)amine (20.0 g, 136 mmol) was suspended in triethyl orthoformate (101.5 mL). Sodium azide (31.7 g, 488 mmol) was added to the reaction mixture and acetic acid (81 mL) was added drop wise at 0 °C. The reaction mixture was heated at 100 °C for 8 h. Afterwards concentrated hydrochloric acid (40 mL) was added at ambient temperature and the solvent was removed under reduced pressure. The residue was neutralized by sodium hydroxide and extracted with ethyl acetate. The product precipitated after one day from the aqueous solution (4.1 g, 13 mmol, 10 %).

m. p. 142 °C °C, dec. 199 °C.

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3441 (m), 3145 (m), 3014 (w), 2977 (w), 2951 (w), 2899 (w), 2847 (m), 2831 (m), 1734 (w), 1688 (w), 1635 (w), 1483 (s), 1454 (m), 1435 (s), 1384 (m), 1351 (m), 1303 (m), 1281 (m), 1253 (m), 1202 (w), 1174 (m), 1153 (m), 1118 (s), 1100 (vs), 1046 (m), 1030 (m), 995 (m), 966 (m), 975 (m), 877 (m), 871 (m), 737 (vw), 723 (vw), 677 (m), 645 (m), 536 (m).

^{1}H NMR (*d6*-DMSO) δ: 3.02 (t, 2H, ^{3}J = 6.53 Hz, CH_2), 4.42 (t, 2H, ^{3}J = 6.53 Hz, CH_2), 9.15

(s, 1H, C*H*).

^{13}C NMR (*d6*-DMSO) δ: 45.9 (CH_2), 52.6 (CH_2), 144.5 (C_q).

m/z (DEI) 306 (M+H), 278, 253, 250, 228, 208, 180.

elemental analysis: calcd (%) for $C_9H_{15}N_{13}$: C 35.41, H 4.95, N 59.64; found: C 35.26, H 5.03, N 59.39.

4.4.2 Synthesis of [$(C_9H_{15}N_{13})_2Cu$]$(NO_3)_2$ 3

Tris(2-(1*H*-tetrazol-1-yl)ethyl)amine 1 (2.0 g, 7 mmol) was dissolved in 2N nitric acid and a solution of copper(II)nitrate trihydrate (3.0 g, 12 mmol) in 2N nitric acid was added. The copper complex precipitated within 6 h to 12 h from the acidic solution (4.0 g, 5 mmol, 71 %).

dec. 135 °C, 168 °C, 190 °C.

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3114 (w), 3022 (w), 2986 (w), 2426 (vw), 1668 (vw), 1630 (w), 1506 (w), 1436 (m), 1384 (vs), 1321 (m), 1262 (w), 1171 (m), 1107 (m), 1038 (w), 1004 (w), 991 (w), 978 (w), 935 (vw), 906 (vw), 888 (vw), 829 (vw), 819 (vw), 783 (vw), 772 (vw), 717 (vw), 674 (vw), 662 (w), 644 (vw), 554 (vw).

elemental analysis: calcd (%) for $C_{18}H_{30}CuN_{28}O_6$: C 27.09, H 3.79, N 49.14; found: C 26.81, H 3.67, N 48.91.

4.4.3 Synthesis of $(Cu(C_6H_{14}N_{12})(NO_3)_2)$*0.5 H_2O

1,2-Bis(5-monomethylhydrazinyl-1*H*-tetrazolyl)ethane **1** (500 mg, 2.0 mmol) and copper(II) nitrate heptahydrate (460 mg, 2.0 mmol) were suspended in water (5 mL) and heated to 100 °C. The complex precipitated as violet crystals after some time from the clear solution (720 mg, 1.6 mmol, 84 %).

dec. 180 °C.

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3564 (m), 3487 (m), 3444 (m), 3175 (m), 3076 (m), 2929 (m), 2715 (vw), 2426 /vw), 2385 (vw), 1658 (s), 1582 (m), 1476 (m), 1417 (s), 1384 (vs), 1356 (vs), 1341 (vs), 1267 (m), 1218 (m), 1143 (m), 1126 (m), 1083 (m), 1040 (w), 1033 (w), 1004 (w), 962 (w), 918 (w), 826 (W), 729 (w), 719 (w), 696 (w), 684 (w), 674 (w), 630 (vw), 485 (vw).

elemental analysis: calcd (%) for $C_{12}H_{30}N_{28}Cu_2O_{13}$: C 15.99, H 3.35, N 43.50; found C 15.82, H 3.33, N 43.26.

4.5 Crystallographic Data

4.5.1 Synthesis and Characterization of a Three-dimensional Coordination Polymer Based on Copper(II)nitrate and a Tridented Tetrazole Ligand

CCDC-746454 (**1**) and -746453 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

Table 4. Selected crystal data for **1** and **3**.

	1	**3**
Formula	$C_9H_{15}N_{13}$	$C_{18}H_{30}N_{28}O_6Cu$
M_r [g mol^{-1}]	305.31	798.17
Crystal system	monoclinic	triclinic
Space group	*P*21/*c*	*P*-1
a [Å]	8.85380(10)	8.5850(5)
b [Å]	8.86260(10)	8.9606(5
c [Å]	17.8227(3)	11.9532(7)
α [°]	90	70.215(5)
β [°]	91.450(2)	76.919(5)
γ [°]	90	69.639(5)
V [Å³]	1398.06(3)	805.02(8)
Z	4	2
F(000)	640	411
$\rho_{calc.}$ [g cm^{-3}]	1.451	1.647
μ [mm^{-1}]	0.105	0.764
2 theta [°]	53.99	53.99
Index range	-11 ≤ h ≤ 11	-10 ≤ h ≤ 10
	-11 ≤ k ≤ 11	-11 ≤ k ≤ 11
	-22 ≤ l ≤ 22	-15 ≤ l ≤ 15
λ [Å]	0.71073	0.71073
T [K]	200(2)	200(2)
Reflections collected	30653	11017
Unique reflections	3040	3497
Parameter	259	301
S	1.058	1.055
R_{int}	0.0269	0.0223

R_1/ wR_2 [I>2σ(I)]	0.0297/ 0.0739	0.0295 / 0.0735
R_1/ wR_2	0.0415/ 0.0778	0.0408 / 0.0779

4.5.2 Synthesis of a One-Dimensional Coordination Polymer Based on Copper(II) nitrate and 1,2-Bis(5-monomethylhydrazinyl-1*H*-tetrazolyl)ethane

CCDC-752243 (5) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

Table 5. Crystal data of **5**.

	5
Formula	$C_6H_{14}CuN_{14}O_{6.49}$
M_r [g mol^{-1}]	449.69
Crystal system	orthorhombic
Space group	*Pbca*
a [Å]	12.2706(4)
b [Å]	15.3391(8)
c [Å]	17.3953(4)
α [°]	90
β [°]	90
γ [°]	90
V [Å³]	3274.1(2)
Z	8
F(000)	1831.2
$\rho_{calc.}$ [g cm^{-3}]	1.824
μ [mm^{-1}]	1.403
2 theta [°]	49.98
Index range	$-11 \leq h \leq 14$
	$-18 \leq k \leq 18$
	$-20 \leq l \leq 20$
λ [Å]	0.71073
T [K]	200(2)
Reflections collected	15491
Unique reflections	2875
Parameter	286
S	0.920
R_{int}	0.0756
R_1/ wR_2 [I>2σ(I)]	0.0423/0.1005
R_1/ wR_2	0.0902/0.1197

4.6 References

(1) a) E. Makino, N. Iwasaki, N. Yagi, H. Kato, Y. Ito, H. Azuma, *Chem. Pharm. Bull*. **1990**, *38*, 201; b) C. V. Reddy Sastry, *Ind. J. Chem*. **1990**, *29B*, 396; c) C. T. Alabaster, *J. Med. Chem*. **1989**, *32*, 575; d) M. Uchida, M. Komatsu, S. Morita, T. Kanbe, K. Nagakawa, *Chem. Parm. Bull.* **1989**, *37*, 322.

(2) T. M. Klapötke, J. Stierstorfer, B. Weber, *Inorg. Chim. Acta* **2009**, *362*, 2311.

(3) A. Faccetti, A. Abbotto, L. Beverina, S. Bradamante, P. Mariani, C. L. Stern, T. J. Marks, A. Vacca, G. A. Pagani, *Chem. Commun.* **2004**, 1770-1771.

(4) H. Schmidbaur, W. Bublak, B. Huber, G. Reber, G. Müller, *Angew. Chem.* **1986**, *98*, 1108-1109.

(5) a) R. K. Jaiswal, N. Jaiswal, S. S. Parmar, E. C. James, *J. Heterocycl. Chem.* **1983**, *20*, 615-617; b) O. N. Verkhozina, V. N. Kizhnyaev, L. I. Vereshchagin, A.V. Rokhin, A. I. Smirnov, *Russ. J. Org. Chem.* **2003**, *39*, 1792-1796; c) A. Chafin, D. J. Irvin, M. H. Mason, S. L. Mason, *Tetrahedron Lett.* **2008**, *49*, 3823-3826.

(6) a) Y. Satoh, N. Marcopulos, Tetrahedron Lett. **1995**, *36*, 1759-1762; b) O. H. Justiz, R. Fernandez-Lafuente, J. M. Guisan, P. Negri, G. Pagani, M. Pregnolato, M. Terreni, *J. Org. Chem.* **1997**, *62*, 9099-9106; c) N. Hassan, P. Weinberger, K. Mereiter, F. Werner, G. Molnar, A. Bousseksou, M. Valtiner, W. Linert, *Inorg. Chim. Acta* **2008**, *361*, 1291-1297.

(7) T. Steiner, *Cryst. Rev.* **1996**, *6*, 1-57.

(8) a) M. Suceska, *Test Methods for Explosives*, Springer, New York, **1995**, p. 21 (impact), p. 27 (friction); b) http://www.bam.de/.

(9) 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 a.>80 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.

(10) a) M. Suceska, *Proc. of 30th Int. Annual Conference of ICT, Karlsruhe, Germany*, ed.

Fraunhofer-Institut für chemische Technologie, DWS Werbeagentur und Verlag GmbH, Karlsruhe, 1999, 50/1; b) EXPLO5.V2, Computer program for calculation of detonation parameters, P, M. Suceska, *Proc. of 32nd Int. Annual Conference of ICT, Karlsruhe, Germany*, ed. Fraunhofer-Institut für chemische Technologie, DWS Werbeagentur und Verlag GmbH, Karlsruhe, 2001, pp. 110/1.

(11) T. M. Klapötke, M. Stein, J. Stierstorfer, *Z. Anorg. Allg. Chem.* **2008**, *634*, 1711-1723.

(12) a) N. Wiberg, *Lehrbuch der Anorganischen Chemie / Holleman-Wiberg*, 101. Ed., de Gruyter, Berlin, **1995**, 141; b) N. Wiberg, *Lehrbuch der Anorganischen Chemie / Holleman-Wiberg*, 101. Ed., de Gruyter, Berlin, **1995**, pp 250, 859 and 1176; c) http://webbook.nist.gov/chemistry/

(13) O. Isayev, B. Rasuley, L. Gorb, J. Leszczynski, *Mol. Diversity*, **2006**, *10*, 233-245.

(14) a) H. Stucki, *Chimia* **2004**, *58*, 409-413; b) M. M. Perchermeier, F. Kiefer, F. J. Wiebel, *Toxicol. Lett.* **1994**, *72*, 53-7; c) G. B. FitzGerald, A. Austin, N. DiGuilio, *Report* **1991**, (Order No. AD-A236 352), 76.

(15) a) M. Friedrich, J. C. Galvez-Ruiz, T. M. Klapötke, P. Mayer, B. Weber, J. J. Weigand, *Inorg. Chem.* **2005**, *44*, 8044-8052; b) G. Geisenberger, T. M. Klapötke, J. Stierstorfer, *Eur. J. Inorg. Chem.* **2007**, 4743-4750; c) T. M. Klapötke, J. Stierstorfer, B. Weber, *Inorg. Chim. Acta* **2009**, *362*, 2311-2320.

5. Energetic Materials Based on 1,2,3-Triazoles

Abstract: The chemistry of 1,2,3-triazoles was investigated by using several derivatives of 1,2,3-triazole with methoxy-substitutents as model compounds. The corresponding nitrate esters and azides were prepared, whereas the synthesis of the nitramines could not be realized. By taking the results into account, the corresponding polymeric 1,2,3-triazoles were prepared by using GAP and polyvinyl azide as starting materials. Whereas the triazoles themselves proved to be low explosives, the corresponding polymeric derivatives showed good explosive properties. Their sufficiently high thermal and physical stability renders these polymers into promising candidates for the development of new binder systems.

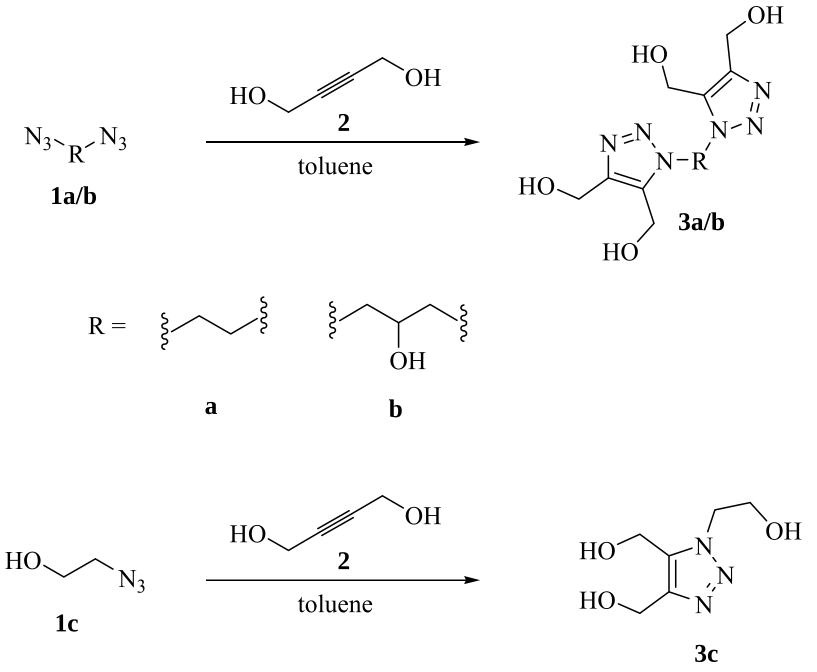
5.1 Introduction

Besides tetrazoles, triazoles are common backbones for the synthesis of energetic materials. Triazoles possess higher thermal and physical stabilities compared to tetrazoles. However, the nitrogen content of triazoles is lower than that of tetrazoles, but in contrast to tetrazoles, triazoles can bear three functionalities (two substituted carbon atoms and one substituted nitrogen atom), whereas tetrazoles are only capable of bearing two functionalities (one substituted carbon atom and one substituted nitrogen atom). Therefore, triazoles offer more possibilities for the introduction of energetic moieties. Another advantage of triazoles, especially 1,2,3-triazoles, is the simple synthesis by the reaction of a derivative of acetylene with an alkyl azide.[1] Besides the easy formation of triazoles, the availability of azide containing polymers like GAP or polyvinyl azide as starting materials renders the polymerization reactions reported in the previous paragraphs unnecessary. In order to investigate the reactivity of the triazoles and the methods to introduce common energetic moieties like nitrate esters, azides and nitramines, the experiments were first conducted and optimized using the ethyl, 2-propanol and hydroxyethyl derivatives, before the know-how was transferred to perform the corresponding polymer-analogue reactions.

5.2 Investigation of Energetic Materials Based on 1,2,3-Triazoles

5.2.1 Synthesis of the 1,2,3-Triazoles

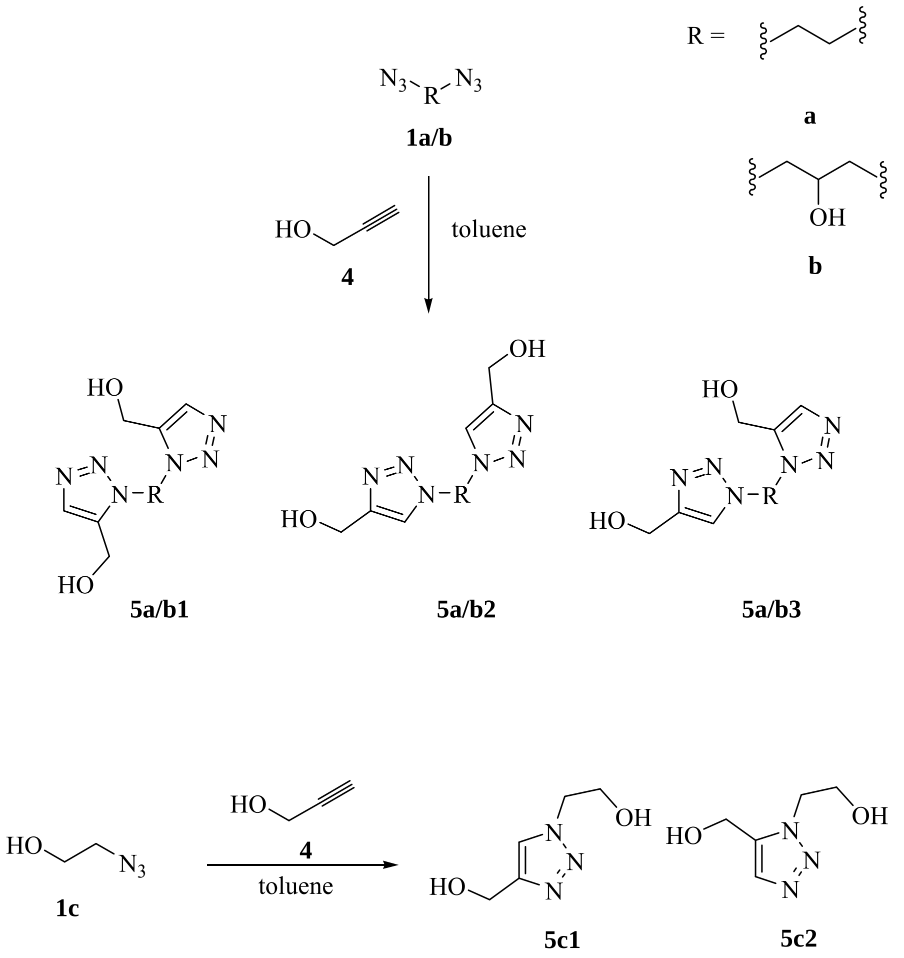
The synthesis of the triazoles was performed according to known methods.[2] In order to investigate the suitability of different triazoles as energetic compounds, three different hydroxyl-triazoles **3** were synthesized (*Scheme 1*).



Scheme 1. Synthesis of the triazoles **3a-c**.

The reaction was carried out by refluxing a suspension of **1a**/**b** and **2** in toluene for 12 h. The triazoles **3** precipitate as brown solid (in case of **3a** and **b**) and could be recovered by filtration. Compound **3** was purified by extraction with hot ethyl acetate and a subsequent recrystallization from propan-2-ol.

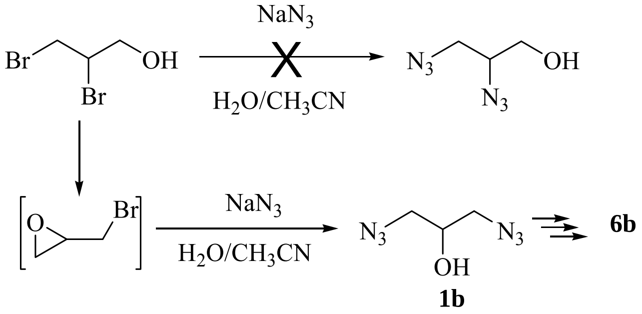
Another promising acetylene derivative for the preparation of triazoles represents the propargyl alcohol. The advantage of **4** compared to **2** is the low boiling point (115 °C). Carrying out the reaction, the triazoles could be recovered by removal of the solvent and the starting material under reduced pressure. The problem arising was the formation of isomers. The reaction with **1c** yielded two, the reaction of **1a** and **b** three different isomers (*Scheme 2*).



Scheme 2. Formation of the isomers **5** using propargyl alcohol.

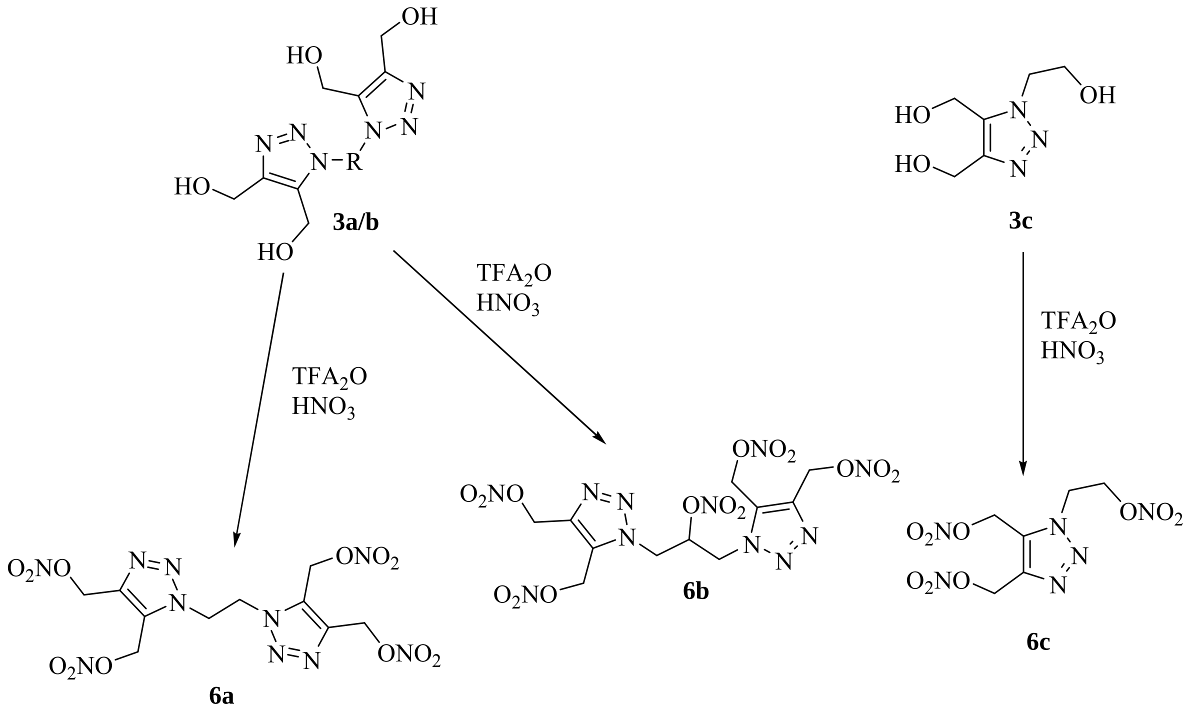
Despite our efforts to separate the different isomers, we were not successful. Although it is possible to influence the formation of isomers by adding copper cations,[3] we decided to not further investigate the compounds **5**. Even if the isomers of **5** could be separated, the energetic properties would never reach the performances of the compounds bearing two hydroxyl groups and as a result two energetic moieties per triazole. Therefore, the synthesis of these compounds would be interesting, but without any further benefit.

Besides the reported triazoles, efforts were undertaken to synthesize a fourth derivative. To investigate the different melting points, the asymmetric isomer of **3b** was tried to prepare. Therefore, the 2,3-dibromo-1-propanol was used to synthesize the corresponding diazide. But instead of the 2,3-diazido-1-propanol, the symmetric 1,3-diazido-2-propanol was formed. The isomerization could be understood by an epoxide formation as intermediate (*Scheme 3*).



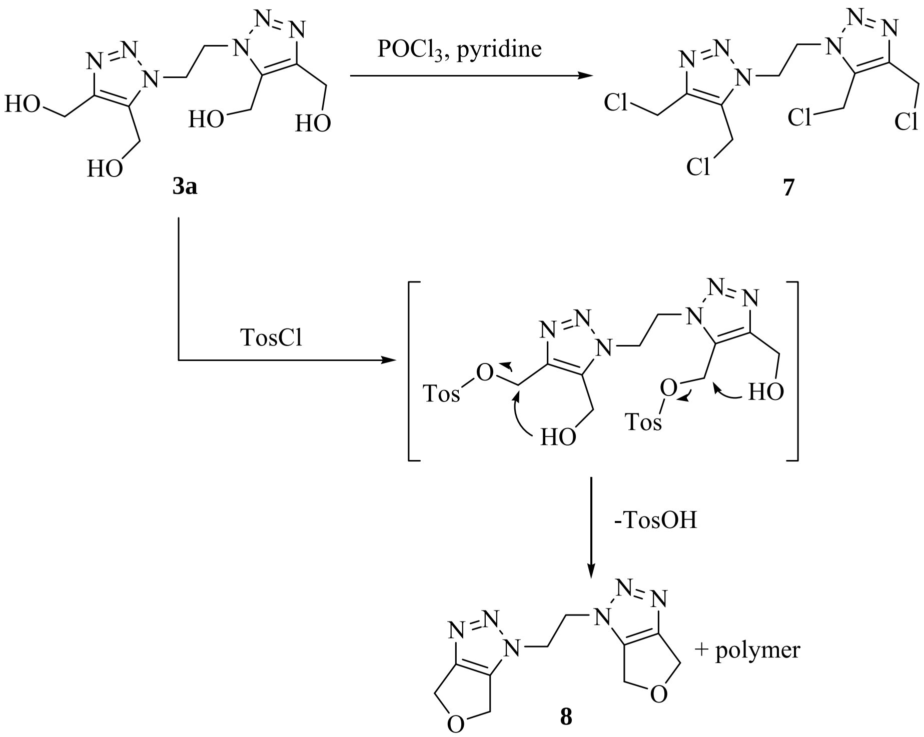
Scheme 3. Isomerization of 2,3-dibromo-1-propanol to form **1b**.

In order to convert the hydroxyl groups into energetic moieties, the triazoles **3** were nitrated. The nitration was carried out in a mixture of trifluoroacetic anhydride (TFA$_2$O) and fuming nitric acid at 0 °C (*Scheme 4*).



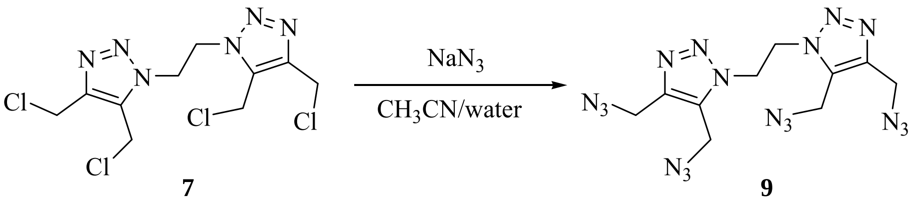
Scheme 4. Nitration of **3**.

To prepare energetic compounds with an improved thermal stability, the corresponding azide of **3a** was synthesized. Therefore, compound **3a** was chlorinated by heating **3a** in a mixture of phosphorous oxychloride and pyridine. Trials to transform the hydroxyl groups into tosyl groups were fruitless, because of an intramolecular attack of the hydroxyl group at the first formed tosyl group leading to the ether structure **8** (*Scheme 5*). Despite variation of the reaction conditions and the proportions of the starting materials, we were not able to obtain any pertosylated species of **3a**.



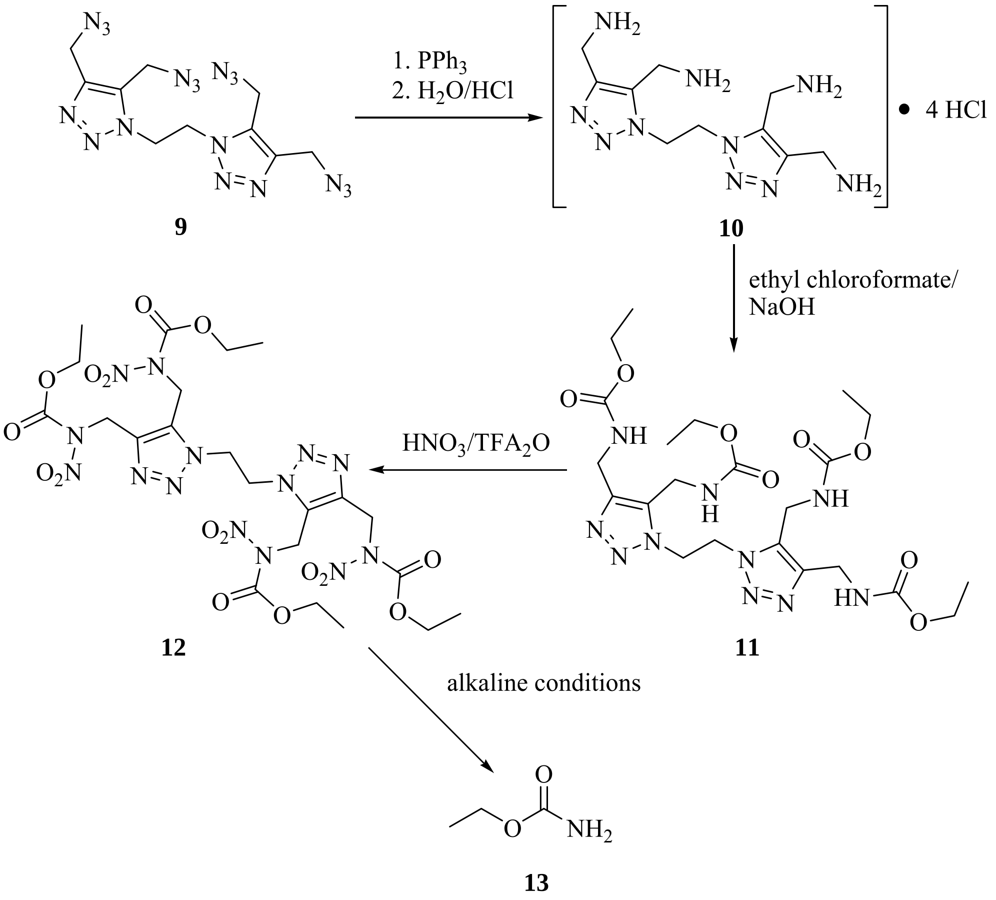
Scheme 5. Chlorination of **3a**.

The chlorine atoms of **7** were then substituted by sodium azide. To date, several methods for this substitution reaction are reported using water,[4] DMF[5] or acetonitrile[6] as solvent. Carrying out the reaction only a mixture of acetonitrile and water proved to be suitable for the substitution reaction of chlorine atoms with sodium azide (*Scheme 6*).



Scheme 6. Formation of **9**.

Besides the nitrate esters and azide moieties, nitramines are another common energetic group. The preparation of nitramines is carried out by the protection of the amine using ethyl chloroformate with a subsequent nitration and deprotection of the formed nitramine.[7] Therefore, the azide **9** was converted into the corresponding hydrochloride of the amine by a Staudinger reaction.[8] The amine **10** was protected using common reactions of ethyl chloroformate in an aqueous solution of sodium hydroxide.[9] The protected amine was then nitrated using TFA_2O and nitric acid. The protected nitramine **11** was characterized by IR spectroscopy, along with mass spectrometry and elemental analysis. The last step of the nitramine synthesis was the deprotection of **11** to yield **12**. We tried several conditions with various bases (ranging from cyclohexyl amine to potassium hydroxide), but we were not able to isolate any product. Instead, we obtained ethyl carbamate **13**, being a hint for decomposition during the deprotection reaction (*Scheme 7*).



Scheme 7. Trial to synthesize the nitramine.

5.2.2 Energetic Properties of the Triazoles

In order to investigate the energetic properties of the triazoles, their thermal (DSC-data) and physical stabilities (according to BAM standards[10]) along with their energetic characteristics were determined.

The thermal stability of the nitrate esters **6a** to **c** is low, compared to the azide derivative **9**. The decomposition points of **6a** to **c** are found between 140 °C and 150 °C (149 °C, 145 °C and 139 °C), whereas the decomposition point of **9** with 213 °C is by 60 °C higher than the decomposition points of the nitrate esters. All compounds are sensitive towards impact (>5 J to >8 J). Whereas the impact sensitivities do not differ much, the nitrate esters are more stable towards friction than the azide derivative **9** (192 N/160 N in contrast to 28 N of **7**). As a result, **6a** to **c** are sensitive and **7** very sensitive towards friction.

The energetic properties were determined by bomb calorimetric measurements along with calculations using the EXPLO5 software.[11]

Table 1. Energetic properties of **6a, 6b**, **6c** and **9.**

	6a	**6b**	**6c**	**9**
molecular formula	$C_{10}H_{12}N_{10}O_{12}$	$C_{11}H_{13}N_{11}O_{15}$	$C_6H_8N_6O_9$	$C_{10}H_{12}N_{18}$
M (g mol^{-1})	464.3	539.1	308.2	384.3
T_{dec} (°C)	149	145	139	213
density (g cm^{-3})[a]	1.5	1.32	1.57	1.55
sensitivity towards friction (N)	> 192	> 160	> 160	> 28
sensitivity towards impact (J)	> 6	> 6	> 8	> 5
$-\Delta U_{comb.}$ (cal g^{-1})[b]	2583	2508	2477	4494
ΔH_{comb} (kJ mol^{-1})[c]	-648	-547	-321	1570
$\Delta_f H_m$ (kJ mol^{-1})[d]	-690	-595	-349	1533
Values calculated by EXPLO5 V5.02				
$-\Delta_E U_m°$ (kJ kg^{-1})[e]	3814	4207	4722	4506
T_E (K)[f]	3125	3527	3700	3140
$p_{C\text{-}J}$ (kbar)[g]	154	136	207	214
D (m s^{-1})[h]	6604	6411	7418	7794
Gas vol. (L kg^{-1})[i]	721	765	751	688
I_s (s)[l]	176	207	218	216

[a] estimated from structure determination or experimental data; [b] experimental (constant volume) combustion energy; [c] experimental molar enthalpy of combustion; [d] molar enthalpy of formation; [e] energy of explosion; [f] explosion temperature; [g] detonation pressure; [h] detonation velocity; [i] assuming only gaseous products; [k] obtained from the database of EXPLO5 (V5.02); [l] specific impulse (isobaric combustion, chamber pressure 60 bar, frozen expansion); [m] specific impulse of a mixture containing 75 % ammonium dinitramide as oxidizer.

The comparison of the $-\Delta_E U_m°$ values (the work performed by the detonation) of the triazoles **6a**, **6b**, **6c** and **9** gives the best results for **6c**. $-\Delta_E U_m°$ of **6c** is by nearly 20 % higher than the value of **6a**. Compared to TNT or RDX (*paragraph 2.3.1.3*) the triazoles are moderate to low explosives. The detonation velocities *D* of the triazoles are in the range of TNT. Along with the low thermal stability and high sensitivity, the triazoles are not suitable for an application as energetic material. The usage of azide groups instead of nitric esters (**9** compared to **6a**) leads to a rise of $-\Delta_E U_m°$ of nearly 20 %. Moreover, the decomposition point of the azide compound **9** is by 64 °C higher than that of **6a**, whereas the impact sensitivity is similar (>6 J in case of **6a**, >5 J in case of **9**). Nevertheless, the friction sensitivity of **9** is by more than 150 N (**9**: >28 N, **6a**: >192 N) higher than the friction sensitivity of the nitrate ester.

5.2.3 Crystal Structure of 9

Compound **9** crystallizes in the monoclinic space group $P2_1/c$ with two molecular formulas per unit cell (*Figure 1*). There can be no inter- or intramolecular interactions be found. The arrangement of **7** in the crystal structure is that way that the azide and the triazole moieties are arranged next to each other (*Figure 2*). The close arrangement of the molecules leads to the – for organic compounds – high density.

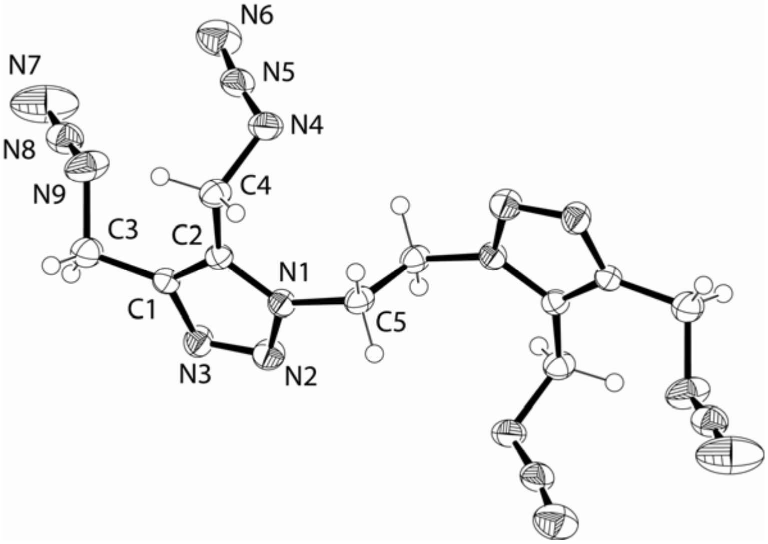


Figure 1. Molecular structure of **9**. Thermal ellipsoids are drawn at the 50% probability level.

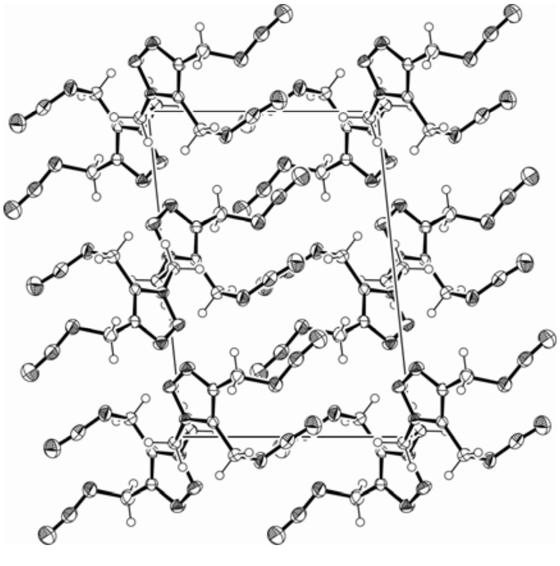
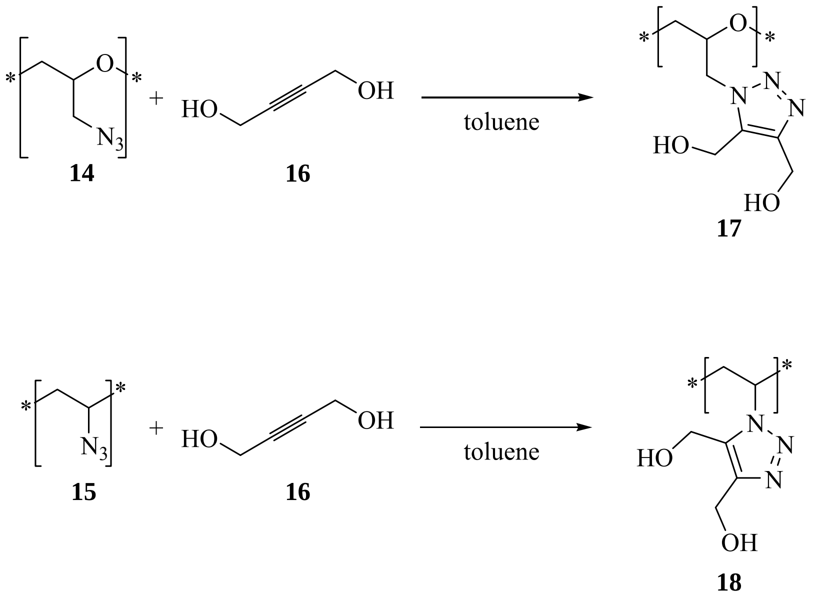


Figure 2. View of the unit cell along the y-axis. Thermal ellipsoids are drawn at the 50% probability level.

5.3 Energetic Polymers Based on 1,2,3-Triazoles

5.3.1 Synthesis and Analysis of the Polymers

To investigate the energetic properties of polymers based on 1,2,3-triazoles, two different structures were synthesized, polymers based on the glycidyl backbone (**14**/**17**) and polymers based on the polyvinyl backbone (**15**/**18**). The advantage of the polyvinyl backbone is the reduced content of carbon, compared to the glycidyl backbone. The disadvantage of polyvinyl polymers bearing good releasing groups (like chloride, azide, nitrate…) is their tendency to undergo elimination reactions, as it is known for polyvinyl chloride.[12] The 1,2,3-triazoles were prepared according to known methods by using the [2+3] cycloaddition reaction of a covalent azide moiety and derivatives of acetylene.[13] In order to obtain 1,2,3-triazoles with a high content of functional groups 2-butyne-1,4-diol (**16**) was used for the formation of the triazole (*Scheme 8*).



Scheme 8. Synthesis of triazole containing polymers **17** and **18**.

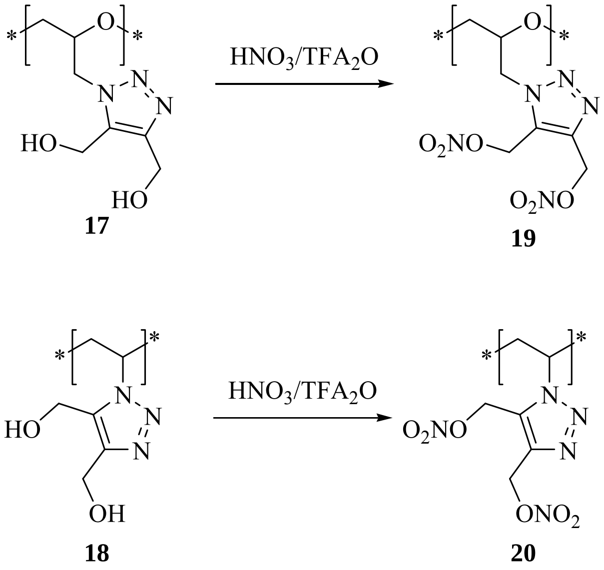
Glycidyl azide polymer[14] (GAP, **14**), a common energetic binder, was used as obtained from commercial sources with a M_n value of 2000 g mol^{-1}. Polyvinyl azide (**15**) was synthesized by the reaction of commercially available polyvinyl chloride with a low molecular weight (M_n~48000 g mol^{-1}) and sodium azide in DMF.[15] The molecular weights of the polymers prepared could not be determined by us, because of the insolubility of the polymers in common solvents. In case of **17** and **18** (both possess a good solubility in water), a degradation of the polymer chain was very unlikely to happen, because of the mild reaction condition applied and an investigation of the molecular weight was unnecessary.

If the synthesis of **15** was carried out at temperatures higher than 60 °C gelation takes place and a black unidentified polymer was formed.[15] The constitution of polymer **15** showed great differences compared to the polyvinyl azide of Gilbert. The elemental analysis of the polymer formed after a reaction time of 10 h published by Gilbert[15] gave a constitution of the polymer of six azide groups, four remaining chloride atoms and one elimination product (ethene moiety) per repeating unit (calc.: $C_2H_3N_3$: C 34.78 %, H 4.38 %, N 60.84 %; reported: C 38.27 %, H 4.67 %, N 36.52 %).[15] By optimizing the reaction conditions, we were able to obtain much higher contents of nitrogen. After a time of reaction of 96 h, compound **15** possessed 53 % nitrogen. The determination of the chlorine content by elemental analysis revealed, that the polymer did not contain any chlorine. ($C_2H_3N_3$: calc.: C 34.78 %, H 4.38 %, N 60.84 %; found: C 37.90 %, H 4.37 %, N 52.65 %). Especially regarding an application as energetic binder, it is very important to obtain chlorine-free polymers, because during the decomposition formed hydrogen chloride leads to severe erosion of the metallic parts of the devices. Moreover, the formation of toxic gases should be reduced and therefore toxic side products are avoided.

The preparation of the triazoles was performed in both cases in toluene as solvent. A suspension of the polymer **14**/**15** and **16** was heated at 80 °C for 12 h and **17** and **18** could be recovered by filtration. Best yields could be obtained by the utilization of a 1.5fold excess of **16** per azide group. The remaining amount of unconsumed alkine could be removed by extraction with hot ethyl acetate. The application of different solvents like acetonitrile, DMF or ethyl acetate lowered the degree of triazole-formation or just yielded starting materials. Polymer **17** still contained traces of **16** which could not be removed, due to the highly viscous character of the polymer along with intermolecular interactions of the hydroxyl groups of **16** with **17** ($C_7H_{11}N_3O_3$: calcd.: C 45.40 %, H 5.99 %, N 22.69 %; found: C 45.23 %, H 5.62 %, N 19.05 %). Nevertheless, traces of azide groups were still present, even after using a 10fold excess of **16**, and could be proved by IR spectroscopy (2021 cm^{-1}). In case of polymer **18**, the elemental analysis gave roughly six triazole moieties and two elimination products per repeating unit (the sample contained three molecules of water per repeating unit: $C_{20}H_{35}N_9O_9$: calc. C 44.03 %, H

6.47 %, N 23.11 %; found: C 45.37 %, H 5.97 %, N 22.59 %). This finding points out the tendency of the vinyl polymer to undergo elimination reactions. In this case, one triazole/azide moiety per repeating unit was lost during the cyclisation reaction.[12]

The first reaction for the insertion of energetic groups was the nitration of **17** and **18** (*Scheme 9*).



Scheme 9. Nitration of **17** and **18**.

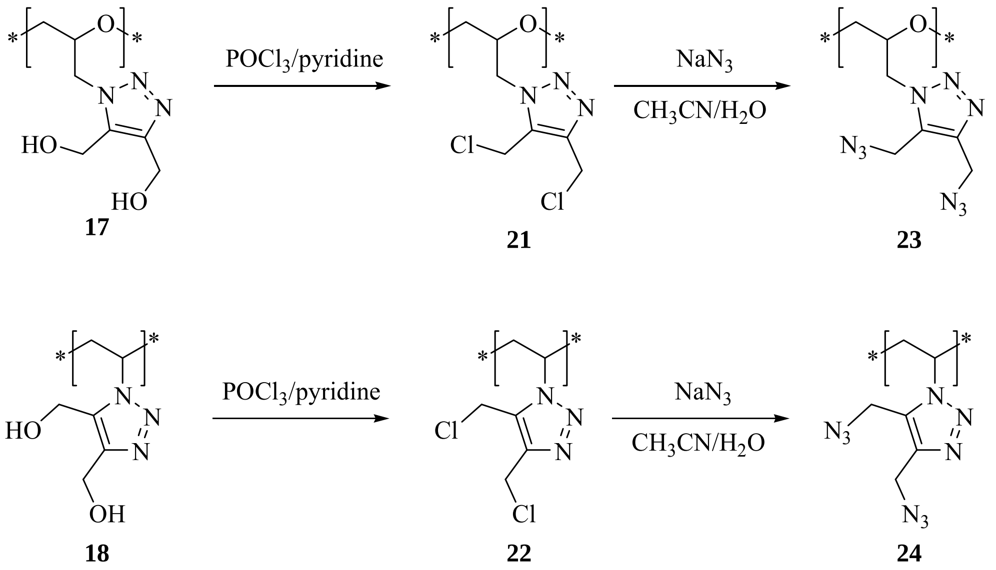
The nitrated polymers **6** and **7** were obtained with yields ranging between 60 % and 70 %. The nitration was carried out according to common methods.[16] Instead of nitrosulfuric acid, a mixture of trifluoroacetic anhydride (TFA_2O) and fuming nitric acid was used. The advantage of trifluoroacetic anhydride compared to a nitration in acetic anhydride is the much lower boiling point of trifluoroacetic anhydride (39 °C compared to 140 °C). As a result, traces of trifluoroacetic anhydride can be removed easily under reduced pressure, in contrast to traces of acetic anhydride. The purification of the polymers was carried out by pouring the suspension on an ice-water mixture with a subsequent filtration. The elemental analysis of polymer **19** was in good accordance with the calculated values. The lower nitrogen content of **19** could be explained by an incomplete conversion of the azide groups into the corresponding triazole moieties of **17**. In case of **20**, the elemental analysis was also close to the calculated values. The IR spectrum of

20 revealed traces of azide groups (2116 cm^{-1}) and trifluoroacetic anhydride (1788 cm^{-1}). A purification of **20** according to the purification of **19** was not possible. The traces of trifluoroacetic anhydride of polymer **19** could only be removed completely by stirring **19** for several hours in water at 90 °C. The tendency to undergo elimination reactions of polymer **20** along with hydrolysis reactions of the nitric esters led to a slow decomposition of the polymer under these conditions. Therefore, the traces of trifluoroacetic anhydride were removed by reduced pressure and stirring in water at ambient temperature but a complete removal of the trifluoroacetic anhydride of polymer **20** was not possible.

Other suitable energetic groups are azide groups. The advantage of azide groups, compared to nitrate esters are their higher thermal stability (up to 200 °C in case of GAP). Azides can be inserted by substitution reactions of halogens with sodium azide.[17] Several methods for the halogenation of the hydroxyl groups were tested, but only the chlorination using phosphorous oxychloride and pyridine led to a high conversion (*Scheme 3*). Other methods like bromination with hydrobromic acid, iodination using hydriodic acid or other common chlorinations with thionyl chloride or sulfuryl chloride resulted either in a decomposition of the triazole or led to a low degree of halogenation. The degree of chlorination was determined by elemental analysis. In case of **21**, the degree of chlorination can be roughly determined with one hydroxyl group per seven chloride atoms ($C_7H_9Cl_2N_3O$: calc. C 37.86 %, H 4.08 %, Cl 31.93 %, N 18.92 %; $C_{28}H_{37}Cl_7N_{12}O_5$ calc.: C 38.66 %, H 4.29 %, Cl 28.53 %, N 19.32 %; found: C 37.17 %, H 4.31 %, Cl 28.74 %, N 19.53 %). As polymer **17**, **21** still contained traces of azide groups (proved by IR spectroscopy: weak azide vibration at 2101 cm^{-1}). In case of polymer **22**, the content of chlorine was determined by elemental analysis to be 26.70 %, compared to the calculated value of 36.92 %.

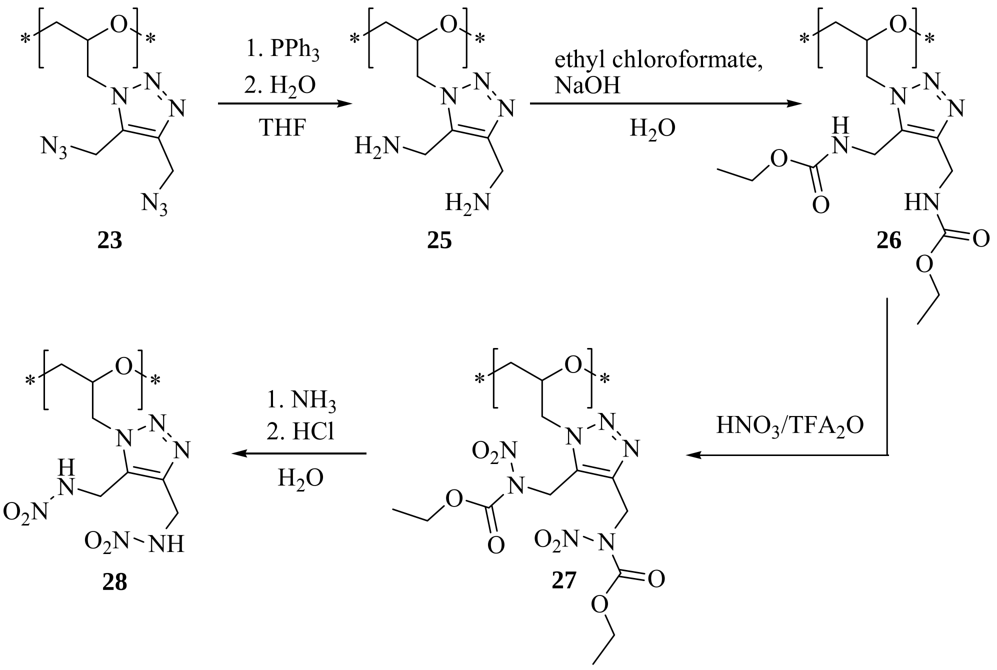
The halogen-azide exchange reaction was conducted in a mixture of water and acetonitrile at 70 °C for 12 h (*Scheme 10*). If DMF was used as solvent, the nitrogen content of the polymer dropped by 10 %. Another advantage of the water/acetonitrile mixture was that the solvent could be removed more easily, because of the lower boiling point of water and acetonitrile compared to DMF. The elemental analysis of polymer **23** gave a degree of substitution of seven azide moieties and one hydroxyl group per repeating unit. The hydroxyl group was a result of a substitution reaction of the chlorine atom with a molecule of water (the sample contained one molecule of water per two triazole moieties: $C_7H_8N_9O$: calc.: C 35.90 %, H 3.44 %, N 53.83 %;

$C_{28}H_{41}N_{33}O_7$: calc. C 35.33 %, H 4.34 %, N 48.56 %; found: C 35.49 %, H 4.01 %, N 48.45 %). In case of polymer **23**, the nitrogen content determined by elemental analysis was much lower than the calculated value. An explanation could be the low degree of chlorination of polymer **22**. The complete exchange of the chloride atoms was proved by the chlorine content of **23** of 0.00 %, determined by elemental analysis ($C_6H_7N_9$: C 35.12 %, H 3.44 %, N 61.44 %; $C_{40}H_{59}N_{45}O_8$: calc.: C 37.01 %, H 4.58 %, N 48.55 %; found: C 37.53 %, H 4.25 %, N 47.49 %).



Scheme 10. Synthesis of azide containing polymers **23** and **24**.

Further reactions to investigate the formation of primary nitramines were conducted using **23** as starting material (*Scheme 11*). Due to the tendency of eliminations of the chlorine and azide/triazole moieties of the vinyl polymers **15**, **18**, **20** and **24** during the previous reactions only polymer **23** was converted into the corresponding nitramine polymer. The azide moieties of **23** were reduced to amine groups by Staudinger reaction conditions[18] using triphenylphosphine in THF. In contrast to common methods (ambient temperature), the reaction mixture had to be heated at 60 °C for 2 h before the (imino)triphenylphosphorane was cleaved by the addition of water. Nevertheless it was never possible to obtain a complete conversion of the azide into amine groups, even if the amine-containing polymer was used for another reduction with triphenylphosphine. The polymer was purified by washing with methylene chloride to remove residues of triphenylphosphine and triphenylphosphine oxide. A direct nitration of amine groups to primary nitramines is not possible. Therefore, the amine had to be protected by a carbamate protecting group. Polymer **25** was converted into the protected polymer **16** by the reaction of ethyl chloroformate in sodium hydroxide. The resulting polymer **26** was nitrated by a mixture of fuming nitric acid and trifluoroacetic anhydride at 0 °C. In order to investigate the influence of the nitration time on the degree of nitro groups, the reaction time was varied between 20 min to 60 min, but the formed polymer had the same composition after each experiment. The introduction of the nitro groups can be proved by IR spectroscopy (shift of the C=O-carbamate vibration from 1708 cm^{-1} to 1776 cm^{-1} and the appearance of the asymmetric N-NO_2-vibration at 1583 cm^{-1}).[19] The nitrated polymer **27** was deprotected by heating **27** in concentrated ammonia at 100 °C until the polymer was dissolved. After acidification of the reaction mixture with concentrated hydrochloric acid, the protonated polymer **28** precipitated. The reaction conditions and bases (ammonia, sodium hydroxide, cyclohexyl amine) used for the deprotection reaction were varied, but we were not able to achieve a complete deprotection of **27**. The elemental analysis allows the assumption, that only half of the protecting groups were cleaved ($C_7H_{10}N_7O_5$: calc.: C 30.89 %, H 3.70 %, N 36.02 %; $C_{10}H_{14}N_7O_7$: calc.: C 34.89 %, H 4.10 %, N 28.48 %; found: C 36.35 %, H 4.61 %, N 29.28 %).



Scheme 11. Synthesis of nitramine containing polymer **28**.

5.3.2 Energetic Properties of the Polymers

In order to analyse the energetic properties of the polymers the sensitivities towards impact and friction were determined according to BAM methods.[10] Polymers **15**, **24** and **28** are insensitive towards friction (>360 N), in case of **24** and **28** sensitive (>6 J and >11 J) and in case of **15** very sensitive towards impact (>3 J). The nitric ester-containing polymers **19** and **20** are both very sensitive towards impact (>2 J).

The thermal stability of the polymers was determined by DSC measurements. Polymers **19** and **20** possessed the lowest decomposition points (126 °C and 153 °C). Especially the decomposition point of **19** was astonishing low, compared to other nitric esters (T_{dec} ~ 150 °C)[21] or polymer **7**, bearing the same nitrated triazole moieties. The thermal stability of the azide containing polyvinyl polymers **15** and **24** was equal (189 °C and 188 °C), whereas the decomposition point of **23** was found to be 20 °C higher (206 °C). Polymer **28** possessed a broad range of decomposition between 250 °C and 280 °C. The decomposition could not be detected by

DSC, but was determined by a melting point analyzer.

The energetic properties were calculated by using experimental values obtained by bomb calorimetric measurements. Using these values, the enthalpy of formation was calculated by applying the Hess thermo chemical cycle, as reported in literature.[22] The heats of formation of H_2O (l) and CO_2 (g) -286 kJ mol^{-1} and -394 kJ mol^{-1} were used as reported.[23] The energetic properties like detonation velocity and work performed by the explosion ($\Delta_E U_m°$) were calculated by using the EXPLO5 program. A comparison of the energetic properties of the polymers revealed the improved characteristics of the polymers compared to the starting material **2**. The $\Delta_E U_m°$ value of **15** classifies **15** as low explosive, despite its high nitrogen content. **19** and **20** possess a lower physical stability and lower explosive characteristics compared to GAP. Polymers **19, 20** and **28** proved to be rather low explosives with low detonation velocities and low values of $\Delta_E U_m°$, whereas the polymers **19** and **20** possess moderate energetic properties. The advantage of polymers **19** and **20** is their high density compared to GAP (1.56 g cm^{-3}/1.75 g cm^{-3} instead of 1.3 g cm^{-3}). The detonation velocity depends on the density of the material;[24] therefore high densities are a sought property of explosives. The comparison of the glycidyl polymers **19** and **23** with the corresponding vinyl polymers **20** and **24** revealed the better properties of the glycidyl polymers in case of **23** despite the higher carbon content of the glycidyl backbone, whereas the nitrated derivative **19** possesses a lower energetic character than **20**. The disadvantage of **20** is its tendency to undergo elimination reactions. As a result, the polymer could be destroyed under basic conditions.

Table 2. Energetic properties of **2**, **6**, 7, **10**, **11** and **15** compared with the common binder GAP.

	GAP	**2**	**6**	**7**	**10**	**11**	**15**
formula[a]	$C_3H_5N_3O$	$C_{1516}H_{2098}N_{1805}O_{152}$	$C_{156}H_{228}N_{88}O_{135}$	$C_{4384}H_{5780}N_{2948}O_{4434}$	$C_{127}H_{172}N_{149}O_{32}$	$C_{4066}H_{5525}N_{4410}O_{891}$	$C_{167}H_{254}N_{115}O_{102}$
molecular mass (g mol^{-1})[a]	99	48000	5496	170000	4300	130400	5500
density (g cm^{-3})[b]	1.3	1.65	1.56	1.67	1.76	1.75	1.5
decomposition point (°C)	216	189	126	153	206	188	250 - 280
impact sensitivity (J)	> 7	>3[l]	>2[l]	>2[m]	>6[m]	>11[n]	>30[m]
friction sensitivity (N)	>360	>360[l]	>360[l]	>160[m]	>360[m]	>360[n]	>240[m]
-$\Delta U_{\text{comb.}}$ (cal g^{-1})[c]	-	4667	3180	2957	4577	4819	4090
ΔH_{comb} (kJ mol^{-1})[d]	-	41716	-16916	-442135	7776	231722	-7796
$\Delta_f H_m$ (kJ mol^{-1})[e]	-	36693	-17475	-458444	7339	218311	-8379
Values calculated by EXPLO5 V5.02							
-$\Delta_E U_m°$ (kJ kg^{-1})[f]	4444	2173	2514	3060	3921	3804	3070
T_E (K)[g]	2860	1789	2085	2467	2683	2568	2280
$p_{C\text{-}J}$ (kbar)[h]	135	164	119	154	258	250	127
D(m s^{-1})[i]	6629	7074	5928	6511	8167	8081	6209
Gas vol. (L kg^{-1})[j]	738	688	693	688	684	680	701
I_s (s)[k]	195	149	148	152	187	183	156

[a] estimated from the composition of the polymer without degradation of the polymer backbone; [b] determined experimentally; [c] experimental (constant volume) combustion energy; [d] experimental molar enthalpy of combustion; [e] molar enthalpy of formation; [f] energy of explosion; [g] explosion temperature; [h] detonation pressure; [i] detonation velocity; [j] assuming only gaseous products; [k] specific impulse (isobaric combustion, chamber pressure 60 bar, frozen expansion); [l] rubber-like solid with a grain size ranging from > 500 µm; [m] powder with a grain size < 100 µm; [n] powder with a grain size of 100 µm to 500 µm.

5.3.3 Conclusions

The energetic nitrogen rich polymers (4,5-bis(nitroxymethyl)-1*H*-1,2,3-triazol-1-yl)glycidyl polymer, (4,5-bis(azidomethyl)-1*H*-1,2,3-triazol-1-yl)glycidyl polymer, (4,5-bis(nitraminomethyl)-1*H*-1,2,3-triazol-1-yl)glycidyl polymer, polyvinyl azide, polyvinyl-4,5-di(azidomethyl)-1*H*-1,2,3-triazole and polyvinyl-(4,5-di(nitroxymethyl)-1*H*-1,2,3-triazole) were investigated**.** The triazoles were prepared in high yields by the reaction of 2-butyne-1,4-diol and common azide containing polymers. The azide and nitramine containing polymers show moderate energetic properties along with a sufficiently high thermal stability. They are insensitive towards friction and sensitive towards impact. The polymers containing nitric esters show low thermal stabilities (<150 °C) and moderate energetic properties. The nitrogen rich polymers without nitric esters are environmental friendly options to common explosives bearing toxic nitro groups. Another advantage of the polymers compared to the common binder GAP is their high density (between 1.5 g cm^3 to 1.7 g cm^3) leading to improved explosive characteristics.

5.4 Experimental Section

CAUTION! Alkyl azides and nitric esters are highly energetic compounds with sensitivity towards heat and impact. Although we had no problems in synthesis, proper protective measures (safety glasses, face shield, leather coat, earthened equipment and shoes, Kevlar® gloves and ear plugs) should be used when undertaking work involving these compounds.

5.4.1 Investigation of Energetic Materials Based on 1,2,3-Triazoles

The 1-(2-hydroxyethyl)-1*H*-1,2,3-triazole-4,5-dimethanol **3c** was prepared according to the general preparation of **3**; the analytical data was compared with known values.[25]

5.4.1.1 General Synthesis for the (1,2,3-Triazol-1-yl) alkanes 3

The azide (**3a**: 32 mmol, **3b**: 68 mmol) and but-2-in-1,4-diol (6.0 g, 70 mmol) were suspended in toluene (200 mL) and stirred at 80 °C for 12 h. The hot toluene was decanted and the brown residue was washed with hot ethyl acetate three times. The crude triazoles were recrystallized from propan-2-ol.

5.4.1.2 1,2-Bis(4,5-di(hydroxymethyl)-1*H*-1,2,3-triazol-1-yl)ethane (3a)

m. p.: 168°C.

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3338 (w), 3112 (w), 2884 (vw), 2847 (vw), 2718 (vw), 1467 (w), 1442 (w), 1424 (w), 1313 (w), 1299 (w), 1267 (w), 1231 (w), 1189 (vw), 1103 (w), 1040 (m), 1017 (vs), 959 (vw), 816 (m), 778 (w), 758 (w), 725 (w), 675 (w), 650 (m).

^{1}H NMR (D_2O) δ: 4.53 (s, 1H, CH_2-N), 4.65 (s, 1H, CH_2-C5), 4.97 (s, 1H, CH_2-C4).

^{13}C NMR (D_2O) δ: 48.3 (*C*H_2-N), 50.6 (*C*H_2-C5), 53.8 (*C*H_2-C4), 135.2 (*C5*), 144.7 (*C4*).

m/z (DCI+): 285 (4 %) [M+H], 130 (5), 58 (30), 57 (100), 56 (29), 55 (5), 53 (2), (44 (5), 43 (100), 42 (18), 41 (33), 40 (2), 39 (21), 29 (7), 27 (6).

$C_{10}H_{16}N_6O_4$ calculated: C 42.25, N 29.56, H 5.67; found C 42.56, N 28.84, H 5.73.

5.4.1.3 1,3-Bis(4,5-bis(hydroxymethyl)-1*H*-1,2,3-triazol-1-yl)propan-2-ol (3b)

m. p.: 122°C.

IR (KBr, cm^{-1}): ṽ = 3359 (vw), 3209 (w), 2878 (vw), 1473 (w), 1442 (vw), 1426 (vw), 1404 (w), 1351 (vw), 1333 (vw), 1261 (vw), 1245 (vw), 1219 (w), 1178 (w), 142 (w), 1106 (vw), 1096 (vw), 1002 (vs), 977 (m), 872 (w), 814 (w), 791 (w), 775 (m), 742 (vw), 672 (vw).

^{1}H NMR (D_2O) δ: 4.51-4.78 (m, 5H, C*H_2*C*H*OHC*H_2*), 4.72 (s, 4H, C*H_2*-C4), 4.80 (s, 1H, C*H_2*-C5).

^{13}C NMR (D_2O) δ: 51.0, 51.6, 53.9, 68.8, 135.4 (*C5*), 144.7 (*C4*).

m/z (DEI+): 314 (5 %) [M], 313 (4), 297 (3), 296 (11), 278 (4), 266 (7), 255 (5), 250 (4), 239 (5), 237 (4), 221 (6), 220 (5), 209 (4), 207 (7), 193 (7), 191 (6), 187 (10), 186 (48), 185 (21), 184 (6), 182 (4), 181 (4), 179 (5), 175 (4), 173 (5), 172 (31), 170 (7), 169 (5), 168 (12), 167 (10), 163 (8), 161 (4), 157 (12), 156 (13), 155 (4), 154 (8), 152 (4), 151 (6), 150 (7), 149 (5), 144 (10), 143 (29), 142 (16), 141 (8), 140 (23), 139 (18), 138 (19), 137 (5), 136 (6), 135 (4), 131 (6), 130 (80), 129 (7), 128 (30), 127 (14), 126 (47), 125 (15), 124 (9), 123 (9), 122 (11), 121 (9), 120 (5), 115 (9), 114 (29), 113 (11), 112 (59), 111 (100), 110 (57), 109 (19), 108 (18), 102 (8), 101 (5), 100 (21), 99 (9), 98 (38), 97 (22), 96 (50), 95 (12), 94 (14), 93 (7), 92 (7), 86 (14), 85 (25), 84 (58), 83 (19), 82 (33), 81 (12), 80 (34), 79 (5), 73 (7), 72 (9), 71 (12), 70 (77), 69 (18), 68 (42), 67 (18), 66 (62), 65 (6), 58 (11), 57 (55), 56 (36), (55 (41), 54 (67), 53 (22), 52 (18), 45 (9), 44 (11), 43 (28), 42 (28), 41 (46), 40 (11), 39 (26), 31 (40), 30 (14), 29 (27), 28 (26), 27 (16).

$C_{11}H_{18}N_6O_5$ calculated: 314.1339; found: 314.1336.

5.4.1.4 General Synthesis for the Nitrated (1,2,3-Triazol-1-yl) alkanes 6

3 (1.0 g) was added dropwise at 0 °C to a mixture of trifluoroacetic anhydride (6.0 g, 29 mmol) and fuming nitric (3.0 g, 48 mmol). The suspension was stirred until the triazole was dissolved and then decanted on an ice-water mixture (150 mL). The reaction mixture was stirred for 30 min and was extracted two times with methylene chloride (100 mL). The organic layers were combined and washed with 0.5 N sodium hydroxide solution. After drying over sodium sulfate and removal of the solvent under reduced pressure, the triazoles were obtained as colorless solid (**6a** and **6b**).

In case of **6c**, the crude hydroxyl triazole was nitrated and the impurities removed by sublimation at 100 °C (impurities possess a lower sublimation point than **6c**). **6c** was obtained as slightly brown oil.

5.4.1.5 1,2-Bis(4,5-di(nitroxymethyl)-1*H*-1,2,3-triazol-1-yl)ethane (6a)

m. p.: 149°C.

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3028 (vw), 2963 (vw), 2899 (vw), 1625 (vs), 1477 (w), 1446 (w), 1429 (w), 1382 (vw), 1367 (vw), 1335 (vw), 1276 (vs), 1204 (vw), 1173 (vw), 1103 (w) 1087 (w), 1018 (m), 985 (w), 939 (m), 921 (s), 862 (s), 838 (s), 830 (s), 751 (m), 732 (m), 693 (w), 643 (m).

^{1}H NMR (d_6-DMSO) δ: 5.01 (s, 1H, CH_2-N), 5.73 (s, 1H, CH_2-C4), 5.81 (s, 1H, CH_2-C5).

^{13}C NMR (d_6-DMSO) δ: 48.2 (*C*H_2-N), 61.6 (*C*H_2-C5), 65.7 (*C*H_2-C4), 130.0 (*C5*), 140.0 (*C4*).

^{14}N NMR (d_6-DMSO) δ: -43.7 (-ONO_2).

m/z (DCI+): 465 (21 %) [M+H], 418 (19), 401 (5), 400 (6), 372 (6), 371 (40), 353 (5), 324 (13), 277 (6), 88 (11), 73 (5), 72 (4), 59 (20), 58 (46), 57 (100), 56 (29), 55 (4), 48 (13), 43 (100), 42 (10), 41 (22), 39 (37), 29 (11), 27 (5).

elemental analysis: calcd (%) for $C_{10}H_{12}N_{10}O_{12}$: C 25.87, N 30.17, H 2.61; found C 26.17, N 30.32, H 2.58.

5.4.1.6 2-Nitroxy-1,3-bis(4,5-di(nitroxymethyl)-1*H*-1,2,3-triazol-1-yl)propane (6b)

dec.: 145°C.

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3018 (vw), 2919 (vw), 1652 (m), 1632 (m), 1613 (s), 1480 (vw), 1468 (vw), 1429 (vw), 1363 (vw), 1335 (vw), 1286 (vs), 1273 (m), 1244 (w), 1137 (vw), 1106 (vw), 1028 (w), 976 (w), 934 (m), 860 (w), 835 (vs), 773 (w), 754 (w), 692 (w), 675 (vw), 658 (w).

^{1}H NMR (*d6*-DMSO) δ: 4.99 (dd, 2H, ^1J = 15.2 Hz, ^3J = 8.4 Hz), 5.14 (dd, 2H, ^1J = 15.2 Hz, ^3J = 3.3 Hz), 5.78 (s, 4H, CH_2-C5), 5.91 (dd, 2H, *J* = 13.0 Hz, 23.1 Hz, CH_2-C4).

^{13}C NMR (*d6*-DMSO) δ: 48.3, 61.7, 65.7, 79.3, 130.6 (*C5*), 140.3 (*C4*).

^{14}N NMR (*d6*-DMSO) δ: -44.7 ($-ONO_2$).

m/z (DCI+): 540 (1 %) [M+H], 262 (2), 88 (1), 73 (2), 72 (2), 59 (9), 58 (35), 57 (100), 56 (30), 55 (4), 53 (2), 48 (6), 44 (5), 43 (100), 42 (13), 41 (27), 40 (2), 39 (27), 30 (2), 29 (8), 27 (6).

$C_{11}H_{13}N_{11}O_{15}$ calculated: C 24.50, N 28.57, H 2.43; found C 25.21 N 28.15, H 2.39.

5.4.1.7 1-(2-Nitroxyethyl)-4,5-di(nitroxymethyl)-1*H*-1,2,3-triazole (6c)

dec.: 139 °C

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3017 (vw), 2972 (vw), 2906 (w), 2556 (vw), 1643 (vs), 1457 (m), 1432 (m), 1383 (m), 1366 (m), 1281 (vs), 1207 (vw), 1151 (vw), 1110 (vw), 985 (m), 929 (m), 852 (s), 754 (m), 706 (vw), 651 (w), 595 (vw).

^{1}H NMR (*d6*-DMSO) δ: 4.87 (t, 1H, ^{3}J = 4.1 Hz, C*H$_2$*), 4.95 (t, 1H, ^{3}J = 4.1 Hz, C*H$_2$*), 5.74 (s, 1H, C*H$_2$*-C5), 5.86 (s, 1H, C*H$_2$*-C4).

^{13}C NMR (*d6*-DMSO) δ: 46.4, 61.2, 65.7, 71.3, 130.1 (*C5*), 140.1 (*C4*).

^{14}N NMR (*d6*-DMSO) δ: -44.8 (-O*N*O$_2$).

m/z (DCI+): 309 (100 %) [M+H], 264 (18), 57 (70), 43 (16).

$C_{10}H_{12}N_{10}O_{12}$ calculated: C 23.39, N 27.27, H 2.62; found C 23.74, N 26.65, H 2.79.

5.4.1.8 Synthesis of 1,2-Bis(4,5-di(chloromethyl)-1*H*-1,2,3-triazol-1-yl)ethane 7

Pyridine (8.2 g, 104 mmol) was added dropwise to phosphorus oxychloride (130.8 g, 309 mmol) at 0 °C. **3a** (6.0 g, 21 mmol) was added slowly to the reaction mixture and heated at 120 °C for 2 h. After cooling to ambient temperature, the reaction mixture was decanted slowly on an ice-water mixture (500 mL) and stirred for 2 h. The aqueous layer was extracted two times with methylene chloride (200 mL). The combined organic layers were dried using sodium sulfate and the solvent was removed under reduced pressure. **5** was obtained as slightly brown powder (3.00 g, 8 mmol, 40 %).

m. p.: 130°C.

IR (KBr, cm^{-1}): ṽ = 3005 (m), 2965 (m), 2107 (w), 1575 (vw), 1476 (s), 1461 (s), 1440 (s), 1300 (m), 1276 (s), 1256 (s), 1244 (s), 1215 (s), 1094 (vs), 1066 (vs), 923 (m), 889 (w), 799 (s), 765 (vs), 730 (vs), 711 (vs), 687 (vs), 662 (s), 464 (vw).

^{1}H NMR (*d6*-DMSO) δ: 4.91 (s, 1H, C*H$_2$*N), 4.99 (s, 1H, C*H$_2$*-C5), 5.01 (s, 1H, C*H$_2$*-C4).

^{13}C NMR (*d6*-DMSO) δ: 31.4 (*C*H$_2$), 35.7 (*C*H$_2$), 47.6 (*C*H$_2$), 133.0 (*C5*), 142.9 (*C4*).

m/z (DEI+): 358 (24 %) [M], 356 (18), 297 (30), 296 (12), 295 (95), 294 (14), 293 (100), 195 (15), 193 (22), 130 (15), 128 (22), 114 (14), 88 (12), 87 (23), 80 (10), 66 (20), 53 (12), 51 (13), 49 (11), 42 (14).

$C_{10}H_{12}Cl_4N_6$ calculated: 357.9848; found: 357.9867.

5.4.1.9 Synthesis of 1,2-Bis(4,5-di(azidomethyl)-1*H*-1,2,3-triazol-1-yl)ethane (9)

5 (3.0 g, 8 mmol) and sodium azide (14.6 g, 225 mmol) were suspended in a mixture of acetonitrile (200 mL) and water (50 mL) and stirred at 80 °C for 12 h. The acetonitrile was removed under reduced pressure and the aqueous layer was extracted with dichloromethane (200 mL) two times. The combined organic layers were washed with water and dried over sodium sulfate. After removing the solvent under reduced pressure, **7** was obtained as slightly brown solid (3.1 g, 8 mmol, 97 %).

dec.: 213°C.

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3010 (w), 2943 (w), 2107 (vs), 1473 (m), 1437 (m), 1306 (m), 1269 (s), 1229 (s), 1212 (s), 1090 (m), 980 (w), 956 (vw), 900 (w), 879 (m), 810 (m), 788 (m), 763 (m), 709 (vw), 690 (vw), 654 (w), 560 (w), 475 (vw).

^{1}H NMR (*d6*-DMSO) δ: 4.56 (s, 1H, CH_2), 4.70 (s, 1H, CH_2-C5), 4.92 (s, 1H, CH_2-C4).

^{13}C NMR (*d6*-DMSO) δ: 40.8 (CH_2), 44.1 (CH_2), 47.9 (CH_2), 131.4 (*C5*), 141.5 (*C5*).

^{14}N NMR (*d6*-DMSO) δ: -319 (N_α), -169 (N_γ), -133 (N_β).

m/z (DEI+): 385 (3.7 %) [M+H], 286 (23), 121 (18), 120 (16), 108 (20), 107 (82), 95 (17), 94 (32), 93 (30), 81 (39), 80 (35), 79 (21), 69 (14), 68 (23), 67 (48), 66 (47), 55 (17), 54 (100), 53 (31), 52 (42), 42 (33), 41 (37), 40 (30), 39 (22), 28 (79), 27 (15).

$C_{10}H_{12}N_{18}$, calculated M+H: 385.1571, found M+H: 385.1582.

5.4.1.10 Synthesis of 1,2-Bis(4,5-di(aminomethyl)-1*H*-1,2,3-triazol-1-yl)ethane (10)

A solution of triphenylphosphine (25.6 g, 98 mmol) in 100 mL THF was added slowly to a solution of **9** (3.1 g, 8 mmol) in 50 mL THF. The reaction mixture was stirred for 2 h at ambient temperature. Water (10 mL) was added and the reaction mixture was stirred for additional 12 h at ambient temperature. The solvent was removed and the residue suspended in concentrated hydrochloric acid (30 mL). Water was added (50 mL) and the aqueous layer was extracted with methylene chloride (3 × 30 mL). After removing the solvent under reduced pressure, the solid was washed with hot ethanol and obtained as colorless powder (3.0 g, 7 mmol, 86 %).

dec.: 200°C.

IR (KBr, cm^{-1}): $\tilde{v}$ =3432 (s), 3124 (w), 2994 (w), 2959 (w), 2926 (w), 2685 (vw), 2594 (vw), 2103 (w), 1751 (vw), 1733 (vw), 1697 (vw), 1629 (w), 1566 (vw), 1496 (w), 1470 (w), 1384 (w), 1225 (w), 1123 (w), 1055 (vw), 977 (vw), 830 (vw), 801 (vw), 609 (vw).

^{1}H NMR (D_2O) δ: 4.38 (s, 1H, CH_2), 4.51 (s, 1H, CH_2-C5), 5.20 (s, 1H, CH_2-C4).

^{13}C NMR (D_2O) δ: 29.7 (CH_2), 33.6 (CH_2), 47.7 (CH_2), 129.7 (*C5*), 140.8 (*C4*).

^{14}N NMR (D_2O) δ: -351 (s, 1N, NH_2).

m/z (FAB+): 281 (17 %) [M+H], 241 (6), 185 (47), 149 (19), 110 (9), 93 (100), 75.1 (51), 57 (29), 45 (19).

5.4.1.11 Synthesis of 1,2-Bis(4,5-di((ethoxycarbonyl(nitro)amino)methyl)-1*H*-1,2,3-triazol-1-yl)ethane (12)

Ethyl chloroformate (8.9 g, 5 mmol) was added at 0 °C dropwise to a suspension of sodium hydroxide (1.5 g, 38 mmol) and **10** (2.0 g, 5 mmol) in water (20 mL). After stirring for 10 min, the aqueous layer was extracted with methylene chloride (2 × 25 mL). The organic layers were washed with water and dried over sodium sulfate. The solvent was removed under reduced pressure and **11** was obtained as colorless solid. **11** was used without purification for further reactions.

Fuming nitric acid (5.2 g, 83 mmol) were added dropwise at 0 °C to acetic anhydride (7 mL) and a solution of **11** in dichloromethane was added slowly and stirred for 30 min at 0 °C. The reaction mixture was decanted on an ice-water mixture (40 mL) and stirred for 20 min. The aqueous layer was extracted with methylene chloride and the combined organic layers were washed with water and dried over sodium sulfate. The solvent was removed under reduced pressure and **12** was obtained as slightly impure colorless solid (3.3 g).

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2991 (w), 2941 (vw), 2877 (vw), 2459 (vw), 1777 (vs), 1744 (m), 1583 (vs), 1468 (w), 1433 (w), 1384 (m), 1327 (m), 1290 (m), 1235 (vs), 1183 (vs), 1115 (m), 1005 (m), 929 (w), 875 (m), 814 (w), 775 (w), 748 (w), 702 (w), 677 (vw), 635 (vw).

m/z (DCI+): 749 (1 %) [M+H], 389 (8), 316 (7), 191 (6), 162 (40), 147 (8), 119 (28), 118 (12), 90 (57), 76 (17), 57 (100), 47 (19), 43 (14), 39 (7).

elemental analysis: calcd (%) for $C_{22}H_{32}N_{14}O_{16}$: C 35.30, H 4.31, N 26.20; found: C 35.05, H 4.35, N 25.31.

5.4.2 Energetic Polymers Based on 1,2,3-Triazoles

5.4.2.1 Synthesis of (4,5-Bis(hydroxymethyl)-1*H*-1,2,3-triazol-1-yl)glycidyl polymer 17

GAP (4.5 g, M_n~2000 g/mol) was dissolved in toluene and but-2-yne-1,4-diol (17.1 g, 200 mmol) was added. The reaction mixture was refluxed for 18 h. After cooling to room temperature, the toluene was decanted and the residue was washed with methylene chloride, acetone and methanol. (4,5-Bis(hydroxymethyl)-1*H*-1,2,3-triazol-1-yl)glycidyl polymer **4** was obtained as dark brown solid (6.3 g).

dec.: > 300 °C.

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3383 (vs), 2930 (m), 2878 (m), 2425 (vw), 2021 (vw), 1638 (m), 1438 (m), 1355 (m), 1230 (m), 1127 (s), 1020 (vs), 811 (w), 781 (w), 688 (w).

elemental analysis: calcd (%) for $C_7H_{11}N_3O_3$: C 45.40, H 5.99, N 22.69; found: C 45.23, H 5.62, N 19.05.

5.4.2.2 Synthesis of (4,5-Bis(nitroxymethyl)-1*H*-1,2,3-triazol-1-yl)glycidyl polymer 19

4 (1.0 g) was suspended in a mixture of 5 mL of trifluoroacetic anhydride and 3 mL fuming nitric acid. After stirring at room temperature for 18 h, the reaction mixture was poured on a mixture of ice/water and stirred for 2 h at 90 °C. The water was decanted and the polymer was extracted with methanol and ethyl ether and dried under reduced pressure (1.3 g).

dec.: 126 °C.

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3418 (m), 2965 (m), 2924 (m), 2853 (m), 2056 (vw), 1737 (w), 1637 (vs), 1456 (m), 1384 (m), 1282 (m), 1202 (w), 1122 (m), 1100 (m), 1059 (m), 925 (vw), 852 (w), 826 (w), 798 (w), 751 (vw), 718 (vw), 581 (w).

elemental analysis: calcd (%) for $C_7H_9N_5O_7$: C 30.55, H 3.30, N 25.45; found: C 29.97, H 3.35, N 22.51.

5.4.2.3 Synthesis of (4,5-Bis(chloromethyl)-1*H*-1,2,3-triazol-1-yl)glycidyl polymer 21

Pyridine (7.2 g, 87.4 mmol) was added dropwise to phosphoroxy chloride (65.0 mL). **4** (4.1 g) was added and the reaction mixture was heated at 120 °C for 2 h. After cooling to ambient temperature, the reaction mixture was poured on 800 mL of a ice-water mixture and stirred for 10 h. The formed solid was filtered off and washed with 2N sodium hydroxide solution, aetone and methylene chloride. (4,5-Bis(hydroxymethyl)-1*H*-1,2,3-triazol-1-yl)glycidyl polymer **8** was obtained as brownish powder (3.5 g).

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3639 (vw), 2963 (w), 2934 (w), 2875 (w), 2101 (w), 1720 (w), 1662 (m), 1528 (w), 1462 (w), 1440 (w), 1384 (m), 1352 (w), 1280 (s), 1192 (w), 1177 (w), 1091 (m), 1070 (m), 1042 (m), 839 (w), 748 (w), 714 (w), 673 (w), 554 (vw).

elemental analysis: calcd (%) for $C_7H_9C_{l2}N_3O$: C 37.86, H 4.08, N 18.92, Cl 31.93; found: C 37.15, H 4.31, N 19.53, Cl 28.74.

5.4.2.4 Synthesis of (4,5-Bis(azidomethyl)-1*H*-1,2,3-triazol-1-yl)glycidyl polymer 23

8 (3.0 g) and sodium azide (15.0 g, 231 mmol) were suspended in acetonitrile (200 mL) and water (50 mL) and heated to 90 °C for 24 h. After removing the acetonitrile, the formed solid was filtered off and washed with water and acetone. After drying, (4,5-bis(azidomethyl)-1*H*-1,2,3-triazol-1-yl)glycidyl polymer **10** was obtained as brown solid (2.7 g).

dec.: 206 °C.

IR (KBr, cm^{-1}): ṽ = 3414 (w), 3010 (w), 2985 (w), 2970 (w), 2943 (w), 2485 (vw), 2107 (vs), 1640 (vw), 1473 (m), 1465 (m), 1437 (m), 1383 (w), 1347 (w), 1306 (m), 1288 (m), 1269 (m), 1245 (m), 1229 (m), 1212 (m), 1177 (m), 1100 (m), 1090 (m), 980 (m), 956 (w), 900 (w), 879 (m), 810 (m), 788 (m), 763 (m), 709 (w), 690 (w), 654 (w), 560 (w), 547 (w), 475 (vw).

elemental analysis: calcd (%) for $C_7H_9N_9O$: C 35.75, H 3.86, N 53.60; found: C 35.49, H 4.01, N 48.45.

impact sensitivity ≥ 6 J; friction sensitivity ≥ 360 N.

5.4.2.5 Synthesis of (4,5-Bis(aminomethyl)-1*H*-1,2,3-triazol-1-yl)glycidyl polymer 25

10 (1.5 g) was suspended in THF (35 mL) and triphenyl phosphine (10.1 g, 38.5 mmol dissolved in 90 mL of THF) was added. The slurry was heated at 60 °C for 2 h. After cooling to ambient temperature water (10 mL) was added and the reaction mixture was stirred for 12 h. The solid was removed by filtration and suspended in methylene chloride (30 mL) and stirred for 15 min. The solid was filtered off and dried. **12** was obtained as brown solid (1.2 g).

IR (KBr, cm^{-1}): ṽ = 3427 (vs), 2956 (m), 2917 (m), 2868 (m), 2097 (w), 2022 (w), 1631 (m), 1467 (w), 1438 (w), 1384 (w), 1259 (w), 1229 (w), 1114 (m), 1070 (m), 996 (w), 976 (w), 861 (vw), 805 (vw), 754 (vw), 726 (vw), 693 (vw), 543 (vw), 522 (w).

elemental analysis: calcd (%) for $C_7H_{13}N_5O$: C 45.89, H 7.15, N 38.23; found: C 39.66, H 5.81, N 26.30.

5.4.2.6 Synthesis of (4,5-Bis(ethoxycarbonylaminomethyl)-1*H*-1,2,3-triazol-1-yl)glycidyl polymer 26

12 (1.5 g) was suspended in 2N sodium hydroxide solution (11.7 mL) at 0 °C. Ethyl chloroformate (1.3 g, 16.4 mmol) was added dropwise. The reaction mixture was stirred for 10 min and the solid was filtered off and washed with methylene chloride. After drying, **13** was obtained as brownish solid (1.4 g).

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2929 (m), 2873 (m), 2100 (w), 1708 (s), 1635 (s), 1546 (m), 1468 (m), 1440 (m), 1384 (m), 1322 (m), 1260 (s), 1114 (s), 1100 (s), 1067 (m), 1028 (m), 920 (vw), 802 (w), 696 (w), 543 (w).

elemental analysis: calcd (%) for $C_{13}H_{21}N_5O_5$: C 47.70, H 6.47, N 21.39; found: C 43.90, H 6.00, N 28.25.

5.4.2.7 Synthesis of (4,5-Bis(ethoxycarbonylnitraminomethyl)-1*H*-1,2,3-triazol-1-yl)glycidyl polymer 27

Fuming nitric acid (4.6 g, 7.3 mmol) as added at 0 °C dropwise to 9 mL of trifluoroacetic anhydride. **13** (1.4 g) was added and stirred at 0 °C for 1 h. The reaction mixture was then poured on a ice-water mixture and stirred for 1 h. The precipitate was filtered off and dried under reduced pressure (1.5 g).

dec.: 250 °C-280 °C.

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2928 (m), 2642 (w), 2105 (w), 1776 (s), 1741 (m), 1643 (s), 1583 (s), 1432 (m), 1384 (s), 1326 (s), 1283 (s), 1236 (s), 1199 (s), 1116 (m), 1006 (m), 927 (vw), 860 (w), 799 (w), 751 (w), 721 (w), 693 (vw).

elemental analysis: calcd (%) for $C_{13}H_{19}N_7O_9$: C 37.41, H 4.59, N 23.49; found: C 37.23, H 4.19, N 26.01.

5.4.2.8 Synthesis of (4,5-Bis(nitraminomethyl)-1*H*-1,2,3-triazol-1-yl)glycidyl polymer 28

14 (1.2 g) was heated in concentrated ammonia solution (30 mL) for 10 min under reflux, until the polymer was dissolved and a clear solution was formed. After cooling to room temperature, the solution was acidified with concentrated hydrochloric acid and the polymer precipitated, was filtered off and washed with water and acetone. **15** was obtained as orange powder (0.76 g).

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3414 (vs), 3219 (s), 2930 (s), 2103 (m), 1687 (s), 1642 (vs), 1575 (s), 1437 (s), 1408 (s), 1384 (vs), 1318 (vs), 1281 (vs), 1115 (s), 1067 (s), 923 (vw), 850 (w), 812 (w), 728 (w), 692 (w), 631 (w).

elemental analysis: calcd (%) for $C_7H_{11}N_7O_5$: C 30.77, H 4.06, N 35.89; found: C 36.35, H 4.61, N 29.28.

impact sensitivity ≥ 30 J; friction sensitivity ≥ 240 N.

5.4.2.9 Synthesis of Polyvinyl Azide 15

Polyvinyl chloride (6.0 g) and sodium azide (31.2 g, 480 mmol) were suspended in DMF (150 mL) and stirred for 96 h at 55 °C. After cooling to ambient temperature, the reaction mixture was poured on water (500 mL) and stirred for 24 h. The precipitate was filtered off and washed with water and methanol. The solid was stirred in a 1:1 acetone/water mixture for 12 h, filtered off and dried under reduced pressure. **2** was obtained as dark, rubber-like solid (5.1 g).

dec.: 189 °C.

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3439 (vs, moisture), 2956 (w), 2926 (vw), 2500 (vw), 2099 (m), 2037 (m), 1631 (s), 1384 (m), 1261 (w), 1100 (w), 1019 (w), 800 (vw), 615 (vw), 551 (w).

elemental analysis: calcd (%) for $C_2H_3N_3$: C 34.78, H 4.38, N 60.84; found: C 37.90, H 4.37, N 52.65.

impact sensitivity ≥ 3 J; friction sensitivity ≥ 360 N.

5.4.2.10 Synthesis of Polyvinyl-4,5-di(hydroxymethyl)-1*H*-1,2,3-triazole 18

2 (3.0 g) and but-2-in-1,4-diol (9.4 g, 109 mmol) were suspended in toluene (200 mL) and stirred for 20 h at 60 °C. The hot mixture was decanted and the residue was extracted with hot ethyl acetate. The solid was filtered of and washed with diethyl ether and dried under reduced pressure. **5** was obtained as brown powder (5.3 g).

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3426 (s), 2934 (w), 2110 (w), 1630 (w), 1455 (w), 1384 (w), 1261 (vw), 1127 (vw), 1018 (m), 796 (vw), 603 (vw).

elemental analysis: calcd (%) for $C_6H_9N_3O_2$: C 46.45, H 5.85, N 27.08; found: C 45.37, H 5.97, N 22.59.

5.4.2.11 Synthesis of Polyvinyl-4,5-di(chloromethyl)-1*H*-1,2,3-triazole 22

Pyridine (1.1 g, 3 mmol) was added dropwise to phosphorous oxychloride (31.3 g, 208 mmol). **5** (1.0 g) was added slowly and the reaction mixture was heated 2 h at 120 °C. After cooling to ambient temperature, the reaction mixture was poured on an ice/water mixture (200 mL) and stirred for 12 h. The solid was filtered off, washed with water and dried under reduced pressure. **9** was obtained as brown solid (1.0 g).

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3428 (vs), 3009 (w), 2963 (w), 2858 (w), 2107 (m), 1630 (m), 1435 (w), 1384 (w), 1261 (m), 1239 (m), 1150 (w), 1098 (w), 1054 (w), 1016 (w), 764 (vw), 717 (w), 688 (vw).

elemental analysis: calcd (%) for $C_6H_7C_{l2}N_3$: C 37.52, H 3.67, N 21.88, Cl 36.92; found: C 37.76, H 4.26, N 21.96, Cl 26.70.

5.4.2.12 Synthesis of Polyvinyl-4,5-di(azidomethyl)-1*H*-1,2,3-triazole 24

9 (0.9 g) and sodium azide (3.1 g, 47 mmol) were suspended in a mixture of water (20 mL) and acetone (70 mL) and stirred for 72 h at 55 °C. The acetonitrile was removed under reduced pressure and the solid was filtered off. The solid was washed with water and acetone and dried under reduced pressure (0.8 g).

dec.: 188°C.

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3749 (vw), 3441 (vs, moisture), 2964 (w), 2927 (w), 2097 (m), 2012 (m), 1630 (m), 1440 (w), 1384 (w), 1339 (w), 1262 (m), 1100 (m), 1023 (w), 972 (vw), 877 (vw), 801 (w), 551 (vw).

elemental analysis: calcd (%) for $C_6H_7N_9$: C 35.12, H 3.44, N 61.44; found: C 37.53, H 4.25, N 47.49, Cl 0.00.

impact sensitivity ≥ 11 J; friction sensitivity ≥ 360 N.

5.4.2.13 Synthesis of Polyvinyl-(4,5-di(nitroxymethyl)-1*H*-1,2,3-triazole) 20

5 (1.0 g) was suspended in a mixture of trifluoroacetic anhydride (5 mL) and fuming nitric acid (3 mL). After stirring at room temperature for 18 h, the reaction mixture was poured on a mixture of ice/water and stirred for 2 h. The water was decanted and the polymer was extracted with methanol and ethyl ether and dried under reduced pressure. **7** was obtained as orange powder (1.4 g).

dec.: 153°C.

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3418 (m), 3016 (w), 2985 (w), 2924 (m), 2556 (vw), 2116 (m), 1788 (m), 1647 (vs), 1436 (m), 1384 (m), 1359 (m), 1283 (vs), 1220 (m), 1151 (m), 985 (m), 930 (m), 847 (s), 750 (m), 702 (w), 642 (m), 595 (w), 520 (vw).

elemental analysis: calcd (%) for $C_6H_7N_5O_6$: C 29.40, H 2.88, N 28.57; found: C 30.95, H

3.04, N 24.28.

impact sensitivity ≥ 2 J; friction sensitivity ≥ 160 N.

5.5 Crystallographic Data

Table 3. Selected crystal data for **7**.

	7
Formula	$C_{10}H_{12}N_{18}$
M_r [g mol^{-1}]	384.3
Crystal system	monoclinic
Space group	$P2_1/c$
a [Å]	8.5380(5)
b [Å]	7.9402(7)
c [Å]	12.2004(7)
α [°]	90.00
β [°]	96.056(5)
γ [°]	90.00
V [Å³]	822.49(10)
Z	2
F(000)	396
$\rho_{calc.}$ [g cm^{-3}]	1.552
μ [mm^{-1}]	0.12
2 theta [°]	55
Index range	$-10 \leq h \leq 10$
	$-10 \leq k \leq 5$
	$-8 \leq l \leq 15$
λ [Å]	0.71073
T [K]	200(2)
Reflections collected	3498
Unique reflections	1770
Parameter	2369
S	151
R_{int}	0.845
R_1/ wR_2 [I>2σ(I)]	0.0253
R_1/ wR_2	0.0451/0.0700
R_1/ wR_2 (alle Daten)	0.0941/0.0773

5.6 References

(1) a) R. H. Wiley, K. F. Hussung, J. Moffat, *J. Org. Chem.* **1956**, *21*, 190-192; b) R. Huisgen, G. Szeimies, L. Moebius, *Chem. Ber.* **1966**, *99*, 475-490; c) K. Banert, *Chem. Ber.* **1989**, *122*, 123-128.

(2) a) J. O. Fournier, J. B. Miller, *J. Heterocycl. Chem.* **1965**, *2*, 488-490; b) D. L. Coffen, R. I. Fryer, D. A. Katonak, F. Wong, *J. Org. Chem.* **1975**, *40*, 894-897; c) M. Ikeda, F. Tabusa, Y. Nishimura, S. Kwon, Y. Tamura, *Tetrahedron Lett.* **1976**, *27*, 2347-2350.

(3) a) K. Cheng, J. Liu, X. Liu, H. Li, H. Sun, J. Xie, *Carbohydr. Res.* **2009**, *344*, 841-850; b) J. Broggi, H. Kumamoto, S. Berteina-Raboin, S. P. Nolan, L. A. Agrofoglio, *Eur. J. Org. Chem.* **2009**, *12*, 1880-1888; c) I. Jlalia, F. Meganem, J. Herscovici, C. Girard, *Molecules* **2009**, *14*, 528-539.

(4) J. M. Dyke, A. P. Groves, A. Morris, J. S. Ogden, A. A. Dias, A. M. S. Oliveira, M. L. Costa, M. T. Barros, M. H. Cabral, A. M. C. Moutinho, *J. Am. Chem. Soc.* **1997**, *119*, 6883-6887.

(5) C. Mazzini, J. Lebreton, V. Alphand, R. Furstoss, *Tetrahedron Lett.* **1997**, *38*, 1195-1196.

(6) E. D. Edstrom, T. Yu, *Tetrahedron* **1997**, *53*, 4549-4560.

(7) a) L. J. Winters, D. B. Learn, S. C. Desai, *J. Org. Chem.* **1965**, *30*, 2471-2472; b) H. M. Curry, J. P. Mason, *J . Am. Chem. Soc.* **1951**, *73*, 5041-5042.

(8) a) Y. Ohba, M. Takatsuji, K. Nakahara, H. Fujioka, Y. Kita, *Chem.-Eur. J.* **2009**, *15*, 3526-3537; b) L. Banfi, R. M. Guiseppe, *Eur. J. Org. Chem.* **2003**, *7*, 1319-1336; c) N. Knouzi, M. Vaultier, L. Toupet, R. Carrie, *Tetrahedron Lett.* **1987**, *28*, 1757-1760.

(9) a) A. Latorre, S. Rodriguez, J. Izquierdo, F. V. Gonzalez, *Tetrahedron Lett.* **2009**, *50*, 2653-2655. b) C. T. Hoang, F. Bouillere, S. Johannesen, A. Zulauf, C. Panel, A. Pouilhes, D. Gori, V. Alezra, C. Kouklovsky, *J. Org. Chem.* **2009**, *74*, 4177-4187.

(10) a) M. Suceska, *Test Methods for Explosives*, Springer, New York, **1995**, p. 21 (impact), p. 27 (friction); b) http://www.bam.de/; c) Impact: insensitive > 40 J, less sensitive > 35 J,

sensitive > 4 J, very sensitive < 4 J; friction: insensitive > 360 N, less sensitive = 360 N, sensitive < 360 N > 80 N, very sensitive < 80 N, extreme sensitive < 10 N; According to the UN Recommendations on the Transport of Dangerous Goods (+) indicates: not safe for transport.

(11) a) M. Suceska, *Proc. of 30th Int. Annual Conference of ICT, Karlsruhe, Germany*, ed. Fraunhofer-Institut für chemische Technologie, DWS Werbeagentur und Verlag GmbH, Karlsruhe, **1999**, 50/1; b) EXPLO5.V2, Computer program for calculation of detonation parameters, P, M. Suceska, *Proc. of 32nd Int. Annual Conference of ICT, Karlsruhe, Germany*, ed. Fraunhofer-Institut für chemische Technologie, DWS Werbeagentur und Verlag GmbH, Karlsruhe, **2001**, pp. 110/1.

(12) a) C.Druesedow, C. F. Gibbs, *Modern Plastics*, **1953**, *30*, 123-128; b) E. J. Arlman, *J. Polym. Sci.* **1954**, *12*, 547-558; c) Z. Vymazal, B. Dolezel, J. Stepek, *Kunststoffe*, **1966**, *56*, 86-91.

(13) a) J. O. Fournier, J. B. Miller, *J. Heterocycl. Chem.* **1965**, *4*, 488-490; b) J. C. Kauer, R. A. Carboni, *J. Am. Chem. Soc.* **1967**, *89*, 2633-2637; c) A. T. Parsons, J. S. Johnson, *J. Am. Chem. Soc.* **2009**, *131*, 3122-3123.

(14) S. Brochu, G. Ampleman, *Macromolecules*, **1996**, *29*, 5539-5545.

(15) E. E. Gilbert, *J. Polym. Sci., Part A: Polym. Chem.* **1984**, *22*, 3603-3606.

(16) a) C.Druesedow, C. F. Gibbs, *Modern Plastics*, **1953**, *30*, 123-128; b) E. J. Arlman, *J. Polym. Sci.* **1954**, *12*, 547-558; c) Z. Vymazal, B. Dolezel, J. Stepek, *Kunststoffe*, **1966**, *56*, 86-91.

(17) a) J. C. Bottaro, R. J. Schmitt, C. D. Bedford, *J. Org. Chem.* **1987**, *52*, 2292-2294; b) M. L. Wolfrom, G. H. McFadden, A. Chaney, *J. Org. Chem.* **1960**, *25*, 1079-1082.

(18) a) E. Tamanini, S. E. J. Rigby, M. Motevalli, M. H. Todd, M. Watkinson, *Chem.-Eur. J.* **2009**, *15*, 3720-3728; b) G. Shaw, B. M. Smallwood, D. V. Wilson, *J. Chem. Soc. C*, **1966**, *10*, 921-924.

(19) a) Y. Ohba, M. Takatsuji, K. Nakahara, H. Fujioka, Y. Kita, *Chem.-Eur. J.* **2009**, *15*, 3526-

3537; b) L. Banfi, R. M. Guiseppe, *Eur. J. Org. Chem*. **2003**, 7, 1319-1336; c) N. Knouzi, M. Vaultier, L. Toupet, R. Carrie, *Tetrahedron Lett.* **1987**, *28*, 1757-1760.

(20) M. Hesse, H. Meier, B. Zeeh, *Spektroskopische Methoden in der organischen Chemie*, 6th edition, Thieme, Stuttgart; New York, **2002**, p. 48 and p. 55.

(21) a) G. Fleury, L. Brissaud, P. Lhoste, *Compt. rend.* **1947**, *224*, 1016-1018; b) S. Zeman, *Thermochim. Acta* **1993**, *230*, 191-206; c) G. M. Nazin, V. G. Prokudin, G. B. Manelis, *Russ. Chem. Bull.* **2000**, *49*, 234-237.

(22) T. M. Klapötke, M. Stein, J. Stierstorfer, *Z. Anorg. Allg. Chem.* **2008**, *634*, 1711-1723.

(23) a) N. Wiberg, *Lehrbuch der Anorganischen Chemie* / Holleman-Wiberg, 101. Ed., de Gruyter, Berlin, **1995**, 141; b) N. Wiberg, *Lehrbuch der Anorganischen Chemie* / Holleman-Wiberg, 101. Ed., de Gruyter, Berlin, **1995**, pp 250, 859 and 1176; c) http://webbook.nist.gov/chemistry/

(24) T. M. Klapötke, *Chemie der hochenergetischen Materialien*, 1. Edition, Walter de Gruyter GmbH & Co. KG, Berlin, **2009**, pp 63.

(25) R. Perion, V. Ferrieres, M. I. Garcia-Moreno, C. Ortiz Mellet, R. Duval, J. M. Garcia Fernandez, D. Plusquellec, *Tetrahedron* **2005**, *61*, 9118-9128.

6. Synthesis and Investigation of 1,2,3,4-Thiatriazol-5-ylcarbamates

Abstract: Several 1,2,3,4-thiatriazol-5-ylcarbamates were synthesized with high yields by the reaction of the corresponding carbon(isothiocyanatidic) acid alkyl esters and sodium azide in aqueous solution. The compounds were characterized by ^{1}H, ^{13}C and ^{15}N NMR, vibrational spectroscopy (IR) and single crystal X-ray diffraction. The thermal stability was investigated by differential scanning calorimetry.

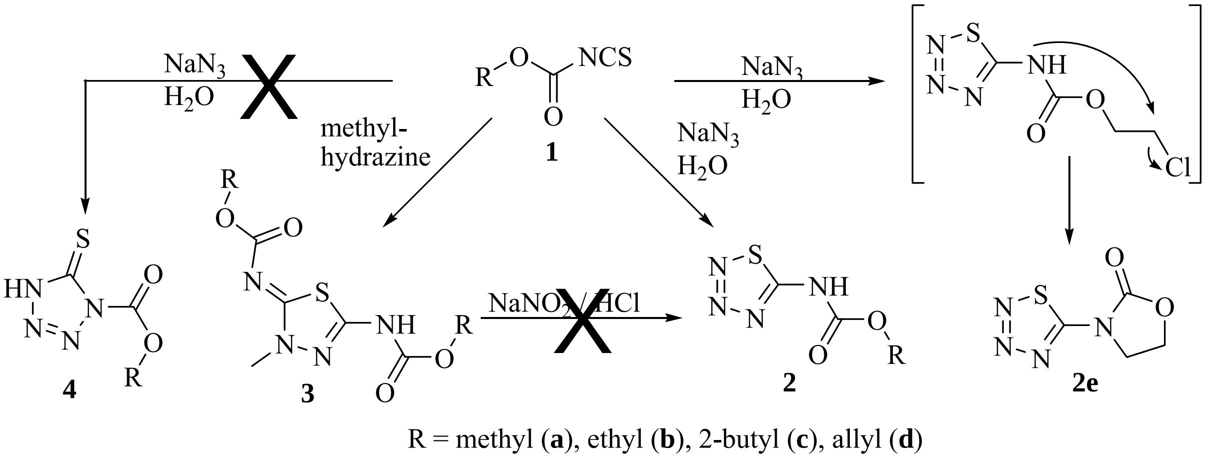
6.1 Introduction

The investigation of the synthesis and thermal behavior of the 1,2,3,4-thiatriazol-5-ylcarbamates was strictly of academic interest, because the sulfur atom prevents these compounds from being used as potential energetic materials. The primary intention of the investigation of carbon(isothiocyanatidic) acid alkyl esters was the hope to obtain either the corresponding thiosemicarbazides, suitable for the preparation of tetrazolyl hydrazines (*paragraph 2.2.1*) or to get the corresponding 1*H*-tetrazole-5-thiones with the sulfur atom as potential leaving group for nucleophilic substitution reactions. Despite being plausible projects in the range of common chemical sense, neither the thiosemicarbazides nor the tetrazoles could be obtained. In case of the thiosemicarbazides, only products containing two carbon(isothiocyanatidic) acid alkyl esters and one monomethyl hydrazine were formed. In case of the tetrazoles only the thiatriazoles were detected.

1,2,3,4-Thiatriazoles have been known for many years. Although the 1,2,3,4-thiatriazoles turned out to be rather nonhazardous compounds, several accidents during the preparation were reported. E. Lieber for example warned, that his synthetic pathway yields rather dangerous intermediates, as the 5-chlor-1,2,3,4-thiatriazole that detonated spontaneously.[1] Besides their interesting structure, thiatriazoles are common intermediates in organic chemistry. Thermal decomposition of derivatives of 1,2,3,4-thiatriazoles yielded the corresponding cyanate[2] or aroyl thiocyanates[3] by loosing N_2 and the sulfur atom.

6.2 Synthesis of 1,2,3,4-Thiatriazol-5-ylcarbamates

The synthesis of the 1,2,3,4-thiatriazol-5-ylcarbamates (**2**) was carried out using sodium azide and the corresponding carbon(isothiocyanatidic) acid alkyl esters (**1**). Common solvents for the cyclisation of isothiocyanates and azide are dioxane,[4] acetonitrile[5] or water. Another method for the preparation of thiatriazoles is the diazotation of thiosemicarbazides.[6] The synthesis of **2** was carried out by adding the corresponding isothiocyanates **1** to a boiling solution of sodium azide in water. The reactivity of the azide anion in aqueous solution is high enough to prevent the highly electrophilic isothiocyanate moiety from hydrolysis. The corresponding sodium salts of **2** that were formed in the aqueous solution could be precipitated as pure powder by acidification of the reaction mixture. The formation of by-products such as 5*H*-tetrazole-5-thiones (**4**) was not observed. Decomposition products as a result of a hydrolysis of **1** could be CO_2, H_2S, HNCO and the corresponding alcohols. Regarding the high yield of **2** a further investigation of these decomposition products was not carried out. In case of **2d**, the thiatriazole could only be obtained as slightly impure compound, due to a decomposition of the allyl moiety.



Scheme 1. Synthesis of the 1,2,3,4-thiatriazol-5-ylcarbamates.

Besides the reaction of **1** with sodium azide, the preparation of thiosemicarbazides bearing a carbamate moiety was investigated. Several attempts for the reaction of hydrazine and the corresponding carbon(isothiocyanatidic) acid alkyl esters **1** to form thiosemicarbazides were performed without success. The reaction of carbon(isothiocyanatidic) acid ethyl ester and monomethyl hydrazine led to a condensation product of two molecules of carbon(isothiocyanatidic) acid ethyl ester and one molecule of monomethyl hydrazine (**3**) (*Scheme 1*).

6.3 Crystal Structures of 2a, 2e and 3

As already mentioned in *Scheme 1*, the formation of the chloroethyl 1,2,3,4-thiatriazol-5-ylcarbamate was not possible, due to an intramolecular attack of the nitrogen atom. Compound **2e** crystallizes in the orthorhombic space group *Fdd*2 with sixteen formula units per unit cell (*Figure 1*). Inter- or intramolecular interactions between the molecules such as hydrogen bridges are not found. The arrangement of the molecules in the crystal structure is in such a manner, that the sulfur atom points towards the O2 of a neighbouring molecule (*Figure 2*). Since the distance between S1 and the neighbouring O2 with 3.28 Å is nearly equivalent with the sum of the van der Waals radii of sulfur and oxygen (3.25 Å[7]), an interaction between S1 and O2 could be excluded. On the other hand, the direction of the sulfur atom towards the oxygen atom allows the assumption, that an intermolecular interaction exists, but a distance equivalent to the sum of the van der Waals radii contradicts this thesis.

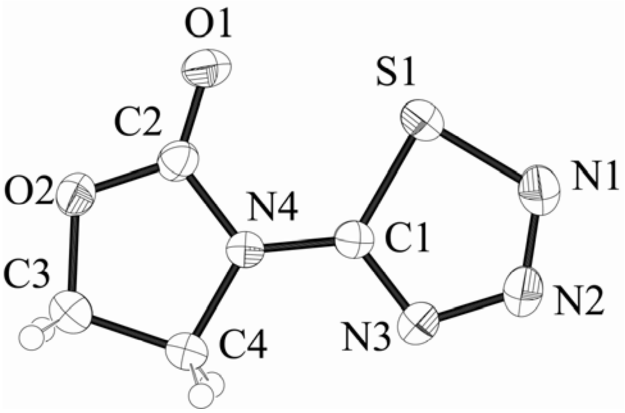


Figure 1. Molecular structure of **2e**. Thermal ellipsoids are drawn at the 50% probability level.

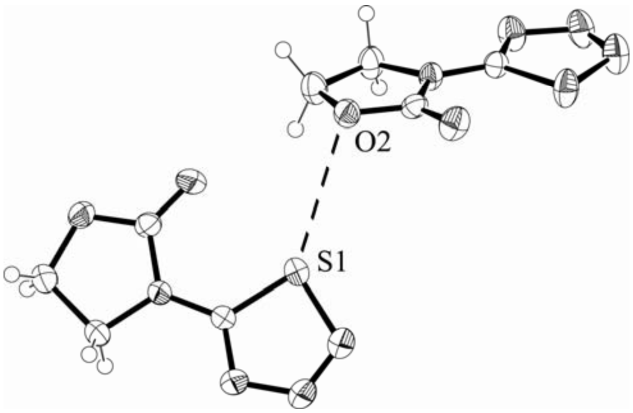


Figure 2. Packing of **2e**. Thermal ellipsoids are drawn at the 50% probability level.

Compound **5** crystallizes in the monoclinic space group *C*2/*m* with four molecular formulas per unit cell. The crystal structure of **5** contains two molecules of crystal water attached to the sodium atom (*Figure 3*). The structure is stabilized by several hydrogen bridges, one between the hydrogen atom H4a of O4 to N4 (D•••A: 2.804 Å, <(DHA): 169.87 °) and the other of the same hydrogen atom to O1 (D•••A: 3.031 Å, <(DHA): 115.38 °). Further hydrogen bridges are formed between the hydrogen atom H4b of O4 to N1 (D•••A: 3.181 Å, <(DHA): 158.14 °) and to O1 (D•••A: 3.031 Å, <(DHA): 112.89 °). The second water molecule forms two hydrogen bridges, on between the hydrogen atom H3a of O3 to N2 (D•••A: 2.899 Å, <(DHA): 178.04 °) and the other between the hydrogen atom H3b of O3 to N3 (D•••A: 2.876 Å, <(DHA): 177.37 °). The sodium atoms are arranged in chains, connected by the bridging oxygen atoms of the crystal water or the O1 atoms of the thiatriazole moieties (*Figure 4*). Thereby, two chains are connected by the hydrogen bridge of H4a to N1.

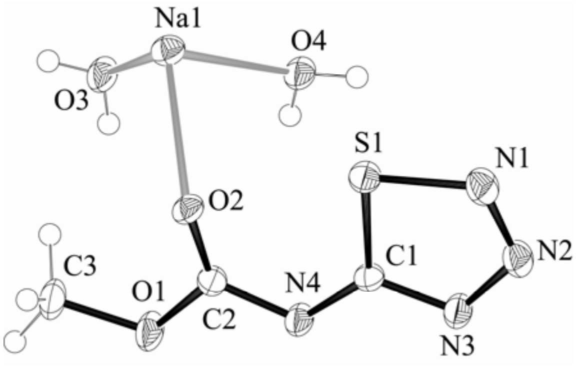


Figure 3. Molecular structure of **5**. Thermal ellipsoids are drawn at the 50% probability level.

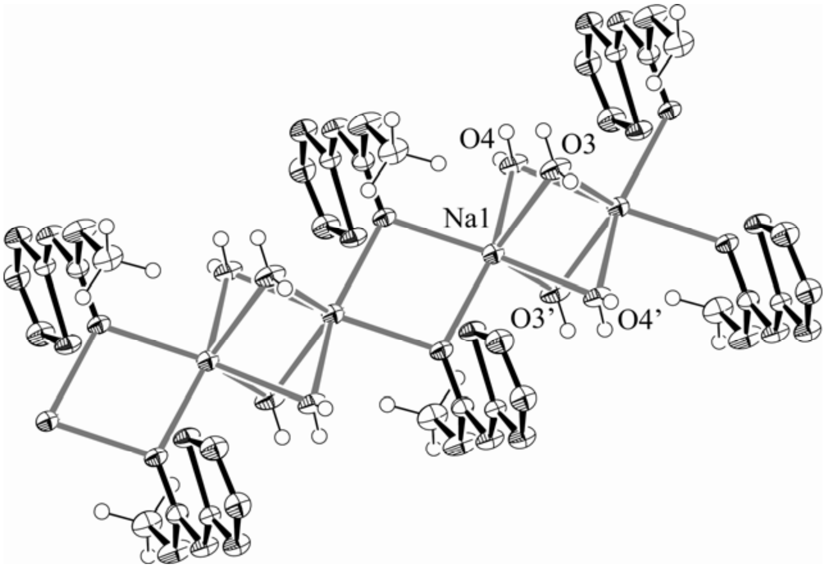


Figure 4. Packing of the sodium salt of **2a**. Thermal ellipsoids are drawn at the 50% probability level.

Compound **3** crystallizes as monohydrate in the triclinic space group *P*-1 with eight formula units per unit cell (*Figure 5*). Three hydrogen bridges stabilize the structure. The first is located between the ring-nitrogen atom N2 as acceptor and N3-H as donor of the neighbouring molecule (D•••A: 3.073 Å, <(DHA): 171.77 °). The water molecule forms two hydrogen bridges, one between O-H as donor to N4 as acceptor (D•••A: 2.947 Å, <(DHA): 177.67 °) and the other between the second proton of the water molecule and O5 of a neighbouring water molecule

(D•••A: 2.785 Å, <(DHA): 1.45.64 °). The proton of **3** was located at N3. Besides this isomer, two more tautomers could be possible, the tautomer protonated at N2 with the double bond between N3 and C1 or the tautomer protonated at N4. An explanation could be the sterical effect of the methyl group C3. A hydrogen bridge to a neighbouring N2-atom is formed by the proton at N3. In case of N4, the methyl group at C3 would complicate these intermolecular interactions due to its sterical hindrance.

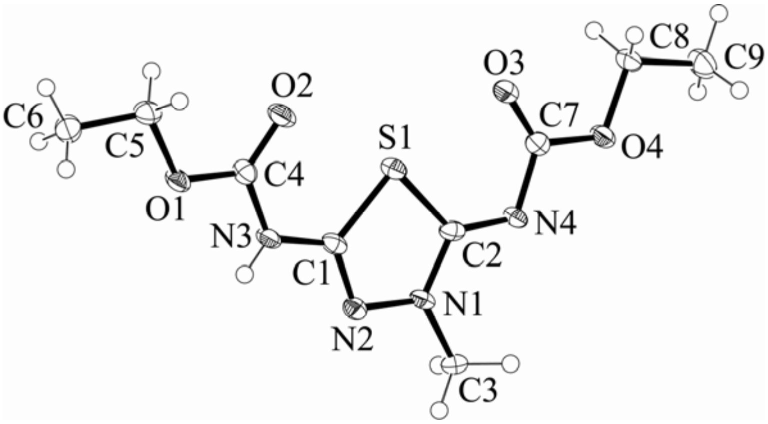


Figure 5. Molecular structure of **3**. Thermal ellipsoids are drawn at the 50% probability level.

6.4 NMR Spectroscopic Data of the1,2,3,4-Thiatriazol-5-ylcarbamates

The ^{13}C NMR shifts of **2a-e** were assigned according to known values from the literature. The quaternary carbon atom of the formate moiety at 155 ppm is independent of the different substituents (ranging from 155.1 ppm to 156.3 ppm, *Table 1*). Comparing the quaternary carbon atoms of the thiatriazole moieties, the difference between **2a-d** and **2e** becomes apparent. In contrast to the structures **2a-d**, with only one substituent at the nitrogen atom N4, the chemical shift of the ring carbon atom of **2e** is shifted about 1.5 ppm upfield (172.0 ppm of **2d** compared to 169.5 ppm of **2e**, *Table 2*). Compared to common ^{13}C NMR values of the quaternary carbon atom of amino-1,2,3,4-thiatriazoles known from literature, the quaternary carbon atom is shifted upfield by about 7 ppm (N-(2,4,6-trimethylpheny1)-1,2,3,4-thiatriazol-5-amine: 179.4 ppm;[8] 5-[2-(ethoxycarbonylvinyl)benzyl]amino-1,2,3,4-thiatriazole: 178.2 ppm, $CDCl_3$[9]). In order to compare the ^{15}N NMR spectra of the two different types of thiatriazoles (**2a-d** and **2e**), ^{15}N NMR spectra of **2a** and **2e** were recorded. The three signals ranging between 67.6 ppm and -47.4 ppm were assigned to the three ring nitrogen atoms. The signals are in accordance with the values of the literature.[10] The comparison between N4 (-267.0 ppm **2a** and 268.3 ppm **2e**) does not show any differences, except in the intensity of the signal. This effect can easily explained by the proton attached to N4 of 2a and the CH_2-moiety in case of **2e**.

Table 2. ^{13}C NMR shifts in ppm of **2a-2e**.

	2a^a	**2b**^{b}	**2c**^{a}	**2d**^{a}	**2e**^{a}
CH_3	54.6	14.4	19.2	-	-
CH_2	-	64.7	73.5	68.1	-
CH	-	-	27.9	-	-
$CH_{2(allyl)}$	-	-	-	132.3	-
$CH_{(allyl)}$	-	-	-	119.5	-
N-CH_2	-	-	-	-	45.6
O-CH_2	-	-	-	-	66.1
C_qO	155.7	154.2	155.5	155.1	156.3
C_qS	171.8	171.6	172.1	172.0	169.5

^{a} measured in *d6*-DMSO; ^{b} measured in $CDCl_3$.

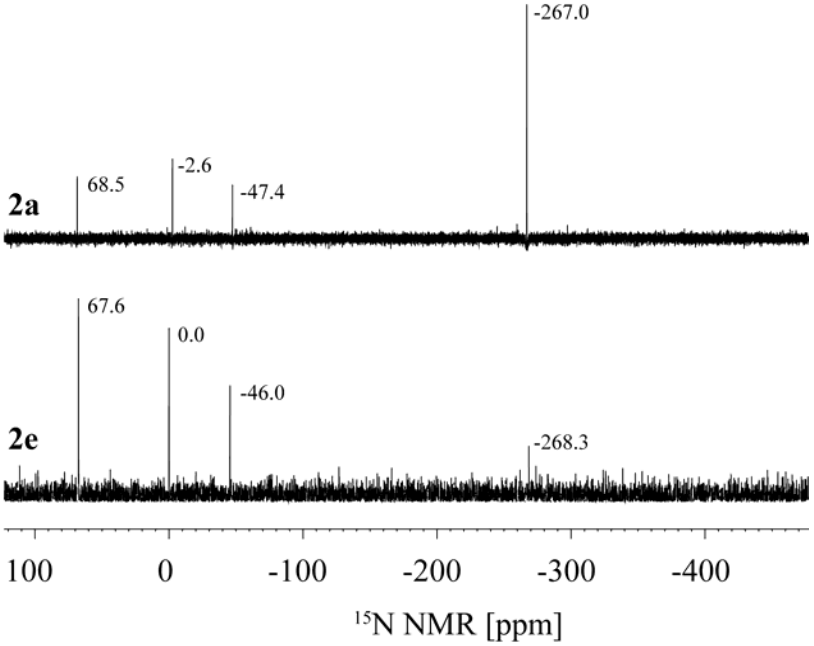


Figure 6. Comparison of the ^{15}N NMR of **2a** and **2e**.

6.5 Thermal Properties and Physical Stabilities of the 1,2,3,4-Thiatriazol-5-ylcarbamates

Besides the analysis of the crystal structures and NMR values, the investigation of the thermal and physical stability is of great interest. A comparison between the thermal stabilities of compounds **2a** to **2e** shows that the point of decomposition depends strongly on the ester moiety. Among the alkyl esters, the 2-butyl derivative **2c** is the most stable compound (119 °C) whereas the point of decomposition of **2a** (109 °C) and **2b** (111 °C) are significantly lower. The allyl derivative **2d** (101 °C) possesses the lowest point of decomposition, **2e** the highest (126 °C). In contrast to the decomposition of compounds **2a-d**, the decomposition of **2e** proceeds in two steps. A possible explanation for the second exothermic signal at about 155 °C could be the second ring system. The point of decomposition at 126 °C could be a result of the decomposition of the thiatriazole ring, whereas the second decomposition at 155 °C could be due to the remaining oxazolidin-2-one moiety. The investigation of the thermal stabilities shows, that unsaturated derivatives (**2d**) are the most unstable compounds, whereas the substitution of the proton of N4 by an alkyl moiety (**2e**) leads to an enhanced thermal stability.

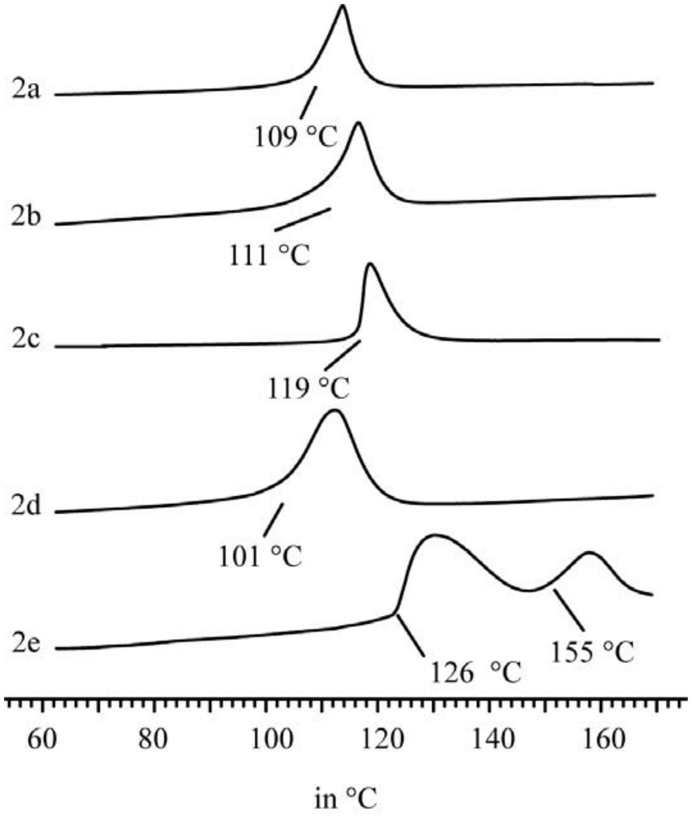


Figure 7. DSC plot of compounds **2a-e** (exo = up).

The determination of the physical stability of **2a-e** shows only insignificant differences between the five compounds. The sensitivity towards friction and impact was determined by BAM standards.[11] The sensitivity towards friction of **2a-e** was determined to be > 360 N, the sensitivity towards impact was < 30 J.

6.6 Conclusions

Methyl 1,2,3,4-thiatriazol-5-ylcarbamate (**2a**), ethyl 1,2,3,4-thiatriazol-5-ylcarbamate (**2b**), 2-butyl 1,2,3,4-thiatriazol-5-ylcarbamate (**2c**), allyl 1,2,3,4-thiatriazol-5-ylcarbamate (**2d**) and 3-(1,2,3,4-thiatriazol-5-yl)oxazolidin-2-one (**2e**) were synthesized and characterized by NMR, vibrational spectroscopy (IR) and single crystal X-ray diffraction. In addition, the thermal behavior of **2a-e** was investigated by differential scanning calorimetry. The thiatriazoles proved to be thermal stable up to 126 °C and showed no sensitivity towards friction but were sensitive towards impact (< 30 J). The advantage of the presented synthesis by using carbon(isothiocyanatidic) acid, alkyl esters is the high yield along with a low preparative effort. The alkyl 1,2,3,4-thiatriazol-5-ylcarbamates can be used as cheap and easy available starting materials for the preparation of the 1,2,3,4-thiatriazol-5-amine or to introduce the 1,2,3,4-thiatriazol moiety into more complex molecules.

6.7 Experimental Section

CAUTION! Azides are highly energetic compounds with sensitivity towards heat and impact. Although we had no problems in synthesis, proper protective measures (safety glasses, face shield, leather coat, earthened equipment and shoes, Kevlar® gloves and ear plugs) should be used when undertaking work involving these compounds.

The used carbon(isothiocyanatidic) acid, alkyl esters **2** were all prepared after known procedures from the literature.[12]

6.7.1 General synthesis for the Preparation of 1,2,3,4-Thiatriazol-5-ylcarbamates 2

Sodium azide (0.75 g, 11.5 mmol) was dissolved in 20 mL water and heated to 70 °C. Carbon(isothiocyanatidic) acid, alkyl ester (7.6 mmol) was dissolved in 1.5 mL hexane and added drop wise to the hot solution of sodium azide in water. The reaction mixture was stirred for 3 h. After cooling to ambient temperature, the aqueous solution was washed with 50 mL ethyl acetate. The aqueous solution was acidified with 2N hydrochloric acid. The neutral 1,2,3,4-thiatriazol-5-ylcarbamates precipitated from the solution and were obtained by filtration.

6.7.2 Methyl 1,2,3,4-thiatriazol-5-ylcarbamate 2a

yield: 75 %.

dec.: 109 °C.

IR (KBr, $\mathrm{cm^{-1}}$): $\tilde{\nu}$ = 3430 (m), 3137 (m), 2962 (m), 2927 (m), 2765 (m), 1717 (vs), 1547 (s), 1468 (m), 1336 (m), 1320 (m), 1271 (s), 1236 (s), 1088 (m), 1020 (w), 948 (vw), 933 (vw), 795(vw), 767 (m), 752 (m), 597 (vw), 581 (vw).

^{1}H NMR (*d6*-DMSO) δ: 3.83 (s, 1H, C*H_3*), 12.29 (br. s, 1H, N*H*).

^{13}C NMR (*d6*-DMSO) δ: 54.6 (*C*H_3), 155.7 (*C*O), 171.8 (CS).

^{15}N NMR (*d6*-DMSO) δ: 68.5, -2.6, -47.4. -267.0.

m/z (DCI$^+$) 161.1 (69%) (M+H), 133 (28), 101 (24), 69 (16), 58 (9), 57 (100), 56 (9), 43 (52), 42 (8), 41 (21), 39 (8), 33 (7).

elemental analysis: calcd (%) for $C_3H_4N_4O_2S$: C 22.50, H 2.52, N 34.98; found: C 22.19, H 2.46, N 34.70.

6.7.3 Ethyl 1,2,3,4-thiatriazol-5-ylcarbamate 2b

yield: 72 %.

dec.: 111 °C.

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3448 (m), 3147 (w), 3086 (w), 3063 (w), 3030 (m), 3004 (m), 2925 (m), 2856 (w), 2769 (w), 1733 (s), 1720 (m), 1604 (w), 1546 (vs), 1384 (w), 1372 (w), 1331 (m), 1316 (m), 1271 (s), 1235 (vs), 1160 (vw), 1091 (m), 1023 (m), 1002 (w), 945 (vw), 877 (vw), 805 (vw), 763 (m), 741 (vw), 590 (vw).

^{1}H NMR ($CDCl_3$) δ: 1.43 (t, 3H, ^3J = 7.2 Hz, C*H_3*), 4.44 (q, 2H, ^3J = 7.2 Hz, C*H_2*), 11.77 (br. s, 1H, N*H*).

^{13}C NMR ($CDCl_3$) δ: 14.4 (*C*H_3), 64.7 (*C*H_2), 154.2 (*C*O), 172.6 (CS).

m/z (DCI$^+$) 175 (40%) (M+H), 147 (12), 133 (10), 132 (21), 58 (12), 57 (100), 56 (11), 47 (8), 43 (71), 42 (9), 41 (25), 39 (8).

elemental analysis: calcd (%) for $C_4H_6N_4O_2S$: C 27.58, H 3.47, N 32.17; found: C 27.73, H 3.52, N 31.90.

6.7.4 2-Butyl 1,2,3,4-thiatriazol-5-ylcarbamate 2c

yield: 76 %.

dec.: 119 °C.

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3427 (m), 3157 (m), 2963 (m), 2915 (m), 2879 (m), 2775 (m), 1731 (vs), 1721 (vs), 1562 (s), 1475 (m), 1466 (m), 1380 (m), 1371 (m), 1345 (m), 1335 (s), 1317 (m), 1277 (s), 1238 (s), 1138 (vw), 1101 (m), 1024 (m), 977 (vw), 966 (vw), 940 (vw), 840 (vw), 799 (w), 770 (m), 756 (m), 594 (vw), 577 (vw), 488 (vw).

^{1}H NMR (*d6*-DMSO) δ: 0.92 (d, 6H, ^3J = 6.8 Hz, CH_3), 1.97 (sept, 1H, ^3J = 6.8 Hz, C*H*), 4.07 (d, 2H, ^3J = 6.8 Hz, CH_2), 13.2 (br. s, 1H, N*H*).

^{13}C NMR (*d6*-DMSO) δ: 19.2 (*C*H$_3$), 27.9 (*C*H), 73.5 (*C*H$_2$), 155.5 (*C*O), 172.1 (CS).

m/z (DCI$^+$) 203 (100%) (M+H), 177 (21), 175 (50), 143 (30), 119 (21), 57 (86), 43 (25), 33 (43).

elemental analysis: calcd (%) for $C_6H_{10}N_4O_2S$: C 35.63, H 4.98, N 27.70; found: C 35.27, H 4.69, N 27.70.

6.7.5 Allyl 1,2,3,4-thiatriazol-5-ylcarbamate 2d

yield: 60 % (slightly impure).

dec.: 101 °C.

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3458 (m), 3159 (m), 2962 (m), 2919 (m), 2765 (m), 1727 (m), 1714 (m), 1647 (m), 1547 (vs), 1454 (m), 1424 (m), 1385 (m), 1359 (m), 1330 (m), 1315 (m), 1262 (vs), 1230 (s), 1097 (m), 1025 (m), 992 (m), 945 (m), 801 (w), 771 (m), 707 (vw), 591 (vw).

^{1}H NMR (*d6*-DMSO) δ: 4.75 (d, 2H, ^3J = 5.50 Hz, CH_2), 5.26 (d, 1H, ^3J = 10.44 Hz, CH_{cis}), 5.37 (d, 1H, ^3J = 17.04 Hz, CH_{trans}), 5.95 (m, 1H, C*H*), 13.25 (br. s, 1H, N*H*).

^{13}C NMR (*d6*-DMSO) δ: 68.1 (*C*H$_2$), 119.5 (*C*H), 132.3 (*C*H$_{2\text{(allyl)}}$), 155.1 (*C*O), 172.0 (CS).

elemental analysis: calcd (%) for $C_5H_6N_4O_2S$: C 32.25, H 3.25, N 30.09; found: C 32.53, H 3.62, N 31.80.

6.7.6 3-(1,2,3,4-Thiatriazol-5-yl)oxazolidin-2-one 2e

yield: 76 %.

dec.: 126 °C.

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3427 (m), 2997 (w), 2924 (vw), 1757 (vs), 1506 (vs), 1486 (s), 1471 (s), 1403 (vs), 1365 (m), 1332 (m) 1311 (m), 1255 (m), 1237 (s), 1127 (s), 1082 (m), 1063 (m), 1022 (s), 954 (m), 895 (vw), 804 (vw), 750 (s), 716 (m), 667 (w), 632 (vw), 567 (vw).

^{1}H NMR (*d6*-DMSO) δ: 4.33 (t, 2H, ^3J = 7.7 Hz, N-CH_2), 4.73 (t, 2H, ^3J = 7.7 Hz, O-CH_2), 13.17 (br. s, 1H, N*H*).

^{13}C NMR (*d6*-DMSO) δ: 45.6 (N*C*H_2), 66.1 (O*C*H_2), 156.3 (*C*O), 169.5 (CS).

^{15}N NMR (*d6*-DMSO) δ: 67.6, 0.0, -46.0, -268.3.

m/z (DCI^+) 173 (100%) (M+H), 162 (32), 145 (24), 113 (33), 103 (14), 88 (19), 57 (84), 43 (28), 41 (12).

elemental analysis: calcd (%) for $C_4H_4N_4O_2S$: C 27.91, H 2.34, N 32.54; found: C 27.66, H 2.30, N 32.11.

6.8 Crystallographic Data

CCDC-740461 (**5**), -740462 (**3**) and -740463 (**2e**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

Table 1. Selected crystal data for **5**, **2e** and **3**.

	5	**2e**	**3**
Formula	$C_3H_3N_4O_2SNa$	$C_4H_4N_4O_2S$	$C_9H_{14}N_4O_4S$
M_r [g mol^{-1}]	182.14	172.17	274.30
Crystal system	monoclinic	orthorhombic	triclinic
Space group	*C*2/*m*	*Fdd*2	*P*-1
a [Å]	15.8754	13.5064	5.1032
b [Å]	6.5299	18.4533	10.8530
c [Å]	8.7428	10.9037	12.8182
α [°]	90	90	66.935
β [°]	110.932	90	88.309
γ [°]	90	90	88.464
V [Å^3]	846.51	2717.61	652.81
Z	4	16	8
F(000)	448.0	1408.0	304.0
$\rho_{calc.}$ [g cm^{-3}]	1.712	1.683	1.528
μ [mm^{-1}]	0.42	0.43	0.73
2 theta [°]	54	54	54
Index range	$-20 \leq h \leq 20$	$-17 \leq h \leq 17$	$-6 \leq h \leq 6$
	$-8 \leq h \leq 8$	$-23 \leq h \leq 23$	$-13 \leq h \leq 13$
	$-11 \leq h \leq 11$	$-13 \leq h \leq 13$	$-16 \leq h \leq 16$
λ [Å]	0.71073	0.71073	0.71073
T [K]	200(2)	200(2)	200(2)
Reflections collected	4644	7195	6818
Unique reflections	1004	1477	2829
Parameter	90	116	236
S	1.067	1.139	0.912
R_{int}	0.0214	0.0223	0.0450
R_1/ wR_2 [I>2σ(I)]	0.0231/0.0629	0.0228/0.0581	0.0380/0.0628
R_1/ wR_2	0.0318/0.0682	0.0265/0.0605	0.0790/0.0628

6.9 References

(1) E. Lieber, C. B. Lawyer, J. P. Trivedi, *J. Org. Chem.* **1961**, *26*, 1644-1646.

(2) a) D. Martin, *Chem. Ber.* **1964**, *97*, 2689-2694; b) D. Martin, *Tetrahedron Lett.* **1964**, *39*, 2829-2832.

(3) C. Christophersen, P. Carlsen, *Tetrahedron*, **1976**, *32*, 745-747.

(4) M. Marchalin, F. Povazanec, A. Martvon, *Collection of Czechoslovak Chemical Communications* **1982**, *47*, 877-883.

(5) M. G. Ponzo, G. Evindar, R. A. Batey, *Tetrahedron Lett.* **2002**, *43*, 7601-7604.

(6) E. Lieber, C. N. Pillai, R. D. Hites, *Can. J. Chem.* **1957**, *35*, 832-842.

(7) A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441-451.

(8) G. Kaugars, J. P. Atherton, F. Han, *J. Org. Chem.* **1992**, *57*, 1671-1676.

(9) G. L'abbe, S. Leurs, I. Sannen, W. Dehaen, *Tetrahedron* **1993**, *49*, 4439-4446.

(10) a) M.-J. Crawford, T. M. Klapötke, P. Klüfers, P. Mayer, P. S. White, *J. Am. Chem. Soc.* **2000**, *122*, 9052-9053; b) M.-J. Crawford, T. M. Klapötke, P. Mayer, M. Vogt, *Inorg. Chem.* **2004**, *43*, 1370-1378.

(11) Impact: insensitive > 40 J, less sensitive > 35 J, sensitive > 4 J, very sensitive < 4 J; friction: insensitive > 360 N, less sensitive = 360 N, sensitive < 360 N > 80 N, very sensitive < 80 N, extreme sensitive < 10 N; According to the UN Recommendations on the Transport of Dangerous Goods (+) indicates: not safe for transport.

(12) a) A. E. Dixon, J. Taylor, *J. Chem. Soc.* **1908**, 18-30; b) C. W. Capp, A. H. Cook, J. D. Downer, I. Heilbron, *J. Chem. Soc.* **1948**, 1340-1345.

7. Synthesis and Investigation of Alkyl Nitramines and *N,N*-Dinitramines

Abstract: Several alkylated nitramines and *N*,*N*-dinitramines were prepared. Whereas the synthesis of primary *N*,*N*-dinitramines by nitration of the corresponding nitramines proved to be a suitable method, we were not able to prepare secondary or tertiary *N*,*N*-dinitramines. The preparation of *N*,*N*-dinitramines by substitution reactions of alkyl halides and silver dinitramide according to Russian publications, was found to be inefficient. The nitramines and *N*,*N*-dinitramines were characterized by IR and NMR spectroscopy, mass spectrometry and elemental analysis. The energetic properties were determined by bomb calorimetric measurements, along with calculations using the EXPLO5 software.

7.1 Introduction

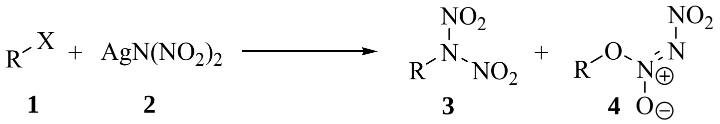
Alkylated nitramines and *N*,*N*-dinitramines are a topic with an apparently exceptional position within this dissertation. However, the synthesis of alkylated *N*,*N*-dinitramines produced important knowledge for the preparation of the energetic materials reported in the previous paragraphs.

Nitramines[1] and *N*,*N*-dinitramines[2] have been known for a long time. Several synthesis, either by substitution reactions of alkyl halides and silver dinitramide[3] or by the nitration of primary nitramines,[2a,4] were reported. Whereas the methyl *N*,*N*-dinitramine is characterized thoroughly,[5] derivatives bearing longer alkyl chains were neglected or the analytical data, which can be found, is incomplete or incorrect. As a consequence, we decided to complete this topic, regarding the analytical data (IR and NMR spectroscopy, mass spectrometry and elemental analysis, along with the determination of the energetic properties).

In order to prove common methods for the preparation of *N*,*N*-dinitramines, the two most convenient syntheses were carried out, the substitution reaction using silver dinitramide and alkyl halides and the nitration of primary nitramines. Due to the fact, that methyl *N*,*N*-dinitramine is well investigated and completely characterized,[5] we excluded this compound from our experiments.

7.2 Synthesis of the *N,N*-Dinitramines by Substitution Reactions of Alkyl Halides and Silver Dinitramide

The synthesis of *N,N*-dinitramines by alkylation reactions of silver dinitramide[3] and mercury(II) dinitramide[6] was published by Luk'yanov (*Scheme 1*).



X = halide; R = alkyl

Scheme 1. Synthesis of the *N,N*-dinitramines **3**.

The *N*,*N*-dinitramines (**3**) were only analysed by IR spectroscopy and the existence of **3** was proved by decomposition reactions. Due to the thin characterization, we decided to perform the same synthesis, but we were not able to isolate any alkylated *N*,*N*-dinitramine.

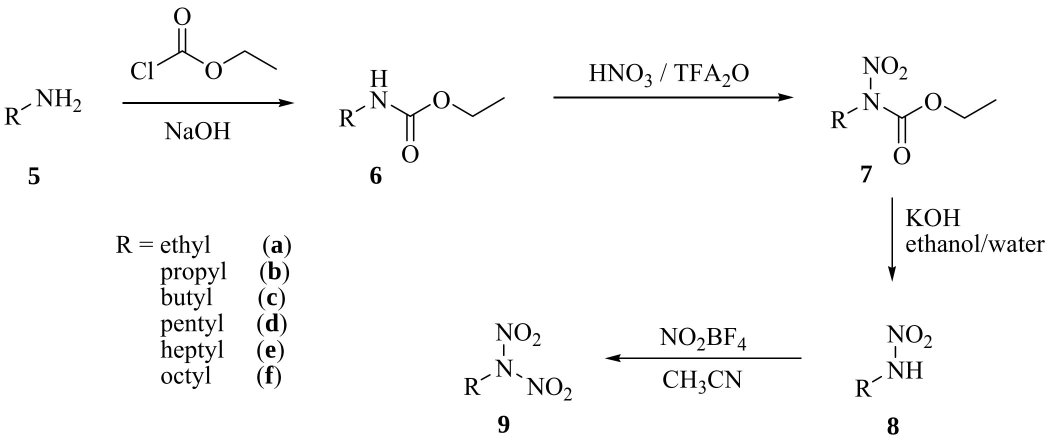
To date, three different silver dinitramide salts are known, the pyridine[7] and acetonitrile adduct and the solvent-free silver dinitramide.[8] Carrying out the reactions using the pyridine adduct, always traces of pyridine were detected, even after using a purification by column chromatography. The disadvantage of the acetonitrile adduct is that the compound can only be obtained with a varying amount of acetonitrile. But regarding the fact, that an excess of the alkyl halide was used, the stoichiometric application of the silver salt was not necessary. The solvent free silver dinitramide was not used, because the reactions were carried out in acetonitrile, leading instantly to the formation of acetonitrile complexes.

In order to investigate the substitution reactions, several alkyl chlorides, bromides and iodides were used. The reactivity of the chlorides was the lowest, whereas the iodides with tertiary alkyl structures (stabilization of the carbocation) proved to possess the highest reactivity (extreme exothermic reaction of *tert*-butyl iodide!). The time of reaction was varied between 12 h and several days. The alkylated *N*,*N*-dinitramine should be recovered by extraction with ethyl ether after water was added to the reaction mixture, but we could not isolate any product. As a consequence we removed the acetonitrile after the reaction was finished and tried to use column chromatography for the purification. As solvent, ethyl ether and ethyl acetate was used in the beginning and the polarity was rised by a slow change to an ethyl acetate/methanol mixture. Only one fraction contained a product in analysable amounts, but the product proved to be a mixture of an acetonitrile adduct of silver *N*,*N*-dinitramide and a second compound. The analysis of the mixture by mass spectrometry always gave the [M-HNO_2] peak (or [M-CH_3-NO_2] peak in case of *tert*-butyl iodide as starting material) of the desired alkylated *N*,*N*-dinitramine. A comparison of the ^{14}N NMR spectrum with the spectra obtained from the alkylated *N*,*N*-dinitramines of *paragraph 7.3* verified, that the mixture did not contain any alkylated *N*,*N*-dinitramine. This finding lead to the assumption, that the alkylated *N*,*N*-dinitramine was formed, but decomposed during the purification by column chromatography. The usage of the working up reported by Luk'yanov lead to a mixture of several compounds and proved not suitable for the synthesis of *N*,*N*-dinitramines. A distillation of the *N*,*N*-dinitramines was tried but then neglected, due to the low decomposition temperature of the compounds.

7.3 Synthesis of *N*,*N*-Dinitramines by Nitration of Nitramines

7.3.1 Synthesis of the *N*,*N*-Dinitramines

The synthesis of the *N,N*-dinitramines (**9**) was carried out, according to a patent by nitration of primary nitramines.[4] The nitramines (**8**) were prepared by the nitration of carbamates (**6**) with a subsequent deprotection of the nitramine (*Scheme 2*).[9]

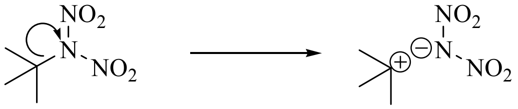


Scheme 2. Synthesis of the *N,N*-dinitramines **9**.

In case of the deprotection of the nitramine **7**, several bases were tried (cyclohexyl amine, sodium hydroxide in water, potassium hydroxide…), but only a concentrated solution of potassium hydroxide in a water-ethanol mixture proved to be suitable for the deprotection of nitramines with short and longer alkyl groups. Whereas the common deprotection using cyclohexyl amine in ethyl ether[9] led to impurities of dicyclohexyl urea, the deprotection with potassium hydroxide yielded pure nitramine.

The conditions of the nitration of **8** to the *N,N*-dinitramine **9** were varied to obtain higher yields than 40 % to 50 %. But in order to purify **9**, the etheric solution had to be washed with 2N aqueous sodium hydroxide solution (removing of **8** and HBF_4). The *N,N*-dinitramines **9** are not stable under alkaline conditions, because they tend to eliminate HNO_2, resulting in the low yields of **9**. Carrying out the experiments, it was for us not possible to isolate derivatives of **9** with longer alkyl chains than pentane. Despite the detection of **9e** and **9f** by NMR spectroscopy, a separation from the corresponding nitramines still present in the reaction mixture could not be achieved. The corresponding sodium salts of **8e** and **8f** were - in contrast to the **8a** to **d** - better soluble in ethyl ether than in the aqueous layer. Other ways of separation (distillation, column chromatography) were neglected, due to the instability **9**.

Besides the primary *N,N*-dinitramines, the preparation of secondary and tertiary *N,N*-dinitramines was investigated. The same reaction conditions as reported for the primary nitramines were used on secondary and tertiary nitramines. But in contrast to the corresponding primary *N,N*-dinitramines, only decomposition products could be detected. The stabilization of the negative charge of the *N,N*-dinitramide anion renders this compound into a good releasing group. As a result, the elimination reaction of the *N,N*-dinitramide anion is eased if the resulting carbocation is stabilized, especially in case of the allyl, benzyl and tert-butyl nitramine. Nevertheless, this theory could not be proved by analytical data and should only be seen as an attempt for an explanation (*Scheme 3*).



Scheme 3. Elimination of the N,N-dinitramide anion.

7.3.2 Analytical Data of 8 and 9

Whereas the analysis of **8** could be performed without any problems, the instability of **9** prevents these compounds to yield proper data, regarding elemental analysis and mass spectrometry. Especially in case of the mass spectrometry, only the [M-HNO_2] peak instead of the molecule peak could be detected. This finding points the tendency of **9** to eliminate HNO_2 to form the corresponding nitrimines out.

Another problem of **9** proved to be the N-N coupling of the amine and the nitro groups within the ^{15}N NMR spectrum. The ^{15}N NMR spectrum of methyl nitramine was reported by Gouesnard (^{15}N NMR: δ = -91.4 ($N(NO_2)_2$)),[5] but in case of longer alkyl chains, we were not able to obtain any signal of the amine nitrogen, due to a heavy splitting of the signal. Therefore, we could only use the ^{14}N NMR spectrum for the assignment of the amine nitrogen (unreliable broad signal).

The vibrations of the IR spectrum of the **9a** and **9c** were assigned by using calculated values. The structure and vibrational frequencies of **9a** and **9c** were computed at the B3LYP level of theory using a correlation consistent polarized double zeta basis (cc-pVDZ).[10] Selected values are given in *Table 1*.

Table 1. Comparison between selected vibrations of **9a** and **9c** with the calculated values using DFT B3LYP/ cc-pVDZ (calculated intensities in parentheses in km mol^{-1}).

9a		**9c**		
$\nu_{calc.}$[cm^{-1}]	ν_{exp} [cm^{-1}]	ν_{calc}[cm^{-1}]	ν_{exp} [cm^{-1}]	vibrations
854 (175)	851	844 (221)	855	ν(N-N)
863 (54)	868	867 (46)	877	δ(ONO)
1296 (279)	1310	1301 (251)	1307	$\nu(NO_2)_{sym}$
1706 (169)	1595	1705 (165)	1609	$\nu(NO_2)_{asym}$
1755 (366)	1638	1755 (379)	1635	$\nu(NO_2)_{asym}$

7.3.3 Energetic Properties of 8 and 9

In order to investigate the suitability of **8** and **9** as energetic materials, the thermal (DSC-data) and physical stability (BAM standards[11,12]) was determined, along with their energetic properties.

The impact sensitivity of the **8** was >40 J, whereas **9** proved to be very sensitive towards impact (>1 J). The sensitivity towards friction was found to be >48 N, in case of **8** and **9**.

The thermal stability of the **8** could not be determined in all cases, because the low boiling point (**8d**: 94 °C) complicates the DSC-measurements. In order to obtain the decomposition point, **8** was sealed in an aluminum container without hole. But only in case of **8a** a decomposition point could be detected. In the other cases, the seal was broken open and the nitramine could escape. The decomposition energy of **8a** was high enough, that the decomposition of the left compound (the evaporation of the nitramine through the untight container takes some time) could be detected. For the other nitramines, no data could be obtained, except for the boiling point in case of **8d**. Nevertheless, the influence of the different alkyl moieties should not lead to big differences of the decomposition points (see **9**). As a consequence, the decomposition points of **8** can be taken as 170 °C, in analogy to the ethyl derivative.

The energetic properties were determined by bomb calorimetric measurements along with calculations using the EXPLO5 software.[13] One problem of bomb calorimetric measurements of high explosive liquids with a low boiling point is the explosion within the bomb instead of a proper burning. Therefore, the usage of benzoic acid pellets (*paragraph 8*) with a cavity filled with the liquid was tested and proved to be improper. As a consequence, the liquid was absorbed by cellulose to obtain a dilution of the explosive liquid. Carrying out the experiments, only *N,N*-dinitramines with an alkyl chain longer than butyl proved to yield reliable values. The values obtained by the bomb calorimetric measurements were checked by calculations (CBS-4M[14]). The comparison between the experimental data of **9a** with the calculated values revealed a big difference, whereas the values obtained for **9c** proved to be in the same range (calc.: 41 kJ kg^{-1}, experiment: -30 kJ kg^{-1}). The results of the bomb calorimetric measurements of **9c** and **9d** were used for the calculations of the energetic properties by the EXPLO5 software.[13]

The energetic properties of **9** are given in *Table 2*, the properties of the **8** in *Table 3*.

Table 2. Energetic properties of **9.**

	9a (calc)	**9c** (calc)	**9c** (exp)	**9d** (exp)
formula	$C_2H_5N_3O_4$	$C_2H_5N_3O_4$	$C_4H_9N_3O_4$	$C_5H_{11}N_3O_4$
molecular mass (g mol^{-1})	132.0	163.1	163.1	177.1
density (g cm^{-3})[a]	1.20	1.15	1.15	1.15
point of decomposition (°C)	80	80	80	82
impact sensitivity (J)	>1	>1	>1	>1
friction sensitivity (N)	>48	>48	>48	>48
$-\Delta U_{\mathrm{comb.}}$ (cal g^{-1})[b]	-	-	4214	4404
ΔH_{comb} (kJ mol^{-1})[c]	-	-	15	-270
$\Delta_f H_m$ (kJ mol^{-1})[d]	-	-	-5	-292
Values calculated by EXPLO5 V5.02				
$-\Delta_E U_m°$ (kJ kg^{-1})[e]	6567	5729	5567	3920
T_E (K)[f]	4656	3581	3553	2577
$p_{C\text{-}J}$ (kbar)[g]	157	111	118	83
D(m s^{-1})[h]	7009	6148	6285	5504
Gas vol. (L kg^{-1})[i]	851	838	847	816

[a] determined experimentally; [b] experimental (constant volume) combustion energy; [c] experimental molar enthalpy of combustion; [d] molar enthalpy of formation; [e] energy of explosion; [f] explosion temperature; [g] detonation pressure; [h] detonation velocity; [i] assuming only gaseous products; [k] obtained from the database of EXPLO5 (V5.02).

Table 3. Energetic properties of **8.**

	8a	**8b**	**8c**	**8d**	**8f**
formula	$C_2H_6N_2O_2$	$C_3H_8N_2O_2$	$C_4H_{10}N_2O_2$	$C_5H_{12}N_2O_2$	$C_8H_{18}N_2O_2$
molecular mass (g mol^{-1})	90.1	104.1	118.1	132.1	174.1
density (g cm^{-3})[a]	1.1	1.15	1.15	1.1	1.1
point of decomposition (°C)	170	-	-	>95 °C	-
impact sensitivity (J)	>40	>40	>40	>40	>40
friction sensitivity (N)	>48	>48	>48	>48	>48
$-\Delta U_{\text{comb.}}$ (cal g^{-1})[b]	4111	4844	5415	5617	7539
$-\Delta H_{\text{comb}}$ (kJ mol^{-1})[c]	92	212	281	539	595
$-\Delta_f H_m$ (kJ mol^{-1})[d]	105	227	298	554	622
Values calculated by EXPLO5 V5.02					
$-\Delta_E U_m°$ (kJ kg^{-1})[e]	4417	3077	2092	535	636
T_E (K)[f]	2829	2057	1569	775	812
$p_{C\text{-}J}$ (kbar)[g]	105	90	76	35	43
D(m s^{-1})[h]	6162	5827	5492	4058	4501
Gas vol. (L kg^{-1})[i]	894	864	850	844	832

[a] determined experimentally; [b] experimental (constant volume) combustion energy; [c] experimental molar enthalpy of combustion; [d] molar enthalpy of formation; [e] energy of explosion; [f] explosion temperature; [g] detonation pressure; [h] detonation velocity; [i] assuming only gaseous products; [k] obtained from the database of EXPLO5 (V5.02).

The comparison of the energetic properties of **9** reveals their high explosive characteristics. Compound **9a** possesses even a higher value of $-\Delta_E U_m$ compared to RDX ($-\Delta_E U_m$ of **9a**: 6567 kJ kg^{-1}; of RDX: 6052 kJ kg^{-1} (*paragraph 2.3.1*)). The elongation of the alkyl moiety in case of **9a** compared to **9c** by two CH_2 groups leads to a drop of $-\Delta_E U_m$ of 800 kJ kg^{-1} and in case of **9c** to **d** (only one CH_2 group) of 1800 kJ kg^{-1}. The detonation velocities of the **9** are slower than that of RDX, because of the low density of the liquids. But despite their excellent properties as energetic materials, their low thermal stability (T_{dec} = 80 °C) along with their high sensitivity towards impact (>1 J) prevents these compounds from any application.

The nitramines **8** possess a sufficient stability towards physical stimuli. The comparison of the energetic properties proves these compounds to be less energetic than TNT ($-\Delta_E U_m$ of **8a**: 4417 kJ kg^{-1}; of TNT: 5099 kJ kg^{-1}). The advantage of the nitramines compared to TNT is their low temperature of explosion (in case of the ethyl derivative by 1000 K lower than that of TNT). The comparison of **8d** and **8f** gives the impression, that the energetic properties of the **8f** are better than the **8d**. This finding can be explained by the extreme low energetic properties of these compounds, leading to similar results using the EXPLO5 software. The values of the **8f** should be neglected.

7.4 Conclusions

Several primary alkyl *N*,*N*-dinitramines and nitramines were synthesized and characterized by vibrational (IR) and NMR spectroscopy. The energetic properties were investigated by calculations along with experimental data. Whereas the synthesis of the alkylated *N*,*N*-dinitramines by substitution reactions of silver dinitramide and alkyl halides proved not to be efficient, the nitration of primary nitramines with nitronium tetrafluoroborate gave the *N*,*N*-dinitramines in moderate yields. The *N*,*N*-dinitramines are high to moderate explosives, but the low thermal and physical stability prevents them from being ever used. The corresponding nitramines possess moderate to low energetic properties, along with sufficiently high thermal and physical stabilities.

7.5 Experimental Section

CAUTION! Nitramines and *N,N*-dinitramines are highly energetic compounds with sensitivity towards heat and impact. Although we had no problems in synthesis, proper protective measures (safety glasses, face shield, leather coat, earthened equipment and shoes, Kevlar® gloves and ear plugs) should be used when undertaking work involving these compounds.

7.5.1 General Synthesis of the Nitramines 8

The amine (320 mmol) was suspended in concentrated sodium hydroxide solution (8 M) and ethyl chloroformate (34.7 g, 320 mmol) was added dropwise at 0 °C. After stirring for 10 min, the precipitate was dissolved in water and extracted with methylene chloride. The combined organic layers were washed two times with water and dried over sodium sulfate. The solvent was removed under reduced pressure.

The protected amine (81 mmol) was added dropwise at 0 °C to a solution of trifluoroacetic anhydride (15 mL) and fuming nitric acid (6 mL). After stirring for 10 min the reaction mixture was decanted on an ice-water mixture and stirred for additional 30 min. The aqueous layer was extracted with methylene chloride. The combined organic layers were dried over sodium sulfate and the solvent was removed under reduced pressure. The nitramine was deprotected by using a solution of potassium hydroxide in a water/ethanol mixture (30 mL/180 mL).

7.5.2 Ethylnitramine 8a

yield: 72 %.

dec.: 170 °C

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3593 (m), 3538 (m), 3289 (vs), 3137 (s, sh), 2986 (s), 2944 (s), 2904 (m), 2886 (m), 2490 (w), 1574 (vs), 1449 (vs), 1396 (vs), 1375 (vs), 1320 (vs), 1159 (s), 1113 (s), 1080 (m), 993 (w), 923 (w), 909 (w), 802 (m), 774 (m), 752 (w), 716 (w), 592 (m), 578 (m).

^{1}H NMR ($CDCl_3$): $\delta = 1.18$ (t, 3H, $^3J = 6.4$ Hz, C*H*$_3$), 3.56-3.54 (m, 2H, C*H*$_2$), 9.41 (s, 1H, N*H*).

^{13}C NMR ($CDCl_3$): $\delta = 11.9$ (*C*H$_3$), 41.3 (*C*H$_2$).

^{14}N NMR ($CDCl_3$): -28 (s, N*N*O$_2$), -214 (s, br *N*NO$_2$).

m/z (DEI+) 90 [M] (9), 85 (10), 83 (15), 75 (100), 59 (7), 46 (29), 43 (35), 42 (28), 30 (25), 29 (21), 27 (12).

elemental analysis: calcd (%) for $C_2H_6N_2O_2$: C 26.67, H 6.71, N 31.10; found: C 26.36, H 6.22, N 30.72.

7.5.3 Propylnitramine 8b

yield: 54 %.

dec.: - .

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3607 (w), 3528 (w), 3288 (s), 3144 (m), 2970 (vs), 2941 (s), 2882 (s), 1577 (vs), 1446 (vs), 1399 (vs), 1331 (vs), 1257 (s), 1154 (m), 1114 (m), 1087 (m), 1038 (w), 979 (w), 893 (w), 870 (w), 774 (m), 633 (w), 615 (w), 596 (m), 579 (m).

^{1}H NMR ($CDCl_3$): $\delta = 0.92$ (dt, 3H, $^3J = 7.3$ Hz, $^4J = 2.0$ Hz, C*H*$_3$), 1.59 (sext, 2H, ^3J = 7.3 Hz, CH$_2$C*H*$_2$CH$_3$), 3.50-3.47 (m, 2H, C*H*$_2$NHNO$_2$), 9.34 (s, 1 H, N*H*).

^{13}C NMR ($CDCl_3$): $\delta = 11.1$ (*C*H$_3$), 20.3 (*C*H$_2$CH$_3$), 48.0 (*C*H$_2$N).

^{14}N NMR ($CDCl_3$):): $\delta = -28$ (s, *N*NO$_2$), -214 (s, br N*N*O$_2$).

m/z (DEI+) 104 [M] (2), 75 (100), 57 (11), 46 (12), 30 (15), 29 (15), 28 (13), 27 (8).

elemental analysis: calcd (%) for $C_3H_8N_2O_2$: C 34.61, H 7.75, N 26.91; found: C 33.80, H 7.53, N 26.05.

7.5.4 Butylnitramine 8c

yield: 76 %.

dec.: - .

IR (KBr, cm^{-1}): ṽ = 3616 (w), 3538 (w), 3290 (vs), 3141 (s), 2963 (vs), 2938 (vs), 2876 (vs), 1577 (vs), 1449 (vs), 1400 (vs), 1324 (vs), 1267 (s), 1232 (s), 1153 (m), 1115 (s), 1023 (w), 996 (w), 917 (w), 804 (w), 775 (m), 743 (m), 618 (m), 580 (m), 501 (w).

^{1}H NMR ($CDCl_3$): δ = 0.93-0.89 (m, 3H, CH_3), 1.40-1.30 (m, 2H, CH_2CH_3), 1.60-1.53 (m, 2H, $CH_2CH_2CH_3$), 3.54 (q, 2H, ^3J = 6.8 Hz, NCH_2), 9.09 (s, N*H*).

^{13}C NMR ($CDCl_3$): δ = 13.6 (CH_3), 19.9 (CH_2CH_3), 28.9 (NCH_2CH_2), 46.1 (NCH_2).

^{14}N NMR ($CDCl_3$): δ = -28 (NNO_2), -214 (br, NNO_2).

m/z (DEI+) 119 [M+H] (1), 75 (100), 72 (12), 56 (6), 55 (5), 46 (11), 43 (26), 41 (25), 39 (7), 30 (39), 29 (8), 28 (15), 27 (15).

elemental analysis: calcd (%) for $C_4H_{10}N_2O_2$: C 40.67, H 8.53, N 23.71; found: C 40.23, H 8.41, N 23.22.

7.5.5 Pentylnitramine 8d

yield: 83 %.

b.p.: 94 °C; dec.: - .

IR (KBr, cm^{-1}): ṽ = 3603 (w), 3547 (w), 3288 (s), 3141 (s), 2960 (vs), 2935 (vs), 2874 (s), 2737 (w), 2685 (w), 2511 (w), 1757 (w), 1578 (vs), 1449 (vs), 1400 (vs), 1329 (vs), 1298 (vs), 1249 (s), 1216 (s), 1153 (m), 1106 (m), 1028 (w), 972 (w), 847 (w), 775 (m), 733 (m), 618 (m), 580 (m).

^{1}**H NMR** ($CDCl_3$): δ = 0.86-0.83 (m, 3H, CH_3), 1.29-1.25 (m, 4H, $CH_2CH_2CH_3$), 1.56 (qui, 2H, ^3J = 7.2 Hz, NCH_2CH_2), 3.51-3.48 (m, 2H, NCH_2), 9.38 (s; N*H*).

^{13}**C NMR** ($CDCl_3$): δ = 13.8 (CH_3), 22.2 (CH_2CH_3), 26.5 ($NCH_2CH_2CH_2$), 28.8 (NCH_2CH_2), 46.3 (NCH_2).

^{14}**N NMR** ($CDCl_3$): δ = -28 (N*N*O_2), -217 (br, *N*NO_2).

m/z (DEI+) 133 [M+H] (1), 86 (7), 85 (7), 83 (10), 75 (100), 70 (9), 69 (38), 59 (5), 57 (15), 56 (8), 55 (9), 46 (14), 43 (13), 42 (9), 41 (51), 39 (10), 30 (87), 29 (42), 28 (20), 27 (14).

elemental analysis: calcd (%) for $C_5H_{12}N_2O_2$: C 45.44, H 9.15, N 21.20; found: C 44.68, H 8.92, N 20.70.

7.5.6 Heptylnitramine 8e

yield: 69 %.

dec.: - .

IR (KBr, cm^{-1}): ṽ = 3517 (w), 3288 (s), 3142 (m), 2956 (vs), 2929 (vs), 2858 (vs), 1696 (w), 1624 (m), 1577 (vs), 1454 (vs), 1399 (vs), 1327 (vs), 1224 (m), 1196 (m), 1153 (w), 1108 (m), 833 (w), 775 (m), 751 (w), 726 (m), 620 (w), 580 (w).

^{1}**H NMR** ($CDCl_3$): δ = 0.85-0.82 (m, 3H, CH_3), 1.29-1.23 (m, 8H, 4 x CH_2), 1.61-1.54 (m, 2H, CH_2CH_2N), 3.53-3.50 (m, 2H, CH_2N), 9.23 (s, 1H, N*H*).

^{13}**C NMR** ($CDCl_3$): δ = 14.0 (CH_3), 22.6 (CH_2), 26.7 (CH_2), 26.8 (CH_2), 28.8 (CH_2), 31.6 (CH_2), 46.4 (CH_2N),

^{14}N NMR (CDCl$_3$): δ = -28 (N*N*O$_2$), -215 (br *N*NO$_2$).

m/z (DEI+) 161 [M+H] (6), 114 (46), 102 (8), 97 (16), 85 (8), 84 (12), 83 (12), 75 (100), 70 (40), 69 (25), 59 (8), 57 (18), 56 (27), 55 (100), 46 (9), 44 (5), 43 (64), 42 (8), 41 (32), 39 (6), 30 (34), 29 (7).

elemental analysis: calcd (%) for $C_7H_{16}N_2O_3$: C 52.48, H 10.07, N 17.48; found: C 52.27, H 9.65, N 16.84.

7.5.7 Octylnitramine 8f

yield: 79 %.

dec.: - .

IR (KBr, cm^{-1}): ṽ = 3609 (w), 3522 (w), 3289 (vs), 3146 (s), 2955 (vs), 2929 (vs), 2857 (vs), 2731 (w), 1578 (vs), 1454 (vs), 1399 (vs),1323 (vs), 1259 (s), 1216 (m), 1190 (m), 1152 (w), 1108 (m), 903 (w), 864 (w), 775 (m), 744 (m), 725 (m), 620 (m), 580 (m).

^{1}H NMR (CDCl$_3$): δ = 0.85-0.82 (m, 3H, C*H$_3$*), 1.30-1.23 (m, 10H, 5 x C*H$_2$*), 1.57 (qui, 2H, ^3J = 6.8 Hz, C*H$_2$*CH$_2$N(H)NO$_2$), 3.55-3.50 (m, 2H, C*H$_2$*N(H)NO$_2$), 9.16 (s, 1 H, N*H*).

^{13}C NMR (CDCl$_3$): δ = 14.1 (*C*H$_3$), 22.6 (*C*H$_2$CH$_3$), 26.7 (*C*H$_2$CH$_2$CH$_3$), 26.8 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 29.1 (*C*H$_2$*C*H$_2$CH$_2$CH$_2$N(H)NO$_2$), 31.8 (*C*H$_2$CH$_2$N(H)NO$_2$), 46.4 (*C*H$_2$N(H)NO$_2$).

^{14}N NMR (CDCl$_3$): δ = -28 (N*N*O$_2$), -219 (br, *N*NO$_2$).

^{15}N NMR (CDCl$_3$): δ = -28 (t, N*N*O$_2$, J = 2.4 Hz), -208 (dd, *N*NO$_2$, J = 96.6 Hz, J = 2.4 Hz)

m/z (DEI+) 175 [M+H] (1), 128 (37), 84 (16), 83 (8), 75 (56), 70 (48), 69 (96), 59 (6), 57 (44), 56 (24), 55 (64), 46 (11), 44 (7), 43 (63), 41 (57), 39 (11), 30 (100), 29 (26), 28 (15), 27 (13).

elemental analysis: calcd (%) for $C_8H_{18}N_2O_2$: C 55.15, H 10.41, N 16.08; found: C 54.62, H 9.96, N 15.96.

7.5.8 General Synthesis of the *N,N*-Dinitramines 9

The nitramine (5 mmol) was dissolved in acetonitrile (5 mL). At 0 °C, nitronium tetrafluoroborate (858 mg, 6.5 mmol) was added slowly and the reaction mixture was stirred until the nitronium tetrafluoroborate was dissolved. The reaction mixture was poured on ice and stirred for 15 min and extracted two times with ethyl ether. The combined organic layers were washed three times with water and two times with 2N aqueous sodium hydroxide solution. After drying over sodium sulfate, the solvent was removed and the *N,N*-dinitramine obtained as slightly yellow oil.

7.5.9 *N,N*-Ethyl dinitramine 9a

yield: 44 %.

dec.: 80 °C.

IR (KBr, cm^{-1}): $\tilde{v}$ = 2992 (m), 2949 (m), 2884 (w), 2552 (w), 1638 (vs), 1595 (vs), 1456 (s), 1440 (s), 1388 (m), 1371 (m), 1310 (s), 1247 (vs), 1153 (m), 1111 (m), 1078 (m), 1047 (m), 964 (w), 868 (s), 851 (s), 805 (vs), 734 (w), 691 (w), 597 (w), 496 (w).

^{1}H NMR ($CDCl_3$): δ = 1.27 (t, 3H, ^3J = 6.9 Hz, CH_3), 4.13 (q, 2H, ^3J = 6.9 Hz, CH_2).

^{13}C NMR ($CDCl_3$): δ = 10.4 (CH_3), 50.2 (CH_2).

^{14}N NMR ($CDCl_3$): δ = -43 ($N(NO_2)_2$), -81 ($N(NO_2)_2$).

***m/z*:** was not possible, due to decomposition.

7.5.10 *N*,*N*-Propyl dinitramine 9b

yield: 40 %.

dec.: 82 °C.

IR (KBr, cm^{-1}): ṽ = 3394 (w), 2976 (s), 2943 (s), 2884 (s), 2550 (w), 1769 (w), 1639 (vs), 1608 (vs), 1463 (s), 1438 (s), 1390 (s), 1376 (s), 1330 (s), 1309 (vs), 1248 (vs), 1177 (w), 1157 (m), 1103 (w), 1060 (m), 1019 (w), 925 (s), 809 (vs), 828 (vs), 769 (s), 738 (w), 693 (w), 642 (w).

^{1}H NMR ($CDCl_3$): δ = 1.04 (t, 3H, ^3J = 7.3 Hz, CH_3), 1.71 (sext, 2H, ^3J = 7.3 Hz, CH_2CH$_3$), 4.07 (t, 2H, ^3J = 7.3 Hz, CH_2N(NO$_2$)$_2$).

^{13}C NMR ($CDCl_3$): δ = 10.9 (CH$_3$), 19.6 (CH$_2$CH$_3$), 56.4 (CH$_2$N(NO$_2$)$_2$).

^{14}N NMR ($CDCl_3$): δ = -38 (N(NO$_2$)$_2$), -80 (N(NO$_2$)$_2$).

m/z (DEI+): 149 [M] (38), 121 (8), 119 (9), 117 (16), 105 (8), 102 (9), 91 (8), 85 (24), 83 (37), 81 (8), 75.1 (39), 73 (10), 71 (20), 70 (16), 69.1 (14), 67 (9), 58 (8), 57 (100), 56 (11), 55 (26), 46 (18), 45 (8), 43 (33), 42 (11), 41 (36), 39 (8), 30 (16), 29 (42), 28 (8), 27 (14).

7.5.11 *N*,*N*-Butyl dinitramine 9c

yield: 41 %.

dec.: 80 °C.

IR (KBr, cm^{-1}): ṽ = 2967 (s), 2940 (s), 2879 (m), 1635 (vs), 1609 (vs), 1469 (m), 1437 (m), 1385 (m), 1358 (w), 1307 (s), 1248 (vs), 1148 (w), 1120 (w), 1069 (w), 954 (w), 855 (s), 803 (s), 766 (m), 693 (w), 638 (w), 500 (w).

^{1}H NMR ($CDCl_3$): δ = 0.94 (t, 3H, ^3J = 7.3 Hz, CH_3), 1.44 (sext, 2H, ^3J = 7.3 Hz, CH_2CH$_3$), 1.67-1.60 (m, 2H, NCH$_2$CH_2), 4.10 (t, 2H, ^3J = 7.3 Hz, NCH_2).

^{13}C NMR ($CDCl_3$): δ = 13.4 (CH_3), 19.4 (CH_2CH_3), 27.8 (NCH_2CH_2), 54.7 (NCH_2).

^{14}N NMR ($CDCl_3$): δ = -43 (NNO_2), -81 ($N(NO_2)_2$).

elemental analysis: calcd (%) for $C_4H_9N_3O_4$: C 29.45, H 5.56, N 25.76; found: C 29.70, H 5.47, N 24.07.

7.5.12 *N,N*-Pentyl dinitramine 9d

yield: 46 %.

dec.: 82 °C.

IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2962 (s), 2936 (s), 2876 (s), 1768 (w), 1637 (vs), 1609 (vs), 1468 (m), 1437 (m), 1381 (m), 1309 (s), 1280 (m), 1247 (vs), 1176 (w), 1151 (w), 1121 (w), 1054 (w), 1001 (w), 875 (m), 825 (s), 733 (w), 694 (w), 638 (w), 597 (w).

^{1}H NMR ($CDCl_3$): δ = 0.89 (t, 3H, ^3J = 7.1 Hz, CH_3), 1.41-1.31 (m, 4H, $CH_2CH_2CH_3$), 1.70-1.63 (m, 2H, CH_2CH_2N), 4.09 (t, 2H, ^3J = 7.3 Hz, CH_2N).

^{13}C NMR ($CDCl_3$): δ = 13.8 (CH_3), 22.1 (CH_2), 25.6 (CH_2), 28.4 (CH_2), 54.9 (CH_2N).

^{14}N NMR ($CDCl_3$): δ = -42 ($N(NO_2)_2$), -84 ($N(NO_2)_2$).

m/z (DCI+): 130 [M-NO_2] (100), 86 (8), 84 (6), 57 (16).

elemental analysis: calcd (%) for $C_5H_{11}N_3O_4$: C 33.90, H 6.26, N 23.72; found: C 36.55, H 6.57, N 19.73.

7.6 References

(1) a) J. Burdon, A. Ramirez, *Tetrahedron*, **1973**, *29*, 4195-4198; b) M. B. Gorichko, O. O. Grygorenko, I. V. Komarov, *Tetrahedron Lett.* **2002**, *43*, 9411-9412.

(2) a) Aerojet-General Corporation, *US Pat. US1126691*, **1968**; b) R. G. Gafurov, B. S. Fedorov, L. T. Eremenko, *U.S.S.R Pat. SU578306*, **1977**; c) J. C. Bottaro, P. E. Penwell, R. J. Schmitt, *Synth. Commun.* **1991**, *21*, 945-949.

(3) O. A. Luk'yanov, N. I. Shlykova, V. A. Tartakovsky, *Russ. Chem. Bull.* **1994**, *43*, 1680-1683.

(4) a) O. A. Luk'yanov, S. N. Shvedova, E. V. Shepelev, O. N. Varfolomeeva, N. N. Malkina, V. A. Tartakovsky, *Russ. Chem. Bull.* **1996**, *45*, 1497-1498; b) Aerojet-General Corporation, US Pat. US1126691, **1968**.

(5) J. Dorie, J.-P. Gouesnard, *Journal de Chimie Physique et de Physicochimie Biologique*, **1985**, *82*, 369-372.

(6) O. A. Luk'yanov, O. V. Anikin, V. A. Tartakovsky, *Russ. Chem. Bull.* **1996**, *45*, 433-440.

(7) H.-G. Ang, W. Fraenk, K. Karaghiosoff, T. M. Klapötke, P. Mayer, H. Nöth, J. Sprott, M. Warchhold, *Z. Anorg. Allg. Chem.* **2002**, *628*, 2894-2900.

(8) T. M. Klapötke, B. Krumm, M. Scherr, *Dalton Trans.* **2008**, *43*, 5876-5878.

(9) H. M. Curry, J. P. Mason, *J. Am. Chem. Soc.* **1951**, *73*, 5043-5046.

(10) M.J. Frisch et al. Gaussian Inc., *Gaussian 03, Revision B04*, Wallingford, CT, **2004**.

(11) a) M. Suceska, *Test Methods for Explosives*, Springer, New York, **1995**, p. 21 (impact), p. 27 (friction); b) http://www.bam.de/.

(12) 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 a.>80 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.

(13) a) M. Suceska, *Proc. of 30th Int. Annual Conference of ICT, Karlsruhe, Germany*, ed. Fraunhofer-Institut für chemische Technologie, DWS Werbeagentur und Verlag GmbH, Karlsruhe, **1999**, 50/1; b) EXPLO5.V2, Computer program for calculation of detonation parameters, P, M. Suceska, *Proc. of 32nd Int. Annual Conference of ICT, Karlsruhe, Germany,* ed. Fraunhofer-Institut für chemische Technologie, DWS Werbeagentur und Verlag GmbH, Karlsruhe, **2001**, pp. 110/1.

(14) a) J. W. Ochterski, G. A. Petersson, and J. A. Montgomery Jr., *J. Chem. Phys.* **1996**, *104*, 2598; b) J. A. Montgomery Jr., M. J. Frisch, J. W. Ochterski, and G. A. Petersson, *J. Chem. Phys.* **2000**, *112*, 6532.

8. Material and Methods

8.1 Chemicals

All chemical reagents and solvents of analytical grade were obtained from Sigma–Aldrich, Acros Organics, ABCR or as found in the laboratory and used without further purification.

Purification by column chromatography was performed using Merck silica gel 60 (Ø 40-60 μm). The solvent is given in the experimental section.

Carrying out the reactions reported in this dissertation, we discovered that inert gas like dry nitrogen or argon is not mandatory for a successful performance of the synthesis.

8.2 General Methods

NMR-spectroscopy: The NMR-spectra were recorded using a *JEOL Eclipse 400* or *JEOL Eclipse 270* instrument. ^{1}H, ^{13}C and ^{15}N NMR spectra were measured in [*d6*]-DMSO, $CDCl_3$, DCl/D_2O or D_2O, if not stated different in the experimental section. The chemical shifts are given relative to tetramethylsilane (^{1}H, ^{13}C) or nitromethane (^{15}N) as external standards. Coupling constants (J) are given in hertz (Hz).

IR-spectroscopy: Infrared (IR) spectra were recorded using a *Perkin–Elmer Spectrum One FT-IR* instrument and KBr pellets or NaCl-plates at room temperature. The intensities are reported in parentheses, distinguishing between very weak (vw), weak (w), medium (m), strong (s) and very strong (vs).

Raman-spectroscopy: Raman spectra were recorded using *Perkin–Elmer Spectrum 2000R NIR FT-Raman* instrument equipped with a Nd:YAG laser (1064 nm). The intensities are reported in percentages relative to the most intense peak and are given in parentheses.

Mass spectrometry: Mass spectrometry was performed on a JEOL MS station JMS-700. The different ionization methods (EI, DEI, DCI and FAB^+) are indicated in the experimental section.

Elemental analysis: Elemental analyses were performed with a *Netsch Simultaneous Thermal Analyzer STA 429*.

DSC-measurements: DSC-measurements were performed by a *Linseis DSC PT-10* instrument at a heating rate of 5 °C min^{-1} in closed aluminum containers with a hole (1 µm) on the top for gas release with a nitrogen flow of 5 mL min^{-1}. The reference sample was a closed aluminum container. If a volatile compound was measured, a closed aluminum container without hole on the top was used.

Melting point: Melting points were either determined using the DSC-data or by using a *Büchi Melting point B-540*.

Density: The density of the compounds was either obtained from the crystal structure or was measured by Quantachrome instruments *Ultrapyc 1200e* using the amorphous compound.

Bomb calorimetric measurements: Bomb Calorimetry was undertaken using a *Parr 1356 Bomb calorimeter* [static jacket] with a *Parr 1108CL* oxygen bomb. For the analysis of solid compounds, 100 mg to 150 mg of the energetic substance was mixed with 950 mg to 1100 mg of benzoic acid. The mixture was converted into a pellet which was used for the measurement. Energetic liquids (100 mg to 150 mg) were absorbed by cellulose.

Crystal structures: The crystallographic data were collected using an *Oxford Xcalibur3 diffractometer* with a Spellman generator (voltage 50 kV, current 40 mA) and a Kappa CCD area detector with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The crystal structures were solved using direct methods (SHELXS-97)[1] and refined using SHELXL-

97.[2] All non-hydrogen atoms were refined anisotropically. Ortep plots showing thermal ellipsoids with 50% probability for the non-hydrogen atoms.

Molecular weights: The average molecular weights of the polymers were determined by external institutions. The molecular weights were measured by Fa. PSS, Mainz using a TSP P1000 HPLC pump with 1.0 mL min^{-1} flow, a TSP AS3000 injection system with 50 µL volume of injection and a Showdex Differentialrefractometer RI 71 as detector. The analysis was done using PSS-WinGPC Unity Version 7.2. As column were used PSS-GRAM, 10µm 30 Å, ID 8.0 mm x 50 mm, PSS-GRAM, 10µm 30 Å, ID 8.0 mm x 300 mm, PSS-GRAM, 10µm 100 Å, ID 8.0 mm x 300 mm and -GRAM, 10µm 3000 Å, ID 8.0 mm x 300 mm. As eluent was used DMF containing 0.01 M $LiNO_3$ or DMSO containing 5 g L^{-1}. The calibration was done using a polystyrene standard.

Impact and friction sensitivity: The impact and friction sensitivity was determined using a BAM drophammer and a BAM friction tester.[3] The sensitivities of the compounds are indicated according to the UN Recommendations on the Transport of Dangerous Goods (+): impact: insensitive > 40 J, less sensitive > 35 J, sensitive > 4 J, very sensitive < 4 J; friction: insensitive > 360 N, less sensitive = 360 N, sensitive < 360 N > 80 N, very sensitive < 80 N, extreme sensitive < 10 N.

8.3 Calculations

Energetic Calculations: The energetic properties of the compounds were determined by bomb calorimetric measurements and the density ρ along with calculations using the EXPLO5 software.[4]

Calculations of the enthalpy of formation: The calculations were performed by Prof. Dr. Thomas M. Klapötke. The enthalpy of formation was calculated using CBS-4M.[5]

Calculations of IR spectra: The calculations of vibrational spectra were obtained by Prof. Dr. Thomas M. Klapötke using DFT BLYP/6-31G* or DFT B3LYP/ cc-pVDZ after optimizing the geometry using the Gaussian 03 software.[6]

8.4 References

(1) G G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**.

(2) G. M. Sheldrick, SHELXS-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**.

(3) a) M. Suceska, *Test Methods for Explosives*, Springer, New York, **1995**, p. 21 (impact), p. 27 (friction); b) http://www.bam.de/.

(4) a) M. Suceska, *Proc. of 30th Int. Annual Conference of ICT, Karlsruhe, Germany*, ed. Fraunhofer-Institut für chemische Technologie, DWS Werbeagentur und Verlag GmbH, Karlsruhe, 1999, 50/1; b) EXPLO5.V2, Computer program for calculation of detonation parameters, P, M. Suceska, *Proc. of 32nd Int. Annual Conference of ICT, Karlsruhe, Germany*, ed. Fraunhofer-Institut für chemische Technologie, DWS Werbeagentur und Verlag GmbH, Karlsruhe, 2001, pp. 110/1.

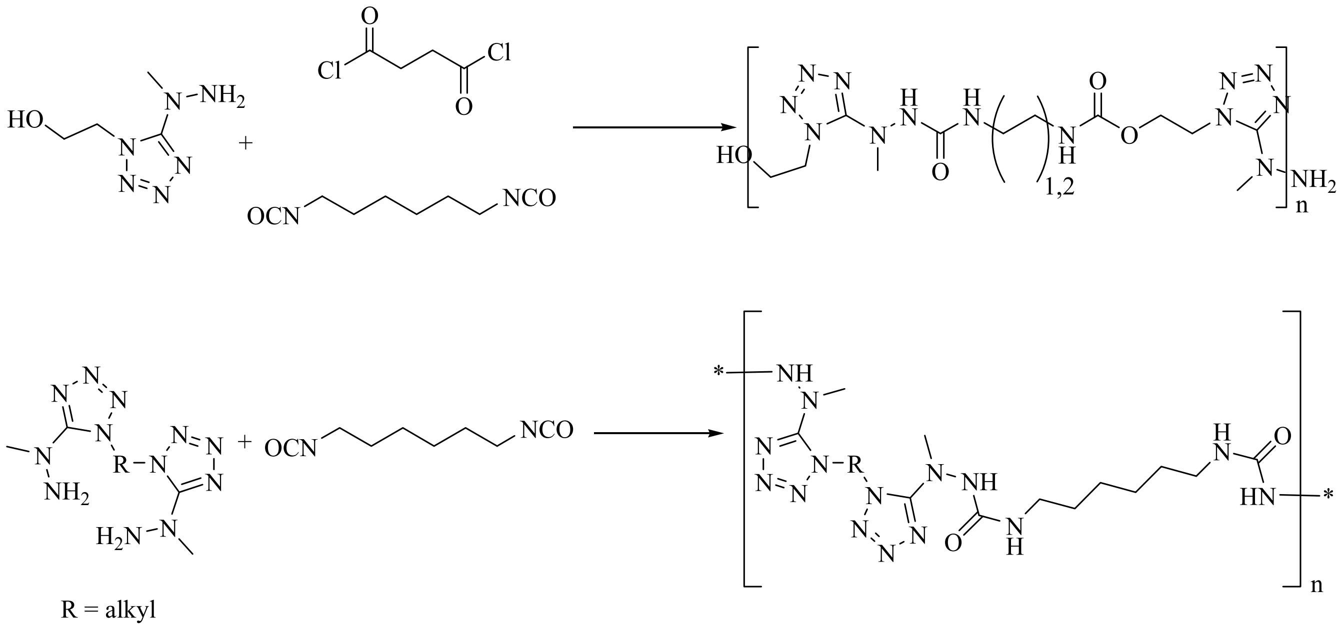
(5) M. J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian, Inc., Gaussian 03, Revision A.1, Pittsburgh, PA, 2003.

(6) Gaussian 03, Revision A.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N.

Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, **2003**.

9. Summary

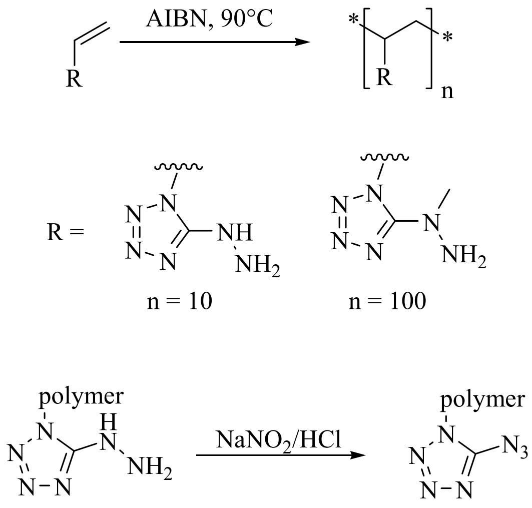
The thesis deals with the synthesis of several nitrogen-rich energetic polymers and related energetic compounds. The most intensively studied topic were polymers based on tetrazolyl hydrazines. One polymer class was obtained by polycondensation and polyaddition reactions of succinyl chloride or hexamethylene diisocyanate with tetrazolyl hydrazines (*Scheme 1*).



Scheme 1. Polymers obtained by polycondensation/polyaddition reactions.

The advantages of these polymers are their high thermal stability along with insensitivity towards impact or friction. Moreover, the carbamate moieties are able to form hydrogen bridges to the energetic filler, leading to increased adhesion forces. The molecular weights of the polymers could be influenced by the addition of alcohols or water leading to a decomposition of the diisocyanate resulting in shorter chains.

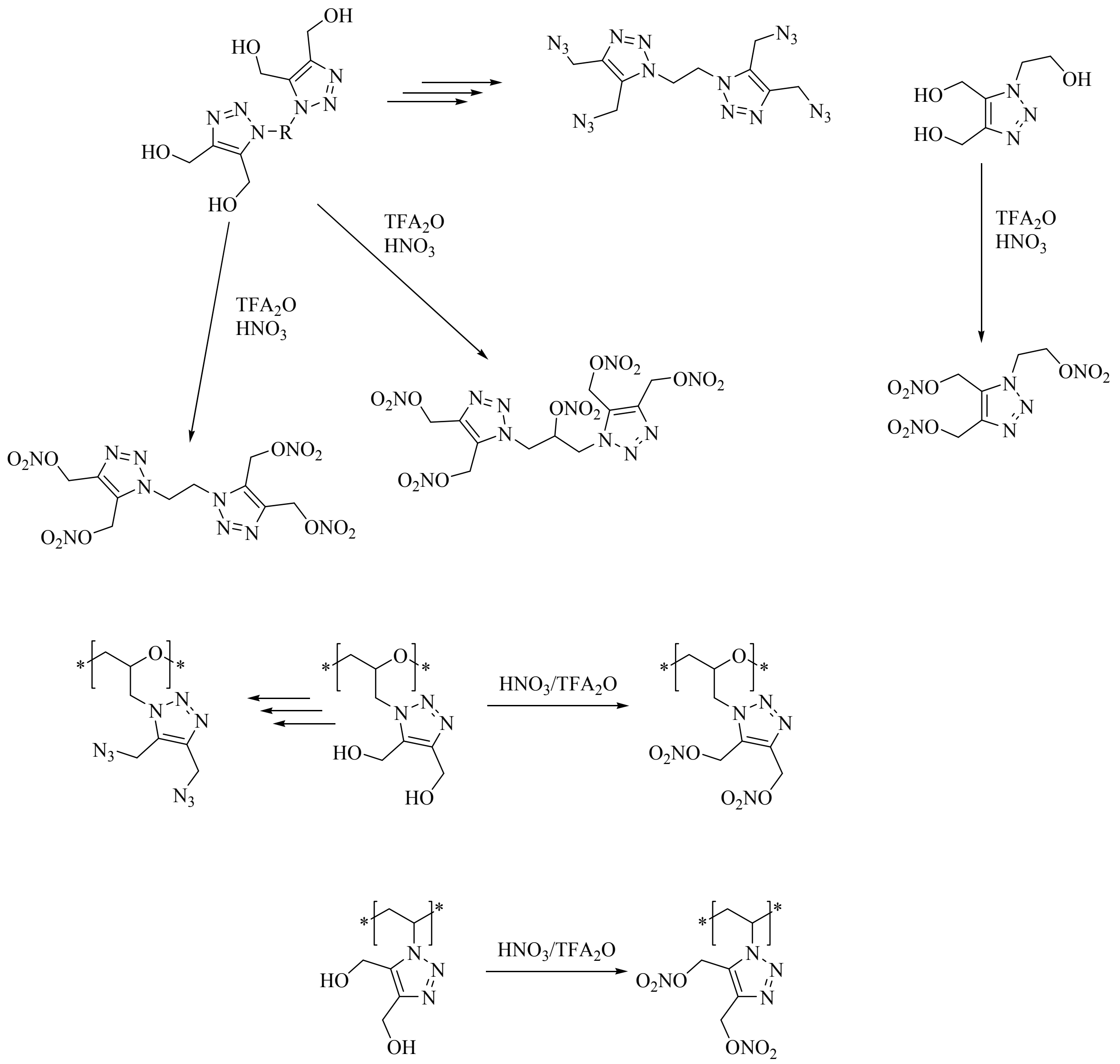
The second polymer class was prepared by radical polymerization of vinyl tetrazoles, obtained by substitution reactions of the bromine atom of 1-vinyl-5-bromo-1*H*-tetrazole (*Scheme 2*).



Scheme 2. Preparation of energetic polymers by radical polymerization.

The polymers containing tetrazolyl hydrazines possess low sensitivities towards impact or friction along with high thermal stabilities. The formation of azidotetrazole containing polymers by diazotation reactions of the hydrazine moiety leads to increased energetic properties along with a decrease of the thermal and physical stability. The diazotation reactions result in a partial decomposition of the polymer.

The third topic dealing with polymers is about polymers based on triazoles. The reactivity and chemistry of the triazoles were investigated by using three different triazoles as model compounds for the preparation of nitrate esters and azides. The experiences were transferred to prepare the corresponding triazole containing polymers using glycidyl azide polymer and polyvinyl azide as starting materials (*Scheme 3*).



Scheme 3. Preparation of triazole containing polymers.

The analysis of the energetic properties of the polymers gave the best results for the diazide polymer. The nitrate esters possessed decomposition points below 150 °C along with low performances, regarding an application as energetic polymers. The diazide polymer possessed moderate energetic properties along with sufficiently high thermal stabilities.

Besides polymers, several energetic materials based on tetrazolyl hydrazines were prepared, such as tetrazenes and azido tetrazoles (*Figure 1* and *Figure 2*). Whereas the tetrazenes proved to be suitable gas generating agents possessing decomposition points at 200 °C along with moderate sensitivities towards impact and friction, the 5-azido tetrazoles were much too sensitive for any application; despite the ethyl bridged derivatives reached the explosive values of RDX.

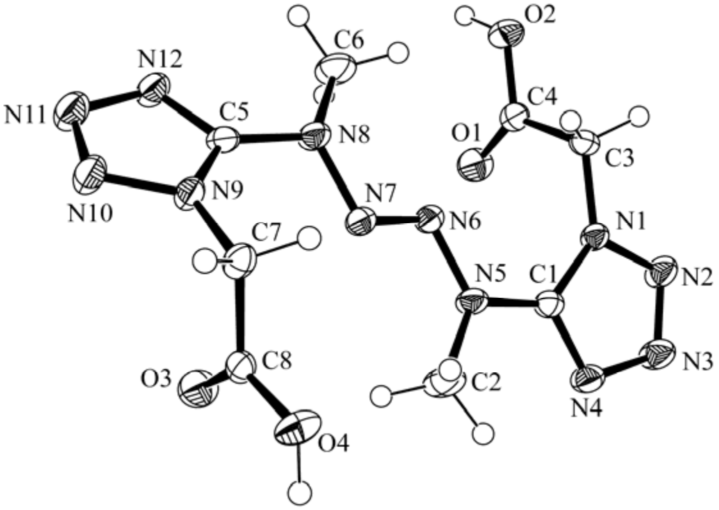


Figure 1. Molecular structure of 1,4-bis[1-carboxymethyl-1*H*-tetrazol-5-yl]-1,4-dimethyl-2-tetrazene.

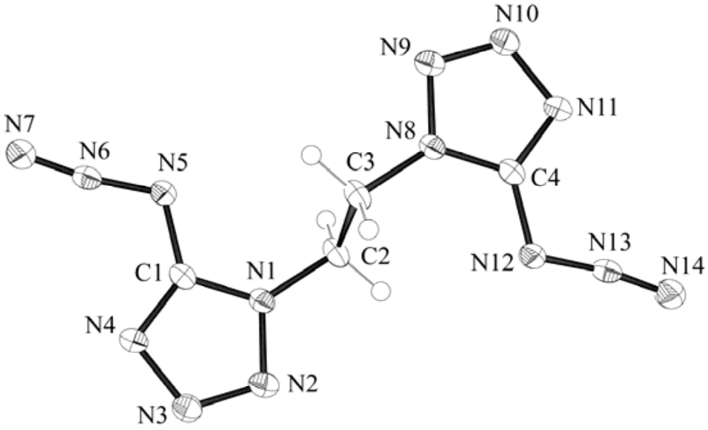


Figure 2. Molecular structure of 1,2-bis(5-azido-1*H*-tetrazol-1-yl)ethane.

Another topic deals with the formation of tetrazole containing complexes. Besides 5-carboxylic-1*H*-tetrazolate (*Figure 3*) bidented and tridented tetrazole ligands were used. The aim of the preparation of complexes was the synthesis of new coloring agents for pyrotechnical formulations. Therefore, the barium, strontium and copper 5-carboxylic-1*H*-tetrazolate were investigated. The complexes showed a high thermal and physical stability. In contrast to the 5-carboxylic-1*H*-tetrazolates, the copper complexes of (2-(1*H*-tetrazol-1-yl)ethyl)amine and 1,2-bis(5-monomethylhydrazinyl-1*H*-tetrazolyl)ethane were very sensitive towards impact and friction. Moreover, the decomposition points of the complexes were lower than the decomposition points of the ligands themselves. As an explanation, the nitrate anion was taken. The close arrangement of the ligand and the oxidising nitrate anion next to each other could lead to the low stability observed.

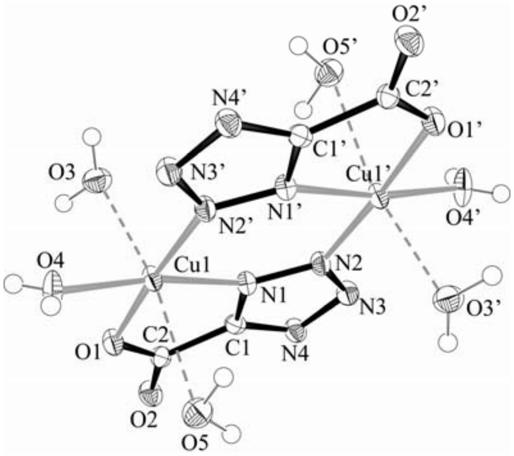
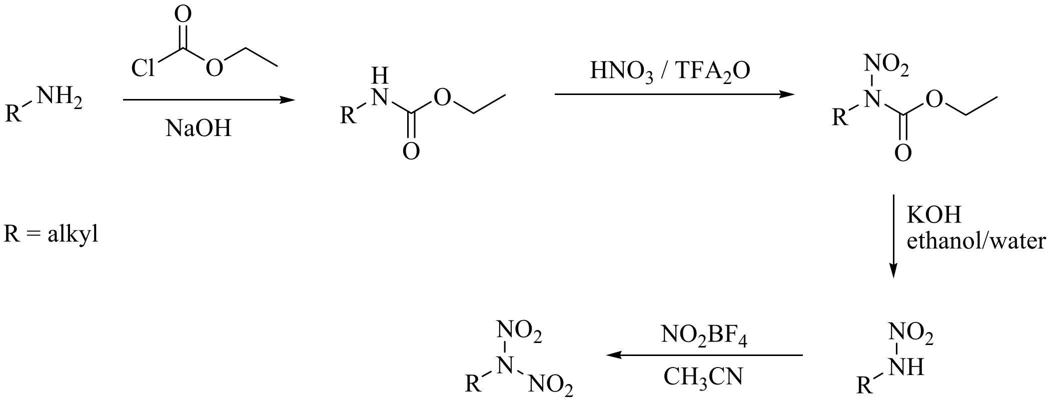


Figure 3. Molecular structure of the copper(II) 5-carboxylic-1*H*-tetrazolate.

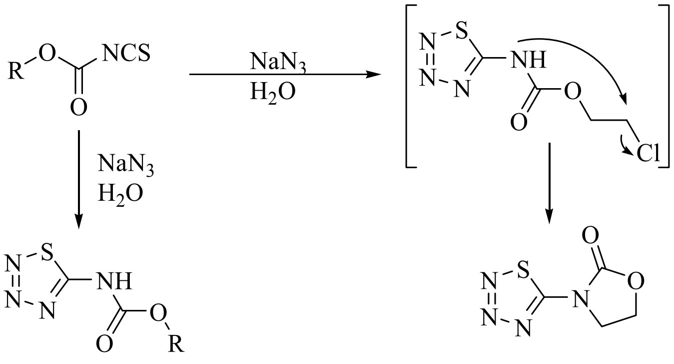
Besides energetic materials based on nitrogen-rich heterocycles, nitramines and *N*,*N*-dinitramines were prepared. These compounds are known for a long time, but were not characterized properly. Therefore, we investigated two different synthetic pathways and determined the physical and thermal stabilities along with the explosive properties. The first preparation was published by Russian chemists and deals with alkylation reactions of silver dinitramide salts. Despite our efforts, we were not able to isolate any alkyl *N*,*N*-dinitramine using this route. The *N*,*N*-dinitramines were prepared according to patents by the nitration of alkyl nitramines using nitronium tetrafluoroborate (*Scheme 4*).



Scheme 4. Preparation of primary alkyl *N*,*N*-dinitramines.

The nitramines proved to be moderate explosives, whereas the corresponding *N*,*N*-dinitramines can be classified as high explosives. The low decomposition points of the *N*,*N*-dinitramine at about 80 °C prevents these compounds from being used as explosives.

The last, strictly academic topic deals with the preparation of thiatriazoles. These heterocycles were obtained by the reaction of sodium azide and carbon(isothiocyanatidic) acid alkyl esters (*Scheme 5*). The application as energetic material of thiatriazoles is neglected, because of the sulfur atom, resulting in the formation of toxic and corrosive SO$_x$ gases during the decomposition reactions



R = methyl (**a**), ethyl (**b**), 2-butyl (**c**), allyl (**d**)

Scheme 5. Preparation of the thiatriazoles.

10. Appendix

10.1 Curriculum Vitae

Name: Stefan Michael Sproll

E-Mail: stefan_sproll@web.de

Birth Date: 27 November 1981, Tübingen (Germany)

Nationality: Germany

Education:	1988-1992	Primary School: Pestalozzi Grundschule Nierstein, Rhineland-Palatinate, Germany
	1992-2001	Secondary School: Carl-Spitzweg-Gymnasium Germering, Bavaria, Germany
	2001-2004	B. Sc. Degree in Chemistry and Biochemistry, Ludwig-Maximilian-University, Munich, Germany
	2004-2006	M. Sc. Degree in Chemistry, Ludwig-Maximilian-University, Munich, Germany
	01.01.2007-	Ph. D. at the Ludwig-Maximilian-University, Munich, Germany

Language knowledge:	German:	native speaker
	English:	fluent
	French:	basic knowledge

Work experience:	2007-present	Doctoral research at the Ludwig-Maximilian University, Munich (supervisor of bachelor and undergraduate research students, teaching lab instructor for 1st, 3rd and 5th/6th semester)
Awards:	2009	Dr. Klaus Römer Award, Ludwig-Maximilian University, Munich, Germany

10.2 Full List of Publications

10.2.1 Articles

1. T. M. Klapötke, S. Sproll, **2-Methylthiosemicarbazide**, *Acta Cryst. E* **2007**, *E63*, o4270.
2. K. Banert, T. M. Klapötke, S. M. Sproll, **Synthesis of *N*-[1-(2-hydroxyethyl)-1*H*-tetrazol-5-yl]-*N*-methylhydrazine as polymeric precursor**, *Eur. J. Org. Chem.* **2009**, *2*, 275–281.
3. J. Heppekausen, T. M. Klapötke, S. M. Sproll, **Synthesis of Functionalized Tetrazenes as Energetic Compounds**, *J. Org. Chem.* **2009**, *74*, 2460-2466.
4. T. M. Klapötke, S. M. Sproll, **Alkyl-Bridged Bis-5-azidotetrazoles: A Safe Way of Preparation**, *Eur. J. Org. Chem.* **2009**, *25*, 4284-4289.
5. T. M. Klapötke, S. M. Sproll, **Synthesis and Investigation of 1,2,3,4-Thiatriazol-5-ylcarbamates**, *Phosphorus, Sulfur and Silicon*, in press.
6. V. Hartdegen, T. M. Klapötke, S. M. Sproll, **Tetrazole-5-carboxylic Acid Based Salts of Earth Alkali and Transition Metal Cations**, *Inorg. Chem.*, **2009**, *48*, 9549-9556.
7. T. M. Klapötke, S. M. Sproll, **Investigation of Nitrogen-rich Energetic Polymers Based on Alkylbridged Bis-(1-methyl-tetrazolylhydrazines)**, *J. Polym. Sci., Part A: Polym. Chem.*, in press.
8. V. Hartdegen, T. M. Klapötke, S. M. Sproll, **Synthesis and Characterization of a Three-dimensional Coordiation Polymer Based on Copper(II) Nitrate and a Tridentate Tetrazole Ligand**, *Z. Naturforsch., B: Chem. Sci. in press*.
9. L. S. Kovacevic, T. M. Klapötke, S. M. Sproll, **Synthesis of a one-dimensional coordination polymer based on copper(II) nitrate and 1,2-bis(5-monomethylhydrazinyl-1*H*-tetrazolyl)ethane**, *Z. Anorg. Allg. Chem.* accepted.
10. T. M. Klapötke, S. M. Sproll, **Nitrogen rich polymers based on 5-bromo-1-vinyl-1*H*-tetrazole**, *Eur. J. Org. Chem.* submitted.

10.2.2 Poster Presentations

1. T. M. Klapötke, S. Sproll, **A Nitrogen Rich, Tetrazole Containing Polymeric Precursor,** *New Trends in Research of Energetic Materials, 10th, Pardubice, Czech Republic*, **2007**.
2. G. Heeb, S. Wilker, T. M. Klapötke, B. Krumm, N. Mayr, S. Sproll, F. X. Steemann, **New Energetic Materials for Nitrocellulose Based Propellants**, *38th Intl. Annual Conf. of ICT*, *Karlsruhe*, *Germany*, **2007**.
3. T. M. Klapötke, S. Sproll, **Synthesis and Characterization of Nitrogen Rich, Energetic Polymers**, *New Trends in Research of Energetic Materials, 11th, Pardubice, Czech Republic*, **2008**.
4. T. M. Klapötke, F. Martin, S. Sproll, J. Stierstorfer, **Azidotetrazoles – Promising Energetic Materials or Waste of Time?** *New Trends in Research of Energetic Materials, 12th, Pardubice, Czech Republic*, **2009**.
5. T. M. Klapötke, S. Sproll, **Bistetrazolyltetrazenes as Energetic, Nitrogen Rich Compounds**, *New Trends in Research of Energetic Materials, 12th, Pardubice, Czech Republic*, **2009**.
6. F. Betzler, T. M. Klapötke, S. Sproll, **New Energetic Polymers Based on Cellulose**, *New Trends in Research of Energetic Materials, 12th, Pardubice, Czech Republic*, **2009**.
7. V. Hartdegen, T. M. Klapötke, S. Sproll, **New Energetic Materials Based on 2H-tetrazole-5-carboxylic Acid**, *New Trends in Research of Energetic Materials, 12th, Pardubice, Czech Republic*, **2009**.

10.3 List of Abbreviations

abbreviation	Meaning	abbreviation	meaning
a.u.	atomic units (Hartree)	NMR	nuclear magnetic resonance
calcd.	calculated	ppm	parts per million
D	detonation velocity	$p_{C\text{-}J}$	detonation pressure
dec.	decomposition	q	quartet
DMF	dimethylformamide	RT	room temperature
DMSO	dimethylsulfoxide	s (NMR)	singlet
DSC	differencial scanning calorimetry	s	solid phase
EI	electron ionization	s (IR)	strong
g	gas phase	T	temperature
h	hours	t (NMR)	triplet
Int.	intensity	vs (IR)	very strong
IR	Infrared	vw (IR)	very weak
I_{sp}	specific impulse	w (IR)	weak
J	coupling constant	Å	Angström (10^{-10} m)
l	liquid phase	δ	chemical shift
m (IR)	medium	ρ	density
m (NMR)	multiplet	Ω	oxygen balance
min	minutes	v	frequency
m.p.	melting point		

Further abbreviations are explained within the thesis.