Dissertation

Azido Liquids
as Potential Hydrazine Replacements
in a Hypergolic Bipropulsion System

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aus

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Danke – ein kleines Wort mit einer unfassbaren Bedeutung:

geliebte Mami **Claudia Karg**, die mir immer alles ermöglichte und fest an mich glaubt, und meine liebe Schwester **Kristina Karg**. Ich kann kaum in Worte fassen, wie viel es mir bedeutet, dass ihr mir sowohl die Freiheit gegeben habt meinen Weg zu gehen als mich auch immer unterstützt habt. Ebenfalls Danke an die tollen Männer unserer Familie, **Wolfgang Doege**, **Helmut Wittmann** und **Stephan Pichler**. Wie sehr ich mich schon auf das gemeinsame Feierbierchen mit euch freue.

Zum Schluss dürfen natürlich meine über alles geliebten Tiere nicht fehlen, die mir jeden Tag aufs neue Kraft und Liebe schenken. Ihr seid die Sonne in meinem Leben: Cooper (unvergessen und immer in meinem Herzen), Louis, Pegaso und meine fünf Besten: Donna, Harvey, Mike, Louis (alias Lulu) und Rachel.

Man muss nichts im Leben fürchten,

man muss nur alles verstehen.

Marie Skłodowska Curie (1867 - 1934)

Physikerin und Chemikerin

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°C	Degree Celsius
Al	Aluminium
AP	Ammonium perchlorate
ASTM	American society for testing and materials
ATR	Attenuated total reflection
BAM	Bundesanstalt für Materialforschung
bs	broad signal
C*	Characteristic exhaust velocity
calcd	calculated
CBS	Complete Basis Set
$CDCl_3$	Chloroform
CEA	Chemical Equilibrium with Applications
cm	Centimetre
COTS	Commercial off-the-shelf
d	doublet
DCC	*N,N'*-dicyclohexylcarbodiimide
DCM	Dichloromethane
dd	double doublet
DDT	Deflagration-to-detonation transition
DMAZ	2-azido-*N,N*-dimethylethan-1-amine
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
DTA	Differential thermal analysis
EA	Elemental analysis
EC_{50}	Half maximal effective concentration

ECHA	European Chemical Agency
EIL	Energetic ionic liquid
EPS	Etage à propergols stockables, storable propellant stage
eq	Equivalent
ESD	Electrostatic discharge
Et_2O	Diethyl ether
EtOH	Ethanol
g	gram
h	hour
H_2O	Water
H_2O_2	Hydrogen peroxide
HEIL	High energetic ionic liquid
HF	Hydrofluoric acid
HTP	High test peroxide
HTPB	Hydroxyl-terminated polybutadiene
Hz	Hertz
ID	Ignition delay
IL	Ionic liquid
IM	Imidazole
IR	Infrared
I_{sp}	Specific impulse
IUPAC	International Union of Pure and Applied Chemistry
J	Joule
K	Kelvin
m	multiplet
m	medium

MAT	Manganese acetate tetrahydrate
mCPBA	*meta*-chloroperoxybenzoic acid
MeOH	Methanol
mL	Millilitre
MMH	Monomethyl hydrazine
mmol	Milli mol
mol	mol
MON	Mixed oxides of nitrogen
N	Newton
N_2O_4	Dinitrogen tetroxide
NASA	National Aeronautics and Space Administration
NC	Nitrocellulose
NG	Nitro-glycerine
NMR	Nuclear magnetic resonance
NO	Nitrogen monoxide
NTO	Dinitrogen tetroxide
O/F	Ratio oxidizer / fuel
OCS	Orbit control system
p	quintet
PETN	Pentaerythritol tetranitrate
ppm	parts per million
PTFE	Polytetrafluoroethylene
q	quartet
RACS	Roll and attitude control system
RCS	Reaction control system
RDX	Cyclotrimethylentriamine

REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
RFNA	Red fuming nitric acid
s	singlet
s	strong
SCAPE	Self Contained Atmospheric Protection Ensembled
SVHC	Substance of very high concern
t	triplet
T_c	Combustion temperature
T_d	Decomposition temperature
THF	Tetrahydrofuran
TMA	Tetramethylammonium
TNT	Trinitrotoluene
UDMH	Unsymmetrical dimethylhydrazine
UN	United nations
$\tilde{v}$	Wavenumber
w	weak
WFNA	White fuming nitric acid
δ	delta

1 Introduction

A compound which contains besides the fuel also the oxidizer and decomposes under energy and gas release is defined according to the ASTM (American society for testing and materials)[1] as an energetic material.[2] The explosive is therefore triggered with an external initiation like heat, impact, pressure, detonation or other forms of external stress. The explosive reaction underlies two important aspects. One the one hand a large amount of heat is formed, which results in a generation of high pressure due to the expansion of the gaseous products. However, this process must be rapid since a slow release of heat does not result in an explosion. An example for a controlled burning instead of detonation or deflagration is charcoal. Therefore, on the other hand the second parameter is the rapidity of deflagration. This aspect distinguishes an explosive reaction since it occurs with high speed.[3]

The speed of an explosive reaction in comparison to a controlled burning can further be divided into deflagration and detonation. In a deflagration reaction, pressure and a flame are formed, but the flame is spread with less speed than the speed of sound. If the reaction front achieves the speed of sound, the deflagration turns into detonation (DDT, Deflagration-to-detonation transition). A detonation reaction is accompanied by a shock wave with a constant velocity.[2]

1.1 Classification of energetic materials

A possibility for a further classification of energetic materials is to divide them according to their individual usage. Therefore, they can be categorized in four sections; as primary explosives, secondary explosives, pyrotechnics and propellants. The classification is shown in Figure 1 below.
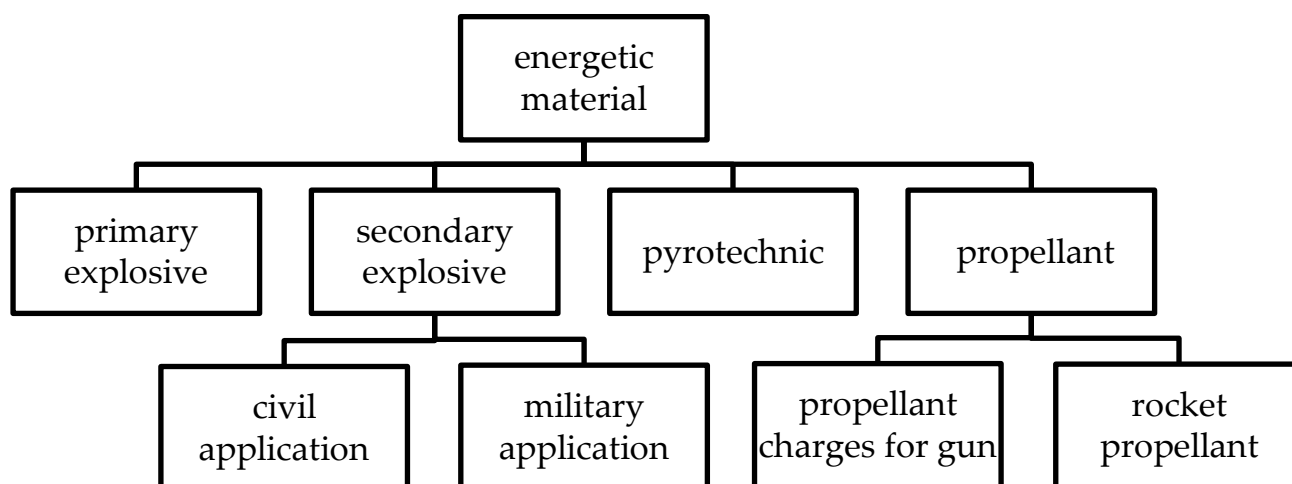
Figure 1: Classification of energetic materials.

Primary explosives, like lead azide ($Pb(N_3)_2$) or lead styphnate, are extremely sensitive towards external stimuli like heat, friction or impact and create a large amount of heat and shockwave during the decomposition. Therefore, their main function is to initiate a secondary explosive and they are used as primers, detonators or percussion caps.

Secondary or high explosives are in comparison relatively insensitive towards external triggers, but after the set off their explosion takes place with a greater violence. As a result, their detonation has a higher velocity and it produces more pressure and heat in comparison to primary explosives. Their application ranges from civil areas, e.g. in mining and quarrying to military operations, like missiles, torpedoes or bombs. Well-known examples of secondary explosives are TNT (trinitrotoluene), RDX (cyclotrimethylentriamine) or PETN (pentaerythritol tetranitrate).

Pyrotechnics are a mixture of substances, which aim at producing special effect like light, smoke, sound or heat. These effects are provided through a non-detonating, self-sustaining exothermic reaction since the substances consist of an oxidizer, a reducing agent and an additive depending on the application. Their usage also ranges from civil application, like fireworks to military application as flares or smoke ammunition.

The fourth section of the classification is the usage of energetic materials as propellants. They are characterized by a controlled decomposition (combustion) with a high generation of gas.

They can be further divided into propellant charges for guns and rocket propellants.[2] The first propellant charge was black powder or gun powder, which consist of potassium nitrate (75%), charcoal dust (15%) and sulphur (10%).[4] To avoid the formation of iron carbide in the gun barrel, the temperature of combustion of an gun explosive must be as low as possible. Single-based propellant charges like nitrocellulose show less erosion problems but also a lower performance than double- or triple based propellant charges. An important property of a propellant charge is also the insensitivity, especially during the handling.[2]

1.2 Rocket propellants

Rocket propellants are also classified to combust in a controlled way (no detonation), but with a slower burning than previously described propellants. They can be further divided into solid propellants and liquid propellants.

- Solid propellants are on the one hand separated into double base propellants, like a homogenous mixture of nitro glycerine and nitrocellulose (NG/NC), or on the other hand in composite propellants, as a heterogenous mixture of a fuel combined with a crystalline oxidizer and a polymeric binder. Such composite propellants can consist of Al (aluminium), AP (ammonium perchlorate) and HTPB (Hydroxyl-terminated polybutadiene).

- Liquid propellants can be divided into monopropellants or bipropellants. Monopropellants are endothermic liquids, as hydrazine, which have the ability to decompose exothermically with the help of a catalyst in absence of oxygen.[5] They generate only a minor thrust and are therefore only applied in small satellites or missiles. Other commonly used monopropellants are hydrogen peroxide (H_2O_2), nitromethane (CH_3NO_2) or isopropyl nitrate ($C_3H_7NO_3$). On the other hand, bipropellants are two separate liquids, an oxidizer and a fuel, transported in separate tanks and only combined in the combustion chamber.[6]

If the propellant must be handled at low temperatures, they are called cryogenic. An example is the combination of H_2 and O_2. Storable propellants can be divided into hypergolic and non-hypergolic propellants. Hypergolicity is described in more detail in section 1.3.

The classification of the rocket propellants is depicted in Figure 2 below.
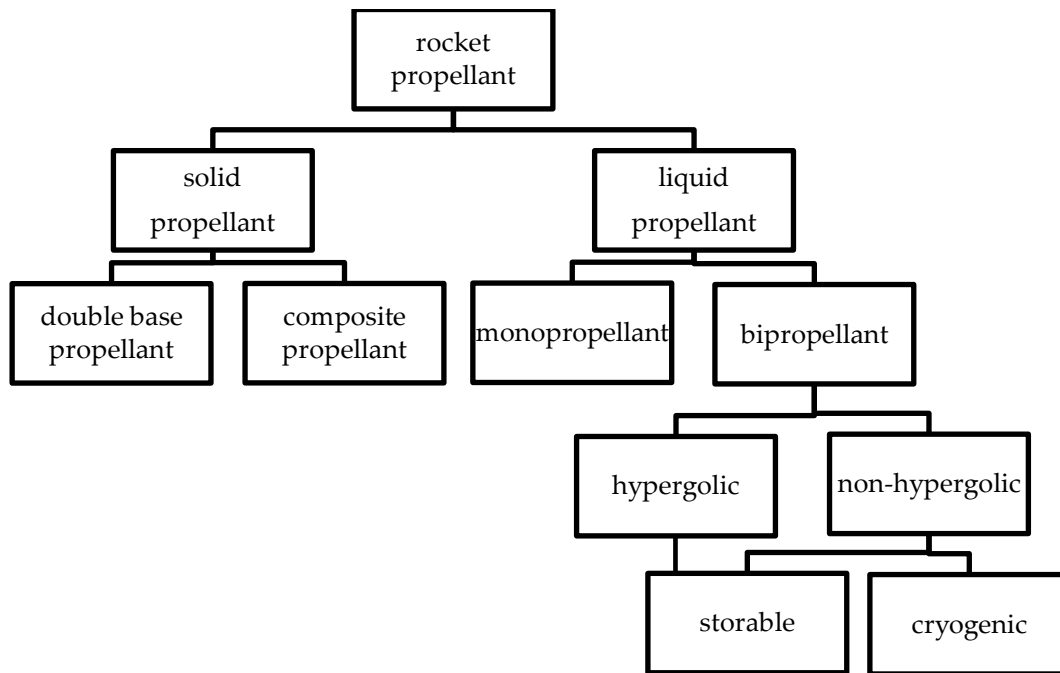
Figure 2: Classification of rocket propellants.

The following sequence of formulae is intended to explain the efficiency of a rocket propellant and the reason for giving special attention to hypergolic propellants.

One of the most important performance parameters of rocket propellants is the specific impulse (I_{sp}). It is defined as the change of impulse per mass unit of the propellant. The equation is shown in formula 1 below. The effective velocity of the gases leaving the nozzle is determined by this parameter which in turn determines the effectivity of a propellant.[2, 7]

$$I_{sp} = \frac{\bar{F} \times t_b}{m} = \frac{1}{m} \times \int_0^{t_b} F(t)dt \qquad \textbf{Formula 1.}$$

The symbols used in Formula 1 are as follows: the thrust of a rocket is the force F, the combustion time (s) is represented as t_b and m is the mass (in kg) of a propellant. Subsequently, the I_{sp} is given in m/s.

Another way to specify the specific impulse is based on the Earth`s gravitational acceleration.

$$I_{sp}^* = \frac{I_{sp}}{g} \qquad \textbf{Formula 2.}$$

The exact description of the specific impulse is given in formula 3.

$$I_{sp} = \sqrt{\frac{2\,\gamma R T_c}{(\gamma-1)M}} \qquad \textbf{Formula 3.}$$

The ratio of specific heat capacities in the gas mixture is γ, the temperature in the combustion chamber is T_c, R is the gas constant and M the average molecular weight of the formed combustion gases.

Therefore, the average thrust of a rocket F can be described by the formula 4 below, where the specific impulse is multiplied by the burned propellant mass Δm divided through the burning time. Hence, the thrust is given in Newton.

$$\bar{F} = I_{sp}\frac{\Delta m}{\Delta t} \qquad \textbf{Formula 4.}$$

The specific impulse is proportional to the root of combustion temperature to molar mass of the formed gases. Formula 5 is depicted below.

$$I_{sp} \propto \sqrt{\frac{T_c}{M}} \qquad \textbf{Formula 5.}$$

A small increase in the specific impulse can have a significant effect on the payload which leads to the rule that an increase of I_{sp} of 20 s can double the payload.[2]

In addition, also the density of the propellant can have a great influence on the propulsion system. The higher the performance, the less amount of propellant is needed which results in a decrease of the payload. Furthermore an increase in the propellant density leads to an decrease of the propulsion system dry mass.[8]

Another important parameter, which has a major effect on the thrust, is the nozzle area expansion ratio, ε. It is defined as

$$\varepsilon = \frac{A_e}{A_t} \qquad \textbf{Formula 6.}$$

There is A_e the thrust chamber exit area and A_t the nozzle throat area.

There is a correlation between the expansion ratio at the nozzle, the chamber pressure and the resulting specific impulse. If the pressure at the nozzle(p_e) is smaller than the ambient pressure (p_a), the thrust equation is negative, and the resulting thrust is decreased. An optimum thrust on the other hand is given, if the pressure at the nozzle is equal to the ambient pressure, $p_e = p_a$.[9] Therefore, the purpose is a higher pressure at the nozzle exit. A higher specific impulse is subsequently achieved, if the chamber pressure is higher and therefore, the nozzle expansion ratio increased.[10]

The ideal thrust equation is therefore depending on many factors and can be given as

$$F = C_F * p_C * A_t$$

Formula 7.

In which C_F stands for the thrust coefficient. It varies from 0.9 to 1.8, depending on the nozzle pressure ratio. If C_F equals the value 1, it is specified as C*, the characteristic exhaust velocity. Next, the thrust is divided through the mass flow and after rearranging the following applies:

$$F = \frac{dm}{dt} C^*$$

Formula 8.

Going back to the specific impulse, it can be defined as

$$I_{sp}^* = \frac{C^*}{g}$$

Formula 9.

Therefore, the exhaust velocity differs only from the specific impulse by dividing the exhaust velocity by the gravity constant.

In the end, the basic rocket equation can be given as

$$v_b = g * I_{sp} * \ln \frac{1}{MR}$$

Formula 10.

and MR stands for the mass ratio m_f (final mass) / m_i (initial mass). [11]

As a result, in a flight to orbit only 10% of the mass may come from the rocket itself, the payload and the engines, while 90% of the mass is due to the propellant.[12]

Subsequently, an attractive way to decrease the mass of the system is the usage of a hypergolic propulsion system since no external ignition sources are needed.

1.3 Hypergolicity

Hypergolicity means that the oxidizer and the fuel ignite spontaneously upon contact. With this reliable ignition reaction, there is no risk of fuel accumulation which could lead to an uncontrolled explosion of the rocket. This hypergolic propulsion system has additional advantages: multiple ignitions to short pulses are possible for manoeuvring. In addition, no external ignition source is needed, which also reduces the possibility of incidents.

Hypergolic ignition systems are used in many space and aircraft systems as in orbiting satellites, manned spacecraft, military aircraft and deep space probes.[13] In space application, hypergolic propulsion is used especially in small thrusters (1-500 N range) as in small or medium satellites, in OCS (orbit control system) or RCS (reaction control system) system of landers or orbiters, or in RACS (roll and attitude control system) of launcher.

An important parameter for a hypergolic ignition is the ignition delay time (ID time). It is defined as the interval between two points in time: from the first contact when mixing the oxidizer and the fuel to a visible ignition, the flame. It should be very low, preferably lower than 50 ms, to prevent a so-called "hard-start".[14] Energy accumulation in the tank could also lead to an uncontrolled explosion. Therefore, the potential fuels must be investigated for their hypergolicity, with different oxidizers, and in addition for their ignition delay time with each oxidizer.

1.4 State of the art

A very good overview about the first research of liquid propellants and the usage of hypergol propulsion systems is given by J. D. CLARK in his book IGNITION! The research of

liquid rocket propellants got high attention during WWII. Systems like "C-Stoff" consisting of hydrazine hydrate, methanol, water and a copper catalyst mixed with hydrogen peroxide were applied in the interceptor *Messerschmitt 163* which used a rocket propulsion system. Since then hydrazine raised attention as the ultimate fuel. It showed hypergolicity, plus a higher performance than other promising fuels like anilines or amines and a higher density.[15]

Until today, Hydrazine and it´s methylated derivatives, monomethyl hydrazine (MMH) and Unsymmetrical dimethylhydrazine (UDMH), are still the commonly used hypergolic fuel and therefore the state-of-the-art fuel in a bipropellant system. Their structures are depicted in Figure 3.
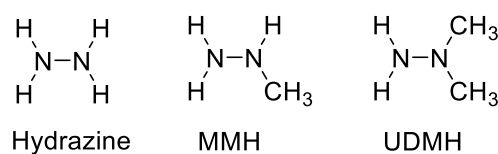
Figure 3: Molecular structures of hydrazine, MMH and UDMH.

They are used together with oxidizers like dinitrogen tetroxide (NTO), or mixtures of nitric acid, e.g. white fuming nitric acid (WFNA) or red fuming nitric acid (RFNA).[16]

Nitric acid was investigated to react hypergol with many compatible fuels. Its reactivity can be improved by combining it with some additives.[17] WFNA is a mixture of over 97% HNO_3, less than 2% NO_2 and around 0.5% water. In comparison, RFNA consist of 83% HNO_3, 13% N_2O_4 and 3% water. Due to the high corrosivity of nitric acid[18], small amounts (about 0.6%) of hydrofluoric acid (HF) are added as a corrosion inhibitor, because fluorine ions have the ability to passivate the construction material in the tank.[19] The oxidizer is then called IRFNA (inhibited red fuming nitric acid).

At room temperature (25 °C), NTO is a colourless gas with a boiling point at 21.69 °C.[20] The colourless gas forms an equilibrium with the radical NO_2, but lower temperatures push the equilibrium on the side of N_2O_4.[21] Stress corrosion cracking of the titanium tanks is prevented by adding nitric oxide (NO) to NTO, which lowers the freezing point. These mixtures are called MON (mixed oxides of nitrogen).[22] The addition of NO also increases the vapour pressure of NTO drastically. As a great disadvantage, NTO has shown to be the

highly toxic, especially towards the mucous membranes. It can cause severe damage of the respiratory system after inhalation, up to death.[23] Therefore, an alternative oxidizer has to be investigated. A green promising alternative would be hydrogen peroxide, since it has only environmentally friendly decomposition products like oxygen and steam. It is commercially available as HTP (high test peroxide) with a content of 85 – 98%.[24] Hydrogen peroxide shows many advantages over other oxidizers, considering its high density of 1.46 g cm^{-3} at 25 °C[25], low vapor pressure of 2.6 mbar at 25 °C [26], relatively low toxicity[27], relatively safe handling and good storability[28]. It is therefore a desirable alternative in a hypergolic bipropellant system. However, due to hypergolicity problems until today it has only been applied as monopropellant, e.g. in the Soyuz launch vehicle.[29]

Getting back to the state of the art fuels, hydrazine and its derivatives show relative low combustion temperatures (hydrazine / NTO ~ 3100 K, MMH / NTO ~ 3250 K, UDMH / NTO ~ 3330 K), good hypergolicity and high I_{sp} values of around 280 s.[30]

In combination with NTO, MMH reveals a high I_{sp} of 310 s.[31] In this combination, it is still in use to propel the storable propellant upper stage (EPS) of the 11th Ariane5 G[32]. The I_{sp} values of UDMH are in the same range but can be increased to 316.7 s by an addition of Aluminium.[33] The Ariane 4 was powered by Viking engines, which used UDMH and NTO.[34] This hypergolic fuel is still in use for the first stage of the Proton rocket and for the side blocks of the Soyuz rocket.[35]

A great disadvantage of hydrazine is the high toxicity, amongst others caused by the high vapour pressure of 21 mbar at 25 °C. In comparison, the vapor pressure of MMH is determined to 50 mbar, UDMH to 164 mbar at 25 °C.[36] Beside the toxic effect on blood, liver, nervous system, lung and mucous membranes[37], in latest studies, hydrazine was found to be carcinogenic[38]. Handling, storage and disposal of hydrazine and its derivatives are under strict precaution and regulations.[39] For example, workers handling hydrazine or derivatives need an extensive protection equipment, like a SCAPE suit (Self Contained Atmospheric Protection Ensembled). In addition, the work time is strictly limited.

Due to the latest findings in cancer studies, the ECHA (European Chemical Agency) included hydrazine in REACH´s candidate list (Registration, Evaluation, Authorisation and

Restriction of Chemicals) as a substance of very high concern (SVHC) in 2011.[40] These candidates are further assessed by experts and industry for the inclusion in the Annex XIV list, which bans the usage of these compounds for the European market. This process of evaluation for restriction may take from 4.5 to 6 years. Although, hydrazine was not yet prioritized for the inclusion in the Annex XIV list, in 2018 the recommendation was close to the prioritisation threshold with a result of hydrazine risk at 15/45. The threshold is defined at 17/45.[41]

In addition, the European Hydrazine Task Force was reactivated in 2019 to continue the investigations for an inclusion of the hydrazine derivatives, MMH and UDMH.

Although hydrazine and its derivatives are not yet banned, many reasons for an urgent need of an alternative are present; for example, the risk of a prohibition, the incalculable cost increase or harsher formalities.

In 2001, the Unites States investigated of 2-azido-*N*,*N*-dimethylethan-1-amine (DMAZ) as a replacement for MMH.[42] DMAZ has shown to be relatively low in toxicity in comparison to MMH, which lead to advantages in handling and transportation.[43] Further studies showed, that DMAZ has a higher density ($0.93 \, \text{g cm}^{-3}$) compared to MMH ($0.88 \, \text{g cm}^{-3}$), higher stability of 135 °C compared to 88 °C and it was defined as insensitive against impact and friction. Additional hypergolicity tests showed an ignition with NTO, but not with RFNA or hydrogen peroxide.[44]

Nowadays research focuses also on the investigation of hypergolic ionic liquids.[45] Due to their low vapor pressure, high thermal stability and low flammability, they are deliberated as green alternative fuels.[46] An ionic liquid (IL) is defined as a liquid salt within the temperature range from −20 °C to +100 °C.[47] These low melting points are achieved through a weak intermolecular interaction, which lead to a lowering of the lattice energy of the ionic material. The lattice energy of an ionic liquid is therefore lower than the thermal energy. The increasing size of ions, anisotropy and internal flexibility have a significant effect on lowering the melting point. The symmetry and diversity of alkyl chains in the cation influence the melting point as well as the viscosity of the IL. [48] Another great advantage is the designability of these compounds and the variation of their physical properties. They can

be modified and combined freely according to the specific requirement of their application and are therefore custom-made. As a result, the design of so-called energetic ionic liquids (EIL´s) becomes a new and vast research field.[49]

Based on the idea of replacing hydrazine and its derivatives with an energetic azide containing liquid or with azide containing ionic liquids, several compounds were chosen for synthesis and for testing them for their potential use as a hypergolic fuel with several oxidizers.

1.5 Organic azides

An azide is the anion (N_3^-) of hydroazic acid (HN_3) which is a highly explosive liquid. This azido group has an energy content of $290 - 365 \, KJ \, mol^{-1}$ and is therefore an energy rich moiety.[50] It decomposes with the release of nitrogen N_2. Since decades, the derived heavy metal salts have also been used in explosives, but they are controversial because of their high toxicity. Azide salts of strongly electropositive metals like sodium or barium are more stabilized and less explosive due to the presence of a linear, resonance stabilized symmetrical N_3^- anion. The bond length between the nitrogens of the azido anion are all equal with 1.18 Å.[51]

In covalent bonded azides, different mesomeric structures can be found. These are shown in Figure 4.
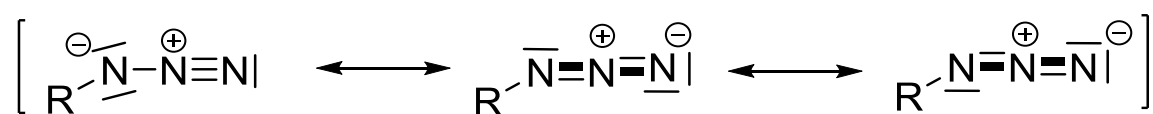
Figure 4: Mesomeric structures of an organic azide.

The binding angle between the nitrogens of organic azides was found to be almost linear with 172.5°.[52] The angle between the residue and the azido group was found to be 105° – 130°.[53]

The labelling of the three equivalent nitrogens in an organic azide signals is done as described in Figure 5 below, whereat the α-nitrogen is bonded to the organic residue followed by β and γ.

$$N\gamma \equiv N_\beta^{\oplus} - N_\alpha^{\ominus}$$
$$\underset{R}{\diagdown}$$
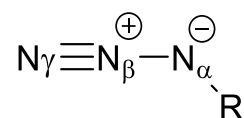
Figure 5: Labelling of nitrogen in azides.

Considering the electronic structure of covalent bonded azides in more detail, the difference in hybridization attracts attention. While the α-nitrogen is sp^2 hybridized, the β- and γ-nitrogens are sp hybridized. The π-bonding takes places between the middle nitrogen and the end nitrogen. The five p orbitals of the three nitrogen's build the molecular orbitals $\pi_y, \pi_y^n, \pi_y^*, \pi_x, \pi_x^*$ where the 14 valence electrons (16 in total minus the 2 electrons in σ_b of the R-N bonding) are allocated in $(\sigma_{bc})^2 (2s)^2 (\sigma_{ab})^2 (\pi_y)^2 (\pi_x)^2 (sp^2)^2 (\pi_y^n)^2$. Two electron excitations take place, one from the highest occupied orbital π_y^n to the highest unoccupied orbital π_x^* and the other from sp^2 to π_y^*. These transitions lead to a UV absorption band at around 290 nm (2870Å; weak) and 210 nm (2160Å; stronger). [54]

Since the discovery of the first organic azide by PETER GRIESS in 1864, the so called phenylazide[55], this class of compounds raised great attention. Azides are widely used in many fields of application[56] as in medicine, biology, material science or as energy density materials and propellants.

1.5.1 Synthesis of organic azides

Several routes[57] for the synthesis of organic azides are described in literature. The most convenient way is a halogen azide exchange reaction via the nucleophilic substitution (Sn2) mechanism with sodium azide as azide source. Since the azide is known as polyatomic analogue of halogens (pseudo halogen), the exchange reaction is an equilibrium reaction in which it must be pushed towards the product side with screening, e.g. using excess amount of sodium azide, individual reaction conditions and solvent. Another way is the conversion of an alcohol to azide via Mitsunobu reaction.[58] It is performed with triphenylphosine (PPh3) and an azodicarboxylate (DEAD or DIAD). Further, azides can also be formed with the use of silyl azides as azide donor. These reagents, like TMSN3 have no direct explosive characteristic, but hydrolyze after a period of time to hydrogen azide.[59]

Due to economic considerations, the cost-efficient, effective and common azide synthesis from commercially available alcohols via the halogen exchange reaction was carried out in this work.

1.5.2 ^{14}N NMR spectroscopy

A suitable method for structure determination is the ^{14}N NMR (nuclear magnetic resonance) spectroscopy, due to relative frequency of occurrence of the ^{14}N isotope of 99.6%. However the short relaxation time, caused by the electromagnetic quadrupole moment of $I = 1$ for the ^{14}N core, leads to broader signals in the spectrum.[60]

Since the α-nitrogen is bonded to the organic residue, it shows the lowest symmetry and shows therefore the broadest signal in ^{14}N NMR spectrometry. Sharp signals are only revealed from the β and γ nitrogen.[61]

The order of the signals appearing in the NMR spectrum depends on the residue of the organic substituent. Electron donating groups lead to an arrangement of N_α, N_γ and the highest frequented signal, which is the N_β. In comparison electron withdrawing substituents change the order to N_α, N_β, N_γ.[62]

1.5.3 IR spectroscopy

Another method for substance identification and the determination of the functional azido group is the infrared (IR) spectroscopy. The IR vibration bands for these covalent bonded azido groups appear as two signals. One appears as a strong signal at 2100 cm^{-1}. This signal can be allocated to the unsymmetrical N≡N stretching absorption band. On the other hand, the symmetric stretching shows up at lower frequencies of around 1200 cm^{-1}.[63]

1.6 Concept and goal

The goal of this work was to synthesize and investigate several liquid azido compounds and test them for their suitability as a fuel in hypergolic propellant formulation.

For a potential practical application, the propellant should fulfil several requirements. These requirements were stated in internal meetings, summarized and listed as "ideal" and "minimum requested" in Table 1.

The toxicity of the new fuel should be as low as possible; however, the allowed hazards include hazards as corrosive, explosive, oxidising, flammable and lower systemic health hazards. The reactivity, respectively the ignition delay time should ideally be under 10 ms, and preferably under 50 ms. As additional requirement, hypergolicity should preferably be achieved with hydrogen peroxide as oxidizer, since it is the greener alternative to the commonly used oxidizers, as described before. The price should not exceed 200 € per kg of fuel, including synthesis, handling and transportation requirements. The availability of the fuel should not be limited. At best, quantities of more than 10 tonnes per year should be available. The new fuel should ideally be storable for more than 15 years, and minimum of one year without decomposing. For transportation, no limits or maximum the standard limitations[64] for propellants should be valid. The specific impulse of the replacement candidate should be higher than 315 s. Here, the parameter of 10 bar and a nozzle expansion ratio of 300 should be used for the calculation. Ideally, no problems in compatibility with the COTS (commercial off-the-shelf) components should occur, but at least the fuel must be stable with stainless steel and polytetrafluoroethylene (PTFE). The liquidity should ideally be given in the temperature range from −15 °C to 150 °C, while the maximum should not surpass the range between 5 °C and 70 °C. The density should be at least be higher than 0.6 g cm⁻³ and the vapour pressure should be lower than 50 mbar, both defined at 25 °C. Ideally the compound should be insensitive towards friction and impact sensitivity, in which the terminal limitation of the sensitivity values must be done implicating the handling difficulty.

Table 1: Ideal and minimum requested propellant requirements.[65]

Property	Ideal	Minimum requested
Toxicity	Non-toxic, not affected by REACH	Low toxic, not affected by REACH
Hazard Classification	No hazards	Allowed: [66]
Reactivity	Hypergolic, ID < 10 ms	Hypergolic, ID < 50 ms
Price	< 20 € per kg	< 200 € per kg
Availability	Commercially available < 10 t per year	> 10 t per year via special manufacturing
Storability	> 15 a	> 1 a
Transport	No transport limitations (land, sea, air)	Standard (as for classical propellants)
Performance	> 323 s (pc = 10 bar, ε = 300)	> 315 s (pc = 10 bar, ε = 300)
Compatible materials	No limitations with COTS components	Stainless steel, PTFE
Temperature range	− 10° C < T < 150 °C	5° C < T < 70 °C
Density	> 1 g cm^{-3}	> 0.6 g cm^{-3}
Vapor pressure	≤ 50 mbar	≤ 200 mbar
Sensitivity	Not sensitive	tbc

1.7 General methods and characterisation

Caution! Organic azides are classified as environmentally toxic and highly explosive. They are sensitive towards mechanical stimuli like impact or friction. Therefore, every reaction involving them was carried out consciously under the appropriate security measures, including ear, hand and body protection. Although no difficulties in handling these energetic materials was experienced, small-scale use is always recommended.

Analytical Methods

Nuclear magnetic resonance (NMR) spectra were recorded using the following instruments: Bruker Avance III (400 MHz), JEOL Eclipse 270 and JEOL Eclipse 400. Regular glass NMR tubes (Ø 5 mm) were used for the measurements. The chemical shifts are listed in ppm relative to ^{1}H and ^{13}C external standard tetramethyl silane and ^{14}N standard MeNO$_2$ and as internal standard the deuterated solvents (CDCl$_3$, DMSO and D$_2$O).

Infrared analysis (IR) was performed on a PERKIN ELMER Spectrum BX-59343 instrument with a SMITHS DETECTION DuraSamplIR II Diamond ATR sensor and spectra were recorded from 4500 cm^{-1} to 650 cm^{-1}.
The absorption bands are reported in wavenumbers (cm^{-1}) and listed as "strong" (s), "medium" (m) and "weak" (w).

Elemental analyses of carbon, hydrogen and nitrogen content were carried on an Elementar Vario el by pyrolysis of the sample and subsequent analysis of the formed gases. Values for liquids are acceptable in a range of ±0.5 of the stated value. Due to measurement method, the determined nitrogen values are often lower than the calculated ones. This is very common, especially for nitrogen-rich compounds and cannot be avoided.

Decomposition temperatures (T_d) were measured via differential thermal analysis (DTA) with an OZM Research DTA 552-Ex instrument at a heating rate of 5 °C min^{-1} and in a range of room temperature to 400 °C. The sample was placed in an open glass tube and the release of heat measured against a reference sample of silica. The decomposition temperatures were

determined at the beginning point of the signal and not at the extrapolated onsets (second derivation of the curve) to achieve a better comparison since most signals are very broad.

The crystal structure was determined by single crystal X-ray diffraction on an Oxford Diffraction Xcalibur 3 diffractometer with a Sapphire CCD detector, four circle kappa platform, Enhance molybdenum Kα radiation source ($\lambda = 71.073$ pm) and Cryostream cooling unit of Oxford Cryosystems. Data collection and reduction were performed with CrysAlisPro.[67] The structures were solved with SIR-92[68], refined with SHELXL-97[69] and finally checked with PLATON[70], all embedded into the WinGX software suite[71]. With the use of checkCIF[72] the finalized CIF files were checked and deposited at the data base of Cambridge Crystallographic Data Centre.[73] Inter- and intramolecular contacts were analysed with Mercury.[74] The illustrations of molecular structures were drawn with ORTEP-3.[75]

Densitiy

Determinations of the densities were carried out using a 1 mL syringe and high precision scale (Excellence Analytical Balance XA204) from Mettler Toledo. The value was determined as average out of five measurements at 22 °C.

Sensitivities

The sensitivities of all synthesized compounds against impact and friction were determined according to BAM[76] (Bundesanstalt für Materialforschung und -prüfung) standards using a BAM drop hammer and a BAM friction apparatus.[77] The compounds were classified in compliance with UN guidelines.[78] For impact sensitivities, values are classified as follows: insensitive >40 J, less sensitive ≥35 J, sensitive ≥4 J, very sensitive ≤ 3 J; Friction sensitivities are: insensitive >360 N, less sensitive = 360 N, sensitive <360 N and >80 N, very sensitive ≤80 N, extremely sensitive ≤10 N. Measurement for sensitivities to electrostatic discharge (ESD) was not possible since all synthesized compounds were liquids.

2 Results and discussion

Within this chapter 2 the synthesis and characterisation of several potential liquid fuel candidates as a replacement for hydrazine and its derivatives are described. If the obtained energetic liquids are already known in the literature, the values received are compared to the literature and the compounds further characterized. In addition, their properties are investigated in more detail. For new compounds, so far unknown in literature, the optimized syntheses are described, the compounds are characterized, and their properties are determined like sensitivities, density or thermal stability.

The candidates are divided into four types of liquid compounds. Energetic azido liquids with carbon backbone are mentioned under section 2.1. Liquid azides with oxygen content are described under section 2.2 and several amino-azido liquids in section 2.3. In the fourth section, 2.5, describes the synthesis and characterisation of energetic salts and ionic liquids.

Chapter 3 covers the theoretical calculations of the structural optimization and for their energy content. In addition, the consequential calculated rocket specific parameters for the synthesized compounds are listed and compared to the requirements mentioned in section 1.6 above.

In chapter 4, the performed hypergolicity tests of the potential candidates with the two different oxidizers, hydrogen peroxide and dinitrogen tetroxide, are investigated. As part of these tests, the suitability of the fuels was studied. In addition, if necessary, the optimized additive for the fuel-oxidizer mixture was tested and the ignition delay time of the sample was determined.

Under chapter 5, the conclusion and outlook of the investigation of new energetic fuels as hydrazine replacement is given.

2.1 C-based azides

Two carbon based azides, an azide derivative of tetrol (ethane-1,1,2,2-tetrol) and the two diazidobutene isomers, were synthesized, further characterized and described in this chapter.

2.1.1 1,1,2,2-Tetraazidomethylethane

The synthesis route and characterisation of 1,4-diazido-2,3-bis(azidomethyl)butane (IUPAC, International Union of Pure and Applied Chemistry) is described, an unknown to literature and new compound. In dependence upon the frequently used name of the precursor, this compound is from now on called 1,1,2,2-tetraazidomethylethane, TAzME **4**.

2.1.1.1 Synthesis

The complete synthesis route to obtain TAzME **4** starting from diethyl malonate is shown in Scheme 1.
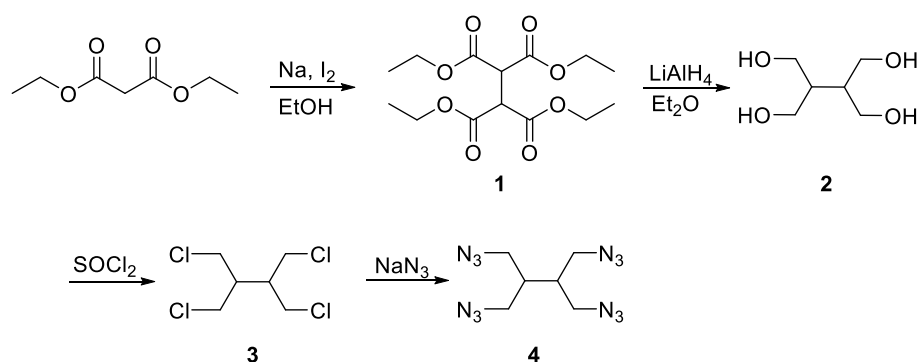
Scheme 1: Synthesis route towards 1,1,2,2-tetraazidomethylethane, TAzME 4.

As first step, an oxidative coupling of the α-carbon of two diethylmalonate molecules was carried out. For this coupling reaction sodium ethoxide was used as deprotonating agent, together with either bromine or iodine to obtain bis(diethylmalonate) (BDEM, **1**) as white needle-shaped crystals.[79] Since the work up of the reaction with bromine is more time-consuming due to the higher toxicity, and the yield with only 30% turned out to be conspicuously lower in comparison to 70% with the iodine route, using iodine is recommended.

Afterwards the desired alcohol precursor 1,1,2,2-tetrahydroxymethylethane, tetrol **2**, was obtained by a reduction of the ester **1** using LiAlH$_4$.[80] Within this reaction step several factors must be taken into account to improve the yield of **2**. On the one hand, only fresh opened LiAlH$_4$ leads to the desired product **2**, on the other hand the reaction solution must be purified with active charcoal, followed by recrystallisation of the crude material in methanol. If these steps are considered, compound **2** can be yielded in 64% as white solid. To continue, compound **2** was chlorinated using sulfuryl chloride and recrystallised from methanol to yield 1,1,2,2-tetrakis(chloromethyl)ethane, TClME **3**, as dark red crystals.[81]

The final reaction step was the halogen azide exchange reaction. Several solvents, like acetone, acetonitrile, water and DMF, different reaction conditions, reflux and room temperature (rt), and variations of the equivalents of sodium azide (4 eq till 12 eq) were tried to obtain 1,1,2,2-tetrakis(azidomethyl)ethane, TAzME **4.** With the reaction conditions of 50 °C for 24h in DMF and excess amount of sodium azide, the desired product **4** was identified among other by-products and first recorded in the NMR spectra. With these findings the reaction time was extended to 4 days to yield product **4** for the first time as yellowish liquid in an amount of 34%. It was further characterized below.

2.1.1.2 Characterisation

The ester **1** and the tetra alcohol **2** were analysed via ^{1}H, ^{13}C NMR spectroscopy in CDCl$_3$ and compared with the literature values.[80] The hydrogen signals of compound **1** can be assigned at 4.15 ppm and 1.20 ppm as multiplet and triplet for the ester and as a singlet at 4.06 ppm for the hydrogen at the tertiary carbons. ^{13}C NMR spectrum shows four signals, at 62.20 ppm and 14.08 ppm for the ethyl carbons, at 167.22 ppm appears the ester carbon and the signal at 51.59 ppm can be allocated for the tertiary carbons. The reduced product **2** shows the expected three hydrogen signals in the ^{1}H NMR spectrum at 3.96 ppm for the hydroxy group, a quartet at 3.45 ppm for the CH$_2$ hydrogens and a quintet at 1.64 ppm for the CH hydrogens. The two carbon signals in the ^{13}C NMR spectrum appear at 60.2 ppm (–CH$_2$OH) and 43.1 ppm (–CH–). All received signals are in accordance with the literature.

The chlorinated compound **3** was also compared to literature[81] via NMR spectroscopy and shows now the CH hydrogens at 2.29 ppm and the CH$_2$ hydrogens appear due to coupling at

3.90 ppm and 3.73 ppm. The carbon signals in the ^{13}C NMR are shifted to 43.2 ppm for the chlorinated carbons and 42.3 ppm for the tertiary carbons. All signals match the literature.

Product **4** was analysed by ^{1}H, ^{13}C and ^{14}N NMR spectroscopy in CDCl$_3$. In the ^{1}H NMR spectrum, the expected two signals can be assigned. The hydrogens of the methylene groups are shifted from 3.90 ppm and 3.73 ppm (compound **3**) to now 3.49 ppm and the signals for the protons of the tertiary carbons appear now at 1.91 ppm (2.29 ppm for **3**). The carbon signals in the ^{13}C NMR spectrum are shifted to 50.7 ppm for the azidated carbons and show up at 38.2 ppm for the tertiary carbons. The typical azide signals in the ^{14}N NMR spectrum appear at −133 ppm (sharp signal, N$_\beta$), −170 ppm (broad signal, N$_\gamma$) and −334 ppm (very broad signal, N$_\alpha$).

The compound was further identified by IR spectroscopy. The asymmetric azide vibration band can be observed as a strong signal at 2083 cm^{-1} and the symmetric vibration band at 1266 cm^{-1}.

For safety reasons the sensitivities towards impact and friction of **4** were determined and accordingly assigned to the UN recommendations on the transport of dangerous goods. In addition, the thermal stability was analysed by DTA measurement. The measured values are listed in Table 2.

Table 2: Sensitivities and decomposition temperature of tetraazide 4.

Compound	Impact sensitivity [J]	Friction sensitivity [N]	T$_d$ [°C]
TAzME 4	2	40	198

According to the UN guideline, the azido liquid **4** is classified as very sensitive in relation to impact and friction. While the sensitivity values are low, no difficulties in handling this compound were observed. However, caution must be strictly adhered to.

The decomposition temperature of **4** was measured at 198 °C. Compared to the methyl derivative 1,3-diazido-2,2-bis(azidomethyl)propane (T$_d$ = 201 °C) is has a slightly decreased stability.

2.1.2 Diazidobutenes

Both stereoisomers, the (Z)-1,4-diazidobut-2-ene (Z)-**6** and the (E)-1,4-diazidobut-2-ene (E)-**6**, were synthesized and characterized in more detail in this chapter.

2.1.2.1 Synthesis

(Z)-1,4-Diazidobut-2-ene, (Z)-**6**, was synthesized from 2–buten–1,4–diol via the chloro derivative, 1,4-dichlorobut–2–ene (Z)-**5**.[82] Reaction scheme is shown in Scheme 2. For the precursor (Z)-**5**, , the so called DARZENS[83] halogenation reaction pathway was used with thionyl chloride as a chlorination agent together with a few drops of pyridine as catalyst.[72] The desired product (Z)-**6** was then yielded by performing an azide halogen exchange reaction.
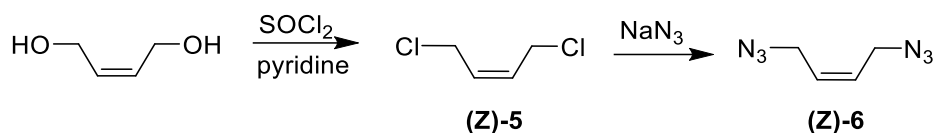
Scheme 2: Synthesis route of (Z)-diazidobutene, (Z)-6.

However, in the nucleophilic substitution of the chloro-derivative (Z)-**5,** an undesired side product is formed, the 2,3-dichlorobut-1-ene **5a**.[73] The expected reaction mechanism is shown in Scheme 3.
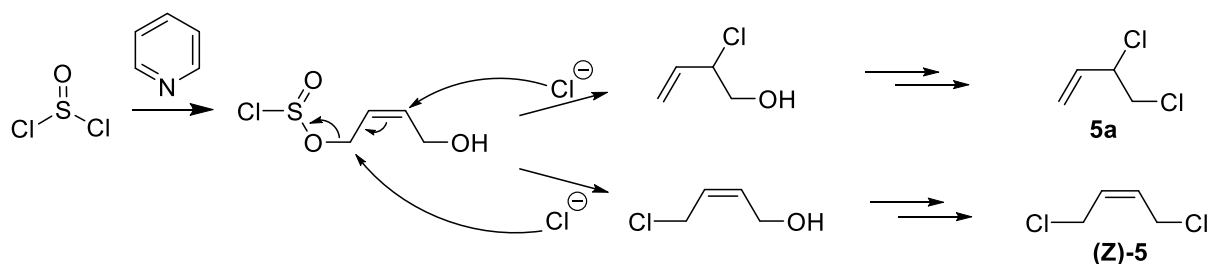
Scheme 3: Reaction mechanism of chlorination to 2-chloro-1,4-diol, (Z)-5, and side product 5a.

This side product **5a** is also formed in the literature instruction, but not further discussed there. After distillation (50 °C, 20 mbar) of the crude product, the desired product (Z)-**5** was yielded in 31% and in sufficient purity for further use for the subsequent azidation reaction.

This reaction was performed with a high excess of sodium azide in DMF. Various conditions during this azidation reaction lead also to various products in different ratios. Besides the desired product (Z)-**6**, also a formation of the side reaction towards 3,4-diazidobut-1-ene **6a**, comparable with the formation of **5a**, can be observed. Possible mechanisms are shown in Scheme 4.
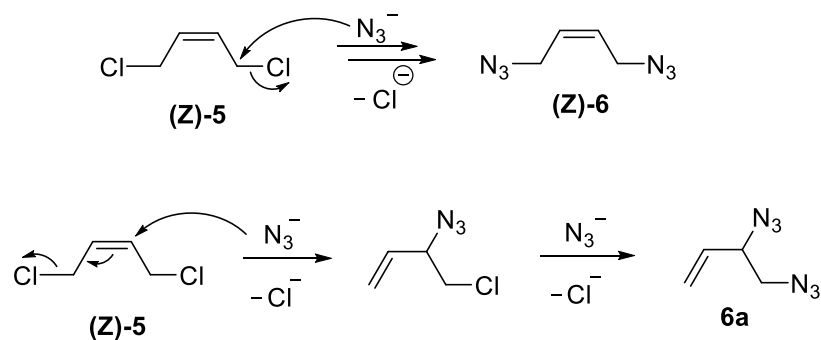
Scheme 4: Reaction mechanism towards 2-azido-1,4-diol, (Z)-6, and side product 6a.

Additionally, also the formation of the stereoisomer (E)-**6** is monitored. An exemplary NMR spectrum is pictured in Figure 6, referenced with CDCl₃.
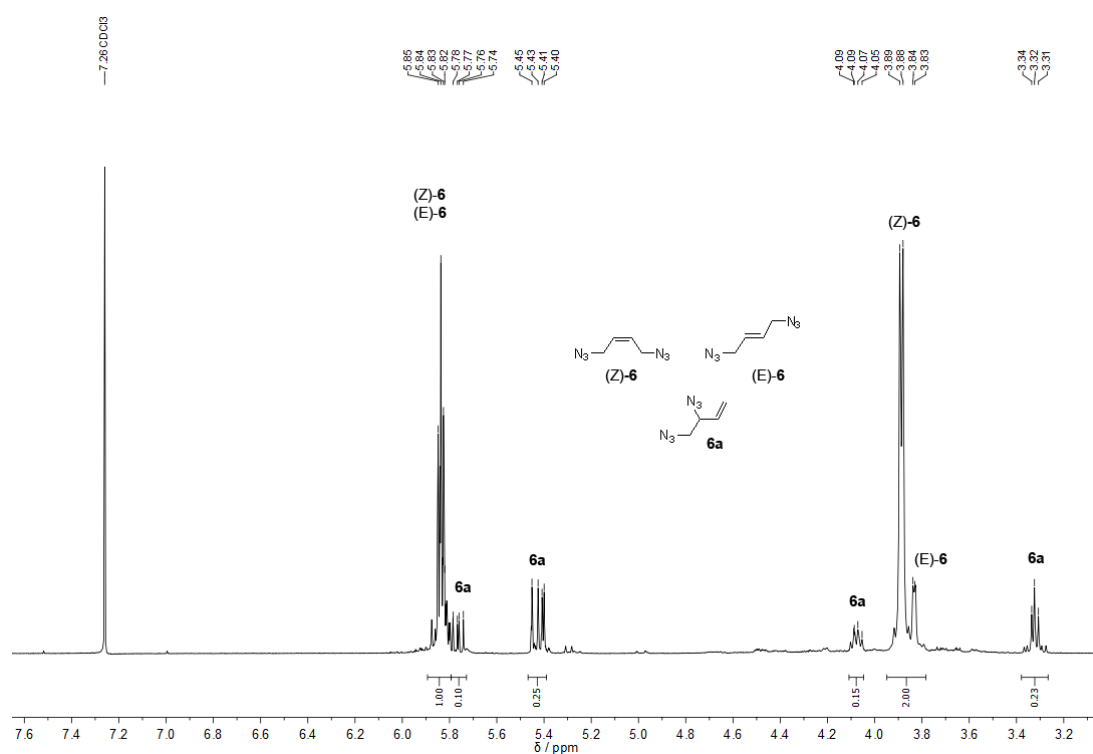
Figure 6: ¹H NMR spectrum of a (Z)-6 synthesis showing signals of (Z)-6, (E)-6 and 6a.

The longer the reaction time, the thermodynamically favoured and more stable compound (E)-**6** is formed. In 2-butene, the standard enthalpy of formation is at −7.89 kcal mol^{-1} for (E)-but-2-ene and at −7.10 kcal mol^{-1} for (Z)- but-2-ene.[84] Therefore performing the reaction with a short reaction time of only 30 min results in a higher yield of the kinetic and desired product (Z)-**6** with over 90% purity. With shorter reaction times, also less formation of the side product **6a** is observed in NMR spectrometry. Optimization of reaction time reduced the yield to less than 5%. Hence (Z)-1,4-diazidobut-2-ene, (Z)-**6,** was yielded as brown liquid in 92%.

On the other hand the thermodynamically stereoisomer (E)-diazidobutene, (E)-**6**, was synthesized from the bromo derivative 1,4-dibromobut-2-ene, displayed in Scheme 5.[85]
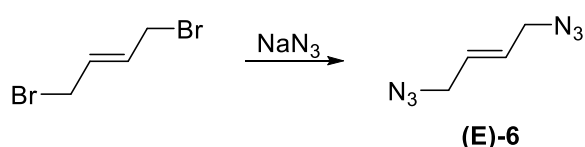
Scheme 5: Synthesis of (E)-diazidobutene, (E)-6.

The same trends like in the synthesis of the (Z)-isomer can be observed within this synthesis. A longer reaction time leads to an increased formation of (E)-**6**, but also the amount of the side product **6a** increases. An exemplary NMR spectrum is given in Figure 7. In comparison to the previously described (Z)-**6** synthesis (Figure 6) the difference in intensity of the azidated CH$_2$-groups of the two stereoisomers can be observed.
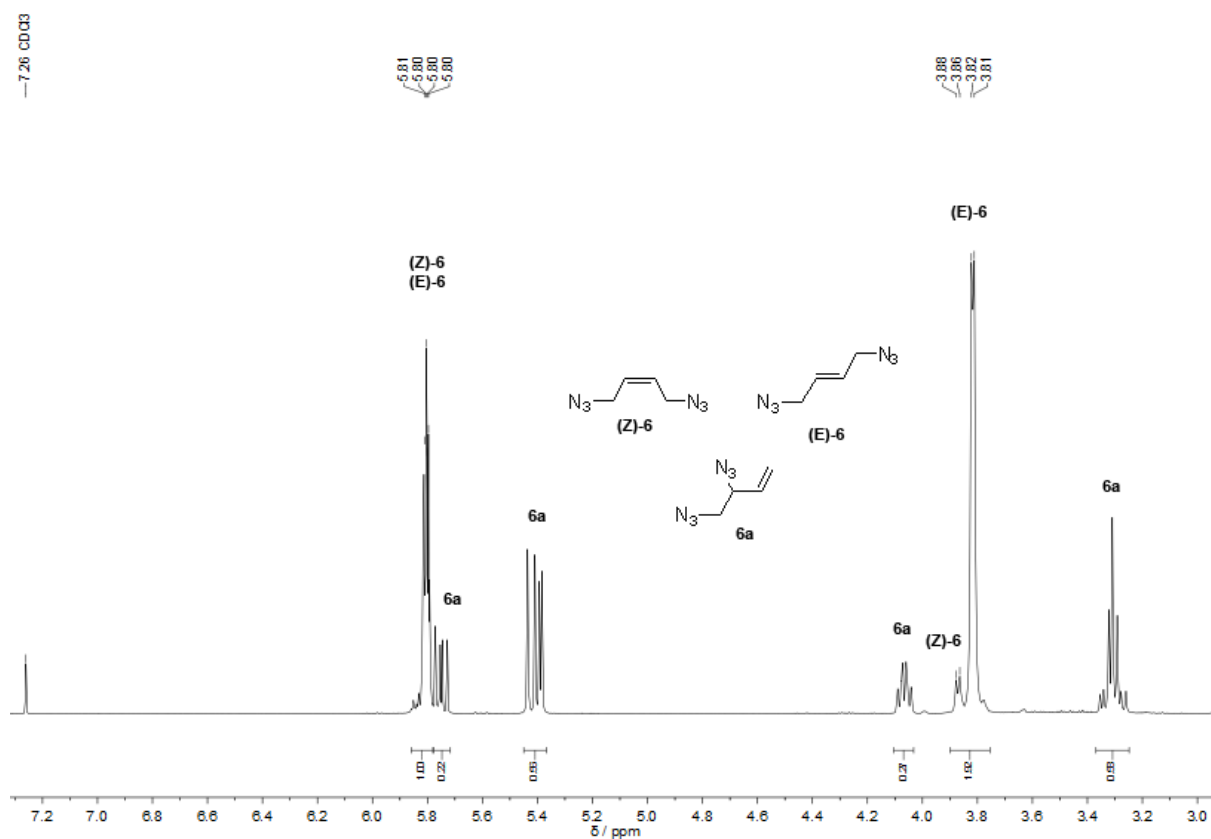
Figure 7: ¹H NMR spectrum of a (E)-6 synthesis showing signals of (Z)-6, (E)-6 and 6a.

Longer reaction time of several hours and optimisation raises the yield of (E)-isomer and sufficiently for further characterisation. (E)-**6** gave a yield in form of a brown liquid in 74%. The lower yield compared to (Z)-**6** can be explained by forming more side product by longer reaction time.

2.1.2.2 Characterisation

(Z)-**5** was identified via ¹H and ¹³C NMR spectroscopy. In the ¹H NMR the CH-signals appear at 5.84 ppm and the CH₂-hydrogens at 4.10 ppm. Carbon signals can be found in the ¹³C NMR at 43.2 ppm for the chlorinated carbon and 42.3 ppm for the alkene carbons. ¹H NMR analysis also suggests a formation of side product **5a** of around 10%. Distillation decreases the side product **5a** to approximately 1%.

The azidated isomers (Z)-**6** and (E)-**6** were also characterized via NMR spectroscopy.

Figure 6 and Figure 7 show the comparison of the shifting of the isomers (Z)-**6** and (E)-**6** and the side product **6a**. The hydrogen signals of the alkene-group appear at 5.84 ppm for both isomers and the CH-hydrogen at 3.89 ppm for (Z)-**6** and 3.83 ppm for of the isomers (E)-**6.**

The impact and friction sensitivities were determined, and the isomeric compounds classified according to UN guidelines. Thermal behaviour in relation to the decomposition temperature was investigated for the yielded batches for (E)-**6** and (Z)-**6**. Purity of the yielded products was around 90%. The values are listed in Table 3 below. Both isomers have the same decomposition temperature with 133 °C, which can be explained by the purity of only 90% and the presence of the isomer and side product. Both isomers are classified as very sensitive towards impact and friction due to the measured values. Because of this low sensitivity values and explosivity, distillation of these compounds is not recommended. Therefore, extreme care must be present while handling these compounds.

Table 3: Sensitivities and decomposition temperature of the diazidobutenes 6.

Compound	Impact sensitivity [J]	Friction sensitivity [N]	T_d [°C]
(Z)-diazidobutene (Z)-6	<1	40	133
(E)-diazidobutene (E)-6	<1	40	133

Densities of both batches of the yielded 1,4-diazidobut-2-enes were determined as average out of five-volume weight measurements as 1.13 g cm^{-3}.

2.1.4 Experimental part

Tetraethyl ethane-1,1,2,2-tetracarboxylate, BDEM 1

Sodium (6.60 g, 287 mmol, 1 eq) was dissolved in EtOH (150 mL) at 0 °C. A solution of diethyl malonate (46.0 g, 287 mmol, 1 eq) was added together with a solution of iodine (36.4 g, 143 mmol, 0.5 eq) in dry Et_2O. The resulting solution was allowed to warm up to room temperature and stirred for 1 h. Afterwards H_2O (150 mL) was added and the solution was extracted with Et_2O (3 x 50 mL). The combined organic phases were washed with saturated $Na_2S_2O_3$ solution (1 x 100 mL), H_2O (1 x 100 mL), Brine (1 x 100 mL) and dried over $MgSO_4$. The solvent was evaporated to 100 mL *in vacuo* and colourless needles of tetraethyl ethane-1,1,2,2-tetracarboxylate (35.3 g, 111 mmol, 77%) crystallized at 5 °C. **¹H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 4.20–4.10 (m, 8H, $-CH_2CH_3$), 4.06 (s, 2H, $-CH$) 1.20 (t, ^3J = 7.1 Hz, 12H, $-CH_3$). **¹³C NMR** (101 MHz, $CDCl_3$): δ (ppm) = 167.22 ($-COO$), 62.20 ($-CH_2$), 51.59 ($-CH$), 14.08 ($-CH_3$). $C_{14}H_{22}O_8$ (318.32 g mol^{-1}).

Ethane-1,1,2,2-tetrol, tetrol 2

To a suspension of $LiAlH_4$ (8.70 g, 229 mmol, 5 eq) in dry Et_2O (60 mL), a solution of tetraethyl ethane-1,1,2,2-tetracarboxylate (14.6 g, 45.9 mmol, 1 eq) in Et_2O (80 mL) was slowly added at 0 °C. The suspension was refluxed for 2 h and stirred at room temperature for additional 20 h. A mixture of H_2O (8.3 g, 460 mmol, 10 eq) and EtOH (30 mL) was carefully added and the pH value was adjusted to ~7 with conc. H_2SO_4. The resulting precipitate was filtered off and refluxed in H_2O (2 x 200 mL). The combined aqueous extracts were evaporated *in vacuo* to half of their volume. Activated charcoal was added to the mixture and stirred for 30 min under heating to 50–60 °C. After filtration the solvent was removed *in vacuo*. The crude product was recrystallized from methanol, yielding ethane-1,1,2,2-tetrol as colourless crystals (4.83 g, 31.9 mmol, 64%). **¹H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 3.96 (s, 4H, $-OH$), 3.49–3.41 (q, ^4J = 4.9 Hz, 8H, $-CH_2OH$), 1.64 (p, ^3J = 4.5 Hz, 2H, $-CH$). **¹³C NMR** (101 MHz, $CDCl_3$): δ (ppm) = 60.2 ($-CH_2OH$), 43.1 ($-CH$). $C_4H_{14}O_4$ (150.17 g mol^{-1}).

1,1,2,2-Tetrakis(chloromethyl)ethane, TClME 3

$SOCl_2$ (7.10 g, 59.7 mmol, 4.5 eq) was added dropwise to ethane-1,1,2,2-tetrol (2.00 g, 13.3 mmol, 1.0 eq) at 0 °C, followed by the careful addition of pyridine (0.20 g, 2.50 mmol, 0.2 eq). The mixture was stirred for 1 h at 90 °C. Ice was added to the reaction solution and the precipitate was filtered, washed with H_2O and dissolved in MeOH. Crystallization from MeOH yielded 1,1,2,2-tetrakis(chloromethyl)ethane (0.59 g, 2.59 mmol, 19%) as dark red crystals. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 3.90 (dd, J = 11.3 Hz, 3.1 Hz, 4H, $-CH_2Cl$), 3.73 (dd, J = 11.4 Hz, 6.2 Hz, 4H, $-CH_2Cl$), 2.34–2.25 (m, 2H, $-CH$). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) = 43.2 (CH_2Cl), 42.3 (CH). $C_4H_{10}Cl_4$ (223.95 g mol^{-1}).

1,1,2,2-Tetrakis(azidomethyl)ethane, TAzME 4

1,1,2,2-Tetrakis(chloromethyl)ethane (0.80 g, 3.50 mmol, 1 eq) was solved in DMF (15 mL) and NaN_3 (2.79 g, 42.9 mmol, 12 eq) was carefully added. The solution was stirred for 4 days at 50 °C. After completion of the reaction H_2O (20 mL) was added and the formed layers were separated. The aqueous phase was extracted with Et_2O (3 × 30 mL). The combined organic phases were washed with H_2O (3 x 30 mL) and brine (7 × 30 mL) and water (3 × 30 mL) to remove the residual DMF. After drying over $MgSO_4$, the solvent was removed *in vacuo* yielding 1,1,2,2-tetrakis(azidomethyl)ethane (0.31 g, 1.20 mmol, 34%) as yellowish oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 3.58–3.39 (m, 8H, CH_2N_3), 1.95–1.87 (m, 2H, CH). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) = 50.71 (CHN_3), 38.19 (CH). **^{14}N NMR** (29 MHz, $CDCl_3$): δ (ppm) = −133 (N_β), −170 (N_γ), −334 (N_α). **IR** (ATR): $\tilde{v}$ = 3346 (w), 2939 (w), 2518 (w), 2083 (s), 1451 (m), 1266 (s), 921 (m). $C_6H_{10}N_{12}$ (250.23 g mol^{-1}) **EA**: calcd. N 67.17, C 28.80, H 4.03%; found N 66.27, C 29.20, H 4.17%. **DTA** (5 °C min^{-1}): T_d = 198 °C. **Sensitives**: IS: 2 J, FS: 40 N.

(Z)-1,4-Dichlorobut-2-ene, (Z)-5

(Z)-1,4-Butenediol (5.00 g, 56.7 mmol, 1.0 eq) was cooled to 0 °C and $SOCl_2$ (20.3 g, 170 mmol, 3 eq) and pyridine (0.50 g, 6.30 mmol, 0.1 eq) were added. The mixture was refluxed for 1.5 h. After cooling down, ice was added, and the solution was extracted with EtOAc (3 x 100 mL). The combined organic phases were washed with brine (1 x 50 mL), dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude product (4.60 g, 36.8 mmol, 65 %) was further

purified by distillation (50 °C, 20 mbar), yielding (Z)-1,4-dichlorobutene (2.18 g, 17.4 mmol, 31%) as colourless liquid. **¹H NMR** (400 MHz, CDCl₃): δ (ppm) = 5.87–5.78 (m, 2H, –C*H*), 4.14–4.07 (m, 4H, –C*H*₂Cl). **¹³C NMR** (101 MHz, CDCl₃): δ (ppm) = 129.7 (–CH) 38.1 (–CH₂Cl). C₄H₆Cl₂ (124.99 g mol⁻¹). **EA**: calcd. C 38.44, H 4.84; found C 38.31, H 4.90.

(Z)-1,4-Diazidobut-2-ene, Z-DAzB 6

(Z)-1,4-Dichlorobut-2-ene (1.00 g, 8.00 mmol, 1 eq) was dissolved in DMF (12 mL) and NaN₃ (4.68 g, 72.0 mmol, 9 eq) was added. The mixture was stirred at 23 °C for 40 min. After the addition of H₂O (30 mL), it was extracted with EtOAc (3 x 50 mL). The combined organic phases were washed with H₂O (2 x 50 mL), Brine (5 x 50 mL) and dried over MgSO₄. The solvent was removed *in vacuo* yielding (Z)-1,4-diazidobutene (1.01 g, 7.30 mmol, 92%) as brown liquid. **¹H NMR** (400 MHz, CDCl₃): δ (ppm) = 5.85–5.80 (m, 2H, –C*H*), 3.89 (d, ^3J = 5.5 Hz, 4H, –C*H*₂N₃). **¹³C NMR** (101 MHz, CDCl₃): δ (ppm) = 127.9 (–CH), 47.1 (–CH₂N₃). **¹⁴N NMR** (29 MHz, CDCl₃): δ (ppm) = −133 (N$_\beta$), −167 (N$_\gamma$), −310 (N$_\alpha$). C₄H₆N₆ (138.13 g mol⁻¹). **DTA** (5 °C min⁻¹): T$_d$ = 133 °C. **Sensitivities**: IS: <1 J, FS: 40 N.

(E)-1,4-Diazidobut-2-ene, E-DAzB 6

(E)-1,4-Dibromobut-2-ene (1.00 g, 4.70 mmol, 1 eq) was dissolved in DMF (10 mL) and NaN₃ (1.22 g, 18.7 mmol, 4 eq) was added. The mixture was stirred at 80 °C for 3 h. After the addition of H₂O (30 mL), it was extracted with EtOAc (3 x 50 mL). The combined organic phases were washed with H₂O (2 x 50 mL), Brine (5 x 50 mL) and dried over MgSO₄. The solvent was removed *in vacuo* yielding (E)-1,4-diazidobutene (0.48 g, 3,5 mmol, 74%) as brown liquid. **¹H NMR** (400 MHz, CDCl₃): δ (ppm) = 5.82–5.79 (m, 2H, –C*H*), 3.83 (d, ^3J = 4.3 Hz, 4H, –C*H*₂N₃). **¹³C NMR** (101 MHz, CDCl₃): δ (ppm) = 128.1 (–CH), 52.0 (–CH₂N₃). **¹⁴N NMR** (29 MHz, CDCl₃): δ (ppm) = −133 (N$_\beta$), −168 (N$_\gamma$), −312 (N$_\alpha$). C₄H₆N₆ (138.13 g mol⁻¹). **DTA** (5 °C min⁻¹): T$_d$ = 133 °C. **Sensitivities**: IS: <1 J, FS: 40 N.

2.2 C-O-based azides

Within this chapter the synthesis of diazidoepoxybutane, several azidoalcohols and azido malonates, and their characterisations are described.

2.2.1 Diazidoepoxibutane

The synthesis towards 2,3-bis(azidomethyl)oxirane (DAZoB, **7**) was not described in literature before. During this work the synthesis and characterisation of **7** was successfully performed and is described below.

2.2.1.1 Synthesis

For this purpose the first attempts were executed, starting from previously described (Z)-1,4-diazidobut-2-ene, (Z)-**6**, with H_2O_2 and formic acid.[76] Several reaction conditions were tried, but using these reactants the desired product **7** could not be yielded. Therefore another synthesis route, described amongst others by SAMOSHIN[86], with the usage of *meta*-chloroperoxybenzoic acid (*m*CPBA) in dry DCM, was carried out. The synthesis route of the epoxide **7** is shown in Scheme 6 below.
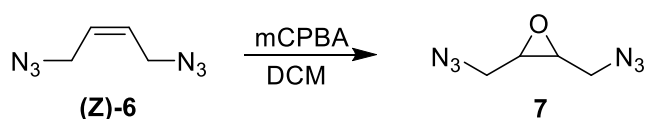
Scheme 6: Synthesis of 2,3-bis(azidomethyl)oxirane, DAzoB 7.

The oxidizing agent *m*CPBA was carefully added at 0 °C and afterwards the reaction solution allowed to slowly warm up to rt. Keeping this reaction condition for two days, DAzoB **7** was obtained as colourless liquid in 58% yield for further characterisation.

2.2.1.2 Characterisation

Compound **7** was analysed by ^1H, ^{13}C and ^{14}N spectroscopy in CDCl_3. In the ^1H NMR spectrum the hydrogens of the CH-group appear at 3.48 ppm and the hydrogens next to the azido group can be found at 3.25 ppm. As previously described, (Z)-**6** shows the signals at 3.88 ppm and 5.83 ppm. The two carbon signals can be observed at 54.05 ppm (CH) and 49.60 ppm (CH_2) and are shifted from 127.9 ppm (–CH) and 47.1 ppm (–CH_2N_3). In the ^{14}N

spectrum the characteristic azido signals appear at −134 ppm (sharp signal, N_β), −167 ppm (broad signal, N_γ) and −319 ppm (very broad signal, N_α).

The density of the epoxide was determined to 1.33 g cm^{-3} and increased in comparison to the densities of the diazidobutenes **6** with 1.13 g cm^{-3}.

For save handling the sensitivities towards impact and friction were measured and the compound categorised according to UN specifications. These values are listed together with the measured decomposition temperature in Table 4.

Table 4: Sensitivities and decomposition temperature of DAzoB 7.

Compound	Impact sensitivity [J]	Friction sensitivity [N]	T_d [°C]
DAzoB 7	2	160	173

Compound **7** is classified as very sensitive towards impact and as sensitive towards friction. In relation to impact, the compound requires caution. Friction sensitivity value is increased in comparison towards (E)-**6** and (Z)-**6**, listed in Table 3, which leads to a decrease in sensitivity and a safer handling of the compound.

2.2.2 Azidoalcohols

In addition, three azidoalcohols, 2-azidoethanol **8**, 1,3-diazidpropanol **9** and 2,3-diazidopropanol **10** were synthesized and further characterized. Their structure formulas are pictured in Figure 8 below.
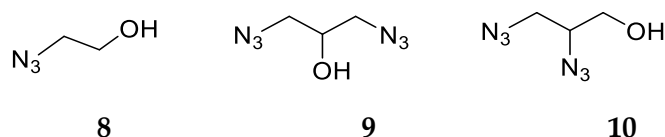
Figure 8: Structure formula of azidoethanol 8 and diazidopropanols 9 and 10.

Because of their liquidity and high energy content they were on the one hand tested itself for their property, on the other hand they were used as a starting material for the synthesis of further azido containing compounds.

2.2.2.1 Synthesis

The synthesis of 2-azidoethanol (AzEtOH, **8**) was carried out starting either from 2-chloroethanol or 2-bromoethanol using 2.5 eq sodium azide in water[87]. The reaction is shown in Scheme 7 below. At 85 € per Kg instead of around 280 € per 500 g for the 2-bromoethanol, the chloro-derivative is with the cheaper reactant.[88] Therefore considering economical aspects, mainly 2-chloroethanol was used for the synthesis of compound **8**.
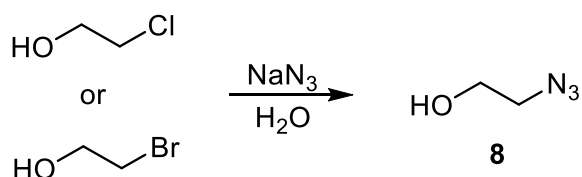
Scheme 7: Synthesis of 2-azidoethanol, AzEtOH 8.

Compound **8** was yielded as colourless oil in 81% and characterized in addition to literature in more detail.

For the synthesis of 1,3-diazido-propan-2-ol **9**, the same reaction conditions as for the synthesis of **8** were used together with 3 eq of sodium azide.[89] Starting from 1,3-dichloropropan-2-ol, the diazidated propanol can be obtained in 83% yield as colourless oily liquid, shown in Scheme 8.
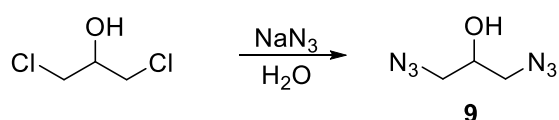
Scheme 8: Synthesis of 1,3-diazidopropan-2-ol, 1,3-DAP 9.

The synthesis of the constitution isomer 2,3-diazido-propan-1-ol, 2,3-DAP **10,** was carried out from the bromo-derivative, 2,3-dibromo-propan-1-ol[90]. Reaction scheme is shown below (Scheme 9).
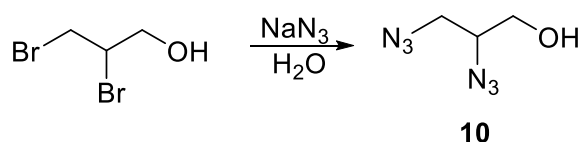
Scheme 9: Synthesis of 2,3-diazidopropan-1-ol, 2,3-DAP 10.

Within this synthesis of **10**, 2-bromoprop-2-en-1-ol, is formed as a side product.[91] It could be shown that a shorter reaction time lead to more formation of the undesired side product. Therefore, the azidation reaction was carried out overnight to reduce the amount of side product to approximately 15%. In the end the bromo allyl alcohol, shown in Scheme 10, can be fully removed while drying the product **10** under high vacuum.
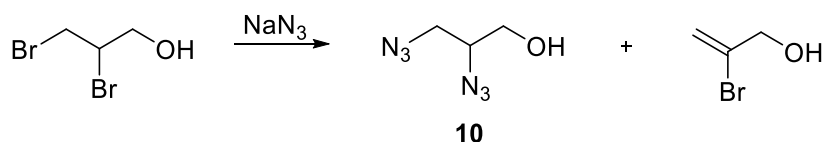
Scheme 10: Formed side product during synthesis of 2,3-DAP 10.

Hence, the yield of compound **10** is with only 61% clearly lower compared to the isomer **9**. All synthesized azidoalcohols **8**, **9** and **10**, were characterized in more detail in the next chapter.

2.2.2.2 Characterisation

^{1}H NMR spectra of **8** shows the expected three signals at 3.77 ppm for the CH_2-hydrogens next to the hydroxyl group, at 3.43 ppm for the ones next to the azido group and at 2.16 ppm for the hydroxyl hydrogen. In the ^{13}C NMR spectra, the two signals can be assigned at 61.6 ppm and 53.7 ppm. The typical azide signals appear in the ^{14}N NMR at −134 ppm (sharp signal, N_β), −171 ppm (broad signal, N_γ) and −319 ppm (very broad signal, N_α).

The product was further identified by IR spectroscopy. The asymmetric azide vibration band can be observed as a strong signal at 2092 cm^{-1} and the symmetric vibration band at 1284 cm^{-1}.

Moreover, an aquatic toxicity test to investigate the influence on the environment and the toxicity of AzEtOH **8** was performed. Within this test, an estimate of the ecological relevance and the possible effects on human health can be given. The test was carried out on a LUMIstox 300 made by the HACH LANGE GmbH (Düsseldorf, Germany) at 15 °C with the usage of liquid dried luminescent bacteria of Vibrio fischeri NRRL-B-11177 as strain. The Half maximal effective concentration (EC$_{50}$) value is the effective concentration for reducing the number of bacteria to half the original number. This value is determined by comparing

the reduction of luminescence to a nontoxic control. The toxicity level (incubation 30 min) is defined as: very toxic (−) < 0.10 g L^{-1}; toxic (o) 0.10–1.00 g L^{-1}; less toxic (+) > 1.00 g L^{-1}.[92] Since this method is just an initial screening test, a toxicity level of "non-toxic" cannot be determined.

The values for **8** are compared with sodium azide, ammonium azide and MMH in the Table 5 below.[93]

Table 5: Results on aquatic toxicity test for 2-azidoethanol 8.

Compound	EC_{50} (15 min) [g L^{-1}]	EC_{50} (30 min) [g L^{-1}]	Toxicity
NaN$_3$	0.25	0.18	o
NH$_4$N$_3$	0.26	0.15	o
MMH	6.00	5.89	+
AzEtOH 8	8.70	8.55	+

With the obtained values of this aquatic bacterium toxicity test AzEtOH can be defined as "less toxic" and seems to be much less critical towards the environment than for example sodium azide. The EC_{50} values for **8** are in addition higher than the values for MMH which indicates less toxicity.

The vapour pressure of 2-azidoethanol was measured by VEREVKIN in 2011 and was determined to be 0.664 mbar at 24.55 °C (297.7 K).[94]

The vapour pressures of the two diazidopropanols **9** and **10** were measured via the transpiration method and could be defined as 0.021 mbar for **9** and 0.012 mbar for compound **10** at 25 °C. Comparing this values with the high ones of hydrazine, MMH and UDMH mentioned in section 1.4, the synthesized azidoalcohols are plenty less volatile and show therefore less toxicity by inhalation.

Compound **9** was also identified via NMR and IR spectrometry. In the ^{1}H NMR, the three signals are at 3.93 ppm for the CH hydrogen, the CH$_2$ hydrogens appear as a broad multiplet at 3.60 ppm and the hydroxyl hydrogen at 3.00 ppm. ^{13}C NMR shows the two expected

signals at 69.5 ppm (CH_2-OH) and 53.8 ppm ($CH-N_3$). The azido signals appear at −136 ppm (sharp signal, N_β), −171 ppm (broad signal, N_γ) and −279 ppm (very broad signal, N_α).

In the measured IR spectrum, the azide vibration bands arise at 2088 cm^{-1} and 1264 cm^{-1}.

Compound **10** was identified via NMR and IR spectrometry as well. In the ^{1}H NMR, now four different signals appear, at 3.75 ppm for the hydrogen of CH-group, two multiplets of the two CH_2-groups at 3.65 ppm and 3.45 ppm and the hydroxyl hydrogen as singlet at 2.31 ppm. ^{13}C NMR shows three carbon signals at 62.8 ppm (CH_2-OH), 62.6 ppm ($CH-N_3$) and 51.7 ppm (CH_2-N_3). Due to the different azido groups, for this compound four azido signals appear at −134 ppm (sharp signal, N_β), −136 ppm (sharp signal, N_β), −170 ppm (broad signal, N_γ) and −277 ppm (very broad signal, N_α).

In the measured IR spectrum, the azide vibration bands arise at 2087 cm^{-1} and 1263 cm^{-1}.

For the three synthesized azidoalcohols, the sensitivities towards impact and friction were measured, as well as their decomposition temperatures. Afterwards, the compounds were categorized. The measured values are listed in Table 6 below.

Table 6: Sensitivities and decomposition temperatures of the azidoalcohols 8, 9 and 10.

Compound	Impact sensitivity [J]	Friction sensitivity [N]	T_d [°C]
AzEtOH 8	> 40	> 360	162
1,3-DAP 9	12.5	160	172
2,3-DAP 10	10	160	164

According to UN guideline 2-azidoethanol **8** is classified as insensitive towards friction and impact. Both diazidopropanols **9** and **10** are categorized as sensitive according to friction and impact. The decomposition temperatures are determined to 162 °C for **8**, 172 °C for **9** and 164 °C for **10.** The higher stability of **9** both towards thermal decomposition and sensitivity can probably be explained by the symmetry.

The densities of the compounds are defined by mass and volume to 1.15 g cm^{-3} for **8** and 1.26 g cm^{-3} for both diazidopropanols, **9** and **10**.

2.2.3 Azido malonates

In addition, further liquid azides derived from malonic acid with a high N-content were synthesized. Therefore, the synthesis was on the one hand focused on the geminal diazidation reaction and on the other hand of the derivatisation of the ester residue. Several paths for the synthesis of α-diazidation of especially malonic acid have been described in literature before. KIRSCH *et al.* suggested a rout involving IBX-SO$_4$K as a mild oxidant.[95] This route is very limited in effectivity due to the low yields of about 20% during the synthesis of IBX-SO$_4$K. A further method was published by KAMBLE *et al.* using NaIO$_4$.[96] Heating to 50 °C within this reaction is necessary. In another route, NaHCO$_3$ was used as a base and the reaction was performed with mild reaction conditions.[97]

2.2.3.1 Synthesis

With these mild reaction conditions and using NaHCO$_3$ as a base, showed in Scheme 11, dimethyl 2,2-diazidomalonate (DM-DAM, **11**) was yielded in shorter reaction time (4 h) and in a higher yield of 62%. In comparison the NaIO$_4$ route took twelve hours for a complete reaction and yielded only 50%.
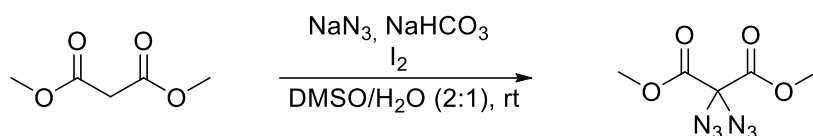
Scheme 11: Synthesis of dimethyl 2,2-diazidomalonate, DM-DAM 11.

The geminal diazidated ethyl analogue derived from diethylmalonate was also synthesized using the same reaction conditions, see Scheme 12. Here the yield was even improved to 81% in less reaction time instead of 61% with the NaIO$_4$ route. Hence diethyl 2,2-diazidomalonate (DE-DAM **12**) was yielded as colourless oil.
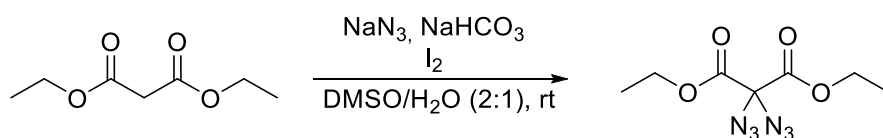
Scheme 12: Synthesis of diethyl 2,2-diazidomalonate, DE-DAM 12.

Considering the aspect of getting a higher energy content, the ester chains were exchanged by an energetic residue. Therefore, three azido malonic acid esters, pictured in Figure 9, were synthesized and characterized.

13 **14** **15**
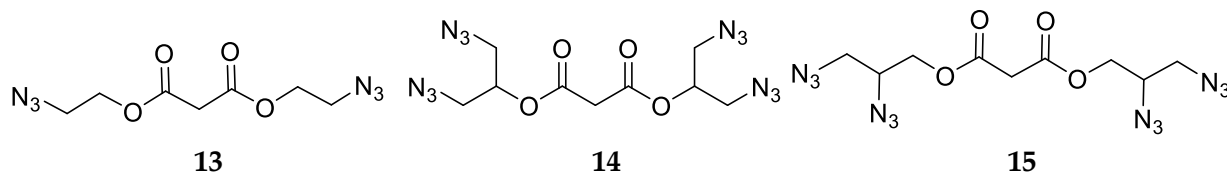
Figure 9: Structure formula of bis(2-azidoethyl) malonate (DAEM 13), bis(1,3-diazidopropyl) 2,2-diazidomalonate (b-1,3-DAPM 14) and bis(2,3-diazidopropyl) 2,2-diazidomalonate (b-2,3-DAPM 15).

The three products **13-15** could be yielded in two different ways.

A) First the esterification reaction can be executed with malonic acid and the respective chloro-alcohols to yield the chloro-esters. Then a chloride azide exchange reaction is performed to obtain the azido esters **13–15**.[98] The reaction steps are shown in Scheme 13.

$R_1 = C_2H_4OH$ (**8**) $R_1' = C_2H_4Cl$ $R_1'' = C_2H_4N_3$ (**13**)
$R_2 = C_3H_5OH$ (**9**) $R_2' = C_3H_5Cl_2,$ $R_2'' = C_3H_5N_6$ (**14**)
$R_3 = C_3H_5OH$ (**10**) $R_3' = C_3H_5Cl_2$ $R_3'' = C_3H_5N_6$ (**15**)
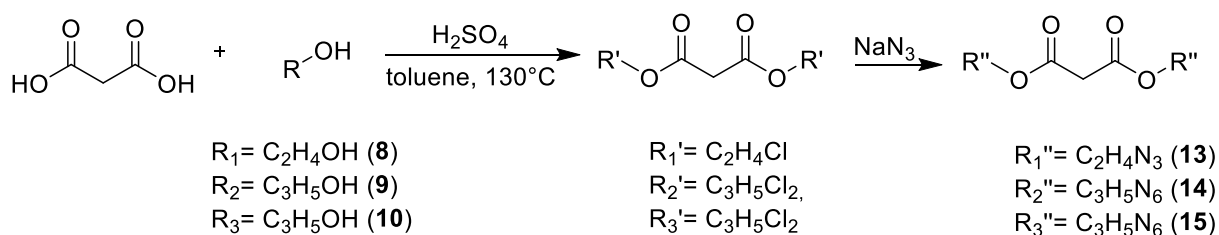
Scheme 13: Reaction scheme towards malonic azido esters via chlorination.

With this route the expected yields of 40% according to literature could not be achieved. Therefore, an alternative route via a direct coupling of previously synthesized azidoalcohols **8-10** was tried.

B) With the use of *N,N'*-dicyclohexylcarbodiimide (DCC) as coupling agent the synthesis of the azido esters was operated under mild reaction conditions.[99] By application of this reactant the desired products **13–15** could be obtained at around 60% yield, shown Scheme 14 and were characterized via NMR and IR spectroscopy.

R₁= C₂H₄OH (**8**)   R₁'= C₂H₄N₃ (**13**)
R₂= C₃H₅OH (**9**)   R₂'= C₃H₅N₆ (**14**)
R₃= C₃H₅OH (**10**)   R₃'= C₃H₅N₆ (**15**)
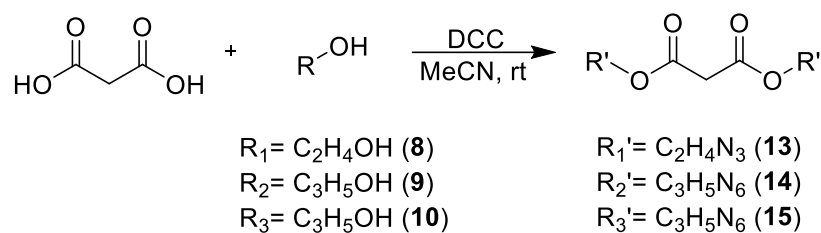
Scheme 14: Reaction scheme towards malonic azido esters via direct coupling with azido alcohols.

Proceeding from this synthesized azido malonic acid liquids **13–15** the α,α-diazidation reaction to the desired compounds **16–18** was performed. They are pictured in Figure 10 below.

16   **17**   **18**
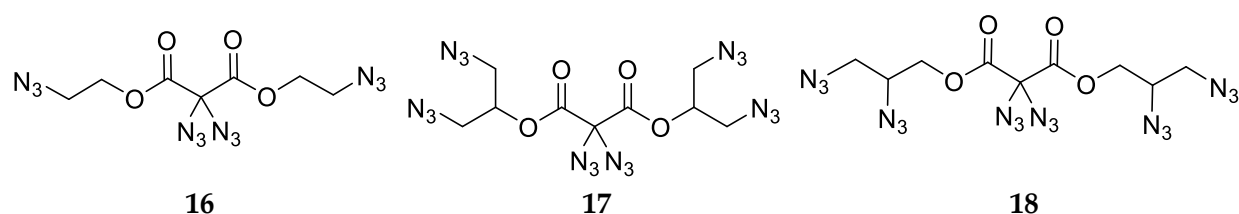
Figure 10: Structure formula of bis(2-azidoethyl) 2,2-diazidomalonate (DA-DAEM 16), bis(1,3-diazidopropyl) 2,2-diazidomalonate (DA-1,3-b-DAPM 17) and bis(2,3-diazidopropyl) 2,2-diazidomalonate (DA-2,3-b-DAPM 18).

However, neither with IBX-SO₄K nor with NaIO₄ the desired compounds, shown in Figure 10, could be obtained. The reaction was tried with milder conditions, using the previously described route with NaHCO₃. This lead to success and the compounds were synthesized for the first time in yields of 50–60%.[100] They have not been described in literature before and were characterized in detail within the next section.

2.2.3.2 Characterisation

Compound **11** was characterized by ^{1}H, ^{13}C and ^{14}N NMR and IR spectroscopy. In the ^{1}H spectrum the methyl hydrogens appear as singlet at 3.91 ppm. The carbon signals can be allocated in the ^{13}C spectrum at 164.1 ppm (CO_2Me), 80.1 ppm ($C(N_3)_2$) and 54.6 ppm (OCH_3). The azido signals appear at −141 (sharp signal, N_β), −155 (broad signal, N_γ), −310 (very broad signal, N_α).

The azide vibration bands appear at 2116 cm⁻¹ and 1228 cm⁻¹ in the measured IR spectrum.

The characterisation of the ethyl malonate **12** was also done with IR and NMR spectroscopy.

The expected two signals for the ethyl residue appear in the ^{1}H NMR spectrum as a quartet at 4.31 ppm for the CH$_2$ hydrogens and as a triplet at 1.28 ppm for the CH$_3$ hydrogens. Measured ^{13}C NMR spectrum showed four signals at 163.5 ppm (CO$_2$Et), 79.8 ppm (C(N$_3$)$_2$), 64.9 ppm (CH$_2$CH$_3$) and 13.9 ppm (OCH$_2$CH$_3$). The nitrogen signals show up in the ^{14}N NMR at −142 ppm (sharp signal, N$_\beta$), −156 ppm (broad signal, N$_\gamma$), −312 ppm (very broad signal, N$_\alpha$).

The measured IR spectrum showed the characteristic azide vibration bands as strong signals at 2119 cm^{-1} and 1226 cm^{-1}.

Azidoethyl ester **13** shows the three expected hydrogen signals in the measured ^{1}H NMR spectrum at 4.33 ppm and 3.52 ppm for the azidoethyl residue and the malonic acid singlet at 3.49 ppm. The four carbon signals appear at 166.0 ppm (COO−), 65.1 ppm (−CH$_2$O), 49.7 ppm (−CH$_2$N$_3$) and 41.2 ppm (−CH$_2$). The nitrogen signals show up at −134 ppm (N$_\beta$), −169 ppm (N$_\gamma$) and −319 ppm (N$_\alpha$) in the ^{14}N NMR spectrum.

The azide vibration bands appear as strong signals at 2101 cm^{-1} and 1731 cm^{-1} in the measured IR spectrum.

The vapour pressures of ester **13** was measured via the transpiration method and could be defined as 0.008 mbar.

The hydrogen signals for the symmetrical propanol ester **14** can be allocated at 5.05 ppm and 3.50 ppm for the propyl residue and at 3.33 ppm for the geminal hydrogens. Carbon signals appear at 165.1 ppm (COO−), 72.0 ppm (−CH), 50.6 ppm (−CH$_2$N$_3$) and 40.9 ppm (−CH$_2$) and the nitrogen signals in the ^{14}N NMR at −135 ppm (N$_\beta$), −170 ppm (N$_\gamma$) and −324 ppm (N$_\alpha$).

The hydrogen signals of the unsymmetrical propanol ester **15** appear in the measured ^{1}H NMR spectrum at 4.33 ppm and 4.25 ppm for the hydrogens of the −CH$_2$N$_3$ group, at 3.81 ppm for the CHN$_3$ hydrogen, the geminal hydrogens at 3.51 ppm and at 3.45 ppm for the CH$_2$. Carbon signals can be allocated in the ^{13}C NMR at 165.5 ppm (COO−), 63.7 ppm (−CH$_2$O), 59.6 ppm (−CHN$_3$), 51.6 ppm (−CH$_2$N$_3$) and 41.0 ppm (−CH$_2$). ^{14}N signals are at −135 ppm (N$_\beta$), −137 ppm (N$_\beta$), −169 ppm (N$_\gamma$) and −323 ppm (N$_\alpha$).

The characterisation of compounds **16–18** was done via ^{1}H, ^{13}C and ^{14}N NMR spectroscopy. The characteristically hydrogen signals at the geminal carbon disappear after the diazidation reaction in the ^{1}H NMR spectrum. Further, the diazidated carbon is then shifted in the ^{13}C NMR to around 80 ppm and the ^{14}N spectrum shows two different N_β signals due to the different surroundings of the azido groups.

For the diazidated azidoethyl ester **16** (DA-DAEM) now only two hydrogen signals for the ethyl residue in the ^{1}H NMR spectrum are left at 4.45 ppm and 3.57 ppm. Carbon signals are at 163.2 ppm (COO−), 66.2 ppm (−CH$_2$O), 49.4 ppm (−CH$_2$N$_3$) and the geminal diazidated carbon appears now at 80.0 ppm (before 65 ppm for **13**). In the ^{14}N NMR the nitrogens can be allocated at −134 ppm (N_β), −142 ppm (N_β), −170 ppm (N_γ) and −320 ppm (N_α).

As expected, the diazidated symmetric azido propanol ester **17** shows now only the hydrogen propyl signals in the ^{1}H NMR spectrum. They are at 5.15 ppm and 3.60 ppm. ^{13}C carbon signals appear at 162.5 ppm (COO−), 74.5 ppm (−CH), 53.8 ppm (−CH$_2$N$_3$) and the geminal diazidated carbon is shifted to 79.8 ppm (−C(N$_3$)$_2$). The nitrogen signals show up at −135 ppm (N_β), −143 ppm (N_β), −171 ppm (N_γ) and −320 ppm (N_α).

The isomeric compound **18** shows three hydrogen signals at 4.40 ppm, 3.85 ppm and 3.45 ppm with the integrals of 4:2:4. Carbon signals can be allocated at 163.0 ppm (COO−), 66.7 ppm (−CH$_2$O), 59.3 ppm (−CHN$_3$) and 51.4 ppm (−CH$_2$N$_3$) and the diazidated carbon at 80.1 ppm (−C(N$_3$)$_2$). In the ^{14}N NMR spectra the signals are at −135 ppm (N_β), −136 ppm (N_β), −142 ppm (N_β), −168 ppm (N_γ), and −327 ppm (N_α).

The densities of the synthesized diazidated azido malonates were determined to 1.49 g cm^{-3} for compound **16,** 1.51 g cm^{-3} for compound **17** and 1.50 g cm^{-3} for compound **18.** The values increase in comparison to the azido liquids **13–15**, with determined densities of 1.38 g cm^{-3} for **13**, 1.38 g cm^{-3} for **14** and 1.30 g cm^{-3} for **15**. The diazidated compounds **11** and **12** show densities of 1.24 g cm^{-3}, respectively 1.21 g cm^{-3}.

The sensitivities towards impact and friction were measured from the synthesized malonic acid azido esters and classified. In addition, the thermal stability was determined. All measured values are listed in Table 7 below.

Table 7: Sensitivities and decomposition temperatures of the azido malonates 11 - 18.

Compound	Impact sensitivity [J]	Friction sensitivity [N]	T_d [°C]
DM-DAM 11	3	60	161
DE-DAM 12	> 40	> 360	147
DAEM 13	> 40	> 360	191
b-1,3-DAPM 14	35	160	162
b-2,3-DAPM 15	35	160	162
DA-bAEM 16	1	36	158
DA-b-1,3-DAPM 17	< 1	36	136
DA-b-2,3-DAPM 18	< 1	36	136

Compound **11** has relatively low sensitivity values. According to the UN guideline, it is therefore classified as very sensitive towards friction and impact. In addition, it decomposes with a loud bang. In comparison, compounds **12** and **13** are classified as insensitive. Stability regarding to sensitivities of the geminal azido moieties seems stabilized through the ethyl residues in **12.** The decomposition temperature for **11** is determined at 161 °C and for **12** at 147 °C. Compound **13** is the most stable compound of the malonic azides regarding heat, with a decomposition temperature of 191 °C. The compounds with propyl residue **14** and **15** are less sensitive towards impact and sensitive according to friction. Their decomposition temperatures were ascertained as being 162 °C. As expected, the geminal diazidated compounds increase their sensitivity and are therefore classified as very sensitive. Therefore, extreme caution while handling these compounds must be applied. While **16** is relatively stable towards heat with a decomposition temperature of around 160 °C, the propyl ones **17** and **18** are less stable and decompose at 136 °C.

2.2.4 Unsuccessful attempts of generating more geminal diazides and a tetraazidoether

The syntheses of other geminal diazidated compounds and a tetraazidoether were tried among others during this work. Some of the attempts without a successful synthesis route are briefly described in the following chapter.

2.2.4.1 Diazidated glutarate ester

Another desired molecule was the diazido bisdiazidopropyl glutarate, shown in Scheme 15.
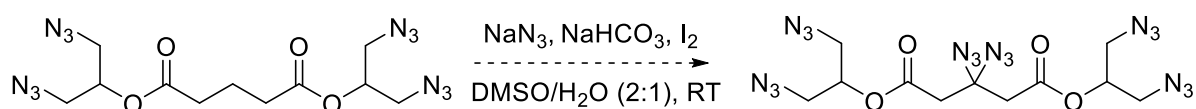
Scheme 15: Synthesis route towards diazido bisdiazidopropyl glutarate.

For trying the geminal diazidation reaction of azido glutarate, first the starting material bisdiazidopropyl glutarate **20** was synthesized from the respective chloro derivative. Bisdichloropropyl glutarate, 1,3-TClPG **19**, was obtained as colourless liquid in 71% yield via the esterification reaction using 2 equivalents of 1,3-dichloropropanol, 1 equivalent glutaric acid and a catalytic amount of sulfuric acid. The reaction is pictured in Scheme 16.[98]
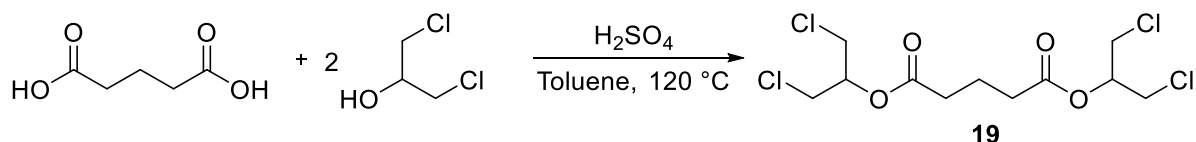
Scheme 16: Synthesis route towards dichloropropyl glutarate 19.

Based on compound **19** the chlorine azide exchange reaction was performed to yield bis(1,3-diazidopropan-2-yl) glutarate, 1,3-TAPG **20**, in over 70%. Compound **20** was characterized via NMR spectroscopy.
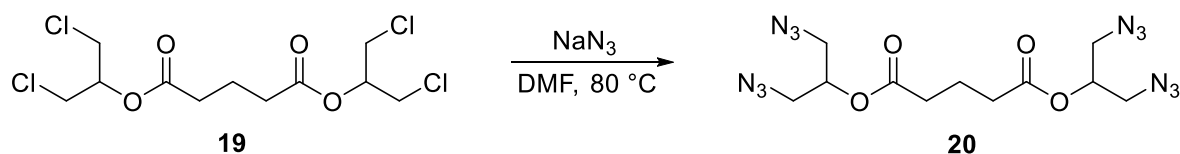
Scheme 17: Synthesis route towards Bis(1,3-diazidopropan-2-yl) glutarate 20.

A spectrum of ^{1}H NMR was measured, showing the quintet at 5.06 ppm (C*H*) and the doublet at 3.46 ppm (C) can be assigned to the diazidopropyl residue. Due to the intensities, the triplet at 2.46 ppm can be allocated to the α-CH$_2$ groups of the glutaric moiety, while the triplet at 1.99 ppm originates from the β-CH$_2$ hydrogens. In the ^{13}C NMR spectrum, the signal at 171.76 ppm was assigned to the carboxyl group. The tertiary carbon appears at 71.01 ppm, the methylene groups of the diazidopropyl residue appear at 50.91 ppm, the α-methylene groups show up at 32.89 ppm and the signal at 19.57 ppm can be assigned to the β carbon. In the ^{14}N spectrum the characteristic azide signals appear at −133 (sharp signal, N$_\beta$), −170 (broad signal, N$_\gamma$) and −326 (very broad signal, N$_\alpha$) ppm.

In addition, the sensitivities towards mechanical stimuli were determined. As a result, bis(1,3-diazidopropan-2-yl) glutarate **20** can be classified as insensitive according to UN guideline. The measured values are listed in Table 8.

Table 8: Sensitivities of bis(1,3-diazidopropan-2-yl) glutarate 20.

Compound	Impact sensitivity [J]	Friction sensitivity [N]
1,3-TAPG 20	40	160

Starting from 1,3-TAPG the geminal diazidation reaction was attempted, using NaHCO$_3$ and Iodine, pictured in Scheme 15 above. With these reaction conditions the desired product DA-1,3-TAPG could not be yielded. However, the acidity of the methylene groups in **20** was apparently not sufficient enough for a deprotonation by sodium hydrogen carbonate. NMR analysis showed only the starting material **20**.

2.2.4.2 Diazidation of acetylacetone

With the same reaction conditions, the geminal diazidation synthesis of acetylacetone was tried to yield 3,3-diazidopentane-2,4-dione. Within these reaction conditions, shown in Scheme 18, the desired product could not be obtained.
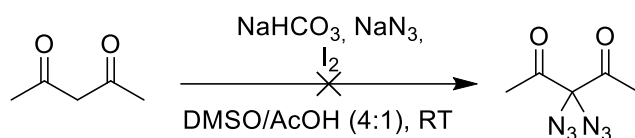
Scheme 18: Unsuccessful synthesis route towards 3,3-diazidopentane-2,4-dione.

2.2.4.3 Diazidation of tetramethoxypropane

Moreover, the synthesis towards 2,2-diazido-1,1,3,3-tetramethoxypropane was tried with three different reaction conditions and reactants. The first attempt was executed using the reaction conditions previously described by KIRSCH *et al.* with IBX-SO$_3$K and NaI in a DMSO-Water mixture.[95a] Second approach used NaIO$_4$ in DMSO and acetic acid[96], the third one was the mild condition route with NaHCO$_3$ in Water-DMSO and rt[97]. The conducted reactions are shown in Scheme 19.
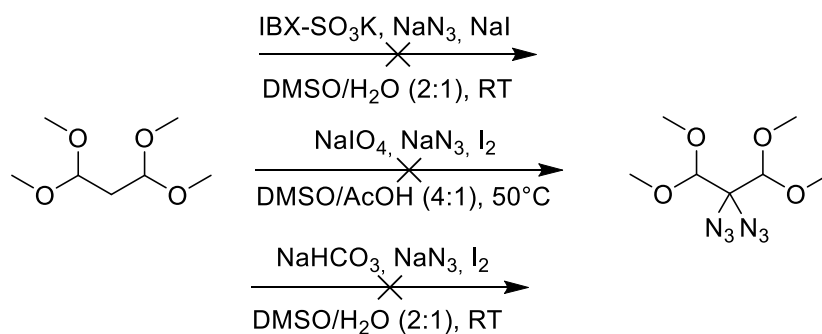
Scheme 19: Unsuccessful synthesis routes towards 2,2-diazido-1,1,3,3-tetramethoxypropane.

None of those routes could yield the desired diazidated compound, 1,1,3,3-tetramethoxypropane.

2.2.4.4 Tetraazidoether

In addition, the synthesis of 2,2'-oxybis-1,3-diazidopropanol was tried. Therefore, the synthesis of chloro-derivative staring from 1,3-dichloropropan-2-ol was attempted, at best followed by a chlorine azide exchange reaction, pictured in Scheme 20.

The synthesis route described by BLANCHARD was used, with sulfuryl chloride as reactant to generate a reactive intermediate and the use of a catalytic amount of pyridine as base to initially deprotonate the alcohol.[101]
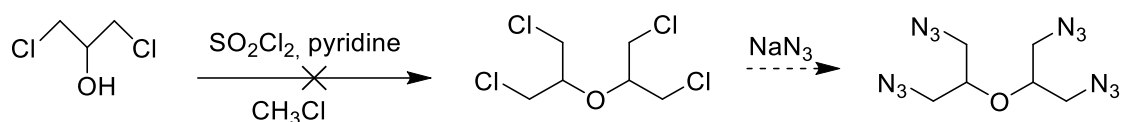
Scheme 20: Unsuccessful synthesis routes towards tetrazidopropylether.

Instead of the intended product, NMR evaluation showed that only the intermediate 1,3-dichloropropan-2-yl sulfurochloridate was yielded, shown in Figure 11.
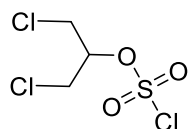
Figure 11: Intermediate 1,3-dichloropropan-2-yl sulfurochloridate.

Surprisingly, the originally as leaving group introduced chlorosulfonic acid moiety proved to be stable enough to remain bound to the molecule with the applied reaction conditions. Despite adding another equivalent of dichloropropanol after isolating, the intermediate could not yield the desired chloroether. Therefore, the further azidation reaction could not be executed.

2.2.5 Experimental part

Diazidoepoxybutane, DAzoB 7

M-chloroperoxybenzoic acid (1.75 g, 10.1 mmol, 1.4 eq) was carefully added at 0 °C to a solution of (Z)-1,4-diazobut-2-ene (1.00 g, 7.20 mmol, 1 eq) in dry dichloromethane (15 mL). The reaction mixture was stirred for 2 days at ambient temperature. Afterwards $CHCl_3$ (20 mL) and saturated Na_2CO_3 solution (20 mL) were added to the mixture and stirred for another 30 min. The organic layer was separated, washed with Na_2CO_3 solution (3 × 30 mL), dried over $MgSO_4$. The solvent was removed *in vacuo* to yield 2,3-epoxy-1,4-diazidobutane (0.64 g, 4.2 mmol, 58%) as colourless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 3.54–3.42 (m, 2H, CH_2CH), 3.28–3.23 (m, 4H, N_3CH_2CH). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) = 54.05 (CH), 49.60 (CH_2). **^{14}N NMR** (29 MHz, $CDCl_3$): δ (ppm) = −134 (N_β), −167 (N_γ), −319 (N_α). $C_4H_6N_6O$ (154.13 g mol^{-1}) **EA**: calcd. N 54.53, C 31.17, H 3.92%; found: N 51.23, C 33.27, H 4.26%. **DTA** (5 °C min^{-1}): T_d = 173 °C. **Sensitivities**: IS: 2 J, FS: 160 N.

Azidoethanol, AzEtOH 8

Sodium azide (14.6 g, 224 mmol, 1.5 eq) was added portion wise to a stirred mixture of 2-chloroethanol (12.0 g, 149 mmol, 1 eq) in H_2O (80 mL) at 0 °C. The reaction mixture was slowly warmed up to room temperature and stirred for another 4 h. Additional sodium azide (9.71 g, 149 mmol, 1 eq) was added and the solution was heated under reflux at 80 °C overnight. After completion, the mixture was extracted with Et_2O (3 x 50 mL) and the combined organic phases were washed with Brine (1 x 10 mL) and dried over $MgSO_4$. The solvent was removed *in vacuo* to yield a colourless oil (10.6 g, 121 mmol, 81%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 3.77 (q, 2H, CH_2−OH), 3.43 (t, 2H, CH_2−N$_3$), 2.16 (s, 1H, −OH). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) = 61.6 (CH_2−OH), 53.7 (CH_2−N$_3$). **^{14}N NMR** (29 MHz, $CDCl_3$): δ (ppm) = −134 (N_β), −171 (N_γ), −319 (N_α). **IR** (ATR): $\tilde{v}$ = 3347 (m), 2936 (w), 2280 (w), 2360 (w), 2340 (w), 2092 (s), 1653 (w), 1635 (w), 1441 (m), 1347 (m), 1284 (s), 1061 (s), 977 (m), 877 (m), 829 (m), and 667 (m). $C_2H_5N_3O$ (87.08 g mol^{-1}) **EA**: calcd. N 48.25, C 27.59, H 5.79 % found N 47.39, C 27.34 H 5.62 %. **DTA** (5 °C min^{-1}): T_d = 162 °C. **Sensitivities**: IS: >40 J, FS: >360 N.

1,3-diazidopropan-1-ol, 1,3-DAP 9

1,3-Dichloropropan-2-ol (5.00 g, 38.8 mmol, 1 eq) was stirred in H_2O (25 mL) at 0 °C while sodium azide (7.58 g, 116 mmol, 3 eq) was added portion wise. The reaction mixture was slowly warmed up to room temperature and stirred for another 4 h. Afterwards additional sodium azide (5.05 g, 77.5 mmol, 2 eq) was added and the reaction mixture was heated at 80 °C overnight. After completion, the mixture was extracted with Et_2O (3 x 50 mL) and the combined organic phases were dried over $MgSO_4$. The solvent was removed *in vacuo* to yield a colourless oil (4.58 g, 32.2 mmol, 83%). **¹H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 3.93 (q, 1H, −C*H*), 3.46–3.73 (m, 2H, −C*H*₂), 3.00 (s, 1H, −O*H*). **¹³C NMR** (101 MHz, $CDCl_3$): δ (ppm) = 69.5 (*C*H₂−OH), 53.8(*C*H−N₃). **¹⁴N NMR** (29 MHz, $CDCl_3$): δ (ppm) = −136 (N_β), −171 (N_γ), −279 (N_α). **IR** (ATR): $\tilde{\nu}$ = 3396 (m), 2930 (w), 2360 (w), 2340 (w), 2088 (s), 1653 (w), 1635 (w), 1442 (m), 1348 (m), 1264 (s), 1086 (m), 1021 (w), 942 (m), 919 (m), 899 (m), 872 (m), 838 (m), 667 (m). $C_3H_6N_6$ (142.1 g mol⁻¹) **EA**: calcd. N 59.13, C 25.35, H 4.26 %; found N 59.14, C 25.04, H 4.25 %. **DTA** (5 °C min⁻¹): T_d = 172 °C. **Sensitivities**: IS: 10 J. FS: 160 N.

2,3-diazidopropan-1-ol, 2,3-DAP 10

2,3-dibromopropan-1-ol (2.00 g, 9.18 mmol, 1 eq) was stirred in H_2O (10 mL) at 0 °C while sodium azide (1.91 g, 29.4 mmol, 3 eq) was added portion wise. The reaction mixture was slowly warmed up to room temperature and stirred for another 4 h. Afterwards additional sodium azide (1.19 g, 18.4 mmol, 2 eq) was added and the reaction mixture was heated at 80 °C overnight. After completion, the mixture was extracted with Et_2O (3 x 10 mL) and the combined organic phases were dried over $MgSO_4$. The solvent was removed *in vacuo* to yield a colourless oil (0.82 g, 5.74 mmol, 61%). **¹H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 3.75 (m, 1H), 3.70–3.61 (m, 2H), 3.51–3.40 (m, 2H), 2.31 (s, 1H, −O*H*). **¹³C NMR** (101 MHz, $CDCl_3$): δ (ppm) = 62.8 (*C*H₂−OH), 62.6 (*C*H−N₃), 51.7 (*C*H₂−N₃). **¹⁴N NMR** (29 MHz, $CDCl_3$): δ (ppm) = −134 (N_β), −136 (N_β), −170 (N_γ), −277 (N_α). **IR** (ATR): $\tilde{\nu}$ = 3375 (m), 2937 (w), 2882 (w), 2508 (w), 2359 (w), 2340 (w), 2087 (s), 1653 (w), 1636 (w), 1444 (m), 1334 (m), 1263 (s), 1042 (m), 970 (w), 929 (m), 896 (m), 827 (m), 667 (m). $C_3H_6N_6$ (142.1 g mol⁻¹) **EA**: calcd. N 59.13, C 25.35, H 4.26 %; found N 58.77, C 25.05, H 4.09 %. **DTA** (5 °C min⁻¹): T_d = 164 °C. **Sensitivities**: IS: 12.5 J. FS: 160 N.

Dimethyl 2,2-diazidomalonate, DM-DAM 11

Dimethylmalonate (0.50 g, 3.78 mmol, 1 eq) was dissolved in a mixture of DMSO/H_2O (2:1, 20 mL). Sodium hydrogen carbonate (1.27 g, 15.12 mmol, 4 eq), sodium azide (0.98 g, 15.12 mmol, 4 eq) and iodine (2.40 g, 9.45 mmol, 2.5 eq) were added to the solution followed by stirring for 4 h at room temperature. To quench the remaining iodine after completion of the reaction, a saturated solution of $Na_2S_2O_3$ was added until the observation of decolouring of the solution. H_2O (15 mL) was added and the reaction mixture was extracted with EtOAc (3 x 25 mL). The combined organic phases were washed with cold water (3 x 25 mL) and brine (3 x 25 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The product was yielded as colourless liquid (0.50 g, 2.30 mmol, 62%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 3.91 (s, 6H, –CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) = 164.1 (CO_2Me), 80.1 ($C(N_3)_2$), 54.6 (OCH_3). **^{14}N NMR** (29 MHz, $CDCl_3$): δ = −141 (N_β), −155 (N_γ), −310 (N_α). **IR** (ATR): $\tilde{v}$ = 2960 (w), 2359 (w), 2116 (s), 1755 (s), 1437 (m), 1366 (w), 1295 (w), 1228 (s), 1069 (m), 1046 (m), 1008 (w), 937 (w), 826 (w), 788 (m), 740 (w), 628 (w), 548 (m), 468 (w). $C_5H_6N_6O_4$ (214.14 g mol^{-1}) **EA**: calcd. N 39.25, C 28.04, H 2.82 %; found N 36.41, C 27.54, H 3.11 %. **DTA** (5 °C min^{-1}): T_d = 161 °C. **Sensitivities**: IS: 3 J, FS: 60 N.

Diethyl 2,2-diazidomalonate, DE-DAM 12

Diethylmalonate (1.00 g, 6.24 mmol, 1 eq) was dissolved in a mixture of DMSO/H_2O (2:1, 20 mL). Sodium hydrogen carbonate (2.10 g, 24.9 mmol, 4 eq), sodium azide (1.62 g, 24.9 mmol, 4 eq) and iodine (3.96 g, 15.6 mmol, 2.5 eq) were added to the solution followed by stirring for 4 h at room temperature. To quench the remaining iodine after completion of the reaction, a saturated solution of $Na_2S_2O_3$ was added until the observation of decolouring of the solution. H_2O (15 mL) was added and the reaction mixture was extracted with EtOAc (3 x 25 mL). The combined organic phases were washed with cold water (3 x 25 mL) and brine (3 x 25 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The product was yielded as colourless oil (1.27 g, 5.03 mmol, 81%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 4.31 (q, J = 7.1 Hz, 4H, –CH_2CH$_3$), 1.28 (t, J = 7.1 Hz, 6H, CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) = 163.5 (CO_2Et), 79.8 ($C(N_3)_2$), 64.9 (–CH_2CH_3), 13.9 (OCH_2CH_3). **^{14}N NMR** (29 MHz, $CDCl_3$): δ (ppm) = −142 (N_β), −156 (N_γ), −312 (N_α). **IR** (ATR): $\tilde{v}$ = 2987 (w), 2359 (w), 2340 (w),

2119 (s), 1754 (s), 1467 (w), 1447 (w), 1393 (w), 1369 (w), 1298 (m), 1226 (s), 1095 (m), 1066 (s), 1043 (s), 1016 (s), 854 (m), 822 (w), 770 (m), 739 (m), 667 (w). $C_7H_{10}N_6O_4$ (242.20 g mol^{-1}) **EA**: calcd. N 34.70, C 34.71 H 4.16 % found N 33.01, C 34.97 H 3.75 %. **DTA** (5 °C min^{-1}): T_d = 147 °C. **Sensitivities**: IS: >40 J, FS: >360 N.

Bis(2-azidoethyl) malonate, DAEM 13

Malonic acid (1.00 g, 9.61 mmol, 1 eq) was dissolved in acetonitrile (20 mL). 2-azidoethanol (1.67 g, 19.2 mmol, 2 eq) and DCC (3.97 g, 19.2 mmol, 2 eq) were added. The mixture was stirred for 30 min at ambient temperature. After completion the mixture was filtered through silica to remove the newly formed urea. The filtrate was washed with water (3 x 30 mL) and brine (3 x 30 mL). After removal of the solvent *in vacuo* the product was obtained as colourless oil (1.43 g, 5.89 mmol, 61%). **^{1}H NMR** (400 MHz, CDCl$_3$): δ (ppm) = 4.34–4.32 (m, 4H), 3.53–3.50 (m, 4H), 3.49 (s, 2H). **^{13}C NMR** (101 MHz, CDCl$_3$): δ (ppm) = 166.0 ($COO-$), 65.1 ($-CH_2O$), 49.7 ($-CH_2N_3$), 41.2 ($-CH_2$). **^{14}N NMR** (29 MHz, CDCl$_3$): δ (ppm) = −134 (N$_\beta$), −169 (N$_\gamma$), −319 (N$_\alpha$). **IR** (ATR): $\tilde{v}$ = 2957 (w), 2101 (s), 1731 (s), 1444 (w), 1412 (w), 1391 (w), 1353 (w), 1274 (m), 1224 (m), 1185 (m), 1144 (m), 1040 (m), 952 (w), 852 (w). $C_7H_{10}N_6O_4$ (242.2 g mol^{-1}) **EA**: calcd. N 34.70, C 34.71, H 4.16 %; found N 30.39, C 34.60, H 4.44 %. **DTA** (5 °C min^{-1}): T_d = 191 °C. **Sensitivities**: IS: >40 J. FS: >360 N.

Bis(1,3-diazidopropan-1-yl) malonate, b-1,3-DAPM 14

Malonic acid (1.00 g, 9.61 mmol, 1 eq) was dissolved in acetonitrile (10 mL). 1,3-diazido-propan- 2-ol (2.73 g, 19.2 mmol, 2 eq) and DCC (3.97 g, 19.2 mmol, 2 eq) were added. The mixture was stirred for 30 min at ambient temperature. After completion the mixture was filtered through silica to remove the newly formed urea. The filtrate was then washed with water (3 x 30 mL) and brine (3 x 30 mL). After removal of the solvent *in vacuo* the product was obtained as colourless oil (2.30 g, 6.55 mmol, 68%). **^{1}H NMR** (400 MHz, CDCl$_3$): δ (ppm) = 5.05 (dd, 2H), 3.53–3.43 (m, 8H), 3.34–3.32 (m, 2H). **^{13}C NMR** (101 MHz, CDCl$_3$): δ (ppm) = 165.1 ($COO-$), 72.0 ($-CH$), 50.6 ($-CH_2N_3$), 40.9 ($-CH_2$). **^{14}N NMR** (29 MHz, CDCl$_3$): δ (ppm) = −135 (N$_\beta$), −170 (N$_\gamma$), −324 (N$_\alpha$). $C_9H_{12}N_{12}O_4$ (352,28 g mol^{-1}) **EA**: calcd. N 47.71, C

30.69, H 3.43 %; found N 45.59, C 30.73, H 3.61 % **DTA** (5 °C min^{-1}): T_d = 162 °C. **Sensitivities**: IS: 35 J. FS: 160 N.

Bis(2,3-diazidopropan-1-yl) malonate, b-2,3-DAPM 15

Malonic acid (1.00 g, 9.61 mmol, 1 eq) was dissolved in MeCN (20 mL). 2,3-diazidopropanol (2.73 g, 19.2 mmol, 2 eq) and DCC (3.97 g, 19.2 mmol, 2 eq) were added. The mixture was stirred for 30 min at room temperature. After completion the mixture was filtered through silica to remove the newly formed urea. The filtrate was washed with water (3 x 30 mL) and brine (3 x 30 mL). After removal of the solvent *in vacuo* the product was obtained as colourless oil (2.06 g, 5.86 mmol, 61%). **^{1}H NMR** (400 MHz, CDCl$_3$): δ (ppm) = 4.36–4.30 (dd, 2H), 4.28–4.22 (dd, 2H), 3.81 (m, 2H), 3.51 (s, 2H), 3.47–3.40 (m, 4H). **^{13}C NMR** (101 MHz, CDCl$_3$): δ (ppm) = 165.5 (COO−), 63.7 (−CH_2O), 59.6 (−CHN_3), 51.6 (−CH_2N_3), 41.0 (−CH_2). **^{14}N NMR** (29 MHz, CDCl$_3$): δ (ppm) = −135 (N_β), −137 (N_β), −169 (N_γ), −323 (N_α). $C_9H_{12}N_{12}O_4$ (342.28 g mol^{-1}) **EA**: calcd. N 47.71, C 30.69, H 3.43 %; found N 46.53, C 30.95, H 3.47 % **DTA** (5 °C min^{-1}): T_d = 162 °C. **Sensitivities**: IS: 35 J. FS: 160 N.

Bis(2-azidoethyl) 2,2-diazidomalonate, DA-DAEM 16

Di-2-azidoethylmalonate (0.50 g, 2.06 mmol, 1 eq) was dissolved in a DMSO/H$_2$O mixture (2:1, 20 mL). Sodium azide (0.54 g, 8.26 mmol, 4 eq), sodium hydrogen carbonate (0.69 g, 8.26 mmol, 4 eq) and iodine (1.15 g, 4,54 mmol, 2.5 eq) were added. The mixture was stirred for 4 h at ambient temperature and after completion a saturated solution of Na$_2$S$_2$O$_3$ was added to quench the remaining iodine. H$_2$O (15 mL) was added and the mixture was transferred to a separation funnel. The mixture was extracted with EtOAc (3 x 50 mL), the combined organic phases were washed with cold water (3 x 50 mL) and brine (30 x 50 mL). The solution was dried over MgSO$_4$ and the solvent was removed *in vacuo*, to yield the product as yellowish oil (0.41 g, 1.28 mmol, 62%). **^{1}H NMR** (400 MHz, CDCl$_3$): δ (ppm) = 4.46–4.45 (m, 2H), 3.58–3.57 (m, 2H). **^{13}C NMR** (101 MHz, CDCl$_3$): δ (ppm) = 163.2 (COO−), 80.0 (−$C(N_3)_2$), 66.2 (−CH_2O), 49.4 (−CH_2N_3). **^{14}N NMR** (29 MHz, CDCl$_3$): δ (ppm) = −134 (N_β), −142 (N_β), −170 (N_γ), −320 (N_α). $C_7H_8N_{12}O_4$ (342.2 g mol^{-1}) **EA**: calcd. N

51.84, C 25.93, H 2.49 %; found N 51.72, C 26.28, H 2.60 % **DTA** (5 °C min^{-1}): T_d = 158 °C. **Sensitivities**: IS: 1 J. FS: 36 N.

Bis(1,3-diazidopropyl) 2,2-diazidomalonate, DA-b-1,3-DAPM 17

Bis(1,3-diazidopropan-1-yl) malonate (0.50 g, 1.42 mmol, 1 eq) was dissolved in a DMSO/H_2O mixture (2:1, 14 mL). Sodium azide (0.36 g, 5.68 mmol, 4 eq), sodium hydrogen carbonate (0.48 g, 5.68 mmol, 4 eq) and iodine (0.90 g, 3.53 mmol, 2.5 eq) were added. The mixture was stirred for 4 h at room temperature and after completion a saturated solution of $Na_2S_2O_3$ was added to quench the remaining iodine. H_2O (15 mL) was added and the mixture was extracted with EtOAc (3 x 50 mL). The combined organic phases were washed with cold water (3 x 50 mL) and brine (3 x 50 mL). The solution was then dried over $MgSO_4$ and the solvent was removed *in vacuo*, to yield the product as yellowish oil (0.27 g, 0.69 mmol, 49%). **^{1}H NMR** (400 MHz, CDCl$_3$): δ (ppm) = 5.19–5.12 (m, 2H), 3.67–3.52 (m, 8H). **^{13}C NMR** (101 MHz, CDCl$_3$): δ (ppm) = 162.5 (COO−), 79.8 (−C(N$_3$)$_2$), 74.5 (−CH), 53.8 (−CH$_2$N$_3$). **^{14}N NMR** (29 MHz, CDCl$_3$): δ (ppm) = −135 (N$_\beta$), −143 (N$_\beta$), −171 (N$_\gamma$), −320 (N$_\alpha$). C$_9$H$_{10}$N$_{18}$O$_4$ (434.30 g mol^{-1}) **EA**: calcd. C 24.89, H 2.32 %; found C 25.55, H 2.52 % **DTA** (5 °C min^{-1}): T_d = 136 °C. **Sensitivities**: IS: <1 J. FS: 36 N.

Bis(2,3-diazidopropyl) 2,2-diazidomalonate, DA-2,3-b-DAPM 18

Bis(2,3-diazidopropan-1-yl) malonate (0.50 g, 1.42 mmol, 1 eq) was dissolved in a DMSO/H_2O mixture (2:1, 14 mL). Sodium azide (0.36 g, 5.68 mmol, 4 eq), sodium hydrogen carbonate (0.48 g, 5.68 mmol, 4 eq) and iodine (0.90 g, 3.53 mmol, 2.5 eq) were added. The mixture was stirred for 4 h at ambient temperature and after completion a saturated solution of $Na_2S_2O_3$ was added to quench the remaining iodine. H_2O (15 mL) was added and the mixture was extracted with EtOAc (3 x 50 mL). The combined organic phases were washed with cold water (3 x 50 mL) and brine (3 x 50 mL). The solution was then dried over $MgSO_4$ and the solvent was removed *in vacuo*, to yield the product as yellowish oil (0.31 g, 0.72 mmol, 51%). **^{1}H NMR** (400 MHz, CDCl$_3$): δ (ppm) = 4.48–4.35 (m, 4H), 3.88–3.83 (m, 2H), 3.52–3.44 (m, 4H). **^{13}C NMR** (101 MHz, CDCl$_3$): δ (ppm) = 163.0 (COO−), 80.1 (−C(N$_3$)$_2$), 66.7 (−CH$_2$O), 59.3 (−CHN$_3$), 51.4 (−CH$_2$N$_3$). **^{14}N NMR** (CDCl$_3$): δ (ppm) = −135 (N$_\beta$), −136 (N$_\beta$), −142

(N$_\beta$), −168 (N$_\gamma$), −327 (N$_\alpha$). C$_9$H$_{10}$N$_{18}$O$_4$ (434.30 g mol^{-1}) **EA**: calcd. C 24.89, H 2.32 %; found C 25.40, H 2.43 %. **DTA** (5 °C min^{-1}): T$_d$ = 136 °C. **Sensitivities**: IS: <1 J. FS: 36 N

Bis(1,3-dichloropropan-2-yl) glutarate, 1,3-TClPG 19

Glutaric acid (2.00 g, 15.14 mmol, 1 eq) and 1,3-dichloropropan-2-ol (3.91 g, 30.28 mmol, 2 eq) were dissolved in toluene (50 mL). Conc. H$_2$SO$_4$ (0.5 mL) was added and the solution was refluxed under constant removal of nascent water via dean-stark conditions at 120 °C for 2 h. The mixture was washed with H$_2$O (3 x 50 mL) and brine (1 x 50 mL), dried over MgSO$_4$ and the solvent was removed *in vacuo*, yielding bis(1,3-dichloropropan-2-yl) glutarate (3.81 g, 10.75 mmol, 71%) as colourless liquid. **^{1}H-NMR** (400 MHz, CDCl$_3$): δ (ppm) = 5.19 (q, 2H, OCH(CH$_2$Cl)$_2$), 3.73 (dd, 2.3 Hz, 8H, CH_2Cl), 2.47 (t, 4H, OOCCH_2), 1.99 (q, 2H, CH$_2$CH_2CH$_2$). **^{13}C-NMR** (101 MHz, CDCl$_3$): δ (ppm) = 171.79 (COO), 71.91 (OCH(CH$_2$Cl)$_2$), 42.54 (CH$_2$Cl), 33.01 (OOCCH$_2$), 19.96 (CH$_2$$CH_2CH_2$). C$_{11}H_{16}Cl_4O_4$ (354.05 g mol^{-1}).

Bis(1,3-diazidopropan-2-yl) glutarate, 1,3-TAPG 20

Bis(1,3-dichloropropan-2-yl) glutarate (1.67 g, 4.72 mmol, 1 eq) was dissolved in DMF (15 mL). Sodium azide (1.84 g, 28.30 mmol, 6 eq) was added at 0 °C. The mixture was stirred at 23 °C for 3 h and sodium azide (1.23 g, 18.92 mmol, 4 eq) was added. It was further stirred at 80 °C for 24 h. H$_2$O (30 mL) was added and the mixture was extracted with EtOAc (3 x 50 mL). The combined organic extracts were washed with H$_2$O (1 x 50 mL), Brine (3 x 50 mL) and dried over MgSO4. The solvent was removed *in vacuo*, yielding bis(1,3-diazidopropan-2-yl) glutarate (1.33 g, 3.50 mmol, 74%) as colourless liquid. **^{1}H-NMR** (400 MHz, CDCl$_3$): δ (ppm) = 5.06 (q, 2H, OCH(CH$_2$N$_3$)$_2$), 3.46 (dd, 1.2 Hz, 8H, CH_2N$_3$), 2.46 (t, 4H, OOCCH_2), 1.99 (q, 2H, CH$_2$CH_2CH$_2$). **^{13}C-NMR** (101 MHz, CDCl$_3$): δ (ppm) = 171.76 (COO), 71.01 (OCH(CH$_2$N$_3$)$_2$), 50.91 (CH$_2$N$_3$), 32.89 (OOCCH$_2$), 19.57 (CH$_2$$CH_2CH_2$). **^{14}N NMR** (CDCl$_3$): δ (ppm) = −133 (N$_\beta$), −170 (N$_\gamma$), −326 (N$_\alpha$). C$_{11}H_{16}N_{12}O_4$ (380.33 g mol^{-1}). **Sensitivities**: IS: 40 J. FS: 160 N.

2.3 C-N-based azides

In this chapter the syntheses of several amino azido liquids are described, the received compounds are compared with literature and characterized in more detail. The chapter is divided into syntheses of secondary amines, tertiary amines and unsuccessful syntheses of amino azido liquids.

2.3.1 Secondary amines

In general: the synthesis of the secondary amino azido liquids is carried out with the chlorination reaction of the respective and commercially available amino alcohols using thionyl chloride as reactant in DCM, followed by an azide exchange reaction with sodium azide in water.[102] Excess thionyl chloride is quenched with methanol after completion of the reaction.

Since the explosivity of amines with azido-methyl residue is described in literature[103], within this thesis only amines with azido-ethyl residue were synthesized and characterized according to their stability.

2.3.1.1 Synthesis

The reaction scheme via the hydrochloride salt towards 2-azido-*N*-methylethan-1-amine, AzEMA **22,** is shown in Scheme 21.
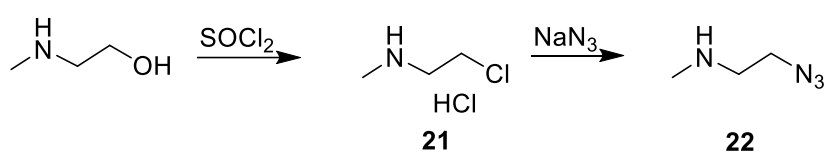
Scheme 21: Synthesis route towards 2-azido-*N*-methylethan-1-amine, AzEMA 22.

While the hydrochloride salt 2-chloro-*N*-methylethan-1-amine **21** was yielded in an almost quantitative yield of 96%, the following chlorine azide exchange reaction lead only to a yield of 56% of compound **22** as a brown sticky oil**.** This lower yield can be explained since the chlorination reaction forms the chlorohydride salt of **21**. To yield compound **22** as a free base, the desalination of the solution must be performed, basifying with sodium hydroxide.

Beside the methylamino azide, also the ethyl derivative 2-azido-*N*-ethylethan-1-amine, AzEEA **24**, was synthesized according to following reaction.
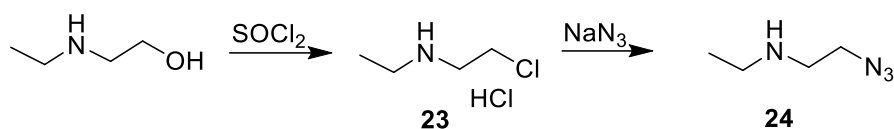
Scheme 22: Synthesis route towards 2-azido-*N*-methylethan-1-amine, AzEEA 24.

During this reaction the same trends as in the synthesis of the methyl derivative can be observed. While the chlorination reaction towards **23** was executed in 99% yield, azido compound **24** was obtained in a lower yield of 55%. The azido liquid **24** was also yielded as a brown sticky oil.

As a third secondary amino liquid the synthesis of bis(2-azidoethyl)amine, DAzEA **26**, was carried out according to Scheme 23.
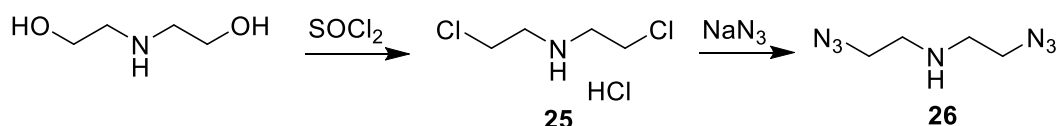
Scheme 23: Synthesis route towards bis(2-azidoethyl)amine, DAzEA 26.

For this reaction diethanolamine was converted with 5 eq of thionyl chloride to the chlorohydrate salt of bis(2-chloroethyl)amine, **25**. It was obtained as white solid in 76% yield. The following azide exchange reaction yielded the desired amino azido liquid **26** as a brown oil in 46%.

The received secondary azido amino liquids **22**, **23** and **26** were characterized using several methods. Using NMR spectroscopy, the resulted NMR shifts were compared to the starting materials and the literature values.[102, 104] The salts of secondary amines can be detected in the NMR by showing a strong characteristic IR vibration band between 1620 to 1560 cm^{-1} in the protonated form.[105]

2.3.1.2 Characterisation

The shifts of azidomethylamine **22** were additionally compared to the shifts of the chloro derivative **21.** The ^{1}H NMR spectrum of compound **21** showed four signals in *d*$_6$-DMSO.

They appear at 9.34 ppm as a broad signal for NH, at 3.93 ppm as a triplet, which can be allocated for the two hydrogens at the CH_2 group next to the chlorine, as another triplet at 3.27 ppm for the NCH_2 hydrogens and as a singlet at 2.55 ppm for the hydrogens of the methyl group. ^{13}C NMR spectrum shows three signals at 49.17 ppm for the CH_2N carbon, at 40.19 ppm for the carbon next to the chloride (CH_2Cl) and at 32.36 ppm for the methyl carbon.

For the azidated compound **22** the NMRs were measured in $CDCl_3$. The hydrogen signals appear as expected as two triplets and one singlet at 3.42 ppm, 2.77 ppm and 2.46 ppm (s). In the ^{13}C spectrum the signals are now shifted to 51.33 ppm (CH_2N), 50.63 ppm (CH_2N_3) and 36.25 ppm (CH_3). These signals match with the literature spectra.[102] The azide signals in the additionally measured ^{14}N NMR can be allocated at 133 ppm (sharp signal, N_β), −171 ppm (broad signal, N_γ) and −314 ppm (very broad signal, N_α).

The measured IR spectrum showed the characteristic azide vibration band as strong signal at 2110 cm^{-1}. Since no strong vibration band between 1620 to 1560 cm^{-1} was observed, compound **22** was yielded as free base.

Azidoethylamine **24** shows in the ^1H NMR spectrum in $CDCl_3$ four hydrogen signals. The typical splitting of the ethyl residue can be overserved as a triplet at 1.08 ppm for CH_3 and as a quartet at 2.67 ppm for CH_2. The signals for the chloro derivative **23** appear in d_6-DMSO at 1.21 ppm and 2.97 ppm. The azidoethyl hydrogens are allocated as triplets at 3.39 ppm for the CH_2 group next to the azide and 2.77 ppm for the CH_2 group next to the amine. In **23** they appeared at 3.92 ppm for CH_2 next to the chlorine and at 3.27 ppm. Carbon signals for **24** are allocated at 51.59 ppm (CH_2N), 48.37 ppm (CH_2N_3), 43.87 ppm (CH_2CH_3) and 15.34 ppm (CH_3) in the ^{13}C spectra. The additionally measured ^{14}N NMR spectrum revealed the azide signals at −134 ppm (sharp signal, N_β), −171 ppm (broad signal, N_γ) and −315 ppm (very broad signal, N_α).

Using IR spectrometry, the azide vibration bands appear at 2101 cm^{-1} and 1282 cm^{-1}. No strong signal for the protonated NH-group was observed.

For the synthesized azido liquid **26** the two hydrogen signals show up at 3.43 ppm for the hydrogens next to the azide and at 2.84 ppm for the hydrogens near the amine. These signals

appear at 3.60 ppm (CH_2Cl) and 3.00 ppm (NCH_2) for the chloro precursor **25**, measured in d_6-DMSO. The two carbon signals are also in accordance with literature values[106] and appear at 51.57 ppm for the carbon next to the azide group and at 48.36 ppm for the carbon near the amine. Chloro precursor signals show up at 48.46 ppm (NCH$_2$) and at 45.10 ppm (CH$_2$Cl). The additionally measured ^{14}N NMR Spectrum revealed the three azide signals at −133 ppm (sharp signal, N$_\beta$), −171 ppm (broad signal, N$_\gamma$) and −313 ppm (very broad signal, N$_\alpha$).

The characteristic azide vibration band for compound **26** can be overserved in the IR spectrum in accordance to literature[106] at 2093 cm^{-1}. No signal for the protonated form was observed.

In addition, the friction and impact sensitivities were measured together with the decomposition temperature of the synthesized secondary amino azido liquids and listed in Table 9 below.

Table 9: Sensitivities and decomposition temperature of the secondary azido amines 22 - 26.

Compound	Impact sensitivity [J]	Friction sensitivity [N]	T_d [°C]
AzEMA 22	40	360	135
AzEEA 24	40	360	149
DAzEA 26	40	360	170

The three compounds **22**, **24** and **26** can be classified as insensitive towards impact and friction according to the UN guideline. No difficulties in handling these explosive compounds were observed. The decomposition temperatures were measured to be 135 °C for **22**, 149 °C for compound **24** and 170 °C for **26**.

Their densities were measured as the average out of five volume-weight measurements and determined to be 0.98 g cm^{-3} for **22**, 1.21 g cm^{-3} for **24** and 1.41 g cm^{-3} for **26**.

2.3.2 Tertiary amines

In this section, the syntheses of several tertiary amino azido liquids are described. Some of the compounds are already described in literature as well, but not fully characterized e.g. regarding their sensitivities.

2.3.2.1 Synthesis

The synthesis of 2-azido-*N*,*N*-dimethylethan-1-amine, DMAZ **28** started also from the commercially available alcohol *N*,*N*-dimethylaminoethanol via a chlorination reaction with thionyl chloride followed by an azide exchange reaction.[102, 107] Reaction syntheses are shown in Scheme 24 below. 2-chloro-*N*,*N*-dimethylethan-1-amine **27** could be obtained as white solid (chlorohydrate salt) in almost quantitative yield. Compound **27** was then converted to the corresponding and desired azide DMAZ **28** with the use of 2.5 equivalents of sodium azide. Using optimized reaction conditions of 50 °C for 2 days and desalination with NaOH, compound **28** was yielded as brown oily liquid in 75%. Performing the reaction with a shorter reaction time resulted in moderate yields of 25%.
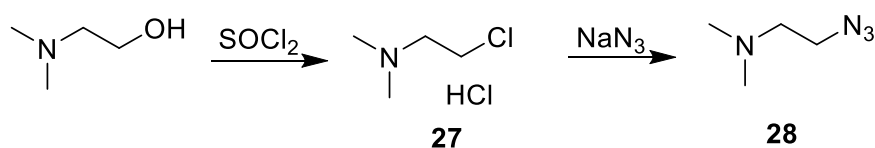
Scheme 24: Synthesis route towards 2-azido-*N*,*N*-dimethylethan-1-amine, DMAZ 28.

In addition, also the ethyl derivative 2-azido-*N*,*N*-diethylethan-1-amine, DEAZ **30** was synthesized via same route, pictured in Scheme 25.
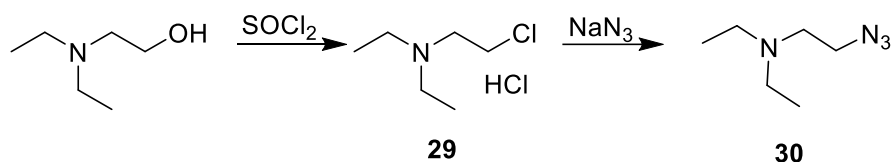
Scheme 25: Synthesis route towards 2-azido-*N*,*N*-diethylethan-1-amine, DEAZ 30.

The chloro derivative **29** was yielded as a white hydrochloride salt in quantitative yield, if reaction time is extended to 16h in comparison to literature.[102] The following chlorine azide

exchange reaction obtained the desired azido liquid **30** in 49% yield as colourless oil. The lower yield can be explained as above due to problems during the desalination reaction.

Derived from **28**, the derivative with propyl chain, 2-azido-*N,N*-dimethylpropan-1-amine, DMAPZ **32**, was also synthesized according to same reaction conditions as mentioned above. The reaction is listed in Scheme 26.
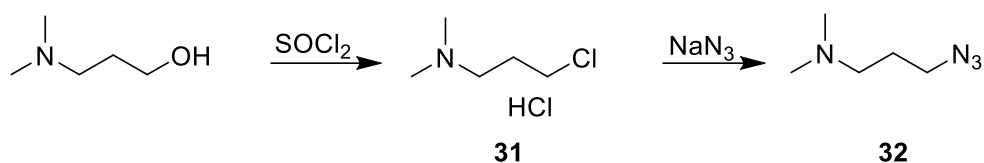
Scheme 26: Synthesis route towards 2-azido-*N,N*-dimethylpropan-1-amine, DMAPZ 32.

Chloropropyl derivative **31** was yielded as a white chlorohydrate salt in very good, almost quantitative yield of 98%.[108] Continuing the reaction to the desired azido liquid **32**, a yield of 74% was obtained as a colourless oil.[109]

In addition, the ethyl derivative 2-azido-*N,N*-diethylpropan-1-amine, DEAPZ **35**, was synthesized according to Scheme 27.
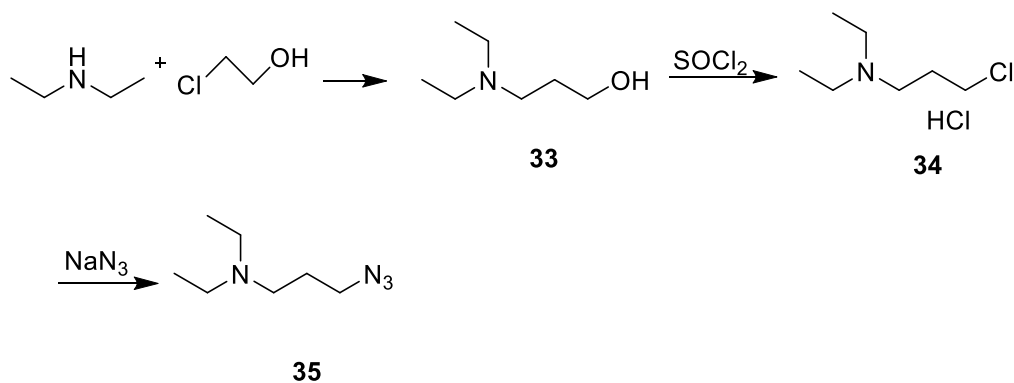
Scheme 27: Synthesis route towards 2-azido-N,N-diethylpropan-1-amine, DEAPZ 35.

For this reaction, as a first step the alcohol precursor 3-(diethylamino)propan-1-ol **33** was obtained from the synthesis of 3-chloropropanol and diethylamine, followed by a desalination using NaOH, as a brownish oil in 43%.[110] The following chlorination reaction yielded 3-chloro-N,N-diethylpropan-1-amine **34** in 72% as a brownish liquid.[111] With this reaction the amino chloride compound **34** was obtained as free base.[112] The subsequent azidation reaction yielded the desired azido product **35** as a yellowish liquid in 32%.

Next, compound 2-azido-*N*-(2-azidoethyl)-*N*-methylethan-1-amine, DAzEMA **37**, was synthesized from the respective alcohol precursor via the chlorine derivative, according to Scheme 28.
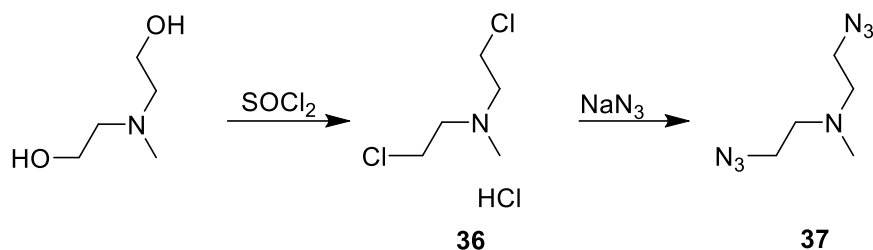
Scheme 28: Synthesis route towards 2-azido-N-(2-azidoethyl)-N-methylethan-1-amine, DAzEMA 36.

The hydrochloride salt of 2-chloro-*N*-(2-chloroethyl)-*N*-methylethan-1-amine **36** was obtained as white solid in 94%.[113] Starting from this compound **36,** the chlorine azide exchange reaction was performed with 5 eq of sodium azide for 2 days at 50 °C.[114] The desired azido liquid **37** was yielded after desalination in 58% as yellowish liquid.

As additional compound, the ethyl derivative of **37** was also synthesized according to Scheme 29. For this purpose, first the alcohol derivative *N*-ethyldiethanolamine **38** was synthesized from diethanolamine, K$_2$CO$_3$ and bromoethane in ethanol.[115] After refluxing the resulting reaction mixture for 4 days, the alcohol **38** was yielded in 51% as colourless oil. The subsequently performed chlorination reaction yielded the chloro precursor, 2-chloro-*N*-(2-chloroethyl)-*N*-ethylethan-1-amine, **39** in 97% as brown chlorohydrate salt.[116] The last step, azidation reaction, obtained the desired azido liquid 2-azido-*N*-(2-azidoethyl)-*N*-ethylethan-1-amine, DAzEEA **40**, in 42% yield as orange oil.
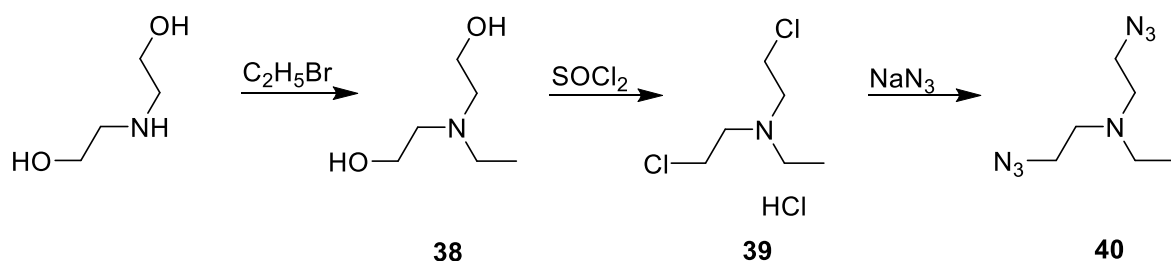
Scheme 29: Synthesis route towards 2-azido-N-(2-azidoethyl)-N-ethylethan-1-amine, DAzEEA 37.

To complete the series of tertiary amino-azido liquids, also the amine with three azidoethyl residues was synthesized. Tris(2-azidoethyl)amine, TAzEA **42**, was yielded according to Scheme 30 below. Synthesis started from triethanolamine via a chlorination reaction to yield tris(2-chloroethyl)amine **41** as white chorohydrate salt in 77% yield.[117] The following azidation reaction lead to azide **42** as yellowish oil in 59% yield.[118]
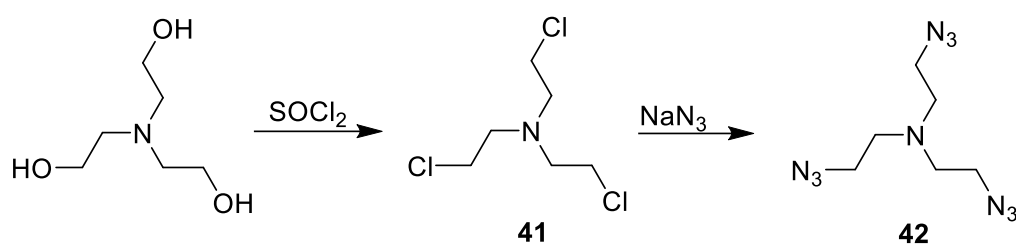
Scheme 30: Synthesis route towards tris(2-azidoethyl)amine, TAzEA 42.

The received tertiary azido amino liquids **28-42** were characterized using several methods. Using NMR spectroscopy, the resulted NMR shifts were compared to the respective literature values. The results are listed in the following chapter.

2.3.2.2 Characterisation

For identification of **28** the NMR shifts were compared to the shifts of the chloro derivative **27** and to literature.[119] The ^{1}H NMR spectrum of **27** shows two triplets at 4.03 ppm and 3.42 ppm for the chloroethyl residue, where the first triplet can be assigned to the CH_2 hydrogens next to the chlorine. The methyl hydrogens show up as a singlet with triple intensity at 2.91 ppm. Carbon signals can be allocated at 58.72 ppm ($ClCH_2$) and 43.64 ppm (NCH_2) for the chloroethyl residue and at 36.85 ppm for the methyl carbon (CH_3). In comparison to the azido compound **28** the hydrogen signals appear now at 3.35 ppm (triplet) and 2.51 ppm (triplet) and 2.28 ppm (singlet). The first triplet is also assigned to the CH_2 group next to the azide. This is also stated in literature.[119] In addition, also the carbon signals in the ^{13}C NMR are now shifted to 58.22 ppm (NCH_2), 49.17 ppm (CH_2N_3) and 45.59 ppm (CH_3). An additionally measured ^{14}N NMR spectrum shows the azide signals at −133 ppm (sharp signal, N_β), −171 ppm (board signal, N_γ) and −313 ppm (very broad signal, N_α).

The measured IR spectrum showed the characteristic azide vibration bands as strong signals at 2094 cm^{-1} and 1275 cm^{-1}.

The hydrogen signals for the diethylamino chloro compound **29** show both triplets of the chloroethyl residue almost on the same position as **28** at 4.05 ppm and 3.35 ppm. The aminoethyl residue can be allocated as multiplet at 3.10 ppm and triplet at 1.43 ppm. ^{13}C NMR reveals the desired four signals at 52.72 ppm (NCH$_2$CH$_2$Cl), 47.23 ppm (CH$_2$CH$_3$), 37.77 ppm (NCH$_2$CH$_2$Cl) and 8.68 ppm (CH$_3$). The signals of the synthesized azido compound **30** were obtained as triplets at 3.25 ppm and 2.60 ppm for azidoethyl side chain, whereas the first one stands for the CH$_2$group next to the azide. The two other ethyl side chain signals appear as quartet in double intensity at 2.53 ppm and as triplet at 1.00 ppm. This is in accordance with the literature.[119] Carbon signals arise at 52.20 ppm (NCH$_2$CH$_2$N$_3$) and 49.50 ppm (NCH$_2$CH$_2$N$_3$) for the azidoethyl chain and at 47.31 ppm (CH$_2$CH$_3$) and 11.85 ppm (CH$_2$CH$_3$) for the two diethyl side chains. Additional measured ^{14}N NMR spectrums shows three signals on almost same positions as the methyl derivative **28** above at −133 (sharp signal, N$_\beta$), −177 (broad signal, N$_\gamma$) and −317 (very broad signal, N$_\alpha$).

The measured IR spectrum revealed the typical strong azide vibration band signals at 2094 cm^{-1} and 1294 cm^{-1}.

The propyl derivative of DMAZ **32** was also characterized via NMR spectroscopy. In this case, in the ^{1}H NMR spectrum of the chloro precursor appear four signals according to literature.[120] The propyl residue show up as a triplet at 3.41 ppm for the CH$_2$ hydrogens next to the chlorine, as a multiplet at 3.03 ppm for the two CH$_2$ hydrogens next to the amino group and as a quintet at 2.05 ppm for the middle CH$_2$ group. Methyl signals can be allocated with integral of 6 at 2.63 ppm. The four carbon signals can be found at 56.25 ppm (NCH$_2$), 43.44 ppm (-CH$_3$), 41.62 ppm (CH$_2$Cl) and 43.64 ppm (CH$_2$CH$_2$Cl). Furthermore, the obtained signals of the ^{1}H NMR spectrum of **32** were compared to literature[112] and the chloro precursor **31**. The four hydrogen signals are now shifted to 3.35 ppm (triplet, CH$_2$N$_3$), 2.35 ppm (triplet, NCH$_2$), 1.75 ppm (CH$_2$CH$_2$Cl) for the propyl chain and at 2.23 ppm for the methyl hydrogens. ^{13}C NMR shows the four signals at 56.71 ppm (NCH$_2$), 49.67 ppm (CH$_2$N$_3$), 45.58 ppm (CH$_3$) and 27.21 ppm (CH$_2$CH$_2$CH$_2$). The nitrogen signals appear at as a sharp signal at −133 ppm (N$_\beta$), as a broader signal at −171 ppm (N$_\gamma$) and a third very broad signal at −310 ppm (N$_\alpha$).

The ethyl propyl derivative **35** was characterized via NMR spectrometry and compared to the alcohol **33** and chloro precursor **34**.

The synthesized alcohol compound **33** shows five signals in the ^{1}H NMR spectrum, as expected. They show up as a quartet at 2.50 ppm and as a triplet at 1.05 ppm for the ethyl residue and at 3.79 ppm for the CH_2 hydrogens next to the amine, at 2.65 ppm for the CH_2 hydrogens next to the hydroxy group and at 1.78 ppm for the middle CH_2 hydrogens.

In comparison, chloro derivative **34** has shifted signals. While the ethyl residues appear almost at the same area, as multiplet and triplet at 2.85 ppm and 0.87 ppm, the three signals for the propyl backbone are clearly shifted. They show up at 3.48 ppm for the CH_2 group next to the chlorine, at 3.25 ppm for the CH_2 hydrogens next to the amine and the middle one appears at 2.05 ppm. Carbon signals show up at 49.71 ppm ($N(CH_2)_2$) and 8.53 ppm ($-CH_3$) for the ethyl residue and at 56.25 ppm (NCH_2), 45.88 ppm (CH_2Cl) and 26.1 ppm (CH_2CH_2Cl) for propyl backbone.

The hydrogen signals of the azido derivative **35** are shifted for the propyl chain to 3.31 ppm (triplet) for the hydrogens next to the azide, to 2.45 ppm (triplet) for the hydrogen next to the amine and at 1.70 ppm (quintet) for the middle hydrogens. Ethyl residue shows up as quartet at 2.49 ppm and triplet at 0.99 ppm. The five carbon signals appear at 47.02 ppm and 11.83 ppm for the ethyl residue and for the propyl chain at 49.93 ppm (CH_2N_3), 49.86 ppm (NCH_2) and 27.21 ppm for the middle carbon. The measured ^{14}N NMR spectrum shows the three azide signals as sharp signal at -133 (N_β), as broad signal at -171 (N_γ) and as a very broad signal at -320 (N_α).

DAzEMA **37** was compared to the chloro precursor **36** and the obtained NMR signals were matched with the literature.[121] The chlorohydrate salt **36** shows the expected three signals in the measured ^{1}H NMR spectrum. They appear as triplets at 3.58 ppm and at 2.69 ppm for the chloroethyl chain and as singlet at 2.28 ppm for the methyl hydrogens. The three carbon signals show up at 59.51 ppm and at 42.28 ppm for the ethyl carbons and at 36.85 ppm for the methyl carbon.

The hydrogen signals of the methyl amino azido liquid **37** appear for the azidoethyl residue now only slightly shifted as triplets at 3.33 ppm and 2.65 ppm. First signal can be assigned to the CH_2 group next to the azide and the second one to the CH_2 hydrogens next to the amine.

The methyl hydrogens show up as singlet at 2.33 ppm. The three carbon signals can be allocated at 56.62 ppm and 49.03 ppm for the azidoethyl residue and at 42.14 ppm for the methyl carbon. ^{14}N NMR spectrum shows the three expected nitrogen signals as sharp, broad and very broad signals at 133 ppm (N_β), −170 ppm (N_γ) and −314 ppm (N_α).

The characteristic azide vibration bands show up at 2100 cm^{-1} and at 1238 cm^{-1}.

The ethyl derivative DAzEEA **40** was characterized via NMR spectroscopy and the signals compared with the synthesized alcohol **38** and chloro **39** precursor[115]. For the amino alcohol **38** in the measured NMR spectrum, the expected two signals for the hydroxyethyl residue are visible as triplets at 3.61 ppm (C*H₂*OH) and 2.63 ppm (NC*H₂*CH₂), in accordance to the literature[115]. The ethyl chain appears as quartet for the CH₂ hydrogens at 2.60 ppm and as triplet for the CH₃ hydrogens at 1.04 ppm. ^{13}C NMR shows the four carbon signals at 51.34 ppm for the CH₂ group of the ethyl alcohol next to the amine, at 48.12 ppm for the ethyl carbon, at 43.64 ppm for the carbon next to the hydroxy group and at 15.10 ppm for the methyl carbon.

In comparison, the hydrogen signals of the chloro derivate **39** are now shifted to 4.10 ppm for the hydrogens next to the chloro group and to 3.50 ppm for the chloroethyl hydrogens next to the amine. The hydrogens of the ethyl chain appear as quartet (CH₂) and triplet (CH₃) at 3.35 ppm and at 1.49 ppm. Carbon signals are shifted to 53.71 ppm (CH₂N), 48.90 ppm (NCH₂CH₃), 36.58 ppm (CH₂Cl) and 8.72 ppm (CH₃).

The hydrogen signals of the amino azido liquid **40** appear for the azidoethyl residue as triplets at 3.33 ppm and 2.65 ppm. The first signal can be assigned to the CH₂ group next to the azide and the second one to the CH₂ hydrogens next to the amine. The ethyl hydrogens show up as quartet and triplet at 2.63 ppm and 1.06 ppm. The four carbon signals show up at 53.60 ppm and 48.56 ppm for the azidoethyl chain, where the first signal can be allocated to the CH₂ group next to the amine and the second one for the CH₂ group next to the azide. The ethyl residue can be allocated at 48.56 ppm (CH₂CH₃) and 12.36 ppm (CH₃). The three expected nitrogen signals appear at −133 ppm (sharp signal, N_β), −170 (broad signal, N_γ) and −313 ppm (very broad signal, N_α).

The azide vibration bands appear at 2100 cm^{-1} and 1283 cm^{-1} in the measured IR spectrum.

The trisazidoethyl amine **42** was also identified via NMR spectroscopy, the signals compared to the chloro precursor and matched with literature.[121-122]

For the trischloroethyl amine **41** the expected two hydrogen signals appear as triplets at 3.51 ppm for the CH_2 hydrogens next to the chlorine and at 2.98 ppm for the CH_2 hydrogens next to the amine. Carbon spectrum shows the expected two signals at 56.93 ppm (CH_2N), and 42.23 ppm (CH_2Cl).

In comparison, the hydrogen signals of the azide **42** show now up as triplets at 3.35 ppm for the hydrogens next to the azide and at 2.79 ppm for the ones next to the amine. The two carbon signals are shifted to 54.09 ppm (NCH_2) and 49.84 ppm (CH_2N_3). ^{14}N NMR spectroscopy reveals three azide signals at −134 ppm (sharp signal, N_β), −171 ppm (broad signal, N_γ) and −316 ppm (very broad signal, N_α).

The characteristic azide vibration bands show up in the measured IR spectrum at 2085 cm^{-1} and 1269 cm^{-1}.

In addition, the friction and impact sensitivities of the synthesized tertiary amino azido liquids **28**-**42** were measured together with the decomposition temperature and listed in Table 10 below.

Table 10: Sensitivities and decomposition temperature of the tertiary azido amines 28 - 42.

Compound	Impact sensitivity [J]	Friction sensitivity [N]	T_d [°C]
DMAZ 28	40	360	135
DEAZ 30	40	360	170
DMAPZ 32	40	360	150
DEAPZ 35	40	360	165
DAzEMA 37	40	360	167
DAzEEA 40	40	360	166
TAzEA 42	15	120	187

The azido compounds **28–40** can all be classified as insensitive towards friction and impact according to the UN guideline. The azido liquid **42** can be classified as sensitive towards impact and insensitive toward friction. While handling these explosive compounds, no difficulties were observed.

The decomposition temperatures were measured to be 135 °C for **28**, 170°°C for compound **30**, 150 °C for **32**, 165 °C for azido liquid **35**, 167 °C for **37**, 166 °C for **40** and 170 °C for **42**.

The densities of the tertiary amino azido liquids were measured as average out of five volume weight measurements and determined to be 0.93 g cm^{-3} for **28**, 0.95 g cm^{-3} for **30,** 1.28 g cm^{-3} for **37,** 1.02 g cm^{-3} for **40** and 1.17 g cm^{-3} for **42**.

2.3.3 Unsuccessful attempts of generating more amino azido liquids

The syntheses of other amino azido compounds were tried among others during this work. Some of the attempts without a successful synthesis route are briefly described in the following chapter.

2.3.3.1 Amino-azido-propan-2-ol

According to 1,3-DAP, the synthesis of amino-azido-propanol was also tried as depicted in Scheme 31.
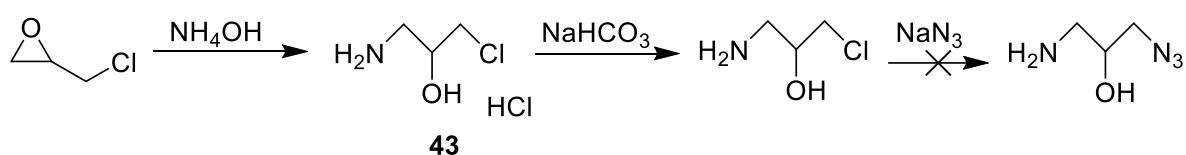
Scheme 31: Synthesis route towards 1-amino-3-azido-propan-2-ol.

For this purpose the alcohol precursor, 1-amino-3-chloro-propan-2-ol **43**, was synthesized from epichlorohydrin and benzaldehyde in ammonia, yielding **43** as hydrochloride salt in 43% as dark yellow solid.[123] It was characterized by NMR spectroscopy. The three hydrogen signals appear at 4.20 ppm for the CH group, at 3.75 ppm for the CH$_2$ hydrogens next to the chlorine and at 3.25 ppm for the CH$_2$ group near the hydroxyl residue. Carbon signals can be allocated at 67.24 ppm for the carbon with an alcohol group attached, at 46.13 ppm for the chloro-carbon and at 42.10 ppm for the carbon next to the amino group.

The following azidation reaction was performed on the one hand from the chlorohydrate salt of **43**, and on the other hand of the free base of **43**, due to consideration of an improvement of solubility. Foor this aim, compound **43** was stirred overnight in excess sodium bicarbonate and the formed sodium chloride precipitated with the addition of ethyl acetate. Compound **43** was therefore obtained as free base as a brownish liquid.

Azidation reaction was executed with different solvents, DMF, acetone and water, with different temperatures, rt till reflux, and different reaction times, 30 min till 4 days. Using a longer reaction time and increasing the reaction temperature, it could be observed that more side product is formed. This side product was assigned to be 2,3-epoxypropylamine as a result of a cyclisation reaction.[124]

Direct azidation reaction of epichlorohydrin, followed by the conversion with ammonia yielded also in the undesired cyclisation product.

With none of the tried reaction conditions, the desired product could be obtained. Existence and stability of 1-amino-3-azdo-propan-2-ol could not be proved.

2.3.3.2 1,3-diazidopropan-2-amine

In addition, synthesis of 1,3-diazidopropan-2-amine, according to Scheme 32, was tried. Starting from the alcohol, 2-aminopropane-2-diol (comm. serinol), the chloro-precursor **44** was yielded as hydrochloride salt in 60% yield.[125]
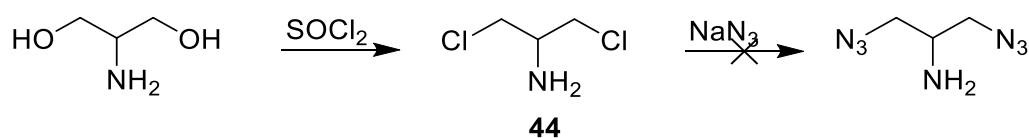
Scheme 32: Synthesis route towards 1,3-diazidopropan-2-amine.

The obtained NMR spectra were compared to literature[126]. As expected, the two signals show up at 3.74 ppm for the CH_2 groups and at 3.39 ppm for the CH hydrogen. Carbon signals appear at 53.35 ppm (CH) and 45.92 ppm (CH_2Cl).

Although the desired compound is already documented in literature, where it is synthesized from the bromo derivative[127], trying several reaction conditions using the chloro derivative

as precursor lead to no success. Therefore, obtaining pure product in a good amount was therefore not possible. It could only be detected in the NMR spectrum, but the amount of non-allocatable by-products was too high for further purification steps. Therefore, a synthesis starting from the chloro-precursor seems not efficient.

2.3.3.3 1-azido-2-methylpropan-2-amine

Then, the synthesis of 1-azido-2-methylpropan-2-amine, pictured in Scheme 33, starting from the alcohol was tried. 2-amino-2-methylpropan-1-ol was chlorinated with thionyl chloride and 1-chloro-2-methylpropan-2-amine **45** was obtained in 83% yield as white chlorohydrate salt.
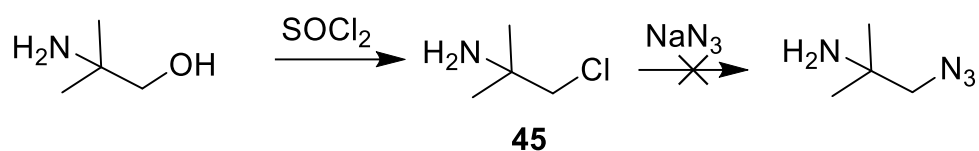
Scheme 33: Synthesis route towards 1-azido-2-methylpropan-2-amine.

The ^{1}H NMR spectrum, measured in d_6-DMSO, shows the amino hydrogens as broad signal at 8.30 ppm and the other expected two signals as singlets at 3.34 ppm for the CH$_2$ hydrogens and at 1.17 ppm for the methyl groups.

The subsequently performed azidation reaction was executed with several reaction conditions and solvents. A direct azidation reaction from the hydrochloride salt as well as starting from the desalinated compound **45** was performed. Reaction solvents DMF and acetone were used, and reaction conditions varying from 30 min to 4 days. With none of these reaction conditions the synthesis of the desired molecule was achieved. A possible explanation is the instability of the product. The measured NMR spectra showed many signals which cannot even be assigned to the starting material. Therefore, a decomposition must have taken place. The only evidence of the existence of this compound is given by LACOTE *et al.*, but they mention no synthesis or analytical data.[128] They justify their synthesis and characterisation based on the paper of WANNAPORN and ISHIKAWA[129], but there the compound isn´t even mentioned. Therefore, the existence of **45** is not proved until now.

2.3.3.4 2-(2-azidoethoxy)-N,N-dimethylethan-1-amine

Another idea was the synthesis of 2-(2-azidoethoxy)-N,N-dimethylethan-1-amine **46**, according to Scheme 34.
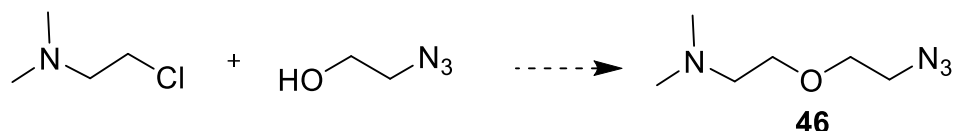
Scheme 34: Synthesis route towards 2-(2-azidoethoxy)-N,N-dimethylethan-1-amine.

At the beginning, the synthesis was tried using 2-(dimethylamino)ethan-1-ol and 1-azido-2-chloroethane, but without success. NMR showed only starting material. The second attempt to obtain the ether was performed using 2-chloro-N,N-dimethylethan-1-amine **27** and 2-azidoethanol **8**, as pictured above. For the synthesis a solution of previously synthesized **8** and sodium hydroxide in water was prepared. A mixture of **27** in Et$_2$O was added. Concentration *in vacuo* yielded a brownish liquid. NMR analysis showed a large amount of **8** an additionally some signals, which can be assigned to the product. The synthesis was also carried out one time after the synthesis of 3-(2-azidoethoxy)prop-1-ene[130]. This method differs from the one described before in the usage of THF as solvent and in the addition of sodium hydride, instead of sodium hydroxide. Also, the reaction was carried out at room temperature. With these conditions only starting material was observed in the NMR spectrometry. The existence of the product **26** was visible in the NMR spectra of the sodium hydroxide route. In the ^{1}H NMR spectrum the CH$_2$O–groups are allocated as a multiplet of two overlapping triplets at 3.64–3.58 ppm. The two other expected triplets are at 3.40–3.37 ppm and 2.55–2.52 ppm. The singlet of the CH$_3$ hydrogens appears at 2.28 ppm. Signals of the starting materials appear at 3.77 ppm (C*H*$_2$–OH) and 3.43 ppm (C*H*$_2$–N$_3$) for **8** and for **27** at 4.03 ppm (C*H*$_2$Cl), 3.42 ppm (NC*H*$_2$) and 2.91 ppm (C*H*$_3$). Therefore, they are clearly shifted which proofs the presence of the desired compound **46**. Carbon NMR analysis showed the signals of compound **46** at 69.91 ppm (NCH$_2$CH$_2$O), 69.54 ppm (N$_3$CH$_2$CH$_2$O), 58.88 ppm (C*H*$_2$N), 50.81 ppm (C*H*$_2$N$_3$) and 45.97 (C*H*$_3$). Unfortunately, trying many different reaction conditions did not lead to a formation of pure product **46** and it does not seem to be

stable enough for further purification steps. But it could be characterized via NMR spectroscopy.

2.3.3.5 N^1,N^1-bis(2-azidoethyl)ethane-1,2-diamine

Several attempts for the synthesis of N^1,N^1-bis(2-azidoethyl)ethane-1,2-diamine were carried out. The first route was the synthesis via the alcohol and chloro precursor, pictured in Scheme 35.
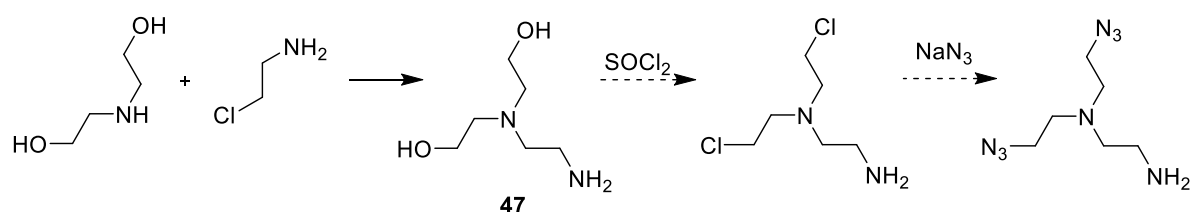
Scheme 35: Synthesis route towards N^1,N^1-bis(2-azidoethyl)ethane-1,2-diamine.

To yield the alcohol 2,2'-((2-aminoethyl)azanediyl)bis(ethan-1-ol) **47,** a reaction of 2-chloroethan-1-amin, which was previously desalinated with sodium hydroxide for a better solubility, and diethanolamine was carried out in water for 3. Compound **47** was yielded as an orange liquid in 83% and characterized via NMR spectroscopy. The obtained signals were compared with the literature.[131] The hydrogen signals appear as expected as very broad signal at 3.87 ppm for the amino and hydroxyl groups. At 3.53 ppm the signals for the CH_2 hydrogens next to the alcohol group appear and at 2.76 ppm the CH_2 hydrogens next to the amine. The hydrogens surrounding the tertiary amine appear as multiplet at 2.55 ppm. This matches with the literature. Afterwards the chlorination reaction was executed several times. using thionyl chloride. Yielding pure product was not possible under used conditions although this compound was already mentioned in literature before.[132]

Because the problems of the chloro precursor occurred before, another approach for the synthesis was investigated. This time, a selective Staudinger amination[133] was tried. For this reaction previously synthesized TAzEA **42** was used with 1 eq of triphenylphosphine, according to Scheme 36 below.
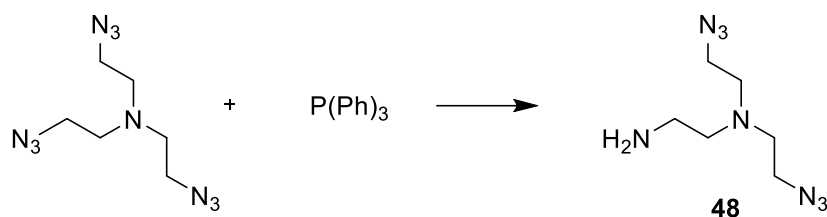
Scheme 36: Synthesis route towards N^1,N^1-bis(2-azidoethyl)ethane-1,2-diamine via Staudinger amination.

For the first attempt, the reaction was carried out in acetonitrile. The amount of triphenylphosphine must be accurately measured and added very slowly to the reaction mixture. Addition of excess lead to an amination of more azido groups. NMR analysis of the product showed that a reaction took place, but the desired compound **48** could not be clearly identified in signals and integrals of the measured spectra. According to LEFFLER, nonpolar solvents are moderating a faster reaction.[134] Therefore the same reaction was subsequently executed in diethyl ether and triphenylphosphine added this time in really small excess of 1.1eq. In addition, a further purification step to remove the residue of triphenylphosphine was carried out. Therefore, zinc(II)chloride and ethanol were added to the solution to precipitate it as triphenylphosphine oxide. With this reaction conditions plus the purification step, compound **48** was identified clearly for the first time via NMR spectroscopy. The NMR showed a broad signal at 6.18 ppm, which can be allocated to the amino hydrogens. At 3.37 ppm appears a large multiplet, with an integral of 6. Here appears the two CH_2 groups next to the tertiary amine and the CH_2 hydrogens next to the amine. The next multiplet at 2.72 ppm has also the integral of 6. At this position the two CH_2 hydrogens next to the azide and the CH_2 hydrogens next to the tertiary amine are allocated. Carbon signals can be assigned at 37.24 ppm for the carbon close to the amino group, at 48.08 ppm for the two carbons next to the azide and at 52.12 ppm for the carbons surrounding the tertiary amine. The NMR signals were compared to the staring material **42** and to 2,2',2''-triaminotriethylamine[135]. Although the product **48** was already successfully characterized via NMR spectroscopy, the obtained yield was too low for further characterisation. Synthesizing **48** with these reaction conditions is possible, but the reaction needs further improvement to yield it in higher amount.

2.3.4 Experimental part

2-Chloro-*N*-methylethan-1-amine hydrochloride, 21

2-(Methylamino)ethan-1-ol (3.00 g, 40.0 mmol, 1 eq) was dissolved in 10 mL DCM and cooled to 0 °C. Thionyl chloride (11.9 g, 100 mmol, 2.5 eq) was slowly added and the mixture was stirred at 50 °C for 1 h. After cooling down to room temperature, 30 mL methanol was added to remove the residual thionyl chloride. The solvent was evaporated *in vacuo* and the chlorohydrate salt of 2-chloro-*N*-methylethan-1-amine (5.02 g, 38.6 mmol, 96%) was obtained as a white solid. **¹H NMR** (400 MHz, d_6-DMSO): δ (ppm) = 9.34 (br, 1H, N*H*), 3.93 (t, 2H, C*H$_2$*Cl), 3.27 (t, 2H, NC*H$_2$*), 2.55 (s, 3H, C*H$_3$*). **¹³C NMR** (101 MHz, d_6-DMSO): δ (ppm) = 49.17 (*C*H$_2$N), 40.19 (*C*H$_2$Cl), 32.36 (*C*H$_3$). **IR** (ATR): $\tilde{v}$ = 3359 (m), 2951 (w), 2753 (w), 2441 (m), 2113 (s), 1468 (w), 1015 (m), 877 (m), 662 (w). C$_3$H$_8$NCl·HCl (130.01 g mol^{-1}).

2-Azido-*N*-methylethan-1-amine, AzEMA 22

2-Chloro-*N*-methylethan-1-amine hydrochloride (3.51 g, 27.0 mmol, 1 eq) was dissolved in 25 mL water and stirred for 1.5 h at room temperature. Afterwards sodium azide (4.39 g, 67.5 mmol, 2.5 eq) was added and the reaction mixture was refluxed at 100 °C over night. After cooling down the pH value was adjusted with NaOH solution to pH 10 and the solution extracted four times with 15 mL DCM. The combined organic phases were dried over sodium sulphate and the solvent removed *in vacuo*, to obtain the product as a brownish solution (1.51 g, 15.1 mmol, 56%). **¹H NMR** (400 MHz, CDCl$_3$): δ (ppm) = 3.43 (t, 2H, C*H$_2$*N$_3$), 2.77 (t, 2H, NC*H$_2$*), 2.46 (s, 3H, -C*H$_3$*). **¹³C NMR** (101 MHz, CDCl$_3$): δ (ppm) = 51.33 (*C*H$_2$N), 50.63 (*C*H$_2$N$_3$), 36.25 (*C*H$_3$). **¹⁴N NMR** (29 MHz, CDCl$_3$): δ (ppm) = −133 (N$_\beta$), −171 (N$_\gamma$), −314 (N$_\alpha$). **IR** (ATR): $\tilde{v}$ = 3289 (m), 2925 (w), 2843 (w), 2110 (s), 1739 (s), 1576 (w), 1456 (m), 1365 (m), 1230 (s), 1205 (s), 1122 (s), 1051 (s), 932 (m), 813 (w), 527 (w). C$_3$H$_8$N$_4$ (130.01 g mol^{-1}). **EA**: calcd. N 55.96, C 35.99, H 8.05 % found N 44.53, C 35.12 H 7.37 %. **DTA** (5 °C min^{-1}): T_d = 135 °C. **Sensitivities**: IS: >40 J, FS: >360 N.

2-Chloro-*N*-ethylethan-1-amine hydrochloride, 23

2-(Ethylamino)ethan-1-ol (5.00 g, 56.1 mmol, 1 eq) was dissolved in 10 mL dichloromethane and cooled to 0 °C. Thionyl chloride (16.7 g, 140 mmol, 2.5 eq) was slowly added and the

mixture was stirred at 50 °C for 1 h. After cooling down to room temperature, 30 mL methanol was added to decompose the residual thionyl chloride. The solvent was evaporated *in vacuo* and the chlorohydrate salt of 2-chloro-*N*-ethylethan-1-amine (7.96 g, 56.0 mmol, 99%) was obtained as a white solid. **¹H NMR** (400 MHz, d_6-DMSO): δ (ppm) = 9.34 (br, 1H, N*H*), 3.92 (t, 2H, C*H*$_2$Cl), 3.27 (t, 2H, NC*H*$_2$), 2.97 (q, 2H, NC*H*$_2$CH$_3$), 1.21 (t, 3H, C*H*$_3$). **¹³C NMR** (101 MHz, CDCl$_3$): δ (ppm) = 52.54 (N*C*H$_2$CH$_2$Cl), 46.98 (*C*H$_2$CH$_3$), 37.57 (NCH$_2$*C*H$_2$Cl), 8.89 (*C*H$_3$). 51.59 (*C*H$_2$N), 48.37 (*C*H$_2$Cl), 43.87 (*C*H$_2$CH$_3$), 15.34 (*C*H$_3$). **IR** (ATR): $\tilde{v}$ = 3369 (m), 2959 (m), 2755 (w), 2467 (s), 1620 (s), 1456 (w), 1037 (w), 753 (w). C$_4$H$_{11}$Cl$_2$N HCl (144.03 g mol^{-1}).

2-Azido-*N*-ethylethan-1-amin, AzEEA 24

2-Chloro-*N*-ethylethanamine hydrochloride (3.93 g, 36.7 mmol, 1 eq) was dissolved in 25 mL water and stirred for 1.5 h at room temperature. Afterwards sodium azide (5.44 g, 83.8 mmol, 2.5 eq) was added and the reaction mixture was refluxed at 100 °C over night. After cooling down the pH value was adjusted with NaOH solution to pH 0 and the solution extracted four times with 15 mL DCM. The combined organic phases were dried over sodium sulphate and the solvent removed *in vacuo*, to obtain the product as a brownish solution (2.09 g, 15.1 mmol, 55 %). **¹H NMR** (400 MHz, CDCl$_3$): δ (ppm) = 3.39 (t, 2H, C*H*$_2$N$_3$), 2.77 (t, 2H, NC*H*$_2$), 2.67 (q, 2H, CH$_3$C*H*$_2$N), 1.08 (t, 2H, C*H*$_3$). **¹³C NMR** (101 MHz, CDCl$_3$): δ (ppm) = 51.59 (*C*H$_2$N), 48.37 (*C*H$_2$N$_3$), 43.87 (*C*H$_2$CH$_3$), 15.34 (*C*H$_3$). **¹⁴N NMR** (29 MHz, CDCl$_3$): δ (ppm) = −134 (N$_\beta$), −171 (N$_\gamma$), −315 (N$_\alpha$). **IR** (ATR): $\tilde{v}$ = 3363 (w), 2944 (w), 2985 (w), 2463 (w), 2101 (s), 1656 (s), 1447 (m), 1348 (m), 1282 (s), 1064 (m), 1041 (m), 625 (w), 503 (w), 419 (w). C$_4$H$_{10}$N$_4$ (114.15 g mol^{-1}) **EA**: calcd. N 49.08, C 42.09, H 8.83 % found N 47.51, C 41.77 H 8.97 %. **DTA** (5 °C min^{-1}): T$_d$ = 149 °C. **Sensitivities**: IS: >40 J, FS: >360 N.

Bis(2-chloroethyl) amine, 25

Diethanolamine (5.00 g, 57.6 mmol, 1 eq) was dissolved in 20 mL DCM and cooled to 0 °C. Thionyl chloride (27.1 g, 238 mmol, 5 eq) was slowly added and the mixture was stirred at 50 °C for 3 h. After cooling down to room temperature, 35 mL methanol was added to remove the residual thionyl chloride. The solvent was evaporated *in vacuo* and the chlorohydrate salt of bis(2-chloroethyl) amine (6.37 g, 36.1 mmol, 76%) was obtained as a

brown solid. **¹H NMR** (400 MHz, CDCl₃): δ (ppm) = 3.60–3.61 (m, 2H, CH_2Cl), 3.03–2.97 (m, 2H, NCH_2) **¹³C NMR** (101 MHz, CDCl₃): δ (ppm) = 48.46 (NCH_2), 45.10 (CH_2Cl). **IR** (ATR): $\tilde{v}$ = 3347 (m), 2959 (m), 2744 (m), 2450 (s), 1586 (s), 1433 (w), 1207 (m), 1064 (w), 1005 (w), 752 (w). $C_4H_9Cl_2N \cdot HCl$ (178.47 g mol⁻¹).

Bis(2-azidoethyl) amine, DAzEA 26

Bis(2-chloroethyl) amine (1.00 g, 7.14 mmol, 1 eq) was dissolved in 25 mL water and stirred for 1.5 h at room temperature. Afterwards sodium azide (2.32 g, 35.7 mmol, 5 eq) was added and the reaction mixture was stirred at 50 °C for 2 days. After cooling down the pH value was adjusted with NaOH solution to pH 10 and the solution extracted four times with 15 mL Et₂O. The combined organic phases were washed with brine (1 x 15 mL), dried over sodium sulphate and the solvent removed *in vacuo*, to obtain the product as a brown oil (0.48 g, 3.10 mmol, 43%). **¹H NMR** (400 MHz, CDCl₃): δ (ppm) = 3.46–3.39 (m, 2H, CH_2N₃), 2.86–2.80 (m, 2H, NCH_2). **¹³C NMR** (101 MHz, CDCl₃): δ (ppm) = 51.57 (CH_2N_3), 48.36 (NCH_2) **¹⁴N NMR** (29 MHz, CDCl₃) δ (ppm) = −133 (N$_\beta$), −171 (N$_\gamma$), −313 (N$_\alpha$) **IR** (ATR): $\tilde{v}$ = 3312 (s), 2934 (s), 2093 (s), 1664 (m), 1446 (s), 1388 (s), 1340 (s), 1269 (m), 1122 (s), 1060 (m), 917 (s), 661 (m), 554 (m). $C_4H_9N_7$ (155.17 g mol⁻¹) **EA**: calcd. N 63.19, C 30.96, H 5.85 % found N 62.19, C 31.70 H 5.38 %. **DTA** (5 °C min⁻¹): T$_d$ = 170 °C. **Sensitivities**: IS: >40 J, FS: >360 N.

2-Chloro-N,N-dimethylethan-1-amine, 27

2-(Dimethylamino)ethan-1-ol (6.00 g, 67.4 mmol, 1 eq) was dissolved in 20 mL dichloromethane and cooled to 0 °C. Thionyl chloride (20.0 g, 165 mmol, 2.5 eq) and 4 drops pyridine were slowly added and the mixture was stirred at 50 °C for 1 h. After cooling down to room temperature, 30 mL methanol was added to decompose the residual thionyl chloride. The solvent was evaporated *in vacuo* and the chlorohydrate salt of 2-chloro-*N,N*-dimethylethan-1-amine (9.43 g, 56.0 mmol, 97%) was obtained as a white solid. **¹H NMR** (400 MHz, CDCl₃): δ (ppm) = 4.03 (t, 2H, CH_2Cl), 3.42 (t, 2H, NCH_2), 2.91 (s, 6H, -CH_3). **¹³C NMR** (101 MHz, CDCl₃): δ (ppm) = 58.72 (ClCH_2), 43.64 (NCH_2), 36.85 (CH_3) **IR** (ATR): $\tilde{v}$ = 3399 (m), 2568 (m), 2473 (m), 1636 (s), 1485 (w), 1217 (m), 1003 (w), 966 (w), 750 (w), 679 (w). $C_4H_{11}Cl_2N \cdot HCl$ (144.03 g mol⁻¹).

2-Azido-*N*,*N*-dimethylethan-1-amine, DMAZ 28

2-Chloro-*N*,*N*-dimethylethan-1-amine (4.22 g, 29.2 mmol, 1 eq) was dissolved in 35 mL water and stirred for 1.5 h at room temperature. Afterwards sodium azide (6.02 g, 92.6 mmol, 2.5 eq) was added and the reaction mixture was stirred at 50 °C for 2 d. After cooling down the pH value was adjusted with NaOH solution to pH 10 and the solution extracted four times with 15 mL DCM. The combined organic phases were washed with brine (1 x 15 mL), dried over sodium sulphate and the solvent removed *in vacuo*, to obtain the product as a brown oil (3.18 g, 27.9 mmol, 75%). **^{1}H NMR** (400 MHz, CDCl$_3$): δ (ppm) = 3.35 (t, 2H, C*H$_2$*N$_3$), 2.51 (t, 2H, NC*H$_2$*), 2.28 (s, 6H, -C*H$_3$*). **^{13}C NMR** (101 MHz, CDCl$_3$): δ (ppm) = 58.22 (NCH$_2$), 49.17 (CH$_2$N$_3$), 45.59 (CH$_3$). **^{14}N NMR** (29 MHz, CDCl$_3$) δ (ppm) = −133 (N$_\beta$), −171 (N$_\gamma$), −313 (N$_\alpha$) **IR** (ATR): $\tilde{v}$ = 2946 (m), 2822 (m), 2772 (m), 2094 (s), 1457 (m), 1347 (w), 1275 (s), 1179 (w), 1152 (w), 1098 (w), 1041 (m), 972 (w), 941 (w), 844 (w), 778 (m). C$_4$H$_{10}$N$_4$ (114.15 g mol^{-1}) **EA**: calcd. N 49.08, C 42.09, H 8.83 % found N 45.94, C 42.50 H 8.44 %. **DTA** (5 °C min^{-1}): T$_d$ = 135 °C. **Sensitivities**: IS: >40 J, FS: >360 N.

2-Chloro-N,N-diethylethan-1-amine, 29

2-(Diethylamino)ethan-1-ol (2.00 g, 17.1 mmol, 1 eq) was dissolved in 20 mL dichloromethane and cooled to 0 °C. Thionyl chloride (3.10 g, 42.7 mmol, 2.5 eq) and 4 drops pyridine was slowly added and the mixture was stirred at 80 °C for 6 h, then at 25 °C for another 10 h. After cooling down to room temperature, 30 mL methanol was added to remove the residual thionyl chloride. The solvent was evaporated *in vacuo* and the chlorohydrate salt of 2-chloro-*N*,*N*-diethylethan-1-amine (2.30 g, 17.0 mmol, 99%) was obtained as a white solid. **^{1}H NMR** (400 MHz, CDCl$_3$): δ (ppm) = 4.07–4.03 (t, 2H, C*H$_2$*Cl), 3.38–3.34 (t, 2H, NC*H$_2$*CH$_2$Cl), 3.27–3.15 (m, 4H, C*H$_2$*CH$_3$), 1.45–1.41 (t, 6H, -C*H$_3$*).**^{13}C NMR** (101 MHz, CDCl$_3$): δ (ppm) = 52.72 (NCH$_2$CH$_2$Cl), 47.23 (CH$_2$CH$_3$), 37.77 (NCH$_2$CH$_2$Cl), 8.68 (CH$_3$). **IR** (ATR): $\tilde{v}$ = 3370 (w), 2988 (w), 2560 (m), 2473 (m), 1630 (w), 1472 (m), 1443 (m), 1385 (m), 1321 (w), 1297 (w), 1269 (w), 1175 (w), 1103 (w), 1045 (w), 1020 (s), 973 (w), 900 (w), 848 (w), 775 (w), 739 (s). C$_6$H$_{14}$ClN·HCl (158.09 g mol^{-1}).

2-Azido-*N*,*N*-diethylethan-1-amine, DEAZ 30

2-Chloro-*N*,*N*-diethylethan-1-amine (1.00 g, 6.33 mmol, 1 eq) was dissolved in 15 mL water and stirred for 1.5 h at room temperature. Afterwards sodium azide (1.24 g, 19.0 mmol, 3 eq) was added and the reaction mixture was stirred at 80 °C over night. After cooling down the pH value was adjusted with KOH solution to pH 10 and the solution extracted four times with 15 mL Et_2O. The combined organic phases were dried over sodium sulphate and the solvent removed *in vacuo*, to obtain the product as a colourless oil (0.44 g, 3.10 mmol, 49 %). **¹H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 3.26–3.23 (t, 2H, C*H*$_2$N$_3$), 2.63–2.59 (t, 2H, NC*H*$_2$CH$_2$N$_3$), 2.56–2.50 (q, 4H, C*H*$_2$CH$_3$), 1.02–0.98 (t, 6H, CH$_2$C*H*$_3$). **¹³C NMR** (101 MHz, $CDCl_3$): δ (ppm) = 52.20 (NCH$_2$CH$_2$N$_3$), 49.50 (NCH$_2$CH$_2$N$_3$), 47.31 (CH$_2$CH$_3$), 11.85 (CH$_2$CH$_3$). **¹⁴N NMR** (29 MHz, $CDCl_3$) δ (ppm) = −133 (N$_\beta$), −177 (N$_\gamma$), −317 (N$_\alpha$) **IR** (ATR): $\tilde{v}$ = 2970 (m), 2936 (w), 2806 (m), 2093 (s), 1455 (w), 1384 (w), 1344 (w), 1294 (s), 1204 (m), 1171 (w), 1123 (w), 1069 (m), 997 (w), 916 (w), 833 (w), 740 (w). $C_6H_{14}N_4$ (142.21 g mol^{-1}) **EA**: calcd. N 39.40, C 50.68, H 9.92 % found N 43.41, C 51.09 H 9.47 %. **DTA** (5 °C min^{-1}): T_d = 170 °C. **Sensitivities**: IS: >40 J, FS: >360 N.

3-Chloro-*N*,*N*-dimethylpropan-1-amine 31

2-(Dimethylamino)propan-1-ol (1.00 g, 9.69 mmol, 1 eq) was dissolved in 20 mL dichloromethane and cooled to 0 °C. Thionyl chloride (2.90 g, 24.2 mmol, 2.5 eq) and 4 drops pyridine was slowly added and the mixture was stirred at 80 °C for 1 h. After cooling down to room temperature, 30 mL methanol was added to remove the residual thionyl chloride. After extraction with EtOAc (3 x 15 mL), the solvent was evaporated *in vacuo* and the chlorohydrate salt of 3-chloro-*N*,*N*-dimethylpropan-1-amine (1.49 g, 9.49 mmol, 98%) was obtained as a white solid. **¹H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 3.42–3.40 (t, 2H, C*H*$_2$Cl), 3.05–3.00 (m, 2H, NC*H*$_2$), 2.63 (s, 6H, -C*H*$_3$), 2.09–2.02 (p, 2H, C*H*$_2$CH$_2$Cl). **¹³C NMR** (101 MHz, $CDCl_3$): δ (ppm) = 56.25 (NCH$_2$), 43.44 (-CH$_3$), 41.62 (CH$_2$Cl), 43.64 (CH$_2$CH$_2$Cl). $C_5H_{12}ClN·HCl$ (157.04 g mol^{-1}).

3-Azido-*N*,*N*-dimethylpropan-1-amine, DMAPZ 32

2-Chloro-*N*,*N*-dimethylpropan-1-amine (5.00 g, 31.8 mmol, 1 eq) was dissolved in 35 mL water and stirred for 1.5 h at room temperature. Afterwards sodium azide (5.17 g, 79.5 mmol, 2.5 eq) was added and the reaction mixture was stirred at 80 °C over night. After cooling down the pH value was adjusted with NaOH solution to pH 10 and the solution extracted four times with 15 mL DCM. The combined organic phases were washed with brine (1 x 15 mL), dried over sodium sulphate and the solvent removed *in vacuo*, to obtain the product as a colourless oil (3.03 g, 23.7 mmol, 74 %). **^{1}H NMR** (400 MHz, CDCl$_3$): δ (ppm) = 3.36–3.32 (t, 2H, C*H*$_2$N$_3$), 2.37–2.34 (t, 2H, NC*H*$_2$), 2.23 (s, 6H, -C*H*$_3$), 1.79–1.72 (p, 2H, C*H*$_2$CH$_2$Cl). **^{13}C NMR** (101 MHz, CDCl$_3$): δ (ppm) = 56.71 (NCH$_2$), 49.67 (CH$_2$N$_3$), 45.58 (CH$_3$), 27.21 (CH$_2$*C*H$_2$CH$_2$). **^{14}N NMR** (29 MHz, CDCl$_3$) δ (ppm) = 133 (N$_\beta$), −171 (N$_\gamma$), −310 (N$_\alpha$). C$_5$H$_{12}$N$_4$ (128.18 g mol^{-1}). **DTA** (5 °C min^{-1}): T$_d$ = 150 °C. **Sensitivities**: IS: >40 J, FS: >360 N.

3-(Diethylamino)propan-1-ol 33

3-Chloropropanol (1.61 g, 17.0 mmol, 1 eq) and diethylamine (2.49 g, 34.1 mmol, 2 eq) were dissolved in 20 mL methanol and stirred at room temperature for 24 h. Afterwards the solution was heated under reflux overnight. 2 g NaOH (50.0 mmol, 1.4 eq) and water (2 mL) were added to the reaction mixture. The aqueous phase was then extracted with diethyl ether (3 × 30 mL), the combined organic extracts dried over MgSO$_4$ and the solvent was removed *in vacuo* to yield 3-(diethylamino)propan-1-ol (0.95 g, 7.2 mmol, 43%) as brownish liquid. **^{1}H NMR** (400 MHz, CDCl$_3$): δ (ppm) = 3.80–3.77 (t 2H, NC*H*$_2$CH$_2$), 2.65 (t, 2H, C*H*$_2$OH), 2.56–2.51 (q, 4H, N(C*H*$_2$CH$_3$)$_2$), 1.70–1.65 (p, 2H, CH$_2$C*H*$_2$CH$_2$), 1.07–1.03 (t, 6H, C*H*$_3$). C$_7$H$_{17}$NO (131.13 g mol^{-1})

3-Chloro-*N*,*N*-diethylpropan-1-amine 34

2-(Diethylamino)propan-1-ol (0.95 g, 7.24 mmol, 1 eq) was dissolved in 20 mL dichloromethane and cooled to 0 °C. Thionyl chloride (2.15 g, 18.1 mmol, 2.5 eq) and 4 drops pyridine was slowly added and the mixture was stirred at 80 °C for 1 h. After cooling down to room temperature, 30 mL methanol was added to remove the residual thionyl chloride. The solvent was evaporated *in vacuo* and 3-chloro-*N*,*N*-diethylpropan-1-amine

(0.75 g, 5.03 mmol, 72%) was obtained as a brownish liquid. **^{1}H NMR** (400 MHz, CDCl$_3$): δ (ppm) = 3.52–3.43 (m, 2H, C*H*$_2$Cl), 3.28–3.24 (m, 2H, NC*H*$_2$), 2.89–2.86 (m, 4H, N(C*H*$_2$CH$_3$)$_2$), 2.09–2.02 (m, 2H, C*H*$_2$CH$_2$Cl), 0.89–0.86 (t, 6H, C*H*$_3$). **^{13}C NMR** (101 MHz, CDCl$_3$): δ (ppm) = 56.25 (NCH$_2$), 49.71 (N(CH$_2$)$_2$), 45.88 (CH$_2$Cl), 26.1 (CH$_2$CH$_2$Cl), 8.53 (CH$_3$). C$_7$H$_{16}$ClN (149.10 g mol^{-1}).

3-Azido-*N*,*N*-diethylpropan-1-amine, DEAPZ 35

3-Chloro-*N*,*N*-diethylpropan-1-amine (0.75 g, 5.03 mmol, 1 eq) was dissolved in 10 mL water and stirred for 0.5 h at room temperature. Afterwards sodium azide (0.98 g, 15.1 mmol, 3 eq) was added and the reaction mixture was stirred at 80 °C for 16 h. After cooling down the solution extracted four times with 15 mL Et$_2$O. The combined organic phases were washed with brine (1 x 15 mL), dried over sodium sulphate and the solvent removed *in vacuo*, to obtain the product as a yellowish oil (0.25 g, 1.60 mmol, 32 %). **^{1}H NMR** (400 MHz, CDCl$_3$): δ (ppm) = 3.32–3.30 (t, 2H, C*H*$_2$N$_3$), 2.51–2.45 (q, 4H, N(C*H*$_2$CH$_3$)$_2$), 2.48–2.44 (t, 2H, NC*H*$_2$), 1.79–1.66 (p, 2H, C*H*$_2$CH$_2$Cl), 1.00–0.97 (t, 6H, C*H*$_3$). **^{13}C NMR** (101 MHz, CDCl$_3$): δ (ppm) = 49.93 (CH$_2$N$_3$), 49.86 (NCH$_2$), 47.02 N(CH$_2$CH$_3$)$_2$, 27.21 (CH$_2$CH$_2$CH$_2$), 11.83 (CH$_3$). **^{14}N NMR** (29 MHz, CDCl$_3$): δ (ppm) = −133 (N$_\beta$), −171 (N$_\gamma$), −320 (N$_\alpha$). C$_7$H$_{16}$N$_4$ (156.14 g mol^{-1}) **DTA** (5 °C min^{-1}): T$_d$ = 165 °C. **Sensitivities**: IS: >40 J, FS: >360 N.

2-Chloro-*N*-(2-chloroethyl)-*N*-methylethan-1-amine 36

N-Methyldiethanolamine (5.00 g, 42.0 mmol, 1 eq) was dissolved in 30 mL dichloromethane and cooled to 0 °C. Thionyl chloride (25.0 g, 210 mmol, 5 eq) was slowly added and the mixture was stirred at 50 °C for 1 h. After cooling down to room temperature, 30 mL methanol was added to remove the residual thionyl chloride. The solvent was evaporated *in vacuo* and the chlorohydrate salt of 2-chloro-*N*-(2-chloroethyl)-*N*-methylethan-1-amine as a white solid (8.12 g, 39.5 mmol, 94 %). **^{1}H NMR** (400 MHz, CDCl$_3$): δ (ppm) = 3.58 (t, 4H, C*H*$_2$Cl), 2.69 (t, 4H, NC*H*$_2$), 2.28 (s, 3H, -C*H*$_3$). **^{13}C NMR** (101 MHz, CDCl$_3$): δ (ppm) = 59.51 (CH$_2$N), 41.28 (CH$_2$Cl), 36.85 (CH$_3$). **IR** (ATR): $\tilde{\nu}$ = 2984 (m), 2437 (w), 1478 (m), 1383 (m), 1328 (m), 1309 (m), 1276 (m), 1125 (m), 980 (m), 949 (w), 911 (w), 778 (w), 741 (m), 741 (m), 668 (m), 518 (s). C$_5$H$_{11}$Cl$_2$N·HCl (192.50 g mol^{-1}).

2-Azido-*N*-(2-azidoethyl)-*N*-methylethan-1-amine, DAzEMA 37

2-Chloro-*N*-(2-chloroethyl)-*N*-methylethan-1-amine (2.00 g, 10.4 mmol, 1 eq) was dissolved in 35 mL water and stirred for 1.5 h at room temperature. Afterwards sodium azide (3.38 g, 51.9 mmol, 5 eq) was added and the reaction mixture was stirred at 50 °C for 2 d. After cooling down the pH value was adjusted with NaOH solution to pH 10 and the solution extracted four times with 15 mL Et$_2$O. The combined organic phases were washed with brine (1 x 15 mL), dried over sodium sulphate and the solvent removed *in vacuo*, to obtain the product 2-azido-*N*-(2-azidoethyl)-*N*-methylethan-1-amine as an orange oil (1.02 g, 6.03 mmol, 58 %). **^{1}H NMR** (400 MHz, CDCl$_3$): δ (ppm) = 3.33 (t, 4H, C*H*$_2$N$_3$), 2.65 (t, 4H, NC*H*$_2$), 2.33 (s, 3H, -C*H*$_3$). **^{13}C NMR** (101 MHz, CDCl$_3$): δ (ppm) = 56.62 (NCH$_2$), 49.03(CH$_2$N$_3$), 42.14 (CH$_3$). **^{14}N NMR** (29 MHz, CDCl$_3$) δ (ppm) = −133 (N$_\beta$), −170 (N$_\gamma$), −314 (N$_\alpha$) **IR** (ATR): $\tilde{\nu}$ = 2100 (s), 1704 (w), 1460 (m), 1355 (m), 1283 (s), 1082 (w), 623 (w). C$_5$H$_{11}$N$_7$ (169.02 g mol^{-1}) **EA**: calcd. N 57.95, C 35.50, H 6.55 % found N 57.49, C 35.38 H 6.45 %. **DTA** (5 °C min^{-1}): T$_d$ = 167 °C. **Sensitivities**: IS: >40 J, FS: >360 N.

N-Ethyldiethanolamine 38

Diethanolamine (5.00 g, 47.6 mmol, 1 eq) was dissolved in 20 mL ethanol. K$_2$CO$_3$ (8.21 g, 59.5 mmol, 1.25 eq) and bromoethane (5.19 g, 47.6 mmol, 1 eq) were added and the mixture was refluxed for 4 d. The solid was filtered off, the filtrate reduced to half of the volume and stored overnight at 4 °C. The obtained with solid was filtered off and the residual solvent was removed *in vacuo*. The obtained residue was distilled under vacuum at 85°C (1.5 mbar). The product *N*-ethyldiethanolamine was obtain (3.20 g, 24.2 mmol, 51%) as a colourless oil. **^{1}H NMR** (400 MHz, CDCl$_3$): δ (ppm) = 3.61 (t, 4H, C*H*$_2$OH), 2.65–2.63 (t, 4H, NC*H*$_2$CH$_2$), 2.64–2.60 (q, 2H, NC*H*$_2$CH$_3$), 1.04 (t, 3H, -C*H*$_3$). **^{13}C NMR** (101 MHz, CDCl$_3$): δ (ppm) = 51.34 (NCH$_2$), 48.12 (CH$_2$CH$_3$), 43.64 (CH$_2$OH), 15.10 (CH$_3$). C$_6$H$_{15}$NO$_2$ (133.19 g mol^{-1}).

2-Chloro-*N*-(2-chloroethyl)-*N*-ethylethan-1-amine 39

N-Ethyldiethanolamine (3.00 g, 22.5 mmol, 1 eq) was dissolved in 30 mL dichloromethane and cooled to 0 °C. Thionyl chloride (13.5 g, 113 mmol, 5 eq) was slowly added and the

mixture was stirred at 50 °C for 2 h. After cooling down to room temperature, 40 mL methanol was added to remove the residual thionyl chloride. The solvent was evaporated *in vacuo* and the chlorohydrate salt of 2-chloro-*N*-(2-chloroethyl)-*N*-ethylethan-1-amine as a brown solid (4.50 g, 21.7 mmol, 97 %). **¹H NMR** (400 MHz, CDCl₃): δ (ppm) = 4.15–4.01 (m, 4H, CH_2Cl), 3.59–3.43 (m, 4H, NCH_2), 3.35 (q, 2H, NCH_2CH₃), 1.49 (t, 3H, -CH_3). **¹³C NMR** (101 MHz, CDCl₃): δ (ppm) = 53.71 (CH₂N), 48.90 (NCH₂CH₃), 36.58 (CH₂Cl), 8.72 (CH₃). **IR** (ATR): $\tilde{v}$ = 2985 (s), 2388 (w), 1729 (s), 1456 (w), 1278 (m), 1015 (m), 986 (m), 787 (m), 756 (w), 732 (w). $C_6H_{14}Cl_2N \cdot HCl$ (206.53 g mol⁻¹).

2-Azido-*N*-(2-azidoethyl)-*N*-ethylethan-1-amine, DAzEEA 40

2-Chloro-*N*-(2-chloroethyl)-*N*-ethylethan-1-amine (1.50 g, 7.26 mmol, 1 eq) was dissolved in 30 mL acetone and stirred for 30 min at room temperature. Afterwards sodium azide (2.36 g, 36.3 mmol, 5 eq) was added and the reaction mixture was stirred at 70 °C for 3 d. After cooling down the pH value was adjusted with NaOH solution to pH 10 and the solution extracted four times with 25 mL Et₂O. The combined organic phases were washed with brine (1 x 15 mL), dried over sodium sulphate and the solvent removed *in vacuo*, to obtain the product 2-azido-*N*-(2-azidoethyl)-*N*-ethylethan-1-amine as an orange oil (0.56 g, 3.05 mmol, 42 %). **¹H NMR** (400 MHz, CDCl₃): δ (ppm) = 3.30 (t, 4H, CH_2N₃), 2.72 (t, 4H, NCH_2), 2.63 (q, 2H, NCH_2CH₃), 1.06 (t, 3H, -CH_3). **¹³C NMR** (101 MHz, CDCl₃): δ (ppm) = 53.60 (NCH₂), 50.04 (CH₂N₃), 48.56 (CH₂CH₃), 12.36 (CH₃). **¹⁴N NMR** (29 MHz, CDCl₃): δ (ppm) = −133 (N$_\beta$), −170 (N$_\gamma$), −313 (N$_\alpha$) **IR** (ATR): $\tilde{v}$ = 2100 (s), 1704 (s), 1460 (m), 1355 (m), 1283 (s), 1082 (w), 623 (w). $C_6H_{13}N_7$ (183.22 g mol⁻¹). **EA**: calcd. N 53.51, C 39.33, H 7.15 % found N 49.33, C 39.30 H 6.63 %. **DTA** (5 °C min⁻¹): T_d= 166 °C. **Sensitivities**: IS: >40 J, FS: >360 N.

Tris(2-chloroethyl)amine 41

Triethanolamine (4.00 g, 26.8 mmol, 1 eq) was dissolved in 30 mL chloroform and cooled to 0 °C. Thionyl chloride (22.3 g, 188 mmol, 7 eq) was slowly added and the mixture was stirred at 50 °C for 2 h. After cooling down to room temperature, 50 mL methanol was added to decompose the residual thionyl chloride. The solvent was evaporated *in vacuo* and the solid was recrystallized from ethyl acetate. The chlorohydrate salt of Tris-(2-chloroethyl)amine

was yielded as a white solid (3.65 g, 20.7 mmol, 77 %). **^{1}H NMR** (400 MHz, CDCl$_3$): δ (ppm) = 3.51 (t, 6H, CH_2Cl), 2.98 (t, 6H, NCH_2). **^{13}C NMR** (101 MHz, CDCl$_3$): δ (ppm) = 56.93 (CH$_2$N), 42.23 (CH$_2$Cl). **IR** (ATR): $\tilde{v}$ = 2985 (s), 2388 (w), 1729 (s), 1456 (w), 1278 (m), 1015 (m), 986 (m), 787 (m), 756 (w), 732 (w). C$_6$H$_{12}$Cl$_3$N·HCl (240.97 g mol^{-1}).

Tris(2-azidoethyl)amine, TAzEA 42

Tris-(2-chloroethyl)amine (3.00 g, 12.4 mmol, 1 eq) was dissolved in 15 mL water and stirred for 30 min at room temperature. Afterwards sodium azide (5.67 g, 87.1 mmol, 7 eq) was added and the reaction mixture was stirred at 100 °C for 2 d. The solution was extracted four times with 25 mL DCM. The combined organic phases were washed with brine (1 x 15 mL), dried over sodium sulphate and the solvent removed *in vacuo*, to obtain the product Tris(2-azidoethyl)amine as a yellowish oil (1.65 g, 7.36 mmol, 59 %). **^{1}H NMR** (400 MHz, CDCl$_3$): δ (ppm) = 3.35 (t, 6H, CH_2N$_3$), 2.79 (t, 6H, NCH_2). **^{13}C NMR** (101 MHz, CDCl$_3$): δ (ppm) = 54.09 (NCH$_2$), 49.84 (CH$_2$N$_3$). **^{14}N NMR** (29 MHz, CDCl$_3$): δ (ppm) = −134 (N$_\beta$), −171 (N$_\gamma$), −316 (N$_\alpha$) **IR** (ATR): $\tilde{v}$ = 2938 (s), 2828 (w), 2085 (s), 1449 (s), 1346 (m), 1269 (s), 1155 (m), 1056 (s), 967 (m), 909 (m), 830 (m), 766 (m), 638 (w), 553 (m). C$_6$H$_{12}$N$_{10}$ (224.25 g mol^{-1}). **EA**: calcd. N 62.47, C 32.14, H 5.39 % found N 62.19, C 32.55 H 5.31 %. **DTA** (5 °C min^{-1}): T$_d$ = 187 °C. **Sensitivities**: IS: 25 J, FS: >360 N.

1-Amino-3-chloro-propan-2-ol 43

Benzaldehyde (8.03 g, 75.7 mmol, 1 eq) was dissolved in 20 mL of ethanol. Afterwards ammonia (25 %) (7.58 mL, 1.90 mmol) was slowly added to the reaction solution and cooled down to 0 °C. During cooling, epichlorohydrin (5.89 mL, 75.5 mmol, 1 eq) was added and the solution stirred for 40 °C overnight. After completion, 20 mL toluol and 5 mL of HCl (2 M) were added and the solution was stirred for additional 3 hours at 45 °C. The aqueous phase was separated, and the organic phase was extracted with water (2 × 30 mL). The combined aqueous phases were concentrated *in vacuo*. The precipitate was recrystallized from ethanol to yield 1-amino-3-chloro propan-2-ol as hydrochloride salt (4.83 g, 33.0 mmol, 43%) as dark yellow solid. **^{1}H NMR** (400 MHz, D$_2$O): δ (ppm) = 4.24-4.14 (m, 1H, CH), 3.79-3.62 (m, 2H,

CH_2Cl), 3.34-3.05 (m, 2H, CH_2NH_2). ^{13}**C NMR** (101 MHz, D$_2$O): δ (ppm) = 67.24 (COH), 46.13 (CH$_2$Cl), 42.10 (CH$_2$NH$_2$). C$_3$H$_8$ClNO·HCl (146.01 g mol^{-1}).

1,3-Dichloropropan-2-amine 44

Thionyl chloride (16.0 mL, 207 mmol, 5 eq) was carefully added to 2-aminopropane-1,3-diol (4.01 g, 44.0 mmol, 1 eq) while cooling. The mixture was then refluxed at 65 °C for 1 h. After 30 minutes a formation of orange foam started and another portion of thionyl chloride (15.0 mL, 194.8 mmol, 4 eq) was added. After another 30 minutes, the reaction mixture was cooled with ice and quenched with water. After neutralization with sodium hydroxide, chloroform was added to the mixture and it was stirred overnight. After separation of the chloroform phase, it was washed with 3 x 10 mL water and the combined organic phases were concentrated *in vacuo*. The crude product was recrystallized in a mixture of ethyl acetate and acetone (2:1) to yield 1,3-dichloropropan-2-amine as hydrochloride salt (4.32 g, 26.3 mmol, 60%). ^{1}**H NMR** (400 MHz, d_6-DMSO): δ (ppm) = 3.74 (d, 4H, CH_2Cl), 3.39 (m, 1H, CH). ^{13}**C NMR** (101 MHz, d_6-DMSO): δ (ppm) = 53.35 (CH), 45.92 (CH$_2$Cl). C$_3$H$_8$Cl$_3$N·HCl (164.46 g mol^{-1}).

1-Chloro-2-methylpropan-2-amine 45

2-amimo-2-methylpropan-1-ol (3.00 g, 33.7 mmol, 1 eq) was dissolved in 20 mL DCM and cooled to 0 °C. Thionyl chloride (10.0 g, 84.3 mmol, 2.5 eq) was slowly added and the mixture was stirred at 50 °C for 1 h. After cooling down to room temperature, 20 mL methanol was added to decompose the residual thionyl chloride. The solvent was evaporated *in vacuo* and the chlorohydrate salt of 1-chloro-2-methylpropan-2-amine as a white solid (4.01 g, 27.8 mmol, 83 %). ^{1}**H NMR** (400 MHz, CDCl$_3$): δ (ppm) = 8.30 (bs, 2H, NH_2), 3.34 (s, 2H, CH_2), 1.17 (s, 6H, -CH_3). **IR** (ATR): $\tilde{v}$ = 3242 (m), 2979 (m), 2034 (s), 1617 (s), 1526 (m), 1506 (m), 1374 (s), 1239 (m), 1139 (w), 1074 (w), 1038 (w), 615 (w). C$_4$H$_{10}$ClN·HCl (144.03 g mol^{-1}).

2-(2-Azidoethoxy)-N,N-dimethylethan-1-amine 46

To a solution of 2-azidoethanol (1.03 g, 11.8 mmol, 1 eq) in sodium hydroxide (2.38 g, 59.5 mmol, 5 eq) in 10 mL water, 2-chloro-*N,N*-dimethyl-ethan-1-amine (2.54 g, 23.6 mmol,

2 eq) was added. The solution was stirred in 10 mL diethyl ether for 30 min and afterwards refluxed overnight at 50 C. After completion, the ether phase was separated, and the aqueous phase washed with diethyl ether (3 × 20 mL). The combined organic phases were dried over sodium sulphate and concentrated in *vacuo*. A brown liquid was obtained (0.58 g, 3.67 mmol, 31%) obtained. **^{1}H NMR** (400 MHz, D_2O): δ (ppm) = 3.64-3.58 (m, 4H, CH_2O), 3.40-3.37 (t, 2H, CH_2N), 2.55-2.52 (t, 2H, CH_2N$_3$), 2.28 (s, 6H, CH_3). **^{13}C NMR** (101 MHz, D_2O): δ (ppm) = 69.91 (NCH_2CH$_2$O), 69.54 (N$_3$$CH_2CH_2$O), 58.88 ($CH_2$N), 50.81 ($CH_2N_3$), 45.97 ($CH_3$). $C_6H_{14}N_4O$ (158.21 g mol^{-1}).

2,2'((2-Aminoethyl)azanediyl)bis(ethan-1-ol), 47

Sodium hydroxide (1.75 g, 43.8 mmol, 2 eq) was dissolved in water and 2-chlorethan-1-amine hydrochloride (2.54 g, 21.9 mmol, 1 eq) was added. This mixture was stirred at 50 °C for 2 h. Afterwards diethanolamine (1.60 mL, 16.9 mmol, 1 eq) was added and this mixture was refluxed for 3 h. The mixture was concentrated *in vacuo* and 2,2'((2-aminoethyl)azanediyl)bis(ethan-1-ol) (2.70 g, 18.2 mmol, 83%) was obtained as orange liquid. **^{1}H NMR** (400 MHz, d_6-DMSO): δ (ppm) = 3.87 (bs, 4H, NH_2, OH), 3.53 (t, 4H, CH_2OH), 2.76 (t, 2H, CH_2NH$_2$), 2.45-2.66 (m, 6H, NCH_2). **^{13}C NMR** (101 MHz, d_6-DMSO): δ (ppm) = 60.46 (NCH_2CH$_2$OH), 57.77 (NCH$_2$$CH_2$OH), 59.24 (N$CH_2CH_2NH_2$), 41.27 (NCH$_2$$CH_2NH_2$). $C_6H_{16}N_2O_2$ (148.12 g mol^{-1}).

N^1,N^1-bis(2-azidoethyl)ethane-1,2-diamine, 48

Tris(2-azidoethyl)amine (1.12 g, 4.46 mmol, 1 eq) was dissolved in 10 mL diethyl ether, as well as triphenylphosphine (1.32 g, 5.02 mmol, 1.1 eq) in another 10 mL. Triphenylphosphine was slowly added with a dropping funnel and gas formation is observed. After 2 hours the gas formation came to an end and water was added to the solution. The ether phase was removed and extracted with water 1 x 50 mL. The combined aqueous phases were concentrated *in vacuo* and to the obtained solution a spatula of zinc(II)chloride and 5 mL ethanol was added to remove the triphenylphosphine as precipitated oxide. This purification step yielded clean N^1,N^1-bis(2-azidoethyl)ethane-1,2-diamine (0.13 g, 0.64 mmol, 14%). **^{1}H NMR** (400 MHz, d_6-DMSO): δ (ppm) = 6.18 (br, 2H, NH_2), 3.37 (m, 6H, NH$_2$CH_2; CH$_2$N$_3$), 2.72

(m, 6H, CH_2NH$_2$), 2.45-2.66 (m, 6H, (N(CH_2)$_3$). **^{13}C NMR** (101 MHz, d_6-DMSO): δ (ppm) = 37.24 (1C, NH$_2$CH$_2$), 48.08 (2C, N$_3$CH$_2$), 52.12 (3C, N(CH$_2$)$_3$). C$_6$H$_{14}$N$_8$ (198.23 g mol^{-1}).

2.5 Salts and Ionic liquids

In this section, the syntheses of salts derived from DE-DAM **12** and several ionic liquids are described. Compounds already known in literature are characterized in more detail and compared to the literature values. The synthesis and characteristics of some new energetic compounds, salts as well as ionic liquids are specified in this chapter.

2.5.1 Salt of DE-DAM

Derived from the previously synthesized compound DE-DAM **12**, two energetic salts, the potassium and the lithium salts, are synthesized and characterized. They have not been described in literature before.

2.5.1.1 Synthesis

For the synthesis of the energetic potassium salt, compound **12** was diluted in water and potassium hydroxide was added. It was observed during the reaction, that the colour changed to a slightly brown solution. The energetic salt potassium 2,2-diazidomalonate, K_2DAM **49**, was obtained as light brown crystals after recrystallisation from acetone in 64% yield. The reaction is shown in Scheme 37.
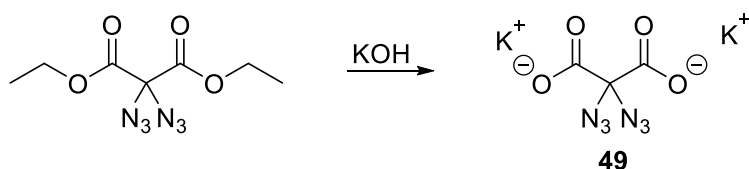
Scheme 37: Synthesis route towards K_2DAM 49.

With same prescription and addition of lithium hydroxide instead of potassium hydroxide, the lithium salt lithium 2,2-diazidomalonate, Li_2DAM **50**, was also synthesized and is depicted in Scheme 38. This lithium salt was yielded in 64% as light red crystals.
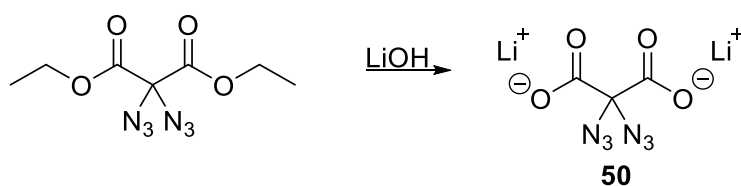
Scheme 38: Synthesis route towards Li_2DAM 50.

Both energetic salts were obtained as crystals and further investigated in the next section.

2.5.1.2 Characterisation

The crystal structure of compound **49** is depicted in Figure 12 below.
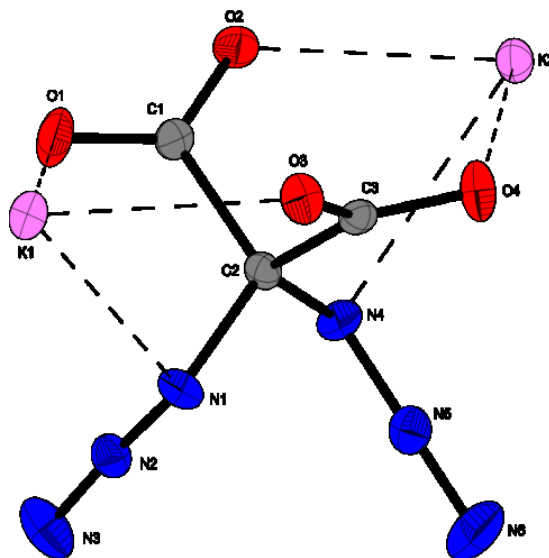
Figure 12: Crystal structure of K₂DAM. Thermal ellipsoids at 50 % probability.

It crystallizes in the triclinic space group P −1 with two molecules in the unit cell. The calculated density of this compound is 1.981 g cm⁻³ at 173 K. The binding angle between O1-C1-O2 and O3-C3-O4 are both around 128°. The angle between C1-C2-C3 is 108° and the angle between N1-C2-N4 is 112°. The angle between the azide groups are both almost linear with 173° based on hyperconjugation effects.[136] Bond length between the azido moiety and the geminal carbon (C2-N1; C2-N4) are 1.48Å. Carbon and oxygen bonds (O1-C1; C1-O2; O3-C3; C3-O3) are around 1.25Å length with a high double bond character and carbon-carbon bonds (C1-C2; C2-C3) are the longest within this molecule with 1.56Å. The bond lengths between N1-N2 and N4-N5 are 1.25Å which is in the range of an N-N double bond. The angles between N3-N2 and N6-N5 are with 1.13Å close to formal triple bond.[51] The potassium salt **49** was also characterized via NMR spectroscopy. As expected, no signals in the measured ¹H NMR were obtained. ¹³C NMR analysis showed the two signals at 171.1 ppm for the carboxy carbon and at 76.5 ppm for the geminal carbon with the two azido groups attached. No loss of the azide groups during the ester hydrolysis was proven via ¹⁴N

NMR spectroscopy. The three signals appear at −138 ppm (N_β), −159 ppm (N_γ) and −283 ppm (N_α).

In comparison, the NMR shifts of the lithium salt **50** appear slightly shifted for the carbon signals at 170.6 ppm (−COO) and at 77.9 ppm ($C(N_3)_2$). The azide signals in the ^{14}N NMR are allocated at −139 ppm (N_β), −160 ppm (N_γ) and −260 ppm (N_α).

Elemental analysis for the lithium salt shows, that one equivalent of crystal water is present in the lithium salt **50**.

The friction and impact sensitivities of the synthesized energetic salts **49** and **50** were measured in addition with the decomposition temperature and listed in Table 11 below.

Table 11: Sensitivities and decomposition temperature of the energic salts derived from DE-DAM 11.

Compound	Impact sensitivity [J]	Friction sensitivity [N]	T_d [°C]
K₂DAM 49	5	288	105
Li₂DAM 50	40	360	98

The potassium salt **49** is classified as sensitive according to UN recommendation. The value for impact sensitivity is relatively low, therefore, this compound must be handled very carefully. In contrast, the lithium salt is classified as insensitive towards friction and impact sensitivity. This can be explained by the presence of crystal water. No difficulties were observed in handling these compounds.

Decomposition temperatures were measured to be 105 °C for the potassium salt **49** and 98 °C for the lithium salt **50**.

2.5.1.3 Unsuccessful attempts derived from DE-DAM 12 and energetic salt 49

It is from high interest to obtain high energetic liquids (HEIL´s) with high N-content. Therefore, geminal diazidated molecules are an interesting building block. A possible method is the transformation of the salt **49** into the acid chloride, which is highly reactive and can be easily derivatized by substitution.

Generally, it is possible to synthesize the acid chloride directly by adding a chlorination agent like thionyl chloride or sulfuryl chloride. Several synthetic attempts were performed on the one hand from DE-DAM **12** and on the other hand from the potassium salt **49** to yield 2,2-diazidomalonyl dichloride according to Scheme 39.
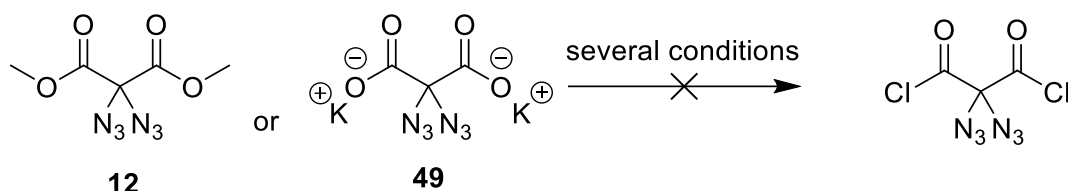
Scheme 39: Synthesis route towards 2,2-diazidomalonyl dichloride.

First the reactions were carried out in neat SOCl$_2$[137], then in chlorinated solvents like chloroform (CDCl$_3$) and dichloromethane (DCM). In addition, sulfuryl chloride and oxalyl chloride was also tested for chlorination[138]. The last approach was executed, adding triethylamine as a base to trap the formed acid. None of these reaction conditions lead to a successful synthesis of the acid chloride. In every attempt, a degradation of the salt was observed. It seems impossible to form the acid chloride because of stability reasons.

To investigate the stability of the potassium salt **49** in more detail, a recoupling with ethanol and DCC as coupling agent was tried. The reaction is depicted in Scheme 40. This reaction did not lead to the desired product either.
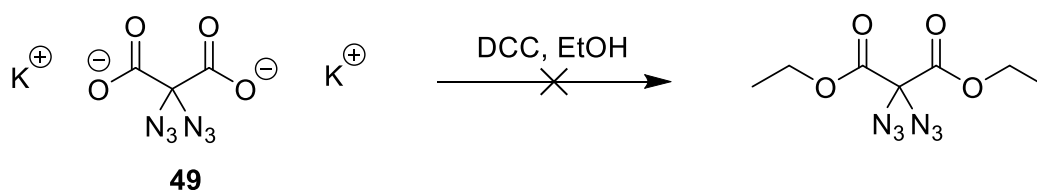
Scheme 40: Synthesis route towards DE-DAM 12 via recoupling.

Furthermore, a cation exchange reaction of the potassium salt **49** together with an imidazolium chloride salt was carried out. Because of the large size of the cation and anion, these reactions should lead to several new ionic liquids.

Cation = [diAIM], [EAIM], [BMIM], [MEIM]
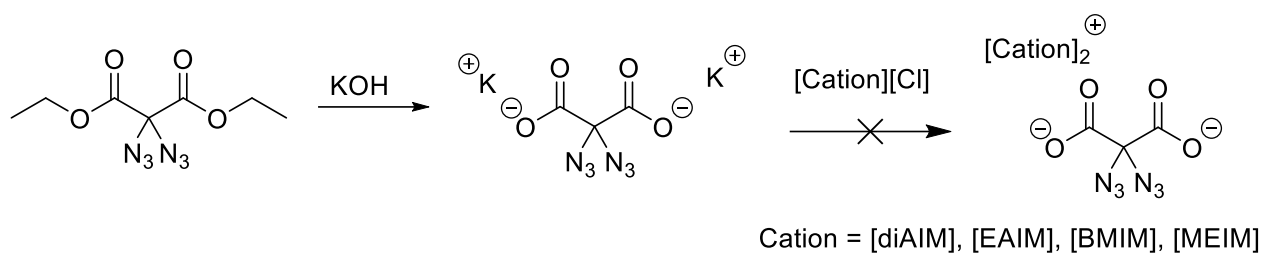
Scheme 41: Cation exchange reaction of K₂DAM 49.

As shown in Scheme 41, the exchange reaction was carried out with the imidazolium salts.

First attempts were executed starting in one case with the previously synthesized 1,3-diallylimidazolium chloride and in the other with 1-allyl-3-ethylimidazolium chloride, described in section 2.5.2. The next one was the exchange reaction of 1-butyl-3-methylimidazolium chloride. Last approach was additional done with the commercially available 1-ethyl-3-methylimidazolium chloride to eliminate the impurity factor.

The exchange reactions were carried out dissolving both salts in THF and merging them. None of the cation exchange reactions took place. Unlike expected during a salt metathesis reaction, no potassium chloride was formed. An explanation could be the large size of the anions and the resulting steric hinderance during the salt formation.

Therefore, the exchange reaction was also carried out using a smaller cation, the tetramethylammonium (TMA) as chloride salt. However, the TMA cation could not be detected in the measured ^{14}N NMR after the exchange reaction. A cation exchange reaction from K₂DAM to form ionic liquids of the energetic anion seems impossible with the tested reaction conditions.

2.5.2 Imidazolium based ionic liquids

For the testing of hypergolicity with hydrogen peroxide, several ionic liquids derived from imidazolium (IM) were synthesized. These IM compounds were chosen by two criteria: the commercial availability and the rising interest in recent research as hypergolic fuel[139]. To the best of our knowledge, investigations to the hypergolic behavior of ILs containing IM-derivatives with HTP are not performed or known in literature. Their hypergolic behaviour was only described with WFNA, showing relatively low ID times with 5 ms.[140] These compounds are all known in literature, where the synthesis and the properties are described.

2.5.2.1 Synthesis

The general synthesis of these cyanoborohydride imidazolium salts starts from imidazole in dry THF, adding sodium hydride to form the sodium imidazolium. A formation of hydrogen can be observed during the addition. In the next step, the respective alkyl halide is added to yield either 1-ethyl imidazole **51** or 1-propylimidazole **52**.[141] Here, the sodium halide was built as precipitate. Compound **51** was obtained in very good 94% yield and compound **52** in 90% yield. No complications occurred during this alkyl imidazole syntheses.
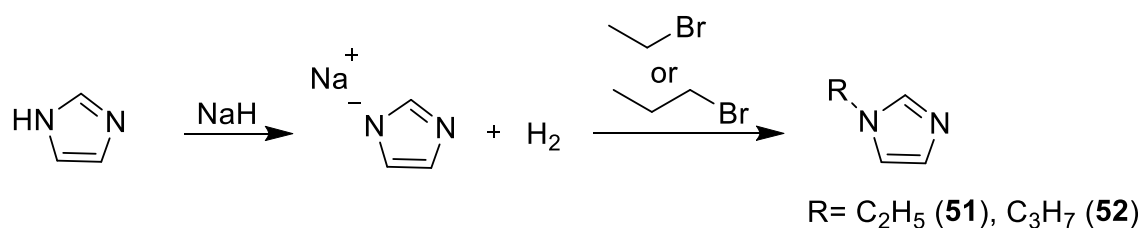
Scheme 42: Synthesis route towards alkyl imidazolium.

1-Methylimidazole is commercially available and was therefore used without further purification for the following alkylation step.

After the synthesis of the alkyl imidazolium compounds, the precursors of the ionic liquid were synthesized by addition of the respective alkyl halide in dry toluene.[142] The reaction is shown in Scheme 43 below.

$R_1 = CH_3, C_2H_5, C_3H_7$

$R_1 = CH_3, C_2H_5, C_3H_7$
$R_2 = C_2H_5, C_3H_7, C_4H_9, C_3H_5$

$X = Br, I$
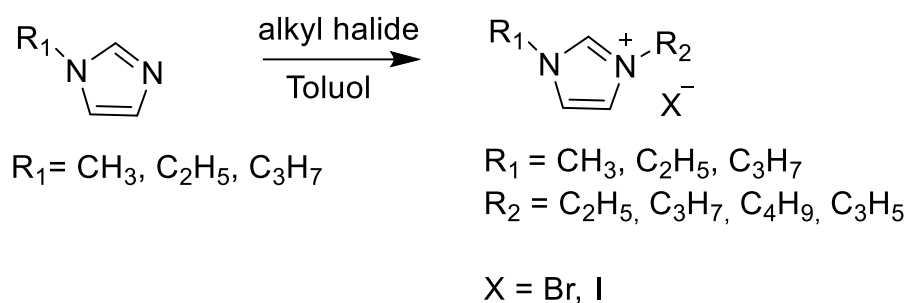
Scheme 43: Synthesis route toward the imidazolium ionic liquid precursor.

Several imidazolium salts with halogen anions were obtained with this reaction. They are pictured in Figure 13 and named after their abbreviations, as follows 3-ethyl-1-methyl-1*H*-imidazol-3-ium bromide **53,** 1-methyl-3-propyl-1*H*-imidazol-3-ium iodide **54**, 3-ethyl-1-propyl-1*H*-imidazol-3-ium bromide **55**, 1,3-dipropyl-1*H*-imidazol-3-ium iodide **56**, 3-allyl-1-methyl-1*H*-imidazol-3-ium bromide **57**, 1-allyl-3-ethyl-1*H*-imidazol-3-ium bromide **58**, 1,3-diallyl-1*H*-imidazol-3-ium bromide **59** and 3-butyl-1-methyl-1*H*-imidazol-3-ium bromide **60**.
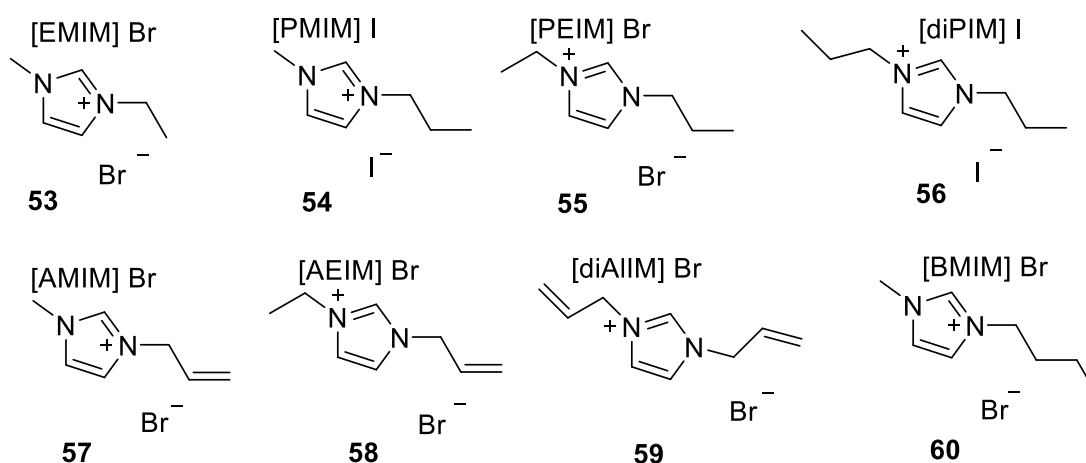
Figure 13: Structure formula of the synthesized alkyl imidazolium salts.

The halogen imidazolium salts were all obtained as light brown till brown viscous oils in almost good yields of 48% up to 69%.

The next step was an anion exchange reaction according to BHOSALE using sodium cyanoborohydride, pictured in Scheme 44.[140] During this reaction, the sodium halogen salt precipitates and is filtered off the solution.

$R_1 = CH_3, C_2H_5, C_3H_7$
$R_2 = C_2H_5, C_3H_7, C_4H_9, C_3H_5$

$X = Br, I$
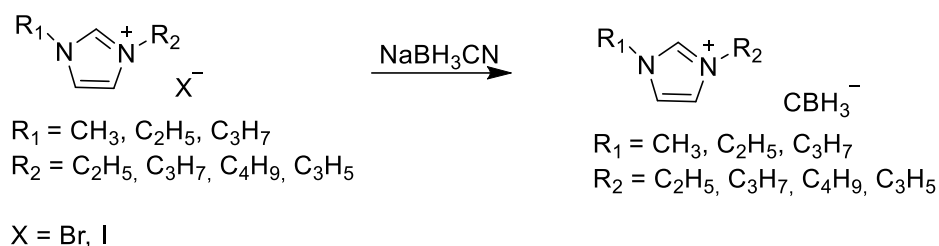
Scheme 44: Synthesis route toward the imidazolium cyanoborohydride ionic liquids.

In Figure 14 below shows all imidazolium ionic liquids **61 - 68** synthesized within this study are mentioned. There are named after their abbreviation as follows, 3-ethyl-1-methyl-1*H*-imidazol-3-ium cyanoborohydride **61**, 1-methyl-3-propyl-1*H*-imidazol-3-ium cyanoborohydride **62**, 3-ethyl-1-propyl-1*H*-imidazol-3-ium cyanoborohydride **63**, 1,3-dipropyl-1*H*-imidazol-3-ium cyanoborohydride **64**, 3-allyl-1-methyl-1*H*-imidazol-3-ium cyanoborohydride **65**, 1-allyl-3-ethyl-1*H*-imidazol-3-ium cyanoborohydride **66**, 1,3-diallyl-1*H*-imidazol-3-ium cyanoborohydride **67** and 3-butyl-1-methyl-1*H*-imidazol-3-ium cyanoborohydride **68**.
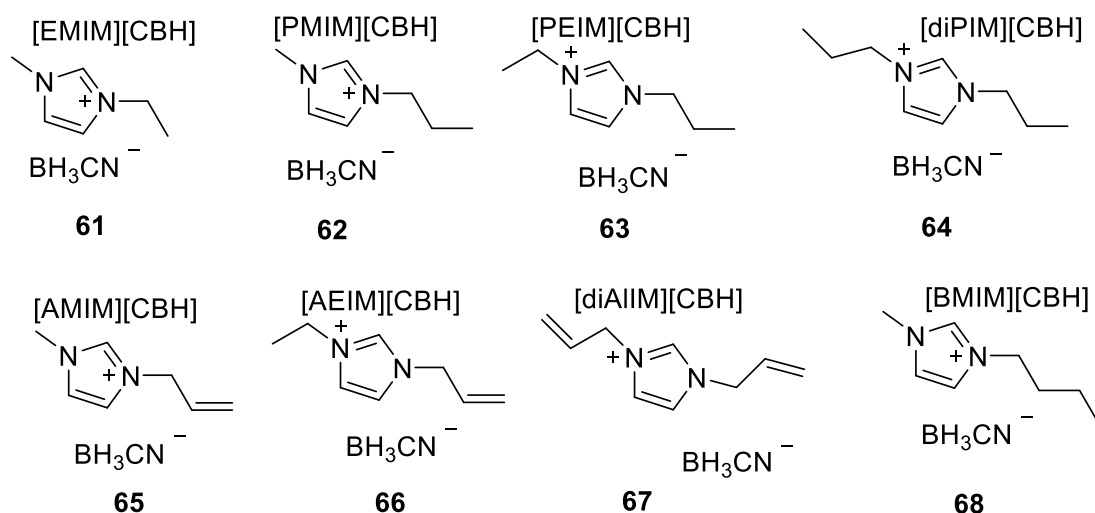
Figure 14: Structure formula of the synthesized ionic liquids derived from imidazolium.

During these exchange reactions several problems were observed within the synthesis of the cyanoborohydride liquids. The yields of the obtained ionic liquids were relatively low, with the lowest yield at 20% and the highest around 40%. Repeating the reaction to obtain a higher amount of the respective ionic liquids showed several purity problems in the NMR spectrum. Although every product was clearly identified, the charges revealed differences in

the peaks and showed several impurities. In the end, it was stated, that within these syntheses of the above-mentioned ionic liquids each batch differed from the other regarding purity and yield, even though exactly the same synthesis was performed. A possible explanation could be in the viscosity, the liquidity and the steric complexity of the ionic liquids. Therefore, an exact and reliable investigation of the hypergolic behaviour cannot be given.

2.5.2.2 Characterisation

Compounds **51** and **52** were characterized via NMR spectroscopy in DMSO and the obtained signals compared with the literature values.[143]

For the ethyl imidazole **51** the hydrogen signals appear as expected, for the imidazole as singlet at 7.64 ppm for the CH group between the two nitrogens and as two doublets at 7.17 ppm and 6.89 ppm for the other CH groups. The ethyl residue shows up as quartet and triplet at 3.95 ppm and 1.33 ppm. Carbon signals in the measured ^{13}C NMR can be allocated at 136.7 ppm (N-CH-N), 128.2/118.8 ppm (N-CH-CH-N), 40.9 ppm (N-CH_2-CH_3) and 16.3 ppm (N-CH_2-*CH_3*).

Propyl imidazole **52** has six signals in the measured ^1H NMR spectrum, which all match the literature values. They show up at 8.29 ppm, 7.43 ppm and 7.36 ppm for the imidazole hydrogens and as triplet (4.02 ppm), multiplet (1.80 ppm) and triplet (0.80 ppm) for the propyl residue. The carbon signals appear at 135.8 ppm (N-CH-N), 120.3 ppm (N-*CH*-CH-N), 48.4 ppm (N-CH_2-CH_2-CH_3), 23.4 ppm (N-CH_2-*CH_2*-CH_3) and 10.5 ppm (N-CH_2-CH_2-*CH_3*).

The halogen imidazolium salts were characterized via ^1H and ^{13}C NMR spectroscopy in DMSO. The obtained signals were compared with the signals of the precursors.

[EMIM]Br **53** shows now six signals in the ^1H NMR spectrum. The signals from the imidazolium scaffold appear at 9.50 ppm, 7.91 ppm and 7.80 ppm. The hydrogens of ethyl residue show up at 4.24 ppm and 1.38 ppm and the methyl hydrogens at 3.80 ppm. Carbon signals can be assigned at 136.2 ppm (N-CH-N), 123.3/121.8 ppm (N-CH-CH-N), 44.0 ppm (N-CH_3), 35.7 ppm (N-CH_2-CH_3) and 15.1 ppm (N-CH_2-*CH_3*).

For [PMIM]I **54** seven hydrogen signals in the measured ^{1}H NMR spectrum were obtained. The ones from the imidazole appear at 9.26 ppm and 7.83 ppm and 7.81 ppm. The propyl residue shows up as two multiplets at 4.20 ppm (hydrogens next to the amine) and 1.80 ppm. The last one can be assigned to the middle CH_2 hydrogens. The CH_3 hydrogens of the propyl residue appear as triplet at 0.83 ppm and the methyl hydrogens at 4.10 ppm. In the measured carbon NMR, there are the seven signals allocated at 135.6 ppm (N-CH-N), 122.3/122.0 ppm (N-CH-CH-N), 50.3 ppm (N-CH_2-CH_2-CH_3), 44.2 ppm (N-CH_3), 22.8 ppm (N-CH_2-CH_2-CH_3) and 10.4 ppm (N-CH_2-CH_2-CH_3).

For the ethyl analogue [PEIM]Br **55** are the hydrogen signals assigned at 9.21 ppm, 7.81 ppm and 7.78 ppm for the imidazole and at 4.10 ppm, 1.80 ppm and 0.84 ppm for the propyl hydrogens and at 4.11 ppm and 0.85 ppm for the ethyl hydrogens. The expected eight carbon signals show up at 135.9 ppm (N-CH-N), 122.4/122.2 ppm (N-CH-CH-N), 50.3 ppm (N-CH_2-CH_2-CH_3), 44.1 ppm (N-CH_2-CH_3), 22.7 ppm (N-CH_2-CH_2-CH_3), 15.0 ppm (N-CH_2-CH_3) and 10.5 ppm (N-CH_2-CH_2-CH_3).

The synthesized dipropyl imidazole, [DiPIM]I **56**, reveals the imidazole hydrogen signals in the ^{1}H NMR at 9.21 ppm and 7.81 ppm, whereby the last one has double intensity. The propyl residue appears due to symmetry as triplet at 4.14 ppm, as multiplet at 1.81 ppm and as another triplet at 0.84 ppm. ^{13}C NMR also shows only five different signals due to symmetry. These can be allocated at 135.9 ppm (N-CH-N) and at 122.4 ppm with double intensity (N-CH-CH-N) for the imidazole scaffold and at 50.3 ppm (N-CH_2-CH_2-CH_3), 22.7 ppm (N-CH_2-CH_2-CH_3) and 10.4 ppm (N-CH_2-CH_2-CH_3) for the propyl carbons.

The allyl methyl imidazole, [AlMIM]Br **57**, shows six different signals in the ^{1}H NMR spectrum. The imidazole hydrogens appear at 9.43 ppm and 7.82 ppm (2H). The allyl residue shows up as mulitplet, triplet and doublet at 6.00 ppm for the CH hydrogen, at 5.30 ppm for the two hydrogens next to the nitrogen and at 4.94 ppm for the last CH_2 hydrogens. The methyl group appears as singlet at 3.90 ppm. The carbon signals were allocated at 136.5 ppm (N-CH-N), 131.7 ppm (N-CH-CH-N), 123.6 ppm (N-CH_2-CH-CH_2), 120.1 ppm (N-CH_2-CH-CH_2), 50.5 ppm (N-CH_2-CH-CH_2) and 35.8 ppm (N-CH_3).

In comparison, the ethyl derivative, [AlEIM]Br **58** shows besides the imidazole hydrogen signals at 9.39 ppm, 7.27 ppm and 7.14 ppm and the allyl signals at 6.05 ppm, 5.32 ppm and 4.85 ppm, now also the ethyl residue at 4.23 ppm and 1.40 ppm. The revealed carbon signals can be allocated at 136.7 ppm (N-CH-N), 131.7 ppm (N-CH-CH-N) and 122.3 ppm (N-CH_2-CH-CH_2) for the imidazole backbone, at 120.3 ppm (N-CH_2-CH-CH_2), 50.8 ppm (N-CH_2-CH-CH_2) and 21.0 ppm (N-CH_2-CH_2-CH_3) for the allyl carbons and at 44.3 ppm (N-CH_2-CH_3) and 15.1 ppm (N-CH_2-CH_3) for the ethyl carbons.

The symmetric imidazolium salt with two allyl residues, [diAlIM]Br **59**, shows only five hydrogen signals due to symmetry reasons. They appear at 9.45 ppm and 7.84 ppm for the imidazolium hydrogens and at 6.05 ppm, 5.33 ppm and 4.93 ppm for the allyl chains. Carbon signals show up at 136.1 ppm (N-CH-N), 131.7 ppm (N-CH-CH-N), 122.6 ppm (N-CH_2-CH-CH_2), 120.2 ppm (N-CH_2-CH-CH_2) and 50.8 ppm (N-CH_2-CH-CH_2).

The synthesized [BMIM]Br **60** shows the hydrogen signals at 9.50 ppm, 7.94 ppm and 7.85 ppm for the imidazole, at 4.20 ppm, 1.72 ppm, 1.18 ppm and 0.82 ppm for the butyl residue and the methyl hydrogens appear at 3.75 ppm. Carbon signals are assigned at 136.4 ppm (N-CH-N), 124.2/122.1 ppm (N-CH-CH-N), 48.3 ppm (N-CH_3), 35.7 ppm (N-CH_2-CH_2-CH_2-CH_3), 31.3 ppm (N-CH_2-CH_2-CH_2-CH_3), 18.6 ppm (N-CH_2-CH_2-CH_2-CH_3) and 13.1 ppm (N-CH_2-CH_2-CH_2-CH_3).

To prove the anion exchange reaction, also a ^{14}N NMR and an ^{11}B NMR was measured for the obtained CBH ionic liquids. The peaks obtained in the measured ^{1}H and ^{13}C NMR differ only slightly from the ones of the halogen salts.

In the ^{1}H NMR of [EMIM][CBH] **61** the hydrogen atoms of the imidazole appear at 9.13 ppm, 7.78 ppm and 7.69 ppm. The ethyl residue is visible at 4.21 ppm and 1.40 ppm, whereas the methyl group is assigned at 3.85 ppm. The carbon shifts are allocated at 136.2 ppm (N-CH-N) and 123.6/122.0 ppm (N-CH-CH-N) for the imidazole, at 44.1 ppm (N-CH_3) for the methyl carbon and at 35.7 ppm (N-CH_2-CH_3) and 15.1 ppm (N-CH_2-CH_3) for the ethyl carbons. The measurement of ^{14}N NMR revealed three nitrogen peaks at −113 ppm, −195 ppm and −209 ppm. ^{11}B NMR shows one peak at 40.7 ppm.

The synthesized [PMIM][CBH] **62** has the seven hydrogen signals at 9.10 ppm, 7.76 ppm and 7.70 ppm for the imidazole nitrogens, as two multiplets (4.12 ppm, .80 ppm) and one triplet (0.85 ppm) for the hydrogens from the propyl chain and as one singlet for the methyl group at 3.85 ppm. The imidazole carbons appear at 136.5 ppm, 123.6 ppm and 122.2 ppm, the propyl carbons at 50.2 ppm (N-CH_2-CH_2-CH_3), 22.8 ppm (N-CH_2-CH_2-CH_3), 10.4 ppm (N-CH_2-CH_2-CH_3) and the methyl carbon at 35.8 ppm. ^{14}N NMR showed three signals at −113 ppm, −196 ppm and −208 ppm and measured ^{11}B NMR one signal at 40.7 ppm.

For the ethyl derivative [PEIM][CBH] **63**, there appears now one additional signal compared to methyl derivative **62**. Imidazole hydrogens can be allocated at 9.10 ppm, 7.72 ppm and 7.70 ppm. The propyl chain is assigned as multiplet at 4.03 ppm for the CH_2 hydrogens next to the amine, as another multiplet at 1.75 ppm for the middle CH_2 group and as triplet at 0.76 ppm for the methyl hydrogens. The ethyl group appears as multiplet at 4.10 ppm and triplet at 1.33 ppm. The eight carbon signals show up in the ^{13}C NMR at 135.6 ppm, 122.4 ppm and 122.2 ppm (imidazole carbons). The propyl carbons are assigned at 50.3 ppm (N-CH_2-CH_2-CH_3), 22.7 ppm (N-CH_2-CH_2-CH_3) and 10.4 ppm (N-CH_2-CH_2-CH_3) and the two ethyl carbons at 44.2 ppm (N-CH_2-CH_3) and 14.9 ppm (N-CH_2-CH_3). The three nitrogen signals are allocated at −114 ppm, −193 ppm and −207 ppm and the single boron signal at 40.7 ppm.

For the symmetrical [DiPIM][CBH] **64** only five signals are revealed in the measured ^{1}H NMR spectrum. The imidazole hydrogens appear at 9.19 ppm for the CH hydrogen between the two nitrogens and at 7.81 ppm for the two others. Propyl hydrogens are assigned as triplet at 4.13 ppm for the CH_2 groups next to the nitrogens, as multiplet at 1.81 ppm for the middle ones and as triplet at 0.85 ppm for the three CH_3 hydrogens. Carbon signals appear at 136.5 ppm (N-CH-N) and 123.0 ppm (N-CH-CH-N) for the imidazole scaffold and at 50.9 ppm (N-CH_2-CH_2-CH_3), 23.2 ppm (N-CH_2-CH_2-CH_3) and 10.9 ppm (N-CH_2-CH_2-CH_3) for the propyl chain. The ^{14}N NMR revealed the three signals at −113 ppm, −192 ppm and −205 ppm and ^{11}B NMR the single signal at 40.7 ppm.

The measured hydrogen signals for the IL [AlMIM][CBH] **65** show up at 9.11 ppm and 7.70 ppm (2 H) for the imidazole hydrogens. The allyl residue is allocated as multiplet at

6.03 ppm for the middle CH hydrogen, as triplet at 5.29 ppm for the CH_2 group next to the nitrogen and as doublet at 4.84 ppm for the CH_2 hydrogens at the end. The methyl hydrogens appear as singlet at 3.90 ppm. The three imidazole carbons appear at 136.5 ppm and with double intensity at 129.5 ppm. Allyl carbons are allocated as multiplet at 6.03 ppm, as triplet at 5.29 ppm and as doublet at 4.84 ppm. The methyl hydrogens appear at 3.90 ppm. Carbon signals show up for the imidazole carbons at 136.5 ppm and 129.5 ppm. The allyl carbons are allocated at 122.3 ppm (N-CH_2-CH-CH_2), 120.1 ppm (N-CH_2-CH-CH_2) and 50.8 ppm (N-CH_2-CH-CH_2). The methyl carbon is assigned at 35.8 ppm. Nitrogen signals are revealed at −115 ppm, −198 ppm and −202 ppm and the boron signal at 40.7 ppm.

For the ethyl derivative [AlEIM][CBH] **66**, there are the imidazole hydrogens at 9.15 ppm, 7.69 ppm and 7.65 ppm. The ethyl group appears as multiplet at 6.05 ppm for the middle, single hydrogen, as triplet at 5.30 ppm for the CH_2 group next to the nitrogen and as doublet for the last CH_2 hydrogens. The ethyl residue is allocated at 4.03 ppm and at 1.43 ppm. The carbons are assigned to 136.7 ppm and 130.5 ppm for the imidazole, for the allyl chain to 121.4 ppm (N-CH_2-CH-CH_2), 120.2 ppm (N-CH_2-CH-CH_2) and 50.8 ppm (N-CH_2-CH-CH_2). The ethyl residue shows up at 44.2 ppm (N-CH_2-CH_3) and 15.0 ppm for the CH_3 carbon. Nitrogen signals appear at −115 ppm, −199 ppm and −203 ppm and the boron signal at 40.7 ppm.

For the symmetrical [diAlIM][CBH] **67** are five hydrogen signals revealed in the measured ^{1}H NMR spectrum. The imidazole hydrogens appear at 9.15 ppm and at 7.73 ppm (2 H). The allyl chain is allocated at 6.05 ppm, 4.84 ppm and 5.33 ppm. The five carbon signals show up at 136.2 ppm (N-CH-N) and 131.7 ppm (N-CH-CH-N) for the imidazole and at 122.8 ppm (N-CH_2-CH-CH_2), 120.6 ppm (N-CH_2-CH-CH_2) and 51.3 ppm (N-CH_2-CH-CH_2) for the allyl carbons. Nitrogen signals are revealed at −114 ppm, −199 ppm and −204 ppm. The signal of the ^{11}B NMR is given at 40.7 ppm.

The last imidazole-based IL [BMIM][CBH] **68** has eight signals in the measured ^{1}H NMR spectrum. The ones at 9.06 ppm, 7.59 ppm and 7.66 ppm are allocated to the imidazole hydrogens. The methyl group appears at 3.75 ppm and the butyl hydrogens are allocated as triplet at 4.05 ppm for the CH_2 hydrogens next to the nitrogen, as multiplet at 1.68 ppm for

the next two hydrogens, as another multiplet at 1.18 ppm for the third CH_2 hydrogens and at 0.79 ppm for the three last hydrogens. The carbon signals show up at 136.5 ppm, 123.6 ppm and 122.2 ppm for the imidazole carbons, at 48.5 ppm for the methyl carbon and at 35.8 ppm ($N-CH_2-CH_2-CH_2-CH_3$), 31.3 ppm ($N-CH_2-CH_2-CH_2-CH_3$), 18.8 ppm ($N-CH_2-CH_2-CH_2-CH_3$) and 13.3 ppm ($N-CH_2-CH_2-CH_2-CH_3$) for the butyl chain. The nitrogen signals appear at −114 ppm, −197 ppm and −209 ppm. The ^{11}B NMR reveals one signal at 40.7 ppm.

All imidazolium based cyanoborohydride **61**-**68** ionic liquids were successfully synthesized and identified via NMR spectroscopy. Their hypergolic behaviour with HTP was investigated.

2.5.3 Ionic liquids from amino-azido liquids

The last field of interest for potential fuel candidates was the ionic liquids derived from the previously synthesized amino azido liquids. The team of SHREEVE investigated the syntheses and hypergolic behaviour of several azido-based ionic amino liquids and nitric acid.[144] They showed especially as dicyanamide salt a relatively low ID time and good stability. Therefore, these compounds were chosen for a further research on hypergolicity with HTP.

2.5.3.1 Synthesis

The first step was the synthesis of the silver dicyanamide salt **69** as anion exchange reactant. It was obtained from sodium dicyanamide mixed with silver nitrate, whereat silver dicyanamide precipitated. It was yielded as white powder in 89% yield.

As azido based ionic liquid, the synthesis of 2-azido-*N*,*N*,*N*-trimethylethan-1-amonium dicyanamide **71** was performed via the iodide salt **70** as precursor. As first step, the methylation was executed from DMAZ **28** using methyl iodide as methylation agent in acetonitrile. 2-azido-*N*,*N*,*N*-trimethylethan-1-amonium iodide **70** was obtained in 54% yield as yellowish solid. The next step was the anion exchange reaction using the previously synthesized silver dicyanamide salt **69**. Silver iodide precipitates during the reaction. Afterwards, the desired compound **71** was yielded in 22% as brownish liquid. The synthesis route is pictured in Scheme 45.
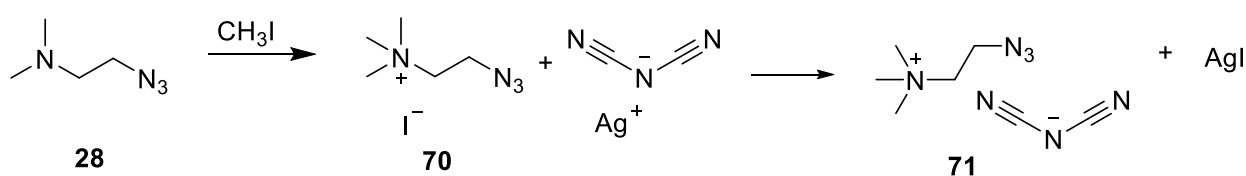
Scheme 45: Synthesis route towards 2-azido-*N*,*N*,*N*-trimethylethan-1-amonium dicyanamide 71.

In addition, the synthesis towards the ionic liquid 2-azido-N-(2-azidoethyl)-N,N-dimethylethan-1-amonium dicyanamide **73** was performed. This time the starting material was the previously synthesized azido amino liquid DAzEMA **37**. Methylation was also performed using methyl iodide and 2-azido-N-(2-azidoethyl)-N,N-dimethylethan-1-

amonium iodide **72** was yielded in 68% as brown oily product. However, the anion exchange reaction with compound **69** was done. In the end, 2-azido-N-(2-azidoethyl)-N,N-dimethylethan-1-amonium dicyanamide **73** was obtained as brownish ionic liquid in 22% yield. The reaction towards the desired IL **73** is depicted in Scheme 46 below.
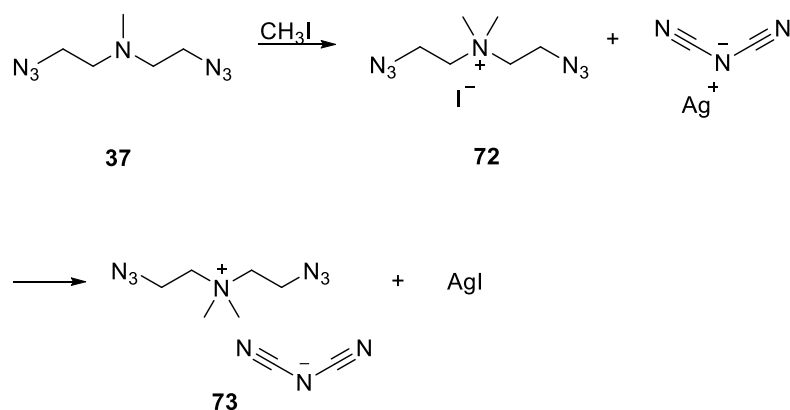
Scheme 46: Synthesis route towards 2-Azido-N-(2-azidoethyl)-N,N-dimethylethan-1-amonium dicyanamide 73.

The obtained ionic liquids **71** and **73** were both characterized via NMR spectroscopy as described in the next section. The received values were compared with the literature.[144]

2.5.3.2 Characterisation

The iodide salt **70** revealed three signals in the ^{1}H NMR spectrum (DMSO). Now they show the intensities of 2:2:9 in comparison of the ones from DMAZ **28** with 2:2:6. They appear as multiplet at 3.95 ppm for the two hydrogens next to the azide, as triplet at 3.52 ppm for the ones next to the amine and at 3.09 ppm for the methyl hydrogens. The carbon signals show up at 63.37 ppm, 52.84 ppm and 44.28 ppm. The first signal can be assigned to the carbon next to the amine, the second one for the carbon next to the azide and the third signal is from the three methyl carbons.

The measured NMR spectra of the ionic liquid **71** after the anion exchange looks almost the same as the previous iodide one **71**. While hydrogen NMR shows the same number of signals and same shifts, the carbon NMR spectra reveals now in comparison four carbon signals for compound **71**. They show up at 119.09 ppm for the carbons of the DCA anion and for the three ones from the amino azido cation on the same previously described positions.

The other synthesized iodine salt **72** has three signals with the intensities of 4:4:6. They appear as triplet at 3.95 ppm for the hydrogens next to the azide, as another triplet at 3.60 ppm for the hydrogens next to the amine and as singlet at 3.10 ppm for the six methyl hydrogens. The carbon shifts appear at 61.97 ppm for the carbon next to the amine, at 51.01 for the carbon next to the azide and at 44.05 ppm for the methyl carbons with double intensity.

The ionic liquid after the anion exchange **73** shows the same signals in the measured ^{1}H NMR spectrum. For the carbon NMR, now the signal of the DCA anion appears at 119.12 ppm, while the others appear at the same positions.

Both DCA ionic liquids **71** and **73** are successfully synthesized and characterized. They were used for the hypergolicity tests.

2.5.4 Unsuccessful attempts of generating more amino azido liquids

The synthesis of other amino azido ionic liquids was tried within this study. Some of the syntheses and anion exchange reactions are briefly described below and an outlook is given on a promising, so far unknown ionic liquid.

2.5.4.1 2-Azido-N,N-dimethylethan-1-aminium iodide

In addition, the synthesis of the ionic liquid derived from AzEMA **22** was tried according to Scheme 47. Therefore, it was also reacted with methyl iodide.
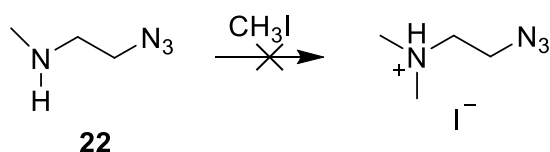
Scheme 47: Synthesis route towards 2-azido-*N,N*-dimethylethan-1-aminium iodide.

Instead of the desired compound *N,N*-dimethylethan-1-aminium iodide, a mixture of three products was obtained. Beside the starting material, the previously synthesized 2-azido-*N,N,N*-trimethylethan-1-amonium iodide **70** and the desired 2-azido-N,N-dimethylethan-1-aminium iodide was yielded. The three compounds are pictured in Scheme 48.
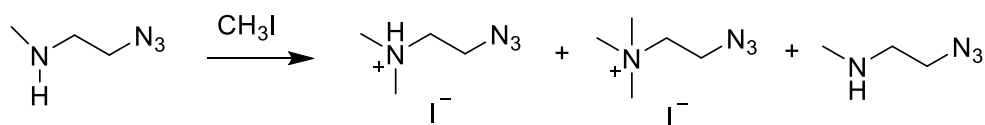
Scheme 48: Products obtained during synthesis of 2-azido-N,N-dimethylethan-1-aminium iodide.

2.5.4.2 2-Azido-N-(2-azidoethyl)-N,N-dimethylethan-1-amonium borohydride

In an additional exchange reaction, also the synthesis of the 2-azido-N-(2-azidoethyl)-N,N-dimethylethan-1-amonium borohydride, pictured in Scheme 49, was tried. Therefore, compound **72** was dissolved in dry acetonitrile under nitrogen atmosphere. Afterwards sodium borohydride was added and the reaction mixture was stirred for 3 days at room temperature under exclusion of air.[139] The obtained product was washed with dry DCM and concentrated *in vacuo*. A brown solution was obtained and characterized via NMR spectroscopy.
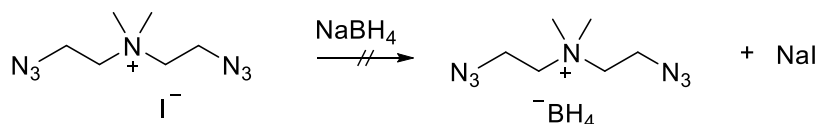
Scheme 49: Anion exchange reaction of 2-Azido-N-(2-azidoethyl)-N,N-dimethylethan-1-amonium iodide 72.

NMR analysis suggested that the anion exchange reaction did not take place. The expected quartet of the borohydride anion does not appear in the NMR spectrum. It should be allocated at around 0.44 ppm.

Although the reaction was executed several times, the boron product could not be yielded after the exchange reaction. A possible explanation can be the decomposition of the sodium borohydride.

2.5.4.3 Tris(2-azidoethyl)methylammonium iodide

As further compound the ionic liquid derived from tris(2-azidoethyl)amine was tried to synthesize with the usage of methyl iodide according to Scheme 50.
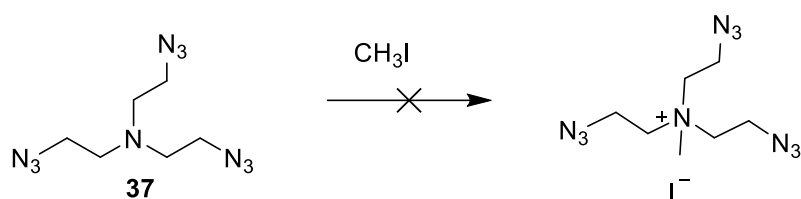
Scheme 50: Synthesis route towards tris(2-azidoethyl)methylammonium iodide.

After refluxing the mixture for the first attempt overnight and the second attempt for 3 days, a brown oil was obtained within both experiments. NMR analysis revealed that the methylation did not take place. The signals were assigned to the starting material **37**.

The next attempt was executed using dimethyl sulphate as methylation agent. After addition, the solution was refluxed for 2 h and a brownish liquid and a viscous precipitate was obtained.
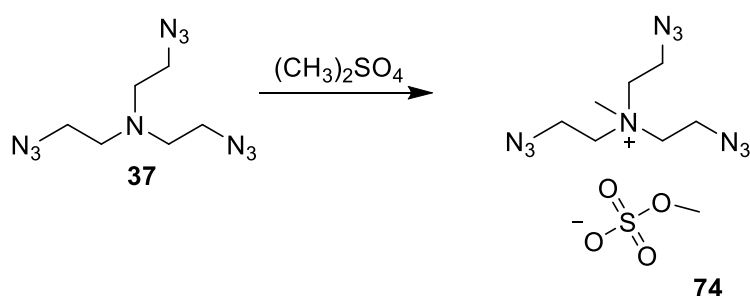
Scheme 51: Synthesis route towards tris(2-azidoethyl)methylammonium sulphate 74.

NMR analysis of the liquid showed that this was still the starting material **37**. However, the remaining signals of the viscous liquid can be assigned to the desired product **74**.

The signals in the ^{1}H NMR appear at 3.95 ppm and 3.61 ppm for the CH_2 groups, where the first one is assigned for the CH_2 group next to the amine. In addition, the methyl signal of the IL shows up at 3.10 ppm and the methyl signal of the methylsulfate anion appears next to the CH_2N signal (3.55 ppm). Carbon shifts are visible at 62.13 ppm (CH_2N), 60.09 ppm (CH_3SO_4), 52.87 ppm (CH_2N_3) and 43.87 ppm (CH_3).

The desired compound **74** was successfully characterized by NMR and the existence was proven, but unfortunately a further anion exchange reaction was not possible.

The exchange was tried according to Scheme 52 with sodium borohydride and in addition with DCA.
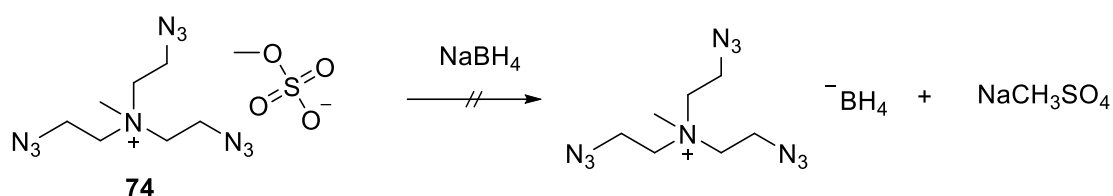
Scheme 52: Anion exchange reaction of tris(2-azidoethyl)methylammonium sulphate 74.

None of the performed exchange reactions was successful. An explanation could be on one hand the steric hinderance of the methylsulfate anion, on other hand a possible decomposition of the reactants or the high stability of compound **74**.

Therefore, only the methylsulfate ionic liquid derived from tris(2-azidoethyl)amine **37** was obtained. It could not be used for the hypergolicity test due to the corrosivity, heaviness and low energy content. Further research for the anion exchange reaction of this compound is needed in future.

2.5.5 Experimental Part

Potassium 2,2-diazidomalonate, K₂DAM 49

Diethyl 2,2-diazidomalonate (1.00 g, 4.13 mmol, 1 eq) was dissolved in H_2O (10 mL) and potassium hydroxide (85 %, 0.47 g, 8.33 mmol, 2 eq) was added. The mixture was stirred for 1 h at room temperature and additional 2 h at 60 °C. A colour change of the solution to slightly brown could be observed. After completion the reaction solution was cooled down and concentrated *in vacuo.* The brown solid was recrystallized in acetone (0.69 g, 2.63 mmol, 64 %). **¹³C NMR** (101 MHz, CDCl₃): δ (ppm) = 171.1 (–COO), 76.5 ($C(N_3)_2$). **¹⁴N NMR** (29 MHz, CDCl₃): δ (ppm) = −138 (N_β), −159 (N_γ), −283 (N_α). $C_3K_2N_6O_4$ (262.27 g mol⁻¹). **EA**: calcd. N 32.04, C 13.74% found N 28.65, C 13.69 %. **DTA** (5 °C min⁻¹): T_d = 105 °C. **Sensitivities**: IS: 5 J, FS: 288 N.

Lithium 2,2-diazidomalonate, Li₂DAM 50

Diethyl 2,2-diazidomalonate (1.64 g, 6.77 mmol, 1 eq) was dissolved in H_2O (15 mL) and lithium hydroxide (0.33 g, 13.5 mmol, 2 eq) was added. The mixture was stirred for 1 h at room temperature and additional 2 h at 60 °C. A colour change to slightly red could be observed. After completion the reaction solution was cooled down and concentrated *in vacuo.* The red solid was recrystallized in acetone (0.80 g, 4.06 mmol, 64 %). **¹³C NMR** (101 MHz, CDCl₃): δ (ppm) = 170.6 (–COO), 77.9 ($C(N_3)_2$). **¹⁴N NMR** (29 MHz, CDCl₃): δ (ppm) = −139 (N_β), −160 (N_γ), −260 (N_α). $C_3Li_2N_6O_4 * H_2O$ (215.96 g mol⁻¹) **EA**: calcd. N 38.91, C 16.68 H 0.93 %; found N 37.23, C 17.65, H 1.03 %. **DTA** (5 °C min⁻¹): T_d = 98 °C. **Sensitivities**: IS: >40 J, FS: >360 N.

General synthesis of the alkyl-imidazoles

To a cooled solution of 12.0 mmol sodium hydride in dry THF, a solution of 12.0 mmol imidazole dissolved in dry THF was slowly added and allowed to warm up to room temperature. After 1 h 18.0 mmol of respective alkyl halide were added and the reaction mixture was stirred at 80 °C over night. After filtration, the solvent was evaporated *in vacuo* and the residue dissolved in DCM. A spatula of active charcoal and sodium sulphate was

added, and the suspension was stirred for two hours. After filtration and evaporation, the alkyl-imidazoles were yielded as yellowish liquids in 50–60 %.

1-Ethlyimidazole 51

¹H NMR (400 MHz, d_6-DMSO): δ (ppm) = 7.64 (s, 1H, N-*CH*-N), 7.17 (d, 1H), 6.89 (d, 1H), 4.00–3.95 (q, 2H, N-C*H$_2$*-CH$_3$), 1.34–1.31 (t, 3H, N-CH$_2$-C*H$_3$*), **¹³C NMR** (101 MHz, d_6-DMSO): δ (ppm) = 136.7 (N-*CH*-N), 128.2/118.8 (N-CH-*CH*-N), 40.9 (N-*CH$_2$*-CH$_3$), 16.3 (N-CH$_2$-*CH$_3$*). $C_5H_8N_2$ (96.13 g mol^{-1}).

1-Propylimidazole 52

¹H NMR (400 MHz, d_6-DMSO): δ (ppm) = 8.29 (s, 1H, N-*CH*-N), 7.43 (s, 1H), 7.36 (s, 1H), 4.04–4.00 (t, 2H, N-*CH$_2$*-CH$_2$-CH$_3$), 1.84–1.75 (m, 2H, N-CH$_2$-C*H$_2$*-CH3), 0.83–0.79 (t, 3H, N-CH$_2$-CH$_2$-*CH3*). **¹³C NMR** (101 MHz, d_6-DMSO): δ (ppm) = 135.8 (s, 1H, N-CH-N), 120.3 (N-*CH*-CH-N), 48.4 (N-*CH$_2$*-CH$_2$-CH$_3$), 23.4 (N-CH$_2$-*CH$_2$*-CH$_3$), 10.5 (N-CH$_2$-CH$_2$-*CH$_3$*). $C_6H_{10}N_2$ (110.16 g mol^{-1}).

General synthesis of the ionic liquid precursor

12.0 mmol of alkyl-imidazole were dissolved in dry toluene (12 mL). Afterwards 18.0 mmol of the respective alkyl-halide was added dropwise under constant stirring. The reaction solution was refluxed at 110 °C for 2 h. The solvent was concentrated *in vacuo* and the halide precursors were yielded as liquids or solids.

[EMIM]Br 53

¹H NMR (400 MHz, d_6-DMSO): δ (ppm) = 9.50 (s, 1H, N-*CH*-N), 7.91 (s, 1H), 7.80 (s, 1H), 4.26–4.21 (m, 2H, N-*CH$_2$*-CH$_3$), 3.80 (s, 3H, N-*CH$_3$*), 1.40–1.36 (t, 3H, N-CH$_2$-*CH$_3$*). **¹³C NMR** (101 MHz, d_6-DMSO): δ (ppm) = 136.2 (N-CH-N), 123.3/121.8 (N-CH-CH-N), 44.0 (N-*CH$_3$*), 35.7 (N-*CH$_2$*-CH$_3$), 15.1 (N-CH$_2$-*CH$_3$*). $C_6H_{11}N_2Br$ (191.07 g mol^{-1}).

[PMIM]I 54

¹H NMR (400 MHz, d_6-DMSO): δ (ppm) = 9.26 (s, 1H, N-*CH*-N), 7.83 (s, 1H), 7.81 (s, 1H), 4.24–4.18 (m, 2H, N-*CH$_2$*-CH$_2$-CH$_3$), 4.15–4.12 (m, 2H, N-C*H$_3$*), 1.85–1.76 (m, 2H, N-CH$_2$-

CH_2-CH$_3$), 0.86–0.81 (t, 3H, N-CH$_2$-CH$_2$-CH_3). **^{13}C NMR** (101 MHz, d_6-DMSO): δ (ppm) = 135.6 (N-CH-N), 122.3/122.0 (N-CH-CH-N), 50.3 (N-CH$_2$-CH$_2$-CH$_3$), 44.2 (N-CH$_3$), 22.8 (N-CH$_2$-CH$_2$-CH$_3$), 10.4 (N-CH$_2$-CH$_2$-CH$_3$). C$_7$H$_{13}$N$_2$I (252.09 g mol^{-1}).

[PEIM]Br 55

^{1}H NMR (400 MHz, d_6-DMSO): δ (ppm) = 9.21 (s, 1H, N-CH-N), 7.81 (s, 1H), 7.78 (s, 1H), 4.15–4.12 (m, 2H, N-CH_2-CH$_2$-CH$_3$), 4.13–4.10 (m, 2H, N-CH_2-CH$_3$), 1.84–1.78 (m, 2H, N-CH$_2$-CH_2-CH$_3$), 0.87–0.83 (t, 3H, N-CH$_2$-CH_3), 0.86–0.82 (t, 3H, N-CH$_2$-CH$_2$-CH_3). **^{13}C NMR** (101 MHz, d_6-DMSO): δ (ppm) = 135.9 (s, 1H, N-CH-N), 122.4/122.2 (N-CH-CH-N), 50.3 (N-CH$_2$-CH$_2$-CH$_3$), 44.1 (N-CH$_2$-CH$_3$), 22.7 (N-CH$_2$-CH$_2$-CH$_3$), 15.0 (N-CH$_2$-CH$_3$), 10.5 (N-CH$_2$-CH$_2$-CH$_3$). C$_8$H$_{15}$N$_2$Br (219.12 g mol^{-1}).

[DiPIM]I 56

^{1}H NMR (400 MHz, d_6-DMSO): δ (ppm) = 9.21 (s, 1H, N-CH-N), 7.81 (d, 2H), 4.16–4.12 (t, 4H, N-CH_2-CH$_2$-CH$_3$), 1.86–1.77 (m, 4H, N-CH$_2$-CH_2-CH$_3$), 0.86–0.83 (t, 6H, N-CH$_2$-CH$_2$-CH_3). **^{13}C NMR** (101 MHz, d_6-DMSO): δ (ppm) = 135.9 (s, 1H, N-CH-N), 122.4 (N-CH-CH-N), 50.3 (N-CH$_2$-CH$_2$-CH$_3$), 22.7 (N-CH$_2$-CH$_2$-CH$_3$), 10.4 (N-CH$_2$-CH$_2$-CH$_3$). C$_9$H$_{17}$N$_2$I (280.15 g mol^{-1}).

[AlMIM]Br 57

^{1}H NMR (400 MHz, d_6-DMSO): δ (ppm) = 9.43 (s, 1H, N-CH-N), 7.82 (s, 2H), 6.07–5.96 (m, 2H, N-CH$_2$-CH-CH$_2$), 5.32–5.28 (t, 4H, N-CH_2-CH-CH$_2$), 4.96–4.92 (d, 4H, N-CH$_2$-CH-CH_2), 3.90 (s, 3H, N-CH_3). **^{13}C NMR** (101 MHz, d_6-DMSO): δ (ppm) = 136.5 (N-CH-N), 131.7 (N-CH-CH-N), 123.6 (N-CH$_2$-CH-CH$_2$), 120.1 (N-CH$_2$-CH-CH$_2$), 50.5 (N-CH$_2$-CH-CH$_2$), 35.8 (N-CH$_3$). C$_7$H$_{11}$N$_2$Br (203.08 g mol^{-1}).

[AlEIM]Br 58

^{1}H NMR (400 MHz, d_6-DMSO): δ (ppm) = 9.39 (s, 1H, N-CH-N), 7.27 (s, 2H), 7.14 (s, 2H), 6.10–6.00 (m, 2H, N-CH$_2$-CH-CH$_2$), 5.35–5.29 (t, 4H, N-CH_2-CH-CH$_2$), 4.89–4.87 (d, 4H, N-CH$_2$-CH-CH_2), 4.26–4.21 (m, 2H, N-CH_2-CH$_3$), 1.43–1.39 (t, 3H, N-CH$_2$-CH_3). **^{13}C NMR** (101 MHz, d_6-DMSO): δ (ppm) = 136.7 (N-CH-N), 131.7 (N-CH-CH-N), 122.3 (N-CH$_2$-CH-

CH$_2$), 120.3 (N-CH$_2$-CH-CH$_2$), 50.8 (N-CH$_2$-CH-CH$_2$), 44.3 (N-CH$_2$-CH$_3$), 15.1 (N-CH$_2$-CH$_3$). C$_8$H$_{13}$N$_2$Br (217.11 g mol^{-1}).

[diAlIM]Br 59

¹H NMR (400 MHz, d_6-DMSO): δ (ppm) = 9.45 (s, 1H, N-CH-N), 7.84 (s, 2H), 6.11–6.01 (m, 2H, N-CH2-CH-CH$_2$), 5.33 (t, 4H, N-CH$_2$-CH-CH$_2$), 4.93 (d, 4H, N-CH$_2$-CH-CH$_2$). **¹³C NMR** (101 MHz, d_6-DMSO): δ (ppm) = 136.1 (N-CH-N), 131.7 (N-CH-CH-N), 122.6 (N-CH$_2$-CH-CH$_2$), 120.2 (N-CH$_2$-CH-CH$_2$), 50.8 (N-CH$_2$-CH-CH$_2$). C$_9$H$_{13}$N$_2$Br (229.12g mol^{-1}).

[BMIM]Br 60

¹H NMR (400 MHz, d_6-DMSO): δ (ppm) = 9.50 (s, 1H, N-CH-N), 7.94 (d, 1H), 7.85 (d, 1H), 4.22–4.19 (t, 2H, N-CH$_2$-CH$_2$-CH$_2$-CH$_3$), 3.75 (s, 3H, N-CH$_3$), 1.76–1.69 (m, 2H, N-CH$_2$-CH$_2$-CH$_2$-CH$_3$), 1.24–1.14 (m, 2H, N-CH$_2$-CH$_2$-CH$_2$-CH$_3$), 0.83–0.80 (t, 3H, N-(C$_3$H$_6$)-CH$_3$). **¹³C NMR** (101 MHz, d_6-DMSO): δ (ppm) = 136.4 (N-CH-N), 124.2/122.1 (N-CH-CH-N), 48.3 (N-CH$_3$), 35.7 (N-CH$_2$-CH$_2$-CH$_2$-CH$_3$), 31.3 (N-CH$_2$-CH$_2$-CH$_2$-CH$_3$), 18.6 (N-CH$_2$-CH$_2$-CH$_2$-CH$_3$), 13.1 (N-CH$_2$-CH$_2$-CH$_2$-CH$_3$). C$_8$H$_{15}$N$_2$Br (219.12 g mol^{-1}).

General synthesis of the Cyanoborohydride ionic liquids

A solution of 6.00 mmol of the cation halide and 6.6 mmol of sodium cyanoborohydride in 20 mL dry THF was stirred at room temperature for 24–48 h. The formed sodium halide was filtered off and the solvent evaporated under reduced pressure to obtain the ionic liquid in yields of 20–40%.

[EMIM][CBH] 61

¹H NMR (400 MHz, d_6-DMSO): δ (ppm) = 9.13 (s, 1H, N-CH-N), 7.78 (s,1H), 7.69 (s,1H), 4.22–4.20 (m, 2H, N-CH$_2$-CH$_3$), 3.85 (s, 3H, N-CH$_3$), 1.45–1.30 (t, 3H, N-CH$_2$-CH$_3$). **¹³C NMR** (101 MHz, d_6-DMSO): δ (ppm) = 136.2 (N-CH-N), 123.6/122.0 (N-CH-CH-N), 44.1 (N-CH$_3$), 35.7 (N-CH$_2$-CH$_3$), 15.1 (N-CH$_2$-CH$_3$). **¹⁴N NMR** (29 MHz, d_6-DMSO): δ (ppm) = −113, −195, −209. **¹¹B NMR** (128 MHz, d_6-DMSO): δ (ppm) = 40.7. C$_7$H$_{14}$N$_3$B (151.02 g mol^{-1}).

[PMIM][CBH] 62

¹H NMR (400 MHz, d_6-DMSO): δ (ppm) = 9.10 (s, 1H, N-CH-N), 7.76 (s, 1H), 7.70 (s, 1H), 4.14–4.11 (m, 2H, N-CH$_2$-CH$_2$-CH$_3$), 3.85 (s, 3H, N-CH$_3$), 1.85–1.76 (m, 2H, N-CH$_2$-CH$_2$-CH$_3$), 0.88–0.84 (t, 3H, N-CH$_2$-CH$_2$-CH$_3$). **¹³C NMR** (101 MHz, d_6-DMSO): δ (ppm) = 136.5 (N-CH-N), 123.6/122.2 (N-CH-CH-N), 50.2 (N-CH$_2$-CH$_2$-CH$_3$), 35.8 (N-CH$_3$), 22.8 (N-CH$_2$-CH$_2$-CH$_3$), 10.4 (N-CH$_2$-CH$_2$-CH$_3$). **¹⁴N NMR** (29 MHz, d_6-DMSO): δ (ppm) = −113, −196, −208. **¹¹B NMR** (128 MHz, d_6-DMSO): δ (ppm) = 40.7. C$_8$H$_{16}$N$_3$B (165.05 g mol^{-1}).

[PEIM][CBH] 63

¹H NMR (400 MHz, d_6-DMSO): δ (ppm) = 9.10 (s, 1H, N-CH-N), 7.72 (s, 1H), 7.70 (s, 1H), 4.13–4.08 (m, 2H, N-CH$_2$-CH$_3$), 4.05–4.01 (m, 2H, N-CH$_2$-CH$_2$-CH$_3$), 1.77–1.68 (m, 2H, N-CH$_2$-CH$_2$-CH$_3$), 1.35–1.31 (t, 3H, N-CH$_2$-CH$_3$), 0.77–0.75 (t, 3H, N-CH$_2$-CH$_2$-CH$_3$). **¹³C NMR** (101 MHz, d_6-DMSO): δ (ppm) = 135.6 (N-CH-N), 122.4/122.2 (N-CH-CH-N), 50.3 (N-CH$_2$-CH$_2$-CH$_3$), 44.2 (N-CH$_2$-CH$_3$), 22.7 (N-CH$_2$-CH2-CH$_3$), 14.9 (N-CH$_2$-CH$_3$), 10.4 (N-CH$_2$-CH$_2$-CH$_3$). **¹⁴N NMR** (29 MHz, d_6-DMSO): δ (ppm) = −114, −193, −207. **¹¹B NMR** (128 MHz, d_6-DMSO): δ (ppm) = 40.7. C$_9$H$_{18}$N$_3$B (179.07 g mol^{-1}).

[DiPIM][CBH] 64

¹H NMR (400 MHz, d_6-DMSO): δ (ppm) = 9.19 (s, 1H, N-CH-N), 7.81 (d,2H), 4.15–4.11 (t, 4H, N-CH$_2$-CH$_2$-CH$_3$), 1.86–1.77 (m, 4H, N-CH$_2$-CH$_2$-CH$_3$), 0.86–0.83 (t, 6H, N-CH$_2$-CH$_2$-CH$_3$). **¹³C NMR** (101 MHz, d_6-DMSO): δ (ppm) = 136.5 (N-CH-N), 123.0 (N-CH-CH-N), 50.9 (N-CH$_2$-CH$_2$-CH$_3$), 23.2 (N-CH$_2$-CH$_2$-CH$_3$), 10.9 (N-CH$_2$-CH$_2$-CH$_3$). **¹⁴N NMR** (29 MHz, d_6-DMSO): δ (ppm) = −113, −192, −205. **¹¹B NMR** (128 MHz, d_6-DMSO): δ (ppm) = 40.7. C$_{10}$H$_{20}$N$_3$B (193.10 g mol^{-1}).

[AlMIM][CBH] 65

¹H NMR (400 MHz, d_6-DMSO): δ (ppm) = 9.11 (s, 1H, N-CH-N), 7.70 (s, 2H), 6.09–5.99 (m, 2H, N-CH$_2$-CH-CH$_2$), 5.31–5.26 (t, 4H, N-CH$_2$-CH-CH$_2$), 4.85–4.83 (d, 4H, N-CH$_2$-CH-CH$_2$), 3.90 (s, 3H, N-CH$_3$). **¹³C NMR** (101 MHz, d_6-DMSO): δ (ppm) = 136.5 (N-CH-N) 129.5 (N-CH-CH-N), 122.3 (N-CH$_2$-CH-CH$_2$), 120.1 (N-CH$_2$-CH-CH$_2$), 50.8 (N-CH$_2$-CH-CH$_2$), 35.8 (N-CH$_3$). **¹⁴N**

NMR (29 MHz, d_6-DMSO): δ (ppm) = −115, −198, −202. **^{11}B NMR** (128 MHz, d_6-DMSO): δ (ppm) = 40.7. $C_8H_{14}N_3B$ (163.03 g mol^{-1}).

[AlEIM][CBH] 66

^{1}H NMR (400 MHz, d_6-DMSO): δ (ppm) = 9.15 (s, 1H, N-CH-N), 7.69 (s, 2H), 7.65 (s, 2H), 6.10–6.02 (m, 2H, N-CH$_2$-CH-CH$_2$), 5.34–5.27 (t, 4H, N-CH_2-CH-CH$_2$), 4.85–4.75 (d, 4H, N-CH$_2$-CH-CH_2), 4.05–3.99 (m, 2H, N-CH_2-CH$_3$), 1.45–1.40 (t, 3H, N-CH$_2$-CH_3). **^{13}C NMR** (101 MHz, d_6-DMSO): δ (ppm) = 136.7 (N-CH-N), 130.5 (N-CH-CH-N), 121.4 (N-CH$_2$-CH-CH$_2$), 120.2 (N-CH$_2$-CH-CH$_2$), 50.8 (N-CH$_2$-CH-CH$_2$), 44.2 (N-CH$_2$-CH$_3$), 21.0 (N-CH$_2$-CH$_2$-CH$_3$), 15.0 (N-CH$_2$-CH$_3$). **^{14}N NMR** (29 MHz, d_6-DMSO): δ (ppm) = −115, −199, −203. **^{11}B NMR** (128 MHz, d_6-DMSO): δ (ppm) = 40.7. $C_9H_{16}N_3B$ (177.06 g mol^{-1}).

[diAlIM][CBH] 67

^{1}H NMR (400 MHz, d_6-DMSO): δ (ppm) = 9.15 (s, 1H, N-CH-N), 7.73 (s, 2H), 6.09–5.99 (m, 2H, N-CH$_2$-CH-CH$_2$), 4.84 (d, 4H, N-CH$_2$-CH-CH_2), 5.38–5.28 (t, 4H, N-CH_2-CH-CH$_2$),. **^{13}C NMR** (101 MHz, d_6-DMSO): δ (ppm) = 136.2 (N-CH-N), 131.7 (N-CH-CH-N), 122.8 (N-CH$_2$-CH-CH$_2$), 120.6 (N-CH$_2$-CH-CH$_2$), 51.3 (N-CH$_2$-CH-CH$_2$). **^{14}N NMR** (29 MHz, d_6-DMSO): δ (ppm) = −114, −199, −204. **^{11}B NMR** (128 MHz, d_6-DMSO): δ (ppm) = 40.7. $C_{10}H_{16}N_3B$ (189.07 g mol^{-1}).

[BMIM][CBH] 68

^{1}H NMR (400 MHz, d_6-DMSO): δ (ppm) = 9.06 (s, 1H, N-CH-N), 7.59 (d, 1H), 7.66 (d, 1H), 4.08–4.04 (t, 2H, N-CH_2-CH$_2$-CH$_2$-CH$_3$), 3.75 (s, 3H, N-CH_3), 1.70–1.62 (m, 2H, N-CH$_2$-CH_2-CH$_2$-CH$_3$), 1.20–1.11 (m, 2H, N-CH$_2$-CH$_2$-CH_2-CH$_3$), 0.81–0.77 (t, 3H, N-(C$_3$H$_6$)-CH_3). **^{13}C NMR** (101 MHz, d_6-DMSO): δ (ppm) = 136.5 (s, 1H, N-CH-N), 123.6/122.2 (N-CH-CH-N), 48.5 (N-CH$_3$), 35.8 (N-CH$_2$-CH$_2$-CH$_2$-CH$_3$), 31.3 (N-CH$_2$-CH$_2$-CH$_2$-CH$_3$), 18.8 (N-CH$_2$-CH$_2$-CH$_2$-CH$_3$), 13.3 (N-CH$_2$-CH$_2$-CH$_2$-CH$_3$). **^{14}N NMR** (29 MHz, d_6-DMSO): δ (ppm) = −114, −197, −209. **^{11}B NMR** (128 MHz, d_6-DMSO): δ (ppm) = 40.7. $C_9H_{18}N_3B$ (179.07 g mol^{-1}).

Ionic Liquids of amines

Silver dicyanamide 69

To a solution of silver nitrate (5.01 g, 29.5 mmol, 1 eq) in 15 mL water sodium dicyanamide (2.64 g, 29.5 mmol, 1 eq) was added and stirred for 1 h at room temperature. After filtration and drying the product was stored protected from light. Silver dicyanamide was obtained as white powder (4.54 g, 26.1 mmol, 89%). AgC_2N_3 (173.91 g mol^{-1}).

2-azido-*N,N,N*-trimethylethan-1-ammonium iodide 70

2-azido-*N,N*-dimethylethan-1-amine **28** (0.71 g, 6.24 mmol, 1 eq) was dissolved in 20 mL acetonitrile and stirred for 15 minutes at room temperature. Methyl iodide (1.03 g, 7.23 mmol, 1.16 eq) was added and the reaction mixture was refluxed at 60 C overnight. After removing the solvent *in vacuo,* washed with n-hexane and 2-azido-*N,N,N*-trimethylethan-1-ammonium iodide as a yellowish solid (0.87 g, 3.39 mmol, 54%) was obtained. **¹H NMR** (400 MHz, d_6-DMSO): δ (ppm) = 3.99–3.93 (m, 2H, C*H*$_2$N$_3$), 3.52 (t, 2H, NC*H*$_2$), 3.09 (s, 9H, C*H*$_3$). **¹³C NMR** (101 MHz, d_6-DMSO): δ (ppm) = 63.37 (NCH$_2$), 52.84 (*C*H$_2$N$_3$), 44.28 (*C*H$_3$). $C_5H_{13}N_4I$ (256.09 g mol^{-1}).

2-azido-*N,N,N*-trimethylethan-1-ammonium dicyanamide 71

2-azido-*N,N,N*-trimethylethan-1-ammonium iodide (0.50 g, 1.95 mmol, 1 eq) was dissolved in 30 mL water and silver dicyanamide (0.65 g, 3.90 mmol, 2 eq) was added. The reaction mixture was stirred overnight at room temperature. After filtration and removing the solvent *in vacuo,* a brownish oily product (0.18 g, 0.72 mmol, 22%) was obtained. **¹H NMR** (400 MHz, d_6-DMSO): δ (ppm) = 3.98–3.92 (m, 2H, C*H*$_2$N$_3$), 3.52 (t, 2H, NC*H*$_2$), 3.08 (s, 9H, C*H*$_3$). **¹³C NMR** (101 MHz, d_6-DMSO): δ (ppm) = 119.09 (N(CN)$_2$), 63.37 (NCH$_2$), 52.84 (*C*H$_2$N$_3$), 44.28 (*C*H$_3$). $C_7H_{13}N_7$ (195.12 g mol^{-1}).

2-Azido-N-(2-azidoethyl)-N,N-dimethylethan-1-ammonium iodide 72

2-Azido-*N*-(2-azidoethyl)-N-methylethan-1-amine **37** (1.03 g, 6.06 mmol, 1 eq) was dissolved in 20 mL acetonitrile and stirred for 15 minutes at room temperature. Methyl iodide

(0.44 mL, 6.91 mmol, 1.15 eq) was added and the reaction mixture was refluxed at 60 C overnight. After removing the solvent *in vacuo*, a brown oily product (1.28 g, 4.11 mmol, 68%) was obtained. **¹H NMR** (400 MHz, *d*₆-DMSO): δ (ppm) = 3.96–3.93 (t, 4H, CH_2N₃), 3.56–3.53 (t, 4H, NCH_2), 3.10 (s, 6H, CH_3). **¹³C NMR** (101 MHz, *d*₆-DMSO): δ (ppm) = 61.97 (NCH_2), 51.01 (CH_2N₃), 44.05 (CH_3). $C_6H_{14}N_7I$ (311.12 g mol^{-1}).

2-Azido-N-(2-azidoethyl)-N,N-dimethylethan-1-ammonium dicyanamide 73

2-Azido-N-(2-azidoethyl)-N,N-dimethylethan-1-ammonium iodide **72** (1.03 g, 3.31 mmol, 1 eq) was dissolved in 30 mL water and silver dicyanamide (1.12 g, 6.67 mmol, 2 eq) was added. The reaction mixture was stirred overnight at room temperature. After filtration and removing the solvent *in vacuo*, 2-azido-N-(2-azidoethyl)-N,N-dimethylethan-1-ammonium dicyanamide was obtained as a brownish oily product (0.18 g, 0.72 mmol, 22%). **¹H NMR** (400 MHz, *d*₆-DMSO): δ (ppm) = 3.95–3.92 (t, 4H, CH_2N₃), 3.58–3.55 (t, 4H (t, 4H, NCH_2), 3.10 (s, 6H, CH_3). **¹³C NMR** (101 MHz, *d*₆-DMSO): δ (ppm) = 119.12 (N(CN)₂), 62.02 (NCH_2), 51.03 (CH_2N₃), 44.09 (CH_3). $C_8H_{14}N_{10}$ (250.27 g mol^{-1}).

2-Azido-*N*,*N*-bis(2-azidoethyl)-*N*-methylethan-1-aminiummethyl sulphate 74

To a mixture of tris(2-azidoethyl)amine **42** (0.26 g, 1.14 mmol, 1 eq) in 4 mL benzene, dimethyl sulphate (0.15 mL, 1.31 mmol, 1.15 eq) was added. The mixture was refluxed at 100 °C for 2 h and the solvent was removed under reduced pressure. **¹H NMR** (400 MHz, *d*₆-DMSO): δ (ppm) = 3.96–3.93 (t, 4H, CH_2N₃), 3.63–3.60 (t, 4H (t, 4H, NCH_2), 3.10 (s, 6H, CH_3). **¹³C NMR** (101 MHz, *d*₆-DMSO): δ (ppm) = 62.13 (NCH_2), 60.09 (CH_3SO_4), 52.87 (CH_2N₃), 43.87 (CH_3). $C_8H_{18}N_{10}SO_4$ (350.36 g mol^{-1}).

3 Calculations (Heat of Formation, optimized O/F ratio, I_{sp}, T_c)

In the following section the executed calculations of the synthesized compounds are shown. For the suggestion of suitability of the compounds as a hypergolic propellant, the heat of formation must be calculated and further applied to determine the theoretical I_{sp} of respective formulations.

3.1 CBS-4m Gaussian calculation

The theoretical values for structure optimization and the enthalpy of formation were calculated with Gaussian 16.[145] The structure optimizations were calculated using the B3LYP functional with the 6-31G basis set.[146] To receive accurate values for the energies, the modified version of Complete Basis Set (CBS-4m) developed by Petersson and co-workers was used.[147]

Further Trouton´s rule[88, 148] was used for the transformation of the enthalpy of gas phase to solid state enthalpy with the estimation for neutral compounds of,

$$\Delta H_{vap.} \left[J\ mol^{-1} \right] = 90\ T_b\ [K] \qquad \textbf{Formula 11. Trouton´s rule.}$$

whereby T_b represents the boiling point of the liquid. If the boiling point is not available, decomposition temperature (T_d) of the liquids was used.

The calculation of the enthalpy of formation is well described in literature.[2] According to Formula 12 the enthalpy of formation H is related to the molar energy of formation U for a high energy compound with the formula $C_a H_b N_c O_d$.[149]

$$H = U + \Delta nRT \qquad \textbf{Formula 12. Enthalpy of formation.}$$

In this equation is R the ideal gas constant and Δn the change of moles in the equation of formation,

$$aC + \frac{b}{2} H_2 + \frac{c}{2} N_2 + \frac{d}{2} O_2\ \rightarrow\ C_a H_b N_c O_d \qquad \textbf{Formula 13. Equation of formation.}$$
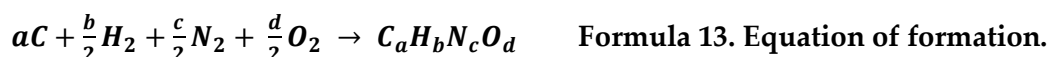
Pictures of the optimized structures were shown in Gaussview 6.1 and applied in the tables below.[150]

Table 12: Calculations of C based azides.
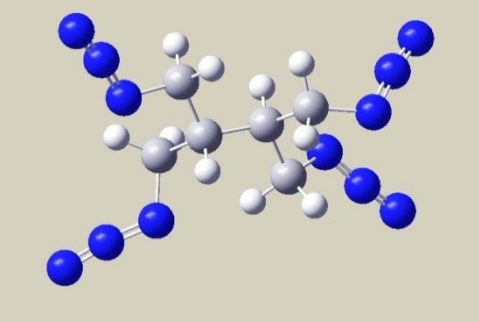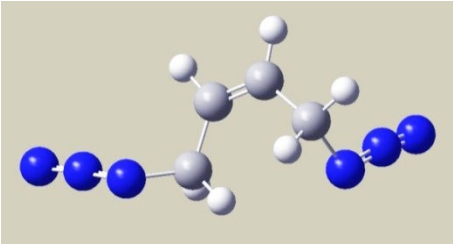
IUPAC Name	Abbreviation	Formula	Optimized structure	T_d [°C]	CBS4m Enthalpy [Hartree]	Heat of Formation [kJ mol^{-1}]	[kJ mL^{-1}]
1,1,2,2-Tetraazido-methylethane	Tetraazide	$C_6H_{10}N_{12}$		198	−890.15	1213.2	/
1,4-Diazidobut-2-ene	DAzB	$C_4H_6N_6$		133	−483.68	677.9	6.43

Table 13: Calculation of diazidoepoxibutane.
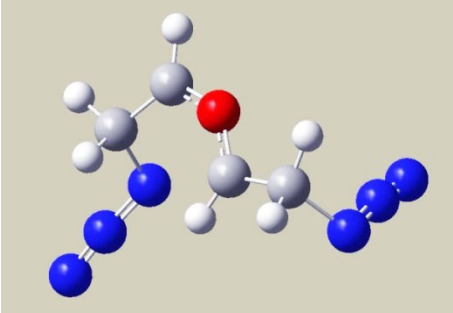
IUPAC Name	Abbreviation	Formula	Optimized structure	T_d [°C]	CBS4m Enthalpy [Hartree]	Heat of Formation [kJ mol⁻¹]	[kJ mL⁻¹]
Diazido-epoxybutane	DAzoB	$C_4H_6N_6O$		173	−558.75	730.8	6.30

Table 14: Calculations of azidoalcohols.
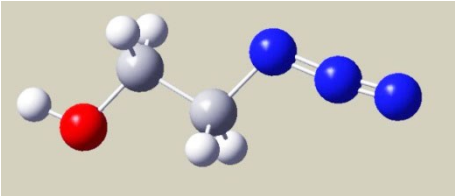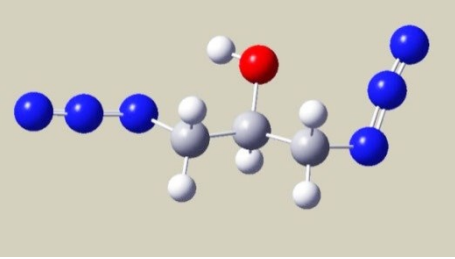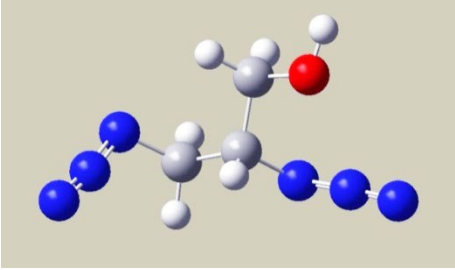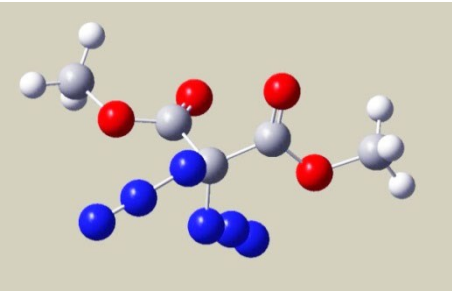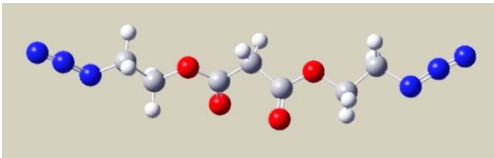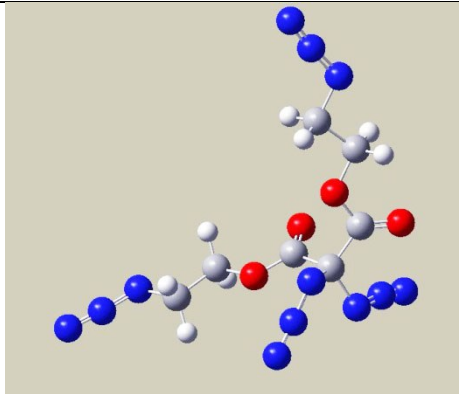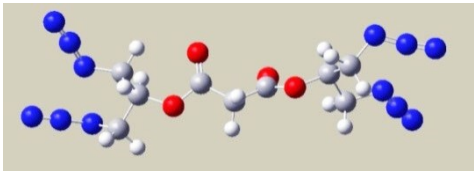
IUPAC Name	Abbreviation	Formula	Optimized structure	T_d [°C]	CBS4m Enthalpy [Hartree]	Heat of Formation [kJ mol^{-1}]	[kJ mL^{-1}]
2-Azidoethan-1-ol	AzEtOH	$C_2H_5N_3O$		162	−318.19	83.5	1.10
1,3-Diazidopropan-2-ol	1,3-DAP	$C_3H_6N_6O$		172	−520.82	397.2	3.53
2,3-Diazidopropan-1-ol	2,3-DAP	$C_3H_6N_6O$		164	−520.81	404.9	3.59

Table 15: Calculations of azido malonic ester.

IUPAC Name	Abbreviation	Formula	Optimized structure	T_d [°C]	CBS4m Enthalpy [Hartree]	Heat of Formation [kJ mol^{-1}]	[kJ mL^{-1}]
Dimethyl 2,2-diazido-malonate	DM-DAM	$C_5H_6N_6O_4$		161	−822.36	−45.2	0.26
Diethyl 2,2-diazido-malonate	DE-DAM	$C_7H_{10}N_6O_4$		147	−900.85	−125.0	0.63

IUPAC Name	Abbreviation	Formula	Optimized structure	T_d [°C]	CBS4m Enthalpy [Hartree]	Heat of Formation [kJ mol^{-1}]	[kJ mL^{-1}]
Bis-(2-azidoethyl)-malonate	DAEM	$C_7H_{10}N_6O_4$		191	−900.85	−124.7	0.71
Bis(2-azidoethyl) 2,2-diazidomalonate	DA-DAEM	$C_7H_8N_{12}O_4$		158	−1227.61	614.6	2.83
Bis(1,3-diazidopropan-1-yl) malonate	b-1,3-DAPM	$C_9H_{12}N_{12}O_4$		162	−1306.10	537.5	1.99
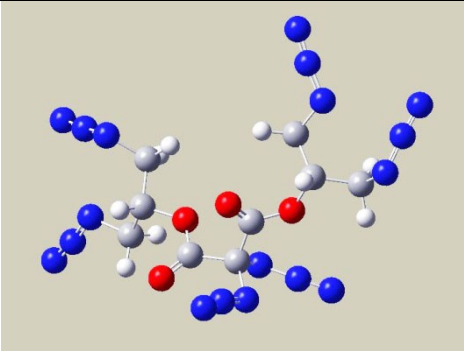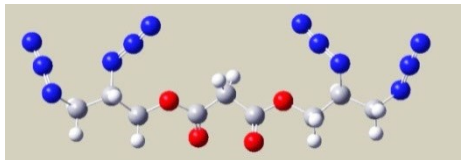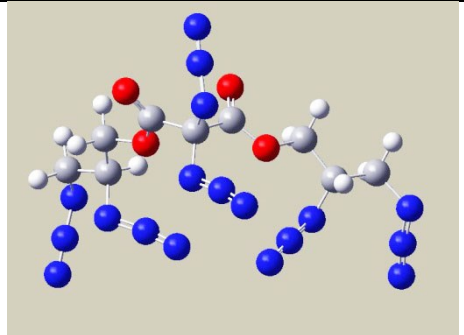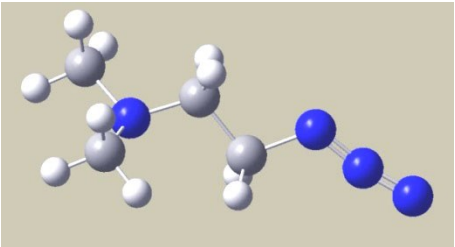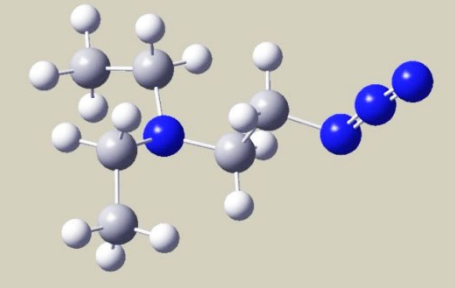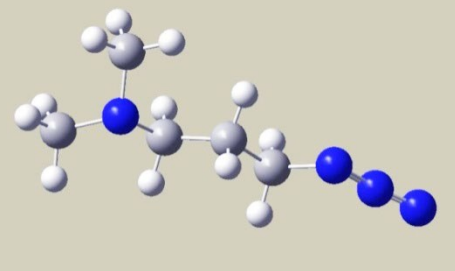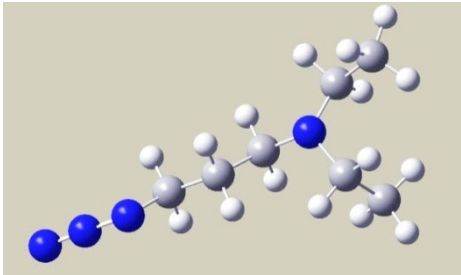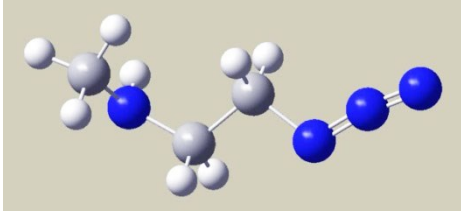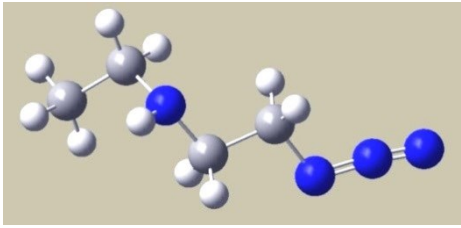
IUPAC Name	Abbreviation	Formula	Optimized structure	T_d [°C]	CBS4m Enthalpy [Hartree]	Heat of Formation [kJ mol^{-1}]	[kJ mL^{-1}]
Bis(1,3-diazidopropyl) 2,2-diazidomalonate	DA-b-1,3-DAPM	$C_9H_{10}N_{18}O_4$		136	−1632.86	1274.3	4.43
Bis(2,3-diazidopropan-1-yl) malonate	b-2,3-DAPM	$C_9H_{12}N_{12}O_4$		162	−1306.10	512.7	2.01
Bis(2,3-diazidopropyl) 2,2-diazidomalonate	DA-2,3-b-DAPM	$C_9H_{10}N_{18}O_4$		136	−1632.87	1247.5	4.31
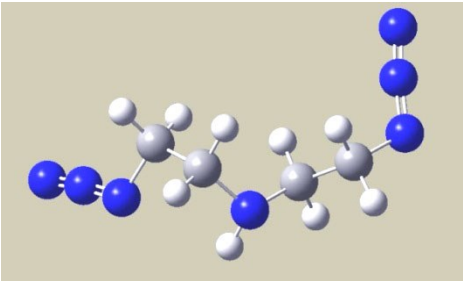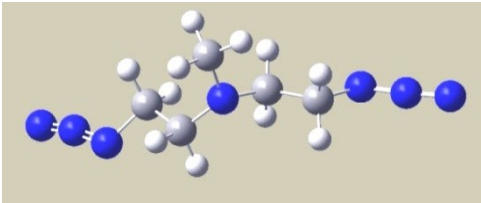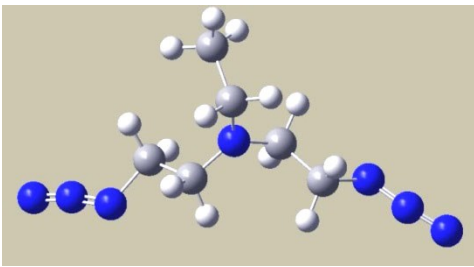
Table 16: Calculations of C-N based azides.

IUPAC Name	Abbreviation	Formula	Optimized structure	T_d [°C]	CBS4m Enthalpy [Hartree]	Heat of Formation [kJ mol^{-1}]	[kJ mL^{-1}]
2-Azido-*N*,*N*-dimethylethan-1-amine	DMAZ	$C_4H_{10}N_4$		135	−377.78	255.9	2.08
2-Azido-*N*,*N*-diethylethan-1-amine	DEAZ	$C_6H_{14}N_4$		170	−455.25	207.7	1.39
3-Azido-*N*,*N*-dimethyl-propan-1-amine	DMAPZ	$C_5H_{12}N_4$		150	−416.01	226.1	/

IUPAC Name	Abbreviation	Formula	Optimized structure	T_d [°C]	CBS4m Enthalpy [Hartree]	Heat of Formation [kJ mol^{-1}]	[kJ mL^{-1}]
3-Azido-*N*,*N*-dimethyl-propan-1-amine	DEAPZ	$C_7H_{16}N_4$		165	−494.49	171.8	/
2-Azido-*N*-methyl-ethan-1-amine	AzEMA	$C_3H_8N_4$		135	−337.54	270.5	2.04
2-Azido-*N*-ethylethan-1-amin	AzEEA	$C_4H_{10}N_4$		149	−376.78	235.2	2.49

IUPAC Name	Abbreviation	Formula	Optimized structure	T_d [°C]	CBS4m Enthalpy [Hartree]	Heat of Formation [kJ mol^{-1}]	[kJ mL^{-1}]
Bis(2-azidoethyl)-amine	DAzEA	$C_4H_9N_7$		170	−540.17	594.8	4.40
2-Azido-*N*-(2-azidoethyl)-*N*-methylethan-1-amine	DAzEMA	$C_5H_{11}N_7$		167	−579.40	591.2	4.48
2-Azido-*N*-(2-azidoethyl)-*N*-ethylethan-1-amine	DAzEEA	$C_6H_{13}N_7$		166	−618.63	570.1	3.17
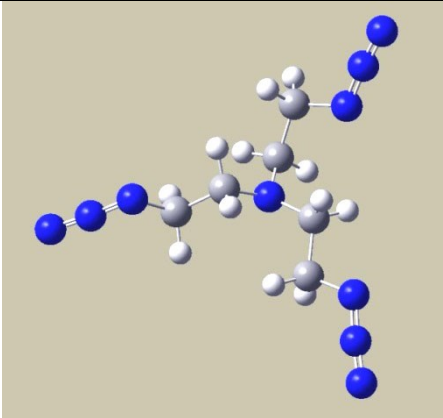
IUPAC Name	Abbreviation	Formula	Optimized structure	T_d [°C]	CBS4m Enthalpy [Hartree]	Heat of Formation [kJ mol^{-1}]	[kJ mL^{-1}]
Tris(2-azidoethyl)-amine	TAzA	$C_6H_{12}N_{10}$		187	−782.02	921.6	4.80

Table 17: Calculation of desirable compounds.
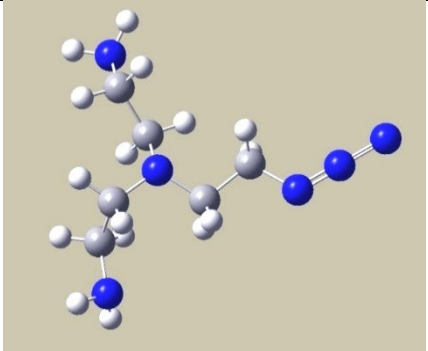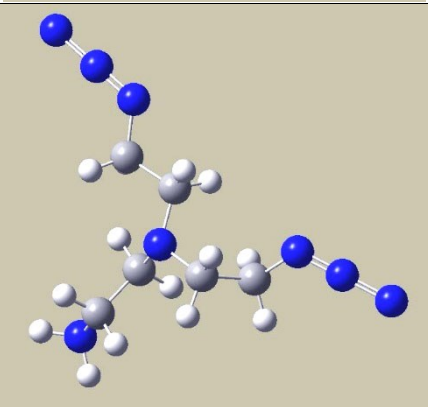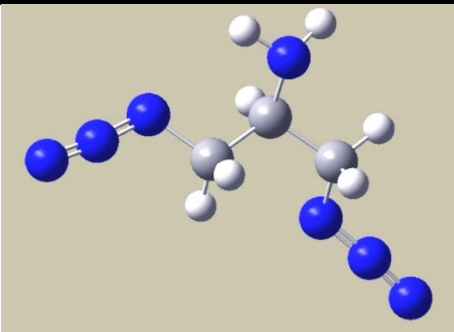
IUPAC Name	Abbreviation	Formula	Optimized structure	T_d [°C]	CBS4m Enthalpy [Hartree]	Heat of Formation [kJ mol^{-1}]
N^1-(2-aminoethyl)-N^1-(2-azidoethyl)ethane-1,2-diamine	DAEAzEA	$C_6H_{16}N_6$		est. 160	−565.80	271.2
N^1,N^1-bis(2-azidoethyl)ethane-1,2-diamine	DAzEAEA	$C_6H_{14}N_8$		est. 160	−673.91	596.6

Table 18: Calculation of serinolazide

IUPAC Name	Abbreviation	Formula	Optimized structure	T_d [°C]	CBS4m Enthalpy [Hartree]	Heat of Formation [kJ mol^{-1}]
1,3-Diazidopropan-2-amine	Serinolazide	$C_3H_7N_7$		est. 160	−500.95	578.6

The calculated heat of formation for TAzME **4** is 1213.2 kJ mol^{-1}.

The heat of formation value for DAzB **6** is 677.9 kJ mol^{-1}, while the synthesized epoxide derivative has a higher value of 730.8 kJ mol^{-1}.

The heat of formations of the three synthesized azidoalcohols are 83.5 kJ mol^{-1} for AzEtOH **8,** 397.2 kJ mol^{-1} for 1,3-DAP **9** and 404.9 kJ mol^{-1} for 2,3-DAP **10**.

The synthesized geminal diazidated malonic acid esters DM-DAM **11** and DE-DAM **12** have negative calculated heat of formation energies with −45.2 kJ mol^{-1} and −125.0 kJ mol^{-1}. The formation of these compounds is exothermic.

The azidoalcohol ester DAEM **13**, b-1,3-DAPM **14**, b-2,3-DAPM **15** have calculated values of −124.7 kJ mol^{-1} (**13**), 537.5 kJ mol^{-1} (**14**) and 512.7 kJ mol^{-1} (**15**). Only azido ester **13** is therefore an exothermic compound.

The geminal diazidated liquids derived from **13–15** have calculated values of 614.6 kJ mol^{-1} for DA-DAEM **16**, 1274.3 kJ mol^{-1} for DA-b-1,3-DAPM **17** and 1247.5 kJ mol^{-1} for DA-b-2,3-DAPM **18**.

The heat of formations for the secondary amines are calculated to be 270.5 kJ mol^{-1} for AzEMA **22**, 235.2 kJ mol^{-1} for the ethyl analogue AzEEA **24** and 594.8 kJ mol^{-1} for DAzEA **26**.

The tertiary amines DMAZ **28** and DEAZ **30** show values of 255.9 kJ mol^{-1} and 207.7 kJ mol^{-1}. Their propyl derivatives DMAPZ **32** and DEAPZ **35** have heat of formations of 226.1 kJ mol^{-1} and 171.8 kJ mol^{-1}. Within these values, it can be observed that the ethyl derivatives have lower heat of formation energies compared to the methyl derivatives.

Same trend can be observed with the derivatives from DAZEA **26,** DAzEMA **37** with methyl residue and DAzEEA **40** with ethyl residue. They have calculated values of 591.2 kJ mol^{-1} (**37**) and 570.1 kJ mol^{-1} (**40**). The compound TAzEA **42** has a heat of formation energy of 921.6 kJ mol^{-1}.
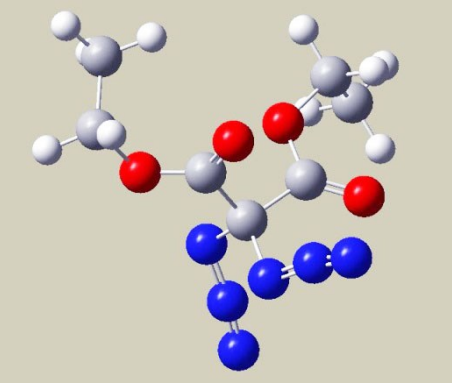
Based on compound **42**, the heat of formation energies for the amino-azido derivatives were calculated. They were assigned to be 271.2 kJ mol^{-1} for DAEAzEA with two aminoethyl chains and 596.6 kJ mol^{-1} for DAzEAEA with the two azidoethyl chains. In addition, the heat of formation of serinolazide was calculated to 578.6 kJ mol^{-1}.

3.2 Rocket specific parameters with Gordon McBride

The theoretical rocket specific parameters for hypergolic mixtures were calculated using the NASA (National Aeronautics and Space Administration) computer program CEA (Chemical Equilibrium with Applications) developed by Dr. S. Gordon, Dr. B. J. McBride and co-workers.[151]

Calculation for rocket problems was executed with input files by assuming frozen composition during expansion, rocket problem case 8 for an infinite area combustor (iac), fixed chamber pressure of 10 bar, determined ratio of chamber pressure to exit pressure of 1000, a supersonic area ratio and nozzle area expansion ratio of 300.[151] These values are commonly used for upper stage engines. Temperature for propellant mixture was set at 285.15 K.

For these hypergolic mixtures calculations on the one hand hydrogen peroxide (H_2O_2) was used as the oxidizer on the other hand dinitrogen tetroxide (N_2O_4).

As important parameters the optimized oxidizer to fuel ratio (O/F), the characteristic velocity of the propellant (C^*), the combustion temperature in the chamber (T_C) and the specific impulse (I_{sp}) are listed in the following tables, Table 19 and Table 20. The calculated I_{sp} is given in the output file as effective exhaust velocity and has to be divided by acceleration of gravity. Therefore the determined value for Munich (Germany) of 9.807232 m s^{-2} was used to obtain the specific impulse value in the common used unit second.[152]

3.2.1 Hypergolic mixture with oxidizer hydrogen peroxide

In Table 19 the calculations of the synthesized azido compounds with the use of hydrogen peroxide as oxidizer are shown. Besides the abbreviation, formula and molar mass of the respective fuels also the heat of formation and density is re-applied. As reference values the parameters of hydrazine, MMH and UDMH are listed above.

Table 19: Theoretical rocket parameters of hypergolic H_2O_2 mixtures.

Abbreviation	Formula	M [g mol^{-1}]	Heat of Formation [kJ mol^{-1}]	ϱ (20-25 °C) [g cm^{-3}]	O/F (opt.)	C* [m s^{-1}]	T_C [K]	I_{sp} [m s^{-1}]	I_{sp} [s]	Ae/At
Hydrazine	N_2H_4	32.05	50.6[153]	1.00[154]	n.a.	n.a.	n.a.	n.a.	n.a.	n.a
MMH	CH_6N_2	46.07	54.2[155]	0.86[156]	2.5	1696	2770	3257.9	332.2	300
UDMH	$C_2H_8N_2$	60.10	48.3[157]	0.79[158]	3.0	1682	2768	3237.1	330.1	300
DMAZ	$C_4H_{10}N_4$	114.15	255.9	0.93	3.0	1653	2905	3199.3	326.2	300
DEAZ	$C_6H_{14}N_4$	142.21	207.7	0.95	3.5	1649	2883	3196.5	325.9	300
DMAPZ	$C_5H_{12}N_4$	149.10	226.1	n.a	3.5	1655	2863	3195.9	325.8	300
DEAPZ	$C_7H_{16}N_4$	156.14	171.8	n.a.	3.5	1649	2857	3193.1	325.6	300

Abbreviation	Formula	M [g mol^{-1}]	Heat of Formation [kJ mol^{-1}]	ϱ (20-25 °C) [g cm^{-3}]	O/F (opt.)	C* [m s^{-1}]	T$_C$ [K]	I$_{sp}$ [m s^{-1}]	I$_{sp}$ [s]	Ae/At
AzEMA	C$_3$H$_8$N$_4$	130.01	270.5	0.98	2.5	1660	2909	3201.2	326.4	300
AzEEA	C$_4$H$_{10}$N$_4$	114.15	235.2	1.21	3.0	1650	2897	3193.5	325.6	300
DAzEA	C$_4$H$_9$N$_7$	155.17	594.8	1.14	2.5	1633	2960	3156.9	321.9	300
DAzEMA	C$_5$H$_{11}$N$_7$	169.02	591.2	1.28	2.0	1663	2919	3189.8	325.2	300
DAzEE	C$_6$H$_{13}$N$_7$	183.22	570.1	1.02	2.5	1655	2934	3192.7	325.5	300
TAzEA	C$_6$H$_{12}$N$_{10}$	224.25	921.6	1.17	2.0	1655	2991	3183.4	324.6	300
AzEtOH	C$_2$H$_5$N$_3$O	87.08	84.2	1.15	1.5	1626	2895	3130.5	319.4	300
1,3-DAP	C$_3$H$_6$N$_6$O	142.12	397.2	1.26	1.5	1624	2986	3124.1	318.5	300

Abbreviation	Formula	M [g mol^{-1}]	Heat of Formation [kJ mol^{-1}]	ϱ (20-25 °C) [g cm^{-3}]	O/F (opt.)	C* [m s^{-1}]	T_C [K]	I_{sp} [m s^{-1}]	I_{sp} [s]	Ae/At
2,3-DAP	$C_3H_6N_6O$	142.12	404.9	1.26	1.5	1625	2990	3126.6	318.8	300
DM-DAM	$C_5H_6N_6O_4$	214.05	−45.2	1.24	1.5	1568	2851	3012.1	307.1	300
DE-DAM	$C_7H_{10}N_6O_4$	242.08	−125.0	1.21	1.5	1566	2857	3028.0	308.7	300
DAEM	$C_7H_{10}N_6O_4$	242.20	−124.7	1.38	1.5	1566	2857	3028.1	308.8	300
DA-DAEM	$C_7H_8N_{12}O_4$	343.22	614.6	1.49	1.0	1580	2997	3029.0	308.8	300
b-1,3-DAPM	$C_9H_{12}N_{12}O_4$	352.38	537.5	1.38	1.5	1586	2954	3061.6	312.2	300
DA-b-1,3-DAPM	$C_9H_{10}N_{18}O_4$	434.30	1274.3	1.51	1.0	1599	3046	3057.2	311.7	300
b-2,3-DAPM	$C_9H_{12}N_{12}O_4$	352.38	512.7	1.30	1.5	1584	2949	3058.3	311.8	300

Abbreviation	Formula	M [g mol⁻¹]	Heat of Formation [kJ mol⁻¹]	ϱ (20-25 °C) [g cm⁻³]	O/F (opt.)	C* [m s⁻¹]	T_C [K]	I_sp [m s⁻¹]	I_sp [s]	Ae/At
DA-b-2,3-DAPM	$C_9H_{10}N_{18}O_4$	434.30	1247.5	1.50	1.0	1597	3040	3053.5	311.3	300
Tetraazide	$C_6H_{10}N_{12}$	250.23	1213.2	n.a.	1.5	1662	3041	3174.7	323.7	300
DAzB	$C_4H_6N_6$	138.13	677.9	1.31	1.5	1672	3000	3181.4	324.4	300
DAzoB	$C_4H_6N_6O$	154.13	730.8	1.33	1.0	1699	3073	3116.3	317.8	300

M = molar mass; ϱ = density; O/F = optimized oxidizer to fuel ratio; C* = characteristic velocity of the propellant; T_c = combustion temperature in the chamber; I_{sp} = specific impulse

A calculation of the rocket specific parameters of hydrazine and HTP as reference was not possible with the used NASA code due to the absence of carbon in this molecule.

The calculated reference I_{sp} values for MMH and UDMH with HTP are 332 s and 330 s with O/F ration of 2.5, respectively 3.0 with combustion temperatures of 2770 K and 2768 K. The characteristic velocities are 1696 m s^{-1} and 1682 m s^{-1}.

The values of the promising alternative DMAZ **28** are with an optimized O/F of 3.0 the following: I_{sp} is a little lower compared to the references with 326 s, T_c is with 2905 K higher and C* lower with 1653 m s^{-1}. The calculations of the derivatives DEAZ **30** (3.0 O/F), DMAPZ **32** and DEAPZ **35** (both 1.5 O/F) result the same I_{sp} value of 326 s. Their T_c values are a little lower with 2880 K to 2860 K, and the C* is almost similar with around 1650 m s^{-1}.

The I_{sp} values for the secondary amines AzEMA **22** and AzEEA **24** are also at 326 s with O/F ratios of 2.5 and 3.0. Their T_c differ only slightly with 2909 K and 2897 K, as well as their C* with 1660 m s^{-1} and 1650 m s^{-1}. These two compounds reveal therefore the same I_{sp} value as DMAZ and are even over the ideal required one of >323 s.

DAzEA **26** has the lowest calculated rocket parameters with I_{sp} of 322 s, T_c 2960 K and C* of 1633 m s^{-1} by an optimized O/F ratio of 2.5.

The derived tertiary amines DAzEMA **37**, DAzEEA **40** and TAzEA **42** have specific impulse values of 325 s (O/F 2.0), 326 s (O/F 2.5) and 325 s (O/F 2.0). Their T_c are 2919 K, 2934 K and the highest one with 2991 K. The C* values are 1663 m s^{-1} and 1655 m s^{-1} for **40** and **42**.

All the previously mentioned synthesized amino azido liquids fulfil the minimum requested theoretical I_{sp} value of >315 s and except of compound **26** even the ideal requested one of >323 s.

For the synthesized azidoalcohols, AzEtOH **8**, 1,3-DAP **9** and 2,3-DAP **10**, the calculated I_{sp} values are 319 s for all three alcohols. The calculated T_c are 2895 K, 2986 K and 2990 K. C* was determined to 1626 m s^{-1}, 1624 m s^{-1} and 1625 m s^{-1}. The values between the diazidopropanols differ only slightly, while alcohol **8** has the highest characteristic velocity. Their theoretical I_{sp} values fulfil in all three cases the minimum requested requirement. In

addition, compared to pure EtOH which has an I_{sp} of 246 s with same optimized O/F ration and C^* of 1354 m s^{-1}, the values of AzEtOH **8** increased significantly by adding an azido group to the system.

The geminal diazidated malonic esters DM-DAM **11** and DE-DAM **12** have with 307 s and 309 s impulses in the same range as AzEtOH. The combustion temperatures are 2851 K and 2857 K, while C^* was determined to 1568 m s^{-1} and 1566 m s^{-1}.

If the ester residue of the malonic acid is modified with the azidoalcohols, the following values are obtained for optimized O/F ratio of 1.5. I_{sp} was calculated to 309 s for DAEM **13** and 312 s for b-1,3-DAPM **14** and b-2,3-DAPM **15**. Their T_c is 2857 K, 2954 K and 3046 K. C^* is calculated to be 1566 m s^{-1}, 1586 m s^{-1} and 1599 m s^{-1}.

The geminal diazidation of the above-mentioned compounds **13**-**15** lead to same maximum I_{sp} values for **16**-**18** of 309 s respectively 312 s/ 311 s by an optimized O/F ratio of 1.0. The T_c values increase on the other hand to 2997 K for **16**, 3046 K for **17** and 3040 K for **18**. Also, C^* is increased to 1580 m s^{-1} and 1599 m s^{-1} / 1597 m s^{-1}.

Although the specific impulse values for the synthesized azidoalcohol and the azido malonates fulfil not the requirement of the minimum requested value of >315 s, they are with 309 s only slightly lower and still within a good range.

The synthesized TAzME **4** has a specific impulse of 324 s with an optimized O/F ratio of 1.5. Its T_c is calculated at 3041 K and C^* at 1662 m s^{-1}.

The values of DAzB **6** differ only slightly form the ones of **4**, whereas the epoxy derivative **7** shows with 318 s as I_{sp}, 3073 K as T_c and 1699 m s^{-1} lower calculated values. However, all three would theoretically fulfil the minimum requirement of >315 s and except of **7** even the ideal of >323 s.

As a result, the addition of oxygen to the fuel oxidizer system with HTP lead to lower I_{sp} values compared to molecules without oxygen content. Although all possible calculated fuels obtain lower theoretical I_{sp} values compared to MMH or UDMH, most of them fulfil the minimum requirement and also the majority of them even the ideal one of >323 s.

3.2.2 Hypergolic mixture with oxidizer dinitrogen tetroxide

In Table 20 the calculations of the synthesized azido compounds with the use of dinitrogen tetroxide as oxidizer are shown. Besides the abbreviation, formula and molar mass of the respective fuels also the heat of formation and density is re-applied. As reference values the parameters of hydrazine, MMH and UDMH are listed above.

Table 20: Theoretical rocket parameters of hypergolic N_2O_4 mixtures.

Abbreviation	Formula	M [g mol^{-1}]	Heat of Formation [kJ mol^{-1}]	ϱ (20-25 °C) [g cm^{-3}]	O/F (opt.)	C* [m s^{-1}]	T_C [K]	I_{sp} [m s^{-1}]	I_{sp} [s]	Ae/At
Hydrazine	N_2H_4	32.05	50.6[153]	1.00[154]	n.a.	n.a.	n.a.	n.a.	n.a.	n.a
MMH	CH_6N_2	46.07	54.2[155]	0.86[156]	1.5	1704	2962	3195.4	325.8	300
UDMH	$C_2H_8N_2$	60.10	48.3[157]	0.79[158]	2.0	1684	3091	3171.6	323.4	300
DMAZ	$C_4H_{10}N_4$	114.15	255.9	0.93	1.5	1655	3095	3089.2	315.0	300
DEAZ	$C_6H_{14}N_4$	142.21	207.7	0.95	2.0	1642	3181	3088.7	314.9	300
DMAPZ	$C_5H_{12}N_4$	149.10	226.1	n.a	2.0	1639	3230	3088.2	314.9	300
DEAPZ	$C_7H_{16}N_4$	156.14	171.8	n.a.	2.0	1639	3117	3076.0	313.6	300
AzEMA	$C_3H_8N_4$	130.01	270.5	0.98	1.5	1657	3224	3107.3	316.8	300

Abbreviation	Formula	M [g mol^{-1}]	Heat of Formation [kJ mol^{-1}]	ϱ (20-25 °C) [g cm^{-3}]	O/F (opt.)	C* [m s^{-1}]	T_C [K]	I_{sp} [m s^{-1}]	I_{sp} [s]	Ae/At
AzEEA	$C_4H_{10}N_4$	114.15	235.2	1.21	1.5	1646	3066	3071.9	313.2	300
DAzEA	$C_4H_9N_7$	155.17	594.8	1.14	1.0	1667	3209	3092.1	315.3	300
DAzEMA	$C_5H_{11}N_7$	169.02	591.2	1.28	1.5	1656	3033	3055.1	311.5	300
DAzEEA	$C_6H_{13}N_7$	183.22	570.1	1.02	1.5	1651	3271	3091.2	315.2	300
TAzEA	$C_6H_{12}N_{10}$	224.25	921.6	1.17	1.5	1619	3373	3038.3	309.8	300
AzEtOH	$C_2H_5N_3O$	87.08	84.2	1.15	1.0	1609	3201	2946.7	300.5	300
1,3-DAP	$C_3H_6N_6O$	142.12	397.2	1.26	1.0	1600	3320	3005.1	306.4	300
2,3-DAP	$C_3H_6N_6O$	142.12	404.9	1.26	1.0	1602	3325	3007.9	306.7	300

Abbreviation	Formula	M [g mol⁻¹]	Heat of Formation [kJ mol⁻¹]	ϱ (20-25 °C) [g cm⁻³]	O/F (opt.)	C* [m s⁻¹]	T_C [K]	I_sp [m s⁻¹]	I_sp [s]	Ae/At
DM-DAM	$C_5H_6N_6O_4$	214.05	−45.2	1.24	0.5	1501	3030	2824.2	288.0	300
DE-DAM	$C_7H_{10}N_6O_4$	242.08	−125.0	1.21	1.0	1527	3154	2895.4	295.2	300
DAEM	$C_7H_{10}N_6O_4$	242.20	−124.7	1.38	1.0	1527	3154	2895.5	295.2	300
DA-DAEM	$C_7H_8N_{12}O_4$	343.22	614.6	1.49	0.5	1566	3227	2917.2	297.4	300
b-1,3-DAPM	$C_9H_{12}N_{12}O_4$	352.38	537.5	1.38	1.0	1598	3547	3035.7	309.5	300
DA-b-1,3-DAPM	$C_9H_{10}N_{18}O_4$	434.30	1274.3	1.51	0.5	1598	3325	2962.1	302.9	300
b-2,3-DAPM	$C_9H_{12}N_{12}O_4$	352.38	512.7	1.30	1.0	1595	3539	3031.3	309.1	300
DA-b-2,3-DAPM	$C_9H_{10}N_{18}O_4$	434.30	1247.5	1.50	0.5	1594	3314	2956.3	301.4	300

Abbreviation	Formula	M [g mol⁻¹]	Heat of Formation [kJ mol⁻¹]	ϱ (20-25 °C) [g cm⁻³]	O/F (opt.)	C* [m s⁻¹]	T_C [K]	I_{sp} [m s⁻¹]	I_{sp} [s]	Ae/At
Tetraazide	$C_6H_{10}N_{12}$	250.23	1213.2	n.a.	1.0	1657	3434	3078.7	313.9	300
DAzB	$C_4H_6N_6$	138.13	677.9	1.31	1.0	1675	3395	3099.1	316.0	300
DAzoB	$C_4H_6N_6O$	154.13	730.8	1.33	0.5	1713	3249	3123.8	318.5	300

M = molar mass; ϱ = density; O/F = optimized oxidizer to fuel ratio; C* = characteristic velocity of the propellant; T_c = combustion temperature in the chamber; I_{sp} = specific impulse

As with the calculation of the HTP system before, the rocket parameter values of hydrazine with NTO could not be obtained with the NASA code.

Therefore, the calculated reference I_{sp} values for MMH and UDMH with NTO are 326 s and 323 s with O/F ration of 1.5, respectively 2.0. They are significantly lower as with HTP. The combustion temperatures are 2962 K and 3091 K. Their characteristic velocities are 1704 m s^{-1} and 1684 m s^{-1}.

Since no minimum or ideal I_{sp} values within this bipropellant system was determined, the obtained I_{sp} values were compared to the reference ones.

The values of the promising alternative DMAZ **28** are with an optimized O/F of 1.5 the following: I_{sp} is a little lower compared to the references with 315 s, T_c is with 3095 K higher and C* lower with 1655 m s^{-1}. The derivatives DEAZ **30**, DMAPZ **32** reveal the same I_{sp} value of 315 s, DEAPZ **35** has an I_{sp} of 314 s Their calculated T_c values are a higher with 3117 K to 3230 K, and the C* is around 15 m s^{-1} lower with 1642 m s^{-1} and 1639 m s^{-1}.

The I_{sp} values for the secondary amines AzEMA **22** and AzEEA **24** determined to 317 s and 313 s with O/F ratios of 1.5. Their T_c are 3224 K and 3066 K. The obtained C* values are 1657 m s^{-1} and 1646 m s^{-1}. The I_{sp} value of AzEMA is slightly higher compared to DMAZ but lower than the ones of MMH and UDMH.

In this combination, the values of DAzEA **26** increase. The I_{sp} is calculated to 315 s, T_c to 3209 K and C* to 1667 m s^{-1} by an optimized O/F ratio of 1.0.

The derived tertiary amines DAzEMA **37**, DAzEEA **40** and TAzEA **42** have specific impulse values of 312 s, 315 s and 310 s with an O/F ratio of 1.5. The value of **42** is the lowest of the calculates amino azido compounds. Their T_c are 3033 K, 3271 K and the highest one with 3373 K for **42**. The C* values are 1656 m s^{-1}, 1651 m s^{-1} and 1651 m s^{-1}.

Compared to MMH and UDMH all obtained I_{sp} values are lower. Compared to DMAZ, the I_{sp} of DEAZ **30,** DAzEA **26** and DAzEEA **40** is with 315 s the same and AzEMA **22** has the highest theoretical I_{sp} with 317 s.

For the synthesized azidoalcohols, AzEtOH **8**, 1,3-DAP **9** and 2,3-DAP **10**, the calculated I_{sp} values are 301 s, 306 s and 307 s at an O/F ratio of 1.0. The calculated T_c are 3201 K, 3320 K and 3325 K. C^* was determined to 1609 m s^{-1}, 1600 m s^{-1} and 1602 m s^{-1}. As it was shown in the calculations with HTP before, the specific impulse values decrease with the presence of an oxygen in the fuel. However, all theoretical I_{sp} values of the azidoalcohols are over 300 s.

Contrary to them, the geminal diazidated malonic esters DM-DAM **11** and DE-DAM **12** have with 288 s (O/F 0.5) and 295 s (O/F 1.0) significantly lower specific impulses. The combustion temperatures are 3030 K and 3154 K, while C^* was determined to 1501 m s^{-1} and 1527 m s^{-1}.

If the ester residue of the malonic acid is modified with the azidoalcohols, the following values are obtained for optimized O/F ratio of 1.0. I_{sp} was calculated to 295 s for DAEM **13** and 310 s for b-1,3-DAPM **14** and 309 s for b-2,3-DAPM **15**. Only the value of **13** is lower than 300 s. Their T_c is 3154 K, 3547 K and 3539 K. C^* is calculated to be 1527 m s^{-1}, 1598 m s^{-1} and 1595 m s^{-1}.

The geminal diazidation of the above-mentioned compounds **13**-**15** lead to a higher I_{sp} value for **16** of 297 s and lower values for **17** and **18** of 303 s respectively 301 s by an optimized O/F ratio of 0.5. The T_c values increase on the one hand higher to 3227 K for **16**, and on the other hand lower with 3325 K for **17** and 3314 K for **18**. Also, C^* is increased to 1566 m s^{-1} for **16** and at the same value of 1598 m s^{-1} / 15974m s^{-1} for **17** and **18**.

The synthesized TAzME **4** has a specific impulse of 314 s with an optimized O/F ratio of 1.0. Its T_c is the highest calculated at 3434 K and C^* is determined to 1657 m s^{-1}.

The values of DAzB **6** are calculated to 316 s for I_{sp}, 3395 K for T_c and 1675 m s^{-1} for C^*. Whereas, the epoxy derivative **7** shows with 319 s as I_{sp} at O/F ratio of 0.5, 3349 K as T_c and 1713 m s^{-1} the highest calculated specific rocket parameters in combination with NTO. However, all alternative fuels show lower I_{sp} values compared to MMH and UDMH, but most of them are over 300 s.

4 Hypergolicity tests

After the synthesis of the energetic liquids and the calculation of the rocket specific parameters, the potential replacement candidates for hydrazine were tested for their hypergolicity with the oxidizers HTP and N_2O_4. For this purpose, a simple drop test was performed to get a quick evidence if the tested propellant combination reacts hypergolic.[159] This drop test allows to control the quantities of the liquids involved precisely:

- The oxidizer or fuel is provided in a glass vessel, where it formed a layer covering the whole bottom. Therefore, the amount of liquid in the vessel varies between 0.5 g and 1.0 g.
- The respective combination component is added dropwise with a glass pipette and syringe to ensure the adding of an identical volume of 0.05 ± 0.055 mL, identical for every test run

The drop hight between the glass vessel and the pipette was adjusted to 150 mm. The whole ignition process from the first contact of the droplet until the visibility of the flame is recorded by a high-speed camera, which is able to capture up to 4.000 frames per minute. An additional light source is given to ensure bright pictures. The whole experimental setup is pictured in Figure 15.

Figure 15: Experimental setup for droplet test.

For the executed experiments SPEEDCAM visario g2 high speed camera was used with an adjustment of the frame rate of 2.000 frames per minute. In order to achieve reliable data about the hypergolic behavior and the ID time, the number of tests was set to n = 3. The ID

time [ms] is measured as the frame number between the first frame, where the droplet touches the surface, until the first frame of a visible flame dived trough the frame rate.

$$ID\ time = \frac{Frame_{ignition} - Frame_{contact}}{Frame\ rate}$$

It is then given in seconds as an average out of 3 measurements.

Figure 16 shows an exemplary evaluation on the basis of the frames given by the high speed camera.

Figure 16: Evaluation of ID time.

4.1 Dinitrogen tetroxide - N₂O₄

Due to the high vapor pressure of N_2O_4 of 1.2 bar[26], the low boiling point and it´s high toxicity by inhalation the experimental setting for the hypergolicity test was done observing high safety measures. Previously cooled NTO was provided in a cool glass vessel and instantly put on a cooled copper plate on an ice bath. The fuel was then added dropwise with the glass pipette.

4.1.1 Commercially available amino liquids

The first tests were carried out using commercially available amino liquids, respectively amino alcohols. Therefore, the following compounds listed in Figure 17 were chosen. They were all purchased from Sigma Aldrich[160] and used for the hypergolicity test with NTO without further purification. In addition, no additive was used within these tests.
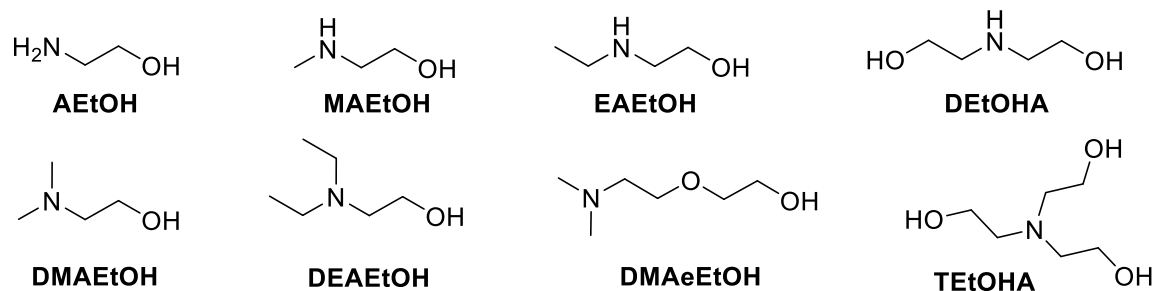
Figure 17: Selected commercially available liquid amino alcohols.

The first tested compound was 2-aminoethanol (AEtOH), followed by the methyl and ethyl derivative *N*-methylethanolamine (MAEtOH) and *N*-ethylethanolamine (EAEtOH). As additional compound, diethanolamine (DEtOHA) was tested for the hypergolicity, as well as the alcohol derivatives of DMAZ and DEAZ, *N,N*-dimethylethanolamine (DMAEtOH) and *N,N*-Diethylethanolamine (DEAEtOH). Furthermore, the ethoxy liquid 2-[2-(dimethylamino)ethoxy]ethanol (DMAeEtOH) was selected, and the trivalent amino alcohol triethanolamine (TEtOHA) as last compound. The results of the hypergolicity test are listed in Table 21 below.

Table 21: Hypergolicity test of amino alcohols and NTO.

Compound	Oxidizer	Hypergolicity	ID time [ms]
AEtOH	N_2O_4	X decomposition	/
MAEtOH	N_2O_4	X strong decomposition	/
EAEtOH	N_2O_4	X strong decomposition	/
DEtOHA	N_2O_4	✓	111
DMAEtOH	N_2O_4	✓	126
DEAEtOH	N_2O_4	✓	106
DMAeEtOH	N_2O_4	✓	158
TEtOHA	N_2O_4	X decomposition	/

X = no hypergolic reaction; ✓ = hypergolic reaction

The usage of AEtOH as a fuel lead only to a decomposition reaction with NTO. No flame or hypergolic ignition occurred. Similar behaviour was observed with the two ethanol amine

derivatives MAEtOH and EAEtOH. With this reaction a stronger decomposition reaction was monitored, but also no hypergolic ignition. In contrast, with the amino alcohol DEtOHA and the two methyl and ethyl derivatives DMAEtOH and DEAEtOH a hypergolic ignition was achieved. In these cases, the measured ID times of 106 – 126 ms are relatively high compared to the requirements of less than 50 ms. Furthermore, the ethoxy compound DMAeEtOH also reacted hypergolic with NTO, even though the determined ID time was very long with 158 ms. Contrary to expectations, triethanolamine showed only a decomposition reaction with NTO and no hypergolicity.

Based on the knowledge of a hypergolic ignition of the azido derivative DMAZ **28** with NTO, these results can give a first impression of the hypergolic behaviour of amino azido liquids.

4.1.2 Synthesized azido liquids

In the next step, the previously synthesized amino azido liquids described in section 2 were tested for the hypergolic reaction with NTO.

First, the reaction of the three azidoalcohols and the azido malonic ester derivatives are described. The tested compounds are depicted in Figure 18 below.
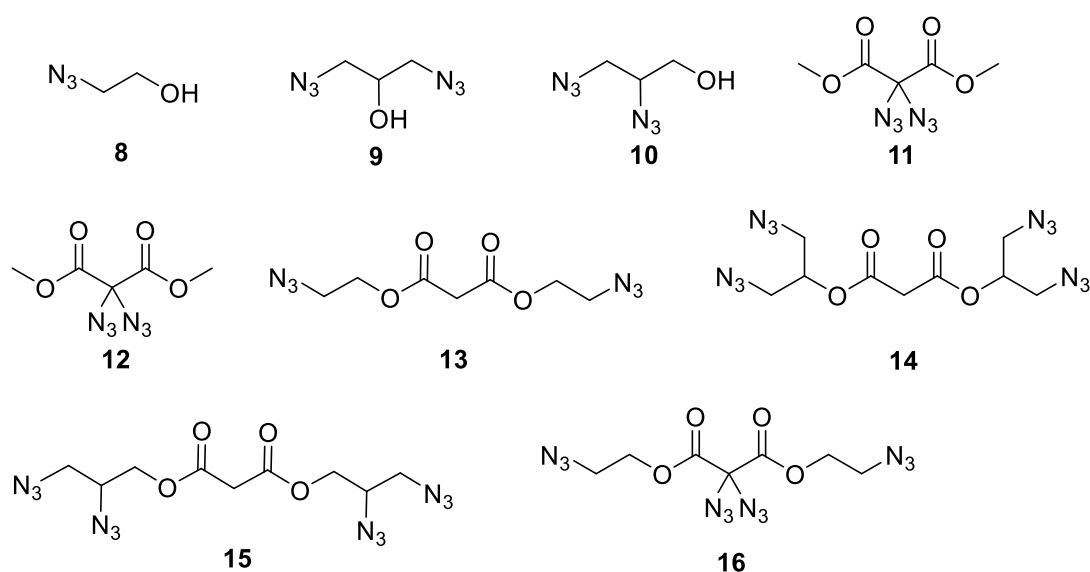
Figure 18: Tested azidoalcohols and azido malonates.

The results and determined ID times of these possible fuels with NTO as oxidizer are given in Table 21 below.

As result, neither the tested azidoalcohol, AzEtOH **8**, nor the two diazidopropanols 1,3-DAP **9** and 2,3-DAP **10** showed a hypergolic reaction with NTO as oxidizer. The tested geminal azidated malonic esters DM-DAM **11** and the ethyl derivative DE-DAM **12** reacted in the same way without a visible ignition. Likewise, the azido substituted derivatives of malonic acid DAEM **13**, b-1,3-DAPM **14** and b-2,3-DAPM **15** and even the geminal diazidated derivative DA-bAEM **16** achieved no hypergolicity with NTO.

Table 22: Hypergolicity test with azidoalcohols and azido malonates with NTO.

Compound	Oxidizer	Hypergolicity	ID time [ms]
AzEtOH 8	N_2O_4	X	/
1,3-DAP 9	N_2O_4	X	/
2,3-DAP 10	N_2O_4	X	/
DM-DAM 11	N_2O_4	X	/
DE-DAM 12	N_2O_4	X	/
DAEM 13	N_2O_4	X	/
b-1,3-DAPM 14	N_2O_4	X	/
b-2,3-DAPM 15	N_2O_4	X	/
DA-bAEM 16	N_2O_4	X	/

X = no hypergolic reaction; ✓ = hypergolic reaction

Resulting from these findings, the next tests were conducted with the synthesized amino azido liquids. The selected compounds for the experiments are shown in Figure 19 below.
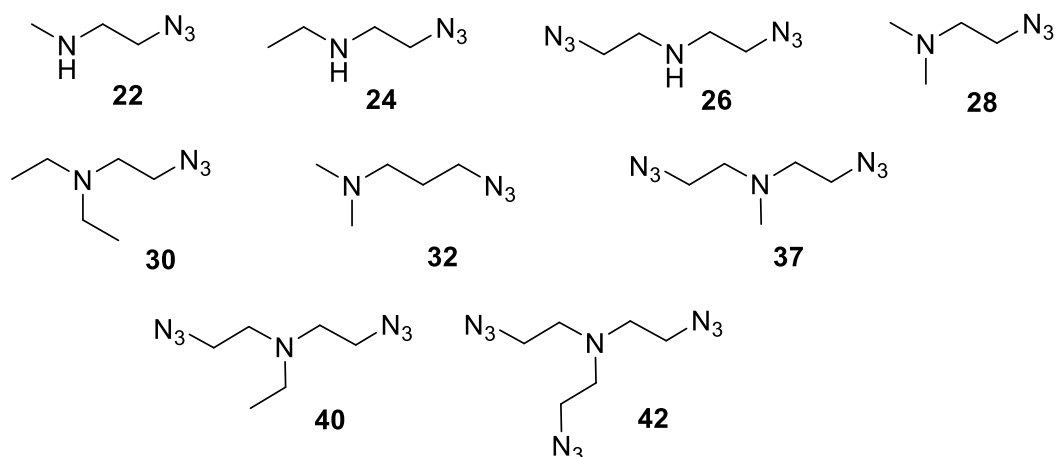
Figure 19: Tested amino azido liquids.

The results of the hypergolicity and the respective measured ID times are listed in Table 23 below.

Table 23: Hypergolicity test with amino azido liquids and NTO.

Compound	Oxidizer	Hypergolicity	ID time [ms]
AzEMA 22	N_2O_4	✓	17
AzEEA 24	N_2O_4	✓	19
DAzEA 26	N_2O_4	✓	17
DMAZ 28	N_2O_4	✓	16
DEAZ 30	N_2O_4	✓	17
DMAPZ 32	N_2O_4	✓	272
DAzEMA 37	N_2O_4	✓	33
DAzEEA 40	N_2O_4	✓	32
TAzEtA 42	N_2O_4	✓	127

X = no hypergolic reaction; ✓ = hypergolic reaction

The synthesized secondary amines, AzEMA **22**, AzEEA **24** and DAzEA **26** achieve a hypergolic ignition with NTO with relatively low ignition delay times of 17 – 19 ms, where the methyl azido amine **22** has the lower ID time with 17 ms compared to its ethyl derivative **24**. The ID time of compound **26** with NTO was also measured at 17 ms. As stated in

literature[44] hypergolicity of DMAZ can be confirmed. Different from what the publication mentioned, the ID time within these tests with 16 ms was significantly lower than the 68 ms determined by PAKDEHI.

In contrast to the other tested amino fuels, the propylene derivative DMAPZ **32** had an extensive longer ID time with 2272 ms. Therefore, it can be stated that the chain length has a significant effect on the ID time.

For the further tested tertiary amines DAzEMA **37** and DAzEEA **40** the measured ID times were 33 ms for compound **37** and 32 ms for compound **40**. The last tested ternary azide TAzEA **42** also showed a long ID time of 127 ms.

A trend can be observed: the greater the steric hinderance of the tested amino azido compounds, the longer the ID time with NTO as oxidizer.

In addition, a good forecast of the hypergolic behavior of the amino azido alcohols can be given, considering the hypergolicity of the amino alcohols. The ones, which showed hypergolicity or a strong decomposition with NTO as alcohol precursor, also revealed hypergolicity and even good ID values as azido derivative.

In summary, NTO showed no hypergolicity with the tested azidoalcohols and malonic acid derivatives, but it reacts hypergolic with all the tested azido amino liquids. In addition, fast ID times were achieved with the tested secondary azido amines and DMAZ, known in literature.

Since NTO is highly toxic and must be handled with high precaution, an alternative oxidizer is preferred.

4.2 Hydrogen peroxide - HTP

As previously described, HTP is an eco-friendly, non-toxic alternative as an oxidizer in a hypergolic bipropellant system. It is commercially available, storable and can also be concentrated to a high degree (>85%) using common labour technique.[161] Therefore, the hypergolicity tests are focused on a HTP propellant combination.

For the performed ignition tests commercially available HTP as Propulse® provided by Evonik Industries with an H_2O_2 content of 98% was used. This content was additionally determined with a density measurement before the conduction of the tests and after each testing period. In every measurement, the guaranteed content of 98% was confirmed.

4.2.1 Additive

Until today, literature has shown that HTP as oxidizer reacts only hypergolic with all the previously tested fuels if an additive is added. These additives can be classified according to their function. On one hand they act as catalysts, if they only decompose the HTP and are not part of the combustion process, and on the other hand they are called promotors, if they actively take part.[162] RARATA AND FLORCZUK showed hypergolicity of methanol and ethanolamine with HTP and an addition of MAT (manganese acetate tetrahydrate) or $CuCl_2$. The measured ignition delay times were only relatively low with 10 ms and 30 ms after an addition of 30% additive MAT or 10% additive $CuCl_2$. [163]

All the synthesized candidates were tested with HTP without an additive. All hypergolicity experiments showed besides decomposition no hypergolic ignition with HTP. Therefore, as a result it can be stated that an additive combined with the synthesized azido liquids is necessary to achieve a hypergolic ignition.

4.2.1.1 Suitable additives for HTP hypergolicity

Therefore, a screening of the most suitable additive was performed. For this purpose, the fuel was combined in weight % with the additive, mixed with a magnetic stirrer for at least 5min and then tested with the oxidizer HTP for ignition. Several salts and complexes were chosen and tested with AzEtOH **8** as a fuel. The results are listed in Table 24 below.

Table 24: Study on suitable additives for HTP.

Additive	Additive amount w/w%	Hypergolicity	ID time [ms]
Cu	10	X	
$Cu(CH_3COO)_2$	10	X	
CuCl	10	X	
$CuCl_2$	10	✓	75
CuBr	10	X	
$CuBr_2$	10	X	175
CuI	10	X	
$Cu(NO_3)_2$	10	X	
$CuCO_3 * Cu(OH)_2$	10	X	
CuO	10	X	
$Cu(acac)_2$	5	X	
$FeCl_2$	5	X (decomp.)	
$FeCl_3$	5	X (decomp.)	
$Fe(NO_3)_2$	5	✓violent	774
$Fe(NO_3)_2$	1	X (decomp.)	
$[Fe(Cp)_2]$	5	✓violent	
$NaNO_3$	10	X	
NaI	10	X	
LiI	10	X	
LiCl	10	X	
LiBr	10	X	
$LiNO_3$	10	X	
K_2CO_3	10	X	

KCl	10	X	
KBr	10	X	
KI	10	✓	285
KNO₂	10	X	
KNO₃	10	X	
Al(SO₄)₃	10	X	
MgCl₂	10	X	
Mg(CH₃COO)₂	10	X	
ZnCl₂	10	X	
ZnBr₂	10	X	
MnO₂	5	✓	27
MnCl₂ * 2 H₂O	10	X (decomp.)	
MnCl₂ * 4 H₂O	10	X (decomp.)	
Mn(acac) ₂	5	✓	210
Mn(acac)₃	5	✓	244
MMT [Mn(C₆H₇)(CO)₃]	5	⚡ explosion	
Ni(acac)₂	10	X	
NH₄Cl	10	X	

X = no hypergolic reaction; ✓ = hypergolic reaction

As a result, considering copper and the copper salts, only two salts where copper is present in the oxidation state (II) achieve hypergolicity with HTP. However, copper (II) chloride showed with 75 ms the lower ignition delay time compared to copper (II) bromide with 175 ms. The tested copper (I) halogen salts, copper (I) chloride / bromide / iodide showed no hypergolic effect, as well as copper oxide, copper acetate, copper acetylacetonate, the basic cooper carbonate and cooper (II) nitrate.

The tested iron salts iron (II/III) chloride showed only decomposition, but no ignition. In comparison, with the addition of iron (II) nitrate and Ferrocene a very violent reaction was

achieved after a long ignition delay time, accompanied by a loud bang. A possible explanation for the violent reaction can be the formation of a reaction similar to the Fenton reaction.[164] Because of the uncontrolled and heavy reaction, the addition of iron salts is not recommended.

The tested sodium salts, sodium nitrate and sodium iodide showed no hypergolicity, neither did the lithium salts, lithium iodide, lithium chloride, lithium bromide and lithium nitrate.

Also, the added potassium salts, potassium carbonate, potassium chloride / bromide, Potassium nitrate and potassium nitrite reached no hypergolic ignition. Only the fuel combination with potassium iodide reacted hypergolic with an ID time of 284 ms.

For an aluminium salt, aluminium sulphate was tested but again a negative result was obtained.

The same results can be stated for the two tested magnesium salts, magnesium chloride and magnesium acetate.

Both, zinc chloride and zinc bromide showed no hypergolic reaction.

In comparison, some positive results were obtained using manganese salts. With manganese dioxide a fast ignition delay time of 27 ms is achieved. While manganese chloride leads only to a visible decomposition, also manganese (II and III) acetylacetonate react hypergolic with HTP. The ignition delay times are 210 ms for the manganese (II) salt and 244 ms for the manganese (III) salt. Furthermore, the liquid manganese complex MMT (methylcyclopentadienyl manganese tricarbonyl) was tested. A great advantage would be the good solubility and mixability of fuel and additive. Unfortunately, the fuel mixture leads to an explosion with only 5 weight %. Additionally, a smaller amount of 1% was tried, but there only decomposition occurs. A screening of the most suitable amount was not possible since no safe ignition could be achieved between 1% and 5%.

Nickel acetylacetonate was not hypergolic in the tested fuel combination, as well as ammonium chloride.

In conclusion, the two additives manganese dioxide and copper (II) chloride showed a low ID time beside hypergolicity and are therefore chosen as a suitable additive for the further hypergolicity tests.

4.2.1.2 Effect on ID time of additive amount

In addition, the effect of the amount of additive was investigated. Therefore, the ignition delay studies were performed using different weight amounts of additives with the fuel. The results are listed in Table 25.

Table 25: Study on the influence of the additive amount.

Additive	Mass w/w %	Hypergolicity	ID time [ms]
$CuBr_2$	10	X	
$CuBr_2$	20	√	174
$CuCl_2$	5	√	105
$CuCl_2$	10	√	75
$CuCl_2$	20	√	52
KI	5	X	
KI	10	√	285
KI	20	√	183
MnO_2	5	√	72
MnO_2	10	√	23

X = no hypergolic reaction; √= hypergolic reaction

From the results listed in the table above, a clear trend for the ID times can be defined. The amount of additive has an obvious influence on the ID time. The more additive is added to the fuel the higher is the decrease on the ID time. Since an amount of 20% of catalyst is no longer profitable, the following tests were performed with a maximum of 10%.

4.2.2 Hypergolicity test performance

Since with the execution of the droplet, HTP can either assume the role of the target layer or the role of the impacting substance, tit was investigated how these changing roles affect the performance.

Therefore, five droplet tests with AzEtOH **8** and 5% / 10% MnO_2 as additive were performed. The results are listed in Table 26.

A providing of the fuel and addition of the oxidizer HTP results in a minor deviation of the determined ignition delay times. In addition to reliable results, lower measured ID times could be shown. With 5% additive the ID time with 27 ms was as fast, as it was when HTP served as target layer and fuel with 10% MnO_2 added. With a mixture of the fuel and 10% MnO_2 and the addition of HTP even ID times of 23 ms could be achieved.

Table 26: Hypergolicity test with HTP provided and HTP addition.

Fuel	Additive	Oxidizer	ID time [ms]					M [ms]
AzEtOH	MnO_2 5%	HTP provided	70	61	94	64	69	72
AzEtOH	MnO_2 10%	HTP provided	25	22	33	35	23	27
AzEtOH	MnO_2 5%	HTP	27	30	25	30	24	27
AzEtOH	MnO_2 10%	HTP	21	23	25	20	25	23

4.2.3 Azidoalcohols / azido malonates

After the evaluation of the most effective additives and the correct setting for the hypergolicity tests, the synthesized candidates were tested with HTP. On one hand MnO_2 was chosen as an additive, on the other hand $CuCl_2$. Considering the payload and effectiveness, a preferably low amount of additive of 5% was chosen.

First, the synthesized azidoalcohols **8–10** and azidomalonates were tested for their hypergolicity with HTP and MnO_2 as additive. The results of the tests performed are listed in Table 27 below.

Table 27: Hypergolicity tests of azidoalcohols and azidomalonates with HTP and additive MnO_2.

Compound	Oxidizer	Additive	Hypergolicity	ID time [ms]
AzEtOH 8	HTP	5%	✓	27
1,3-DAP 9	HTP	5%	✓	57
2,3-DAP 10	HTP	5%	✓	95
DM-DAM 11	HTP	5%	✓	352
DE-DAM 12	HTP	5%	✓	> 500
DAEM 13	HTP	5%	✓	> 500
b-1,3-DAPM 14	HTP	5%	✓	> 500
b-2,3-DAPM 15	HTP	5%	✓	> 500
DA-bAEM 16	HTP	5%	✓	> 500

X = no hypergolic reaction; ✓ = hypergolic reaction

The lowest ID time was measured with AzEtOH **8** as fuel with 27 ms. Despite the fact, that this time can be decreased down to 23 ms with an addition of 10% MnO_2 as additive, the ID time of 27 ms is quite a desired value and fulfils the minimum requested requirement of lower than 50 ms. Furthermore, the tested diazidopropanol **9** touches with 57 ms on the boarder of the requirement. The unsymmetrical derivative reveals an excessively long delay with 95 ms. The geminal diazidated malonic acids **11** and **12** show ID times of 352 ms (**11**) and over 500 ms for compound **12**. A similar behaviour can be overserved from the azidoalcohol ester **13–15**. They all show ID times from more than 500 ms. Likewise, the delay of the geminal diazidated derivative **16** is longer than 500 ms.

In addition, these compounds were also tested with 5% of $CuCl_2$ as additive and the results listed in Table 28.

Table 28: Hypergolicity tests of azidoalcohols and azidomalonates with HTP and additive CuCl$_2$.

Compound	Oxidizer	Additive	Hypergolicity	ID time [ms]
AzEtOH 8	HTP	5%	✓	105
1,3-DAP 9	HTP	5%	✓	153
2,3-DAP 10	HTP	5%	✓	212
DM-DAM 11	HTP	5%	✓	> 500
DE-DAM 12	HTP	5%	✓	> 500
DAEM 13	HTP	5%	✓	> 500
b-1,3-DAPM 14	HTP	5%	✓	> 500
b-2,3-DAPM 15	HTP	5%	✓	> 500
DA-bAEM 16	HTP	5%	✓	> 500

X = no hypergolic reaction; ✓ = hypergolic reaction

In summary, CuCl$_2$ also works as a suitable additive to achieve a hypergolic ignition reaction with HTP. In comparison, the obtained ID times are significantly higher than the ones with MnO$_2$. No one of the measured ID times fulfil the minimum requested criterion of being lower than 50 ms. Therefore, CuCl$_2$ does not seem to be the optimum additive for low ID times with the tested azidoalcohols and azidomalonates.

4.2.4 Amino azido liquids

The synthesized amino azido liquids were also tested for their hypergolicity with HTP. As expected, no hypergolic reaction was achieved within these compounds without additive. Therefore, their ID times were determined using MnO$_2$ and CuCl$_2$ as additives. The results are listed in Table 29 for MnO$_2$ and Table 30 for CuCl$_2$.

Table 29: Hypergolicity test of amino azido liquids with HTP and additive MnO$_2$.

Compound	Oxidizer	Additive	Hypergolicity	ID time [ms]
AzEMA 22	HTP	5%	✓	71
		10%		22
AzEEA 24	HTP	5%	✓	51
		10%		16
DAzEA 26	HTP	5%	✓	245
DMAZ 28	HTP	5%	✓	52
DEAZ 30	HTP	5%	✓	53
DMAPZ 32	HTP	5%	✓	> 500
DAzEMA 37	HTP	5%	✓	85
DAzEEA 40	HTP	5%	✓	84
TAzEtA 42	HTP	5%	✓	> 500

X = no hypergolic reaction; ✓ = hypergolic reaction

Table 30: Hypergolicity test of amino azido liquids with HTP and additive CuCl$_2$.

Compound	Oxidizer	Additive	Hypergolicity	ID time [ms]
AzEMA 22	HTP	5%	✓	103
AzEEA 24	HTP	5%	✓	60
DAzEA 26	HTP	5%	✓	> 500
DMAZ 28	HTP	5%	✓	59
DEAZ 30	HTP	5%	✓	65
DMAPZ 32	HTP	5%	✓	> 500
DAzEMA 37	HTP	5%	✓	133

DAzEEA 40	HTP	5%	✓	132
TAzEtA 42	HTP	5%	✓	> 500

X = no hypergolic reaction; ✓= hypergolic reaction

With the usage of MnO_2 in 5% w/w the ID times of the secondary amines AzEMA **22** and AzEEA **24** are at 51 ms and 71 ms. If the amount of additive is increased to 10%, the ID times can be lowered to 22 ms for **22** and even 16 ms for **24**. These ID times would fulfil the requested requirements. Compound **26** shows a significantly lower delay of 245 ms. The tertiary amines DMAZ **28** and DEAZ **30** achieve ID times of 52 ms and 53 ms, which are similar to the ones of the secondary amines **22** and **24**. These ID times are also only 2 ms respective 3 ms higher than the minimum requirement. An elongation of the azido alkyl chain **32** lead to a clear increase of the ignition time. The measured ID times of derivatives **37** and **40** are 85 ms and 84 ms, which is around 10 ms longer compared to the shortest times. Compound **40** has an ID time of over 500 ms, which fails the limitation.

As stated in Table 30, with the usage of $CuCl_2$ as additive all measured ID times are clearly increased. The shortest one was achieved with DMAZ **28** of 59 ms, followed by 60 ms of **24**, 65 ms of **30** and 103 ms of **22**. Tertiary amines **37** and **40** show ID times of 133 ms, respective 132 ms. As measured with MnO_2 before, the delay of **32** and **42** are higher than 500 ms.

With these compounds, it also seems as if $CuCl_2$ is not the best additive to achieve preferred low ID times.

In addition, the previously mentioned new compound TAzME **4** was also tested for its hypergolicity with HTP and 5% MnO_2 as additive, but no hypergolic ignition reaction was observed.

4.2.5 Ionic liquids

According to expectations, no hypergolic ignition was observed with the pure tested imidazole based ionic liquids and HTP. This was meanwhile also stated by BHOSALE.[165]

Additional test with the synthesized imidazole-based liquids and MnO_2 as additive were performed. The results are listed in Table 31 below.

Table 31: Hypergolicity test of imidazole-based IL`s with HTP and additive MnO$_2$.

Compound	Oxidizer	Additive	Hypergolicity	ID time [ms]
[EMIM][CBH] 61	HTP	5%	✓	16
[PMIM][CBH] 62	HTP	5%	✓	17
[PEIM][CBH] 63	HTP	5%	✓	22
[diPIM][CBH] 64	HTP	5%	✓	23
[AMIM][CBH] 65	HTP	5%	✓	125
[AEIM][CBH] 66	HTP	5%	✓	143
[diAIM][CBH] 67	HTP	5%	✓	> 500
[BMIM][CBH] 68	HTP	5%	✓	88

X = no hypergolic reaction; ✓ = hypergolic reaction

As a result, it can be stated that the length of chains has an influence on the ID time. While the [EMIM][CBH] **61** has the shortest ID time with 16 ms, followed by [PMIM][CBH] **62** with 17 ms, the ethyl propyl derivative **63** and dipropyl derivative **64** achieve longer ID times with 22 ms and 23 ms. An allyl residue has a decreasing effect on the ID time. They have the longest measured ID times with 125 ms for **65**, 143 ms for IL **66** and over 500 ms. The ID time of IL **68** is with 88 ms clearly longer than compared to the ones with propyl residue.

Due to necessity of extensive synthesis, the obtained low yields during synthesis and the irregular purity, these compounds are not recommended, although they show short ID times with MnO$_2$ as additive.

The synthesized IL´s derived from the amino azido liquids were also tested for hypergolicity.

They are pictured in Figure 20 below.
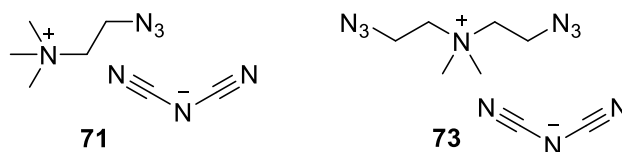
Figure 20: Successfully synthesized IL´s derived from amino azido liquids for hypergolicity test.

No IL candidate showed hypergolic reaction in the tests without an additive. With the addition of MnO_2, a hypergolic reaction was achieved. The results of these tests are given in Table 32.

Table 32: Hypergolicity test of amino azido ionic liquids with HTP and additive MnO_2.

Compound	Oxidizer	Additive	Hypergolicity	ID time [ms]
IL 71	HTP	5%	✓	184
IL 73	HTP	5%	✓	343

X = no hypergolic reaction; ✓ = hypergolic reaction

Both fuels show relatively long ID times with 184 ms (**71**) and 343 ms (**73**) despite an addition of MnO_2 as additive.

By reason of extensive synthesis, low yield and the bad hypergolicity, no further investigation of the hypergolicity of these amino-azido ionic liquids were executed.

5 Summary and conclusion

The general goal of this work was the synthesis and evaluation of potential hydrazine replacement candidates for a hypergolic bipropulsion system. Since hydrazine and its derivatives, MMH and UDMH, are still the state-of-the-art fuel but are shown to be cancerogenic, an alternative is urgent. The focus was therefore placed on the synthesis of liquid azides, since they have a high energy content, would reveal good energetic parameters and decompose into environmentally friendly nitrogen.

Amongst others, the following requirements were stated for the potential candidates:

- The candidates should have a good and easy synthesis, in order to facilitate commercial application.
- The candidates should be insensitive towards friction and impact to ensure a safe handling.
- They should also be less toxic compared to hydrazine, especially regarding the vapour pressure.
- In consideration of the payload, the density of the compounds should be ideally higher than > 1 g cm^{-3}.
- The theoretical specific impulse of the fuel should be at least > 315 s.
- They should provide a reliable hypergolicity for an application in a bipropellant system
- and therefore, show a short ignition delay (ID) time (< 50 ms) to prevent an uncontrolled explosion.

In section 2 of this work, the **synthesis and characterisation** of the potential fuels are described. The potential azido candidates were divided into sections according to their backbone or classification.

Staring with **C-based azides**, the novel compound 1,1,2,2-tetraazidomethylethane, TAzME **4** was synthesized and characterised, followed by the two diazidobutene isomers, (Z)-**6** and (E)-**6**. The compounds are pictured in Figure 21 below.
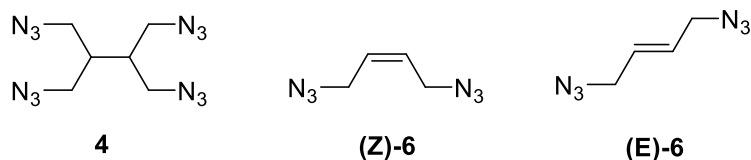
Figure 21: Molecule structures of synthesized C-based azides.

However, all three compounds turned out to be very sensitive towards impact and friction and therefore fail the criteria for insensitivity. In addition, their precursor is only obtained in low yields of around 20%, which is not favoured in an industrial application.

In the next subdivision, the synthesis and characterisation of azides with **oxygen content** is presented. The synthesized molecules are shown in Figure 22 below.
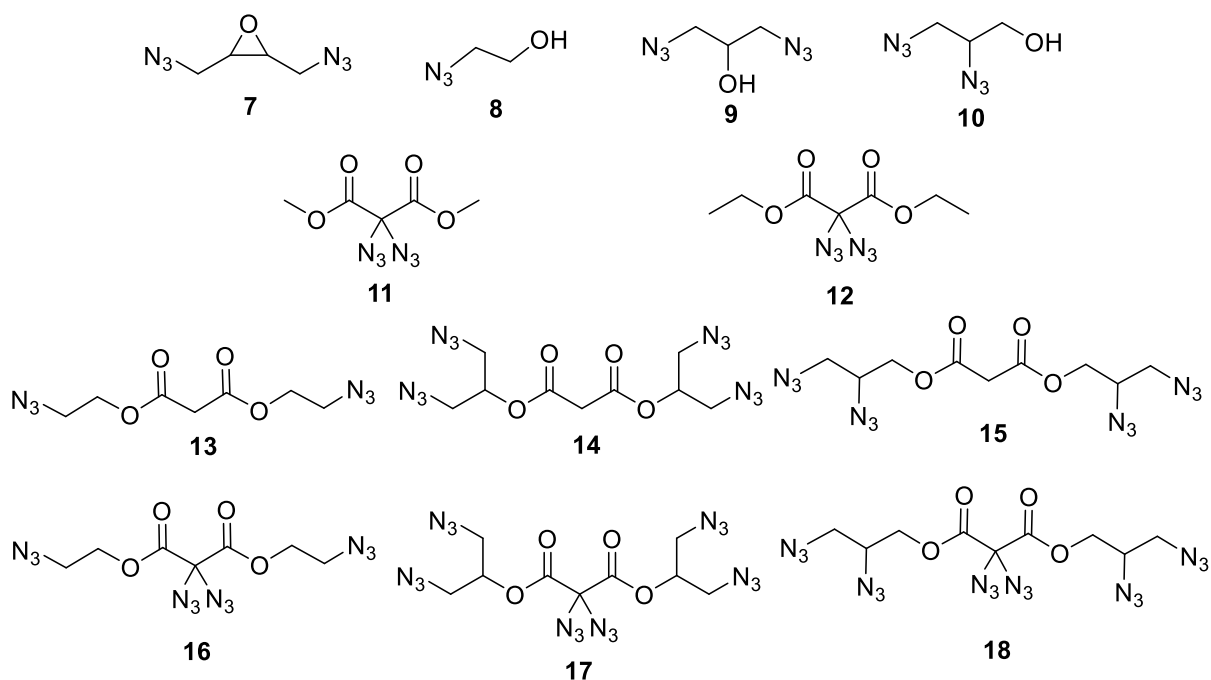
Figure 22: Molecule structures of synthesized C-O-based azides.

First pictured molecule is the compound 2,3-bis(azidomethyl)oxirane (DAZoB **7**), unknown in literature to date. It is obtained from the previously synthesized (Z)-**6** via an epoxidation reaction using H_2O_2 and *m*CPBA. With 173 °C, it has a higher thermal stability compared to (Z)-**6** with 133 °C, but also a low sensitivity towards impact and friction, which is not as desired. Subsequently, the three azidoalcohols, 2-azidoethanol **8**, 1,3-diazidpropanol **9** and 2,3-diazidopropanol **10** were synthesized. They were obtained in high yields (81% for **8,** 83%

for **9** and 61% for **10**) in a simple one-step synthesis from their halogen derivatives and characterized in more detail. While compound **8** was classified as insensitive, the diazidopropanols **9** and **10** are categorized as sensitive. Additionally, AzEtOH **8** passed the aquatic toxicity test of the luminescent bacteria Vibrio fischeri and was determined as "less toxic". Furthermore, all three alcohols have a low vapor pressure of 0.664 mbar (297.7 K)[94] for **8**, 0.021 mbar for **9** (298 K) and 0.012 mbar for **10** (298 K) which reduces the toxicity by inhalation. The densities of the compounds were defined to 1.15 g mol^{-1} for **8** and 1.26 g mol^{-1} for both diazidopropanols, **9** and **10**. Hence, the three azido alchols, especially the insensitive AzEtOH **8**, fullfills beside the synthetical criteria, also the required physical properties.

Furthermore, the synthesis and characterisation of azides derived from malonic acid is described. Beside the geminal diazidation reaction which yielded the derivatives dimethyl 2,2-diazidomalonate (DM-DAM **11**) and diethyl 2,2-diazidomalonate (DE-DAM **12**), the malonic acid was also transformed to contain energetic ester residues. Therefore, the previously synthesized azidoalcohols were converted with malonic acid to obtain bis(2-azidoethyl) malonate (DAEM **13**), bis(1,3-diazidopropyl) 2,2-diazidomalonate (b-1,3-DAPM **14**) and bis(2,3-diazidopropyl) 2,2-diazidomalonate (b-2,3-DAPM **15**). As next step, it was also possible to increase the energy content by performing the geminal diazidation reaction of these esters **13**-**15**. The novel and highly energetic compounds bis(2-azidoethyl) 2,2-diazidomalonate (DA-DAEM **16**), bis(1,3-diazidopropyl) 2,2-diazidomalonate (DA-1,3-b-DAPM **17**) and bis(2,3-diazidopropyl) 2,2-diazidomalonate (DA-2,3-b-DAPM **18**) were obtained. As expected, these compounds **16**-**18** increase their sensitivity and decrease their thermal stability. They are classified as very sensitive compounds. In comparison, compound **13** turned out to be the most stable compound of the malonic azides regarding heat, with a decomposition temperature of 191 °C. It was classified as insensitive as well as liquid **12**. Surprisingly, the ethyl residue of **12** seems to stabilize the central azido groups compared to the very sensitive compound **11**. The determined densities of the synthesized diazidated azidomalonates were all higher than 1.21 g cm^{-3} and the vapour pressure of **13** was definded to 0.008 mbar. Hence, of the synthesized azido malonic acid esters only compound **12** and **13** fulfil the requirements.

In the third synthesis subdivision, several azido **amino liquids** were synthesized and characterized. These compounds were obtained transforming the respective amino alcohols to the chloride derivatives as hydrochloride salt, followed by a chloride azide exchange and desalination reaction. They are pictured in Figure 23 below.
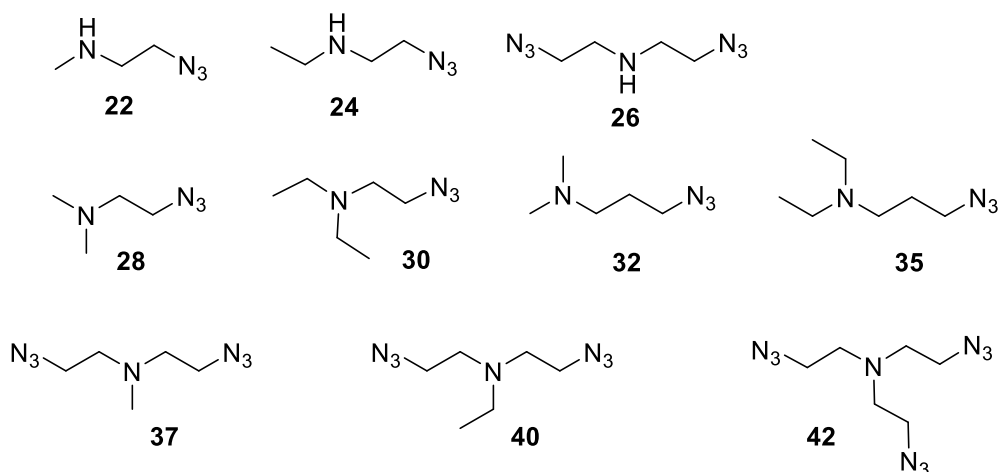
Figure 23: Molecule structures of synthesized C-N-based azides.

The secondary amines 2-azido-*N*-methylethan-1-amine (AzEMA **22**), 2-azido-*N*-ethylethan-1-amine (AzEEA **24**) and bis(2-azidoethyl)amine, (DAzEA **26**) were yielded and classified as insensitive. Their densities were measured to be 0.98 g cm^{-3} for **22**, 1.21 g cm^{-3} for **24** and 1.41 g cm^{-3} for **26**, in which only **22** falls minimally below the benchmark of >1 g cm^{-3}.

As tertiary amines, 2-azido-*N,N*-dimethylethan-1-amine (DMAZ **28**) and 2-azido-*N,N*-diethylethan-1-amine (DEAZ **30**) as well as their propyl derivatives 2-azido-*N,N*-dimethylpropan-1-amine (DMAPZ **32**) and 2-azido-*N,N*-diethylpropan-1-amine (DEAPZ **35**) were synthesized and classified as insensitive. In addition also 2-azido-*N*-(2-azidoethyl)-*N*-methylethan-1-amine, (DAzEMA **37**), 2-azido-*N*-(2-azidoethyl)-*N*-ethylethan-1-amine (DAzEEA **40**) and tris(2-azidoethyl)amine (TAzEA **42**) were synthesized and characterised. Except compound **42**, which was classified as sensitive towards impact and insensitive toward friction, the liquids **37** and **40** are also insensitive. The densities of the tertiary amino azido liquids were determined to be over 1 g cm^{-3} for **37**, **40** and **42** and to be 0.93 g cm^{-3} for **28**, 0.95 g cm^{-3} for **30.** These densities are lower than the ideal requirement.

In the fourth synthesis subdivision, several **salts and ionic liquids** (ILs) are described. Derived from the previously synthesized compound DE-DAM **12**, the two novel energetic salts potassium 2,2-diazidomalonate (K₂DAM **49**) and lithium 2,2-diazidomalonate (Li₂DAM **50**) are described and pictured below.
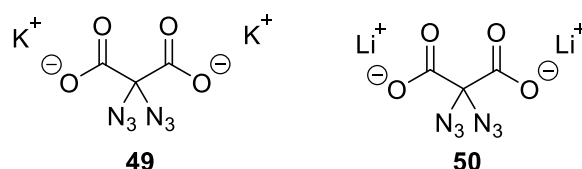
Figure 24: Molecule structures of synthesized energetic DAM salts.

While **49** turned out to be sensitive, salt **50** was determined to be insensitive due to the presence of crystal water.

Furthermore, several ionic liquids derived from imidazolium were synthesized. The general synthesis of these cyanoborohydride imidazolium salts starts from imidazole adding sodium hydride to form the sodium imidazolium. In the next step, the respective alkyl halide is added followed by sodium cyanoborohydride. The following ILs were obtained and pictured in Figure 25 below.
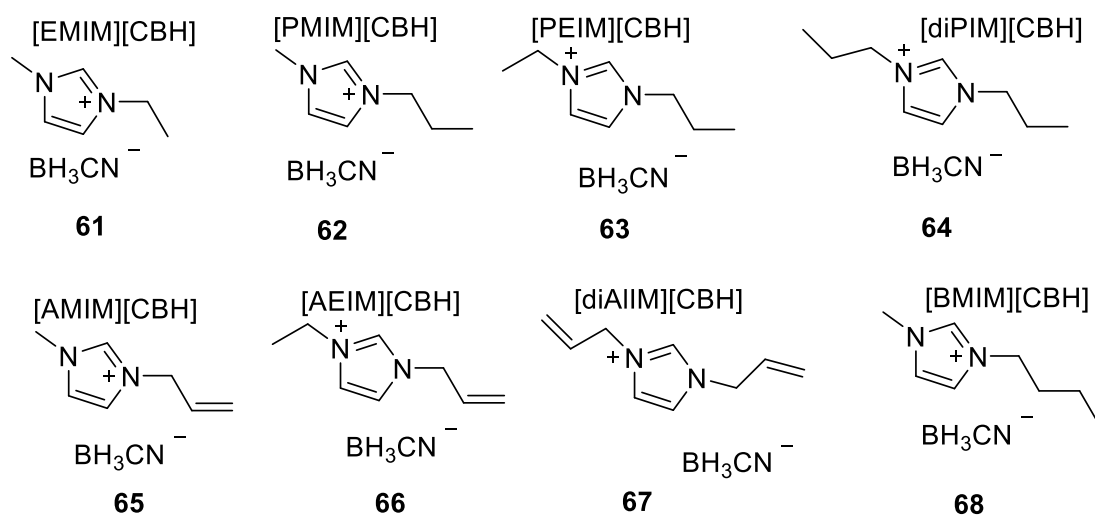
Figure 25: Molecule structures of synthesized imidazolium-based IL´s.

During these syntheses, several problems regarding yields and purity occurred. Therefore, these compounds are not recommended for an industrial use.

In addition, two cyanoborohydride ionic liquids derived from the amino azido liquids were synthesised and characterized. They are shown in Figure 26 below.
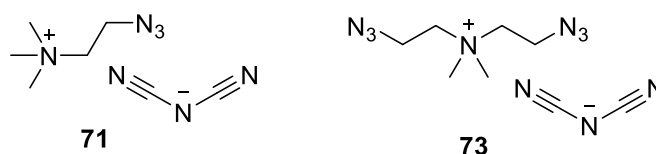
Figure 26: Molecule structures of synthesized amino azido IL´s.

On the one hand, the synthesis of 2-azido-*N,N,N*-trimethylethan-1-amonium dicyanamide **71** was performed using DMAZ as a precursor via the iodide salt. On the other hand, the synthesis of 2-azido-N-(2-azidoethyl)-N,N-dimethylethan-1-amonium dicyanamide **73** was performed using DAzEMA **37** as precursor of the methylation reaction. Both liquids were obtained in low yields of only 22% and therefore not recommended for industrial usage.

In the third section of this thesis the **calculations** of the heat of formation and rocket specific parameters of the previously synthesized compounds are described. These values, especially the I_{sp} give an evidence of the efficiency of the fuel in the bipropellant system. On the one hand, HTP was used as eco-friendly and desirable oxidizer, on the other hand NTO, which is the state-of-the-art oxidizer in the hydrazine / MMH systems.

- In the systems with HTP, the highest I_{sp} in the optimized oxidizer to fuel ratio (O/F) was calculated. Within these calculations, it was shown that the presence of oxygen in the fuel leads to lower I_{sp} values compared to molecules without oxygen content. Although all possible calculated fuels obtain lower I_{sp} values compared to MMH or UDMH, most of them fulfil the minimum requirement. The majority of them even surpass the ideal value of >323 s. For example, high I_{sp} values were achieved with the amino azido compounds AzEMA **22** and AzEEA **24** with 326 s or for the synthesized azidoalcohols, AzEtOH **8,** 1,3-DAP **9** and 2,3-DAP **10** with 319 s. In addition, it could be shown that the calculated I_{sp} value of AzEtOH **8** increased significantly by adding an azido group compared to pure EtOH, which has an I_{sp} of 246 s.

- In the calculations with NTO as oxidizer, same trend as mentioned before was observed. The specific impulse values decrease with the presence of an oxygen in the fuel.

However, all theoretical I_{sp} values of the azidoalcohols are over 300 s. The highest theoretical I_{sp} values within these systems were obtained of AzEMA **22** with 317 s, DMAZ **28** and DAzoB **7** with 319 s.

In the last section of this work, the **hypergolic behaviour** of the fuels was tested with HTP and NTO as oxidizer. For this purpose, a simple drop test was performed to get a quick evidence if the tested propellant combination reacts hypergolic. The ID time was recorded using a high-speed camera.

- For NTO, at first commercially available amino alcohols were tested. Even though these compounds showed long ID times, they gave a first evidence of the hypergolic behaviour of the amino azido liquids. Within these tests, AzEMA **22**, AzEEA **24** and DAzEA **26** achieve a hypergolic ignition with relatively low ignition delay times of 17 – 19 ms, as well as DMAZ **30** and DEAZ **32** with 16 ms respectively 17 ms. The propyl derivatives had a significant increase in the delay time.

Therefore, a trend can be observed: the higher the steric hinderance of the tested amino azido compounds, the longer becomes the ID time with NTO as oxidizer. Surprisingly, no one of the synthesized azidoalcohols or azido malonates showed hypergolicity in this bipropellant system.

- Using HTP as oxidizer, hypergolic ignition was only achieved using an additive. Evaluation of the most suitable additive showed that the shortest ID times were achieved with MnO_2 or $CuCl_2$ as additive, in which the copper salt achieved longer ID times. In addition, the amount of additive has an obvious influence on the ID time. The more additive is added to the fuel, the shorter becomes the ID time. Also, the setup has a significant effect on the ID time. A providing of the fuel and addition of the oxidizer HTP resulted in a minor deviation of the determined ignition delay times. In addition, lower ID times within this setup were measured. The lowest ID times were obtained using AzEtOH **8** as fuel and 5% MnO_2 as additive with 27 ms, respectively 23 ms when 10% were added. For the amino azido compounds, the secondary amines AzEMA **22** and AzEEA **24** have short ID times with 51 ms and 71 ms using 5% additive. If the amount of additive is increased to 10%, the ID times can

be lowered to 22 ms for **22** and even 16 ms for **24**. These ID times would fulfil the requested requirements.

As conclusion and outlook, within this work it was shown that it is possible to find an alternative to hydrazine and its derivatives for a hypergolic bipropellant system.

The most promising candidates, AzEtOH **8**, AzEMA **22** and AzEEA **24**, which comply the requirements are listed in Table 33 below.

Table 33: Most promising azido liquid candidates.

Property	Requirement	AzEtOH 8	AzEMA 22	AzEEA 24
Toxicity	Non-toxic, not affected by REACH	aquatic toxicity test	tbd	tbd
Synthesis	easy, high yield	✓	✓	✓
Reactivity HTP (+ 10% MnO_2)	Hypergolic, ID < 50 ms	23 ms	22 ms	16 ms
Reactivity NTO	Hypergolic, ID < 50 ms	x	17 ms	19 ms
Performance HTP	> 315 s (pc = 10 bar, ε = 300)	319 s	326 s	326 s
Performance NTO	(pc = 10 bar, ε = 300)	301 s	317 s	313 s
Temperature range	− 10° C < T < 150 °C	✓	✓	✓
Density	> 1 g cm^{-3}	1.15 g cm^{-3}	0.98 g cm^{-3}	1.21 g cm^{-3}
Vapor pressure	≤ 50 mbar	0.664 mbar	< 50 mbar	< 50 mbar
Sensitivity	Insensitive	✓	✓	✓

Although HTP would be the preferred oxidizer alternative, it only reacts hypergolic with an additive. If it is applied, the evaluation respectively the synthesis of a suitable and applicable additive must go on. In addition, it could be shown that liquid molecules containing an

energetic azido group reveal good theoretical rocket parameters regarding the I_{sp}. For the ID time, the focus must be put on small molecules with only little steric hinderance as they achieve shorter ID times. For the future, the previously described less toxic and insensitive candidates should be tested further with a calibrated injection nozzle or test bench to get reliable results on the suitability as replacement fuel.

6   Literature

[1]   American Society for Testing and Materials, https://www.astm.org/.

[2]   T. M. Klapötke, *Chemistry of High-Energy Materials*, Walter de Gruyter GmbH & Co. KG: Berlin, **2019**.

[3]   J. P. Agrawal, *High Energy Materials: Propellants, Explosives and Pyrotechnics*, Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, **2015**.

[4]   J. Köhler, R. Meyer, A. Homburg, *Explosivstoffe*, Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, **2012**.

[5]   O. Morgan; D. S. Meinhardt, in *35th Joint Propulsion Conf.* (Ed.: A. P. 99-2595), Los Angeles, CA, **1999**.

[6]   G. P. Sutton, *Rocket propulsion elements, Vol. 6th edition*, John Wiley & Sons: New York, **1992**.

[7]   A. O. Dekker, *Journal of Jet Propulsion*, **1956**, *26*, 572-575.

[8]   S. Schneider, in *34th AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit*, Cleveland,OH, U.S.A, **1998**.

[9]   D. K. Huzel, *Modern Engineering for Design of Liquid-Propellant Rocket Engines*, American Institute of Aeronautics & Astronautics, **1992**.

[10]   V. E. Morell, NATIONAL ADVISORY COMMITTEEFOR AERONAUTICS, NASA Technical Reports Server (NTRS), **1950**.

[11]   J. F. Connors, *National Aeronautics and Space Administration Vol. 196812*, **1968**.

[12]   T. Benson, NASA National Aeronautics and Space Administration, **2014**. https://www.grc.nasa.gov/WWW/K-12/rocket/rktpow.html

[13]   B. Nufer, in *Vol. KSC-2010-045*, NASA Kennedy Space Center, **2010**.

[14]   R. T. Holzmann, *Chemical Rockets and Flame and Explosives Technology*, Marcel Dekker Incorporated: New York, **1969**.

[15]   J. D. Clark, *Ignition!: an informal history of liquid rocket propellants*, RUTGERS UNIV PR, **2017**.

[16]   A. R. Katritzky, *Journal of the American Chemical Society* **2002**, *124*, 6504-6504.

[17]   U. C. Durgapal, P. K. Dutta, G. C. Pant, M. B. Ingalgaonkar, V. Y. Oka, B. B. Umap, *Propellants, Explosives, Pyrotechnics* **1987**, *12*, 149-153.

[18]   N. Kaplan, R. J. Andrus, *Industrial & Engineering Chemistry* **1948**, *40*, 1946-1947.

[19]   C. E. Feiler, in *Vol. NACA-RM-E53L17b*, National Advisory Committee for Aeronautics., **1953**.

[20]   C. H. H. Thienes, Thomas J, *Clinical Toxicology*, Lea & Febiger: Philadelphia, **1972**.

[21]   H. A. Bent, *Inorganic Chemistry* **1963**, *2*, 747-752.

[22]   F. S. Forbes, P. A. Van Splinter, in *Encyclopedia of Physical Science and Technology*, Academic Press: New York, **2003**.

[23]   N. R. Council, D. E. L. Studies, B. E. S. Toxicology, C. Toxicology, C. A. E. G. Levels, *Acute Exposure Guideline Levels for Selected Airborne Chemicals: Volume 11*, National Academies Press, **2012**.

[24]   Evonik   INDUSTRIES, https://www.activeoxygens.com/product/h2o2/en/products/hydrogen-peroxide/pages/default.aspx

[25]   W. M. Haynes, *CRC Handbook of Chemistry and Physics*, CRC Press: Oakville, **2014**.

[26]   T. E. Daubert, R. P. Danner, R. P., *Physical and thermodynamic properties of pure chemicals: Data compilation.*, Taylor & Francis: Washington DC, **1989**.

[27]   B. E. Watt, A. T. Proudfoot, J. A. Vale, *Toxicological reviews* **2004**, *23*, 51-57.

[28]   M. Ventura, in *41st AIAA/ASME/SAE/ASEE Joint Propulsion Conference*, Arizona, **2005**.

[29]   A. Cervone, L. Torre, L. d'Agostino, in AIAA Paper: 2006-5239, *American Institute of Aeronautics and Astronautics* **2006**.

[30]   E. W. Schmidt, *Hydrazine and Its Derivatives: Preparation, Properties, Applications, 2 Volume Set*, Wiley-Interscience, **2001**.

[31]   J. SMITH, R. STECHMAN, in *17th Joint Propulsion Conference*, Colorado Springs, CO, U.S.A, **1981**.

[32]   ArianeGroup, in *V-181 Press Kit*, Space Launch Report: Ariane 5 Data Sheet, **2008**.

[33]   T. L. Varghese, S. C. Gaindhar, J. T. David, J. Jose, R. Muthiah, S. S. Rao, K. Ninan, V. Krishnamurthy, *Defence Science Journal* **1995**, *45*, 25-30.

[34]   ArianeGroup, Space Launch Report: Ariane 4 Data Sheet, **2003**.

[35]   T. V. Koroleva, P. P. Krechetov, I. N. Semenkov, A. V. Sharapova, S. A. Lednev, A. M. Karpachevskiy, A. D. Kondratyev, N. S. Kasimov, *Transportation Research Part D Transport and Environment* **2017**, *58*, 54-69.

[36]   V. K. Shen, D. W. Siderius, W. P. Krekelberg, H. W. Hatch, Eds., NIST Standard Reference Simulation Website, NIST Standard Reference Database Number 173, National Institute of Standards and Technology, Gaithersburg MD, 20899, http://doi.org/10.18434/T4M88Q.

[37]   Public Health Service Agency for Toxic Substances and Disease Registry P. H. Service, U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES, **1997**.

[38]   a) IARC Monographs on the Evaluation of Carcinogenic Risks to Humans Volume 115, *Some Industrial Chemicals*, Lyon, France, **2018**;
        b) IARC Monographs on the Evaluation of Carcinogenic Risks to Humans Volume 71, Lyon, France, **1999**.

[39]   a) National Institute for Occupational Safety and Health, *NIOSH POCKET GUIDE TO CHEMICAL HAZARDS, Vol. DHHS (NIOSH) Publication No. 2005-149* DEPARTMENT OF HEALTH AND HUMAN SERVICES, **2007.**

b) United States. Office of the Director of Defense Research Engineering, *The Handling and Storage of Liquid Propellants*, Office of the Director of Defense Research and Engineering, **1963**.

[40]   European Chemicals Agency, in ED/31/2011, Inclusion of Substances of Very High Concern in the Candidate List, Helsinki, **2011**.

[41]   European Chemicals Agency, Prioritisation Assesment, **2018**.

[42]   D. M. Thompson, Patent *Vol. US6013143A*, **2000**.

[43]   B. Mellior, in *Proceedings of the 2nd International Conference on Green Propellants for Space Propulsion ESA SP-557*, Sardinia, Italy, **2004**.

[44]   S. G. Pakdehi, S. Rezaei, H. Motamedoshariati, M. H. Keshavarz, *Journal of Loss Prevention in the Process Industries* **2014**, *29*, 277-282.

[45]   T. Fei, Y. Q. Zhang, Y. Du, X. F. Xu, l. Yuchuan, S. P. Pang, *Chinese Journal of Energetic Materials* **2016**, *24*, 1017-1028.

[46]   Z. Zhang, Q. Jia, W. Liao, *Handbook on the Physics and Chemistry of Rare Earths, Vol. 48* Elsevier, **2015**, pp. 287-376.

[47]   T. Welton, *Chemical Reviews* **1999**, *99*, 2071-2084.

[48]   S. Zhang, J. Wang, X. Lu, Q. Zhou, *Structures and Interactions of Ionic Liquids*, Springer: Berlin Heidelberg, **2013**.

[49]   E. Sebastiao, C. Cook, A. Hu, M. Murugesu, *Journal of Materials Chemistry A* **2014**, *2*, 8153-8173.

[50]   S. Bräse, K. Banert, *Organic Azides: Syntheses and Applications*, John Wiley & Sons: New York, **2011**.

[51]   E. Wiberg, A. F. Holleman, *Lehrbuch der anorganischen Chemie*, Walter de Gruyter GmbH & Co. KG: Berlin, **2019**.

[52]   M. T. Nguyen, D. Sengupta, T.-K. Ha, *The Journal of Physical Chemistry* **1996**, *100*, 6499-6503.

[53]   a) M. E. C. Biffin, J. Miller, D. B. Paulin, PATAI'S Chemistry of Functional Groups, *The Azido Group*, John Wiley & Sons: New York **1971**, pp. 57-190;
b) I. C. Tornieporth-Oetting, T. M. Klapötke, *Angewandte Chemie Int. Edt.* **1995**, *34*, 511-520.

[54]   W. D. Closson, H. B. Gray, *Journal of the American Chemical Society* **1963**, *85*, 290-294.

[55]   a) P. Grieß, *Justus Liebigs Annalen der Chemie* **1862**, *121*, 257-280;
b) P. Grieß, *Justus Liebigs Annalen der Chemie* **1865**, *135*, 121-121.

[56]   S. Bräse, C. Gil, K. Knepper, V. Zimmermann, *Angewandte Chemie Int. Edt.* **2005**, *44*, 5188-5240.

[57]   E. F. V. Scriven, K. Turnbull, *Chemical Reviews* **1988**, *88*, 297-368.

[58]   H. Loibner, E. Zbiral, *Helvetica Chimica Acta* **1976**, *59*, 2100-2113.

[59]   M. Jafarzadeh, *Synlett* **2007**, *13*, 2144-2145.

[60] M. Hesse, H. Meier, B. Zeeh, *Spektroskopische Methoden in der Organischen Chemie*, 7. Auflage ed. Georg Thieme Verlag: Stuttgart, **2005**.

[61] J. Müller, *Journal of Organometallic Chemistry* **1973**, *51*, 119-123.

[62] D. M. Kanjia, J. Mason, I. A. Stenhouse, R. E. Banks, N. D. Venayak, *Journal of the Chemical Society, Perkin Transactions 2* **1981**, 975-979.

[63] E. Lieber, C. N. R. Rao, T. S. Chao, C. W. W. Hoffman, *Analytical Chemistry* **1957**, *29*, 916-918.

[64] NASA TECHNICAL STANDARD, in *NASA-STD-8719.12A*, **2018**.

[65] Ariane Group, LMU Munich, internal communication.

[66] https://www.reach-compliance.ch/ghsclp/ghspictograms/.

[67] CrysAlisPro, 1.171.37.33, Agilent Technologies, Santa Clara, CA, USA, **2014**.

[68] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *Journal of Applied Crystallography* **1994**, *27*, 435.

[69] G. Sheldrick, *Acta Crystallographica Section C* **2015**, *71*, 3-8.

[70] A. Spek, *Acta Crystallographica Section D* **2009**, *65*, 148-155.

[71] L. Farrugia, *Journal of Applied Crystallography* **1999**, *32*, 837-838.

[72] M. Altamura, E. Perrotta, *The Journal of Organic Chemistry* **1993**, *58*, 272-274.

[73] S. Murahashi, Y. Taniguchi, Y. Imada, Y. Tanigawa, *The Journal of Organic Chemistry* **1989**, *54*, 3292-3303.

[74] C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler, J. van de Streek, *Journal of Applied Crystallography* **2006**, *39*, 453-457.

[75] L. Farrugia, *Journal of Applied Crystallography* **1997**, *30*, 565.

[76] R. W. Alder, A. P. Davis, *Journal of molecular modeling* **2006**, *12*, 649-652.

[77] NATO standardization agreement (STANAG) on explosives. Impact sensitivity tests. No. 4489, Sept. 17, **1999**. WIWEB-Standardarbeitsanweisung 4-5.1.02, Ermittlung der Explosionsgefährlichkeit, hier der Schlagempfindlichkeit mit dem Fallhammer, Nov. 8, **2002**. NATO standardization agreement (STANAG) on explosive. Friction sensitivity tests. No. 4487, 1st ed., Aug. 22, **2002**. WIWEB-Standardarbeitsanweisung 4-5.1.03, Ermittlung der Explosionsgefährlichkeit oder der Reibeempfindlichkeit mit dem Reibeapparat, Nov. 8, **2002**.

[78] Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, United Nations, New York, Geneva, **1999**. 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 and. > 80N, very sensitive ≤ 80 N, extremely sensitive ≤ 10 N

[79] Y. Li, Q. Wang, L. Dong, X. Guo, W. Wang, J. Xie, J. Chang, *Synthesis* **2009**, *20*, 3383-3390.

[80] N. G. Luk'yanenko, O. T. Mel'nik, *Chemistry of Heterocyclic Compounds* **1987**, *23*, 934-939.

[81]   K. Weinges, R. Spänig, *Chemische Berichte* **1968**, *101*, 3010-3017.

[82]   B. Martin, F. Possémé, C. Le Barbier, F. Carreaux, B. Carboni, N. Seiler, J.-P. Moulinoux, J.-G. Delcros, *Bioorganic & Medicinal Chemistry* **2002**, *10*, 2863-2871.

[83]   G. Darzens, *Comptes rendus de l'Académie des sciences* **1911**, *152*, 1314-1317.

[84]   F. A. Carey, R. J. Sundberg, *Advanced Organic Chemistry: Part A: Structure and Mechanisms*, Springer US, **2007**.

[85]   J. J. Blumenstein, C. J. Michejda, *Tetrahedron Letters* **1991**, *32*, 183-186.

[86]   I. Dotsenko, Q. Zhao, A. Franz, P. Batoon, N. Samoshina, V. Samoshin, *Arkivoc* **2014**, *5*, 1641.

[87]   J.-C. Wu, D.-X. Wang, Z.-T. Huang, M.-X. Wang, *The Journal of Organic Chemistry* **2010**, *75*, 8604-8614.

[88]   F. Trouton, *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science* **1884**, *18*, 54-57.

[89]   Farhanullah, T. Kang, E.-J. Yoon, E.-C. Choi, S. Kim, J. Lee, *European Journal of Medicinal Chemistry* **2009**, *44*, 239-250.

[90]   F. Samrin, A. Sharma, I. A. Khan, S. Puri, *Journal of Heterocyclic Chemistry* **2012**, *49*, 1391-1397.

[91]   B. Biannic, J. J. Bozell, T. Elder, *Green Chemistry* **2014**, *16*, 3635-3642.

[92]   C. J. J. Cao, M. S.; Hurley, M. M.; Klapötke, T. M., *JANNAF J. Propuls. Energet.* **2012**, *5*, 41-51.

[93]   S. Heimsch, T. M. Klapotke, *International Journal of Energetic Materials and Chemical Propulsion* **2019**, *18*, 1-8.

[94]   S. P. Verevkin, V. N. Emel'yanenko, M. Algarra, J. Manuel López-Romero, F. Aguiar, J. Enrique Rodriguez-Borges, J. C. G. Esteves da Silva, *The Journal of Chemical Thermodynamics* **2011**, *43*, 1652-1659.

[95]   a) P. Klahn, H. Erhardt, A. Kotthaus, S. F. Kirsch, *Angewandte Chemie International Edition* **2014**, *53*, 7913-7917;
         b) T. Harschneck, S. Hummel, S. F. Kirsch, P. Klahn, *Chemistry – A European Journal* **2012**, *18*, 1187-1193.

[96]   D. A. Kamble, P. U. Karabal, P. V. Chouthaiwale, A. Sudalai, *Tetrahedron Letters* **2012**, *53*, 4195-4198.

[97]   H. Erhardt, A. P. Häring, A. Kotthaus, M. Roggel, M. L. Tong, P. Biallas, M. Jübermann, F. Mohr, S. F. Kirsch, *The Journal of Organic Chemistry* **2015**, *80*, 12460-12469.

[98]   a) D. Kumari, K. D. B. Yamajala, H. Singh, R. R. Sanghavi, S. N. Asthana, K. Raju, S. Banerjee, *Propellants, Explosives, Pyrotechnics* **2013**, *38*, 805-809;
         b) D. Kumari, H. Singh, M. Patil, W. Thiel, C. S. Pant, S. Banerjee, *Thermochimica Acta* **2013**, *562*, 96-104;

c) D. Kumari, A. S. G, C. S. Pant, M. Patil, H. Singh, S. Banerjee, *RSC Advances* **2014**, *4*, 39924-39933.

[99]   M. D. Spantulescu, M. A. Boudreau, J. C. Vederas, *Organic Letters* **2009**, *11*, 645-648.

[100]   M. Claßen, S. B. Heimsch, T. M. Klapötke, *Propellants, Explosives, Pyrotechnics* **2019**, *44*, 1515-1520.

[101]   L. Blanchard, *Bulletin de la Societe Chimique de France* **1928**, *43*, 1202 – 1204.

[102]   C. Xiao, Y. Cheng, Y. Zhang, J. Ding, C. He, X. Zhuang, X. Chen, *Journal of Polymer Science Part A: Polymer Chemistry* **2014**, *52*, 671-679.

[103]   T. M. Klapötke, B. Krumm, M. Scherr, F. X. Steemann, K. Banert, Y.-H. Joo, *Chemistry – A European Journal* **2009**, *15*, 11341-11345.

[104]   S. H. Pang, L.-C. Lee, M. A. Sakwa-Novak, R. P. Lively, C. W. Jones, *Journal of the American Chemical Society* **2017**, *139*, 3627-3630.

[105]   R. A. Heacock, L. Marion, *Canadian Journal of Chemistry* **1956**, *34*, 1782-1795.

[106]   S. Kumar, N. Ranjan, P. Kellish, C. Gong, D. Watkins, D. P. Arya, *Organic & Biomolecular Chemistry* **2016**, *14*, 2052-2056.

[107]   a) A. C. Engler, D. K. Bonner, H. G. Buss, E. Y. Cheung, P. T. Hammond, *Soft Matter* **2011**, *7*, 5627-5637;
        b) I. Dimitrov, K. Jankova, S. Hvilsted, *Journal of Polymer Science Part A: Polymer Chemistry* **2010**, *48*, 2044-2052.

[108]   T. Taguchi, M. Nakao, *Tetrahedron* **1962**, *18*, 245-255.

[109]   A. Mariani, A. Bartoli, M. Atwal, K. C. Lee, C. A. Austin, R. Rodriguez, *Journal of Medicinal Chemistry* **2015**, *58*, 4851-4856.

[110]   J. Walker, *Journal of the Chemical Society (Resumed)* **1945**, 630-633.

[111]   R. A. Dodean, P. Kancharla, Y. Li, V. Melendez, L. Read, C. E. Bane, B. Vesely, M. Kreishman-Deitrick, C. Black, Q. Li, R. J. Sciotti, R. Olmeda, T.-L. Luong, H. Gaona, B. Potter, J. Sousa, S. Marcsisin, D. Caridha, L. Xie, C. Vuong, Q. Zeng, J. Zhang, P. Zhang, H. Lin, K. Butler, N. Roncal, L. Gaynor-Ohnstad, S. E. Leed, C. Nolan, S. J. Huezo, S. A. Rasmussen, M. T. Stephens, J. C. Tan, R. A. Cooper, M. J. Smilkstein, S. Pou, R. W. Winter, M. K. Riscoe, J. X. Kelly, *Journal of Medicinal Chemistry* **2019**, *62*, 3475-3502.

[112]   D.-Y. Zeng, G.-T. Kuang, S.-K. Wang, W. Peng, S.-L. Lin, Q. Zhang, X.-X. Su, M.-H. Hu, H. Wang, J.-H. Tan, Z.-S. Huang, L.-Q. Gu, T.-M. Ou, *Journal of Medicinal Chemistry* **2017**, *60*, 5407-5423.

[113]   M. Vaidyanathan, R. Balamurugan, U. Sivagnanam, M. Palaniandavar, *Journal of the Chemical Society, Dalton Transactions* **2001**, *23*, 3498-3506.

[114]   Y. Gao, L. Chen, Z. Zhang, W. Gu, Y. Li, *Biomacromolecules* **2010**, *11*, 3102-3111.

[115]   N. Salvarese, F. Refosco, R. Seraglia, M. Roverso, A. Dolmella, C. Bolzati, *Dalton Transactions* **2017**, *46*, 9180-9191.

[116] T. K. Hansen, T. Joergensen, F. Jensen, P. H. Thygesen, K. Christiansen, M. B. Hursthouse, M. E. Harman, M. A. Malik, B. Girmay, *The Journal of Organic Chemistry* **1993**, *58*, 1359-1366.

[117] A. S. Singh, P. K. Bharadwaj, *Dalton Transactions* **2008**, *6*, 738-741.

[118] K. Banert, J. Wutke, T. Rüffer, H. Lang, *Synthesis* **2008**, *16*, 2603-2609.

[119] S.-H. Jung, H.-Y. Song, Y. Lee, H. M. Jeong, H.-i. Lee, *Macromolecules* **2011**, *44*, 1628-1634.

[120] P. W. Hickmott, S. Wood, P. Murray-Rust, *Journal of the Chemical Society, Perkin Transactions 1* **1985**, 2033-2038.

[121] E. Haapaniemi, M. Mesilaakso, *Magnetic Resonance in Chemistry* **2012**, *3*, 196-207.

[122] R. Caraballo, M. Saleeb, J. Bauer, A. M. Liaci, N. Chandra, R. J. Storm, L. Frängsmyr, W. Qian, T. Stehle, N. Arnberg, M. Elofsson, *Organic & Biomolecular Chemistry* **2015**, *13*, 9194-9205.

[123] P. Jagdishwarog, L. Velupillai, Patent *WO2015173664 (A1)*, **2015**.

[124] W. Adam, G. Asensio, R. Curci, M. E. Gonzalez-Nunez, R. Mello, *Journal of the American Chemical Society* **1992**, *114*, 8345-8349.

[125] C. E. Williamson, T. J. Sayers, A. M. Seligman, B. Witten, *Journal of Medicinal Chemistry* **1967**, *10*, 511-511.

[126] A. Mansour, T. Kehat, M. Portnoy, *Organic & Biomolecular Chemistry* **2008**, *6*, 3382-3387.

[127] M. J. Abedin, L. Liepold, P. Suci, M. Young, T. Douglas, *Journal of the American Chemical Society* **2009**, *131*, 4346-4354.

[128] M.-H. Larraufie, C. Ollivier, L. Fensterbank, M. Malacria, E. Lacôte, Angewandte Chemie **2010**, *49*, 2178-2181.

[129] D. Wannaporn, T. Ishikawa, *Molecular Diversity* **2005**, *9*, 321-331.

[130] K. Sykam, S. Donempudi, *Polymer* **2015**, *62*, 60-69.

[131] a) U. Asseline, M. Chassignol, J. Draus, M. Durand, J.-C. Maurizot, *Bioorganic & Medicinal Chemistry* **2003**, *11*, 3499-3511;
b) S. Laval, W. Dayoub, L. Pehlivan, E. Métay, A. Favre-Reguillon, D. Delbrayelle, G. Mignani, M. Lemaire, *Tetrahedron* **2014**, *70*, 975-983.

[132] D. C. Ware, B. D. Palmer, W. R. Wilson, W. A. Denny, *Journal of Medicinal Chemistry* **1993**, *36*, 1839-1846.

[133] H. Staudinger, J. Meyer, Helvetica **1919**, *2*, 635-646.

[134] J. E. Leffler, R. D. Temple, *Journal of the American Chemical Society* **1967**, *89*, 5235-5246.

[135] L. González, A. Ladegaard Skov, S. Hvilsted, *Journal of Polymer Science Part A: Polymer Chemistry* **2013**, *51*, 1359-1371.

[136] C. Janiak, T. M. Klapötke, E. Riedel, H. J. Meyer, *Moderne anorganische Chemie*, Walter de Gruyter GmbH & Co. KG: Berlin, **2003**.

[137] F. Matsuda, M. Yanagiya, T. Matsumoto, *Tetrahedron Letters* **1982**, *23*, 4043-4046.

[138]   a) Y. Natori, H. Tsutsui, N. Sato, S. Nakamura, H. Nambu, M. Shiro, S. Hashimoto, *The Journal of Organic Chemistry* **2009**, *74*, 4418-4421;

b) H. M. Peltier, J. P. McMahon, A. W. Patterson, J. A. Ellman, *Journal of the American Chemical Society* **2006**, *128*, 16018-16019.

[139]   D. Chand, J. Zhang, J. n. Shreeve, *Chemistrya- A European Journal* **2015**, *38*, 13297-13301.

[140]   V. K. Bhosale, P. S. Kulkarni, *New Journal of Chemistry* **2017**, *41*, 1250-1258.

[141]   J. E. Bara, *Industrial & Engineering Chemistry Research* **2011**, *50*, 13614-13619.

[142]   W. Chen, F. Liu, *Journal of Organometallic Chemistry* **2003**, *673*, 5-12.

[143]   S. Aher, P. Bhagat, *Research on Chemical Intermediates* **2016**, *42*, 5587-5596.

[144]   Y.-H. Joo, H. Gao, Y. Zhang, J. n. M. Shreeve, *Inorganic Chemistry* **2010**, *49*, 3282-3288.

[145]   M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian 16 Rev. C.01, Wallingford, CT, **2016**.

[146]   a) V. A. Rassolov, J. A. Pople, M. A. Ratner, T. L. Windus, *The Journal of Chemical Physics* **1998**, *109*, 1223-1229;

b) A. D. Becke, *The Journal of Chemical Physics* **1993**, *98*, 5648-5652.

[147]   a) J. W. Ochterski, G. A. Petersson, J. A. M. Jr., *The Journal of Chemical Physics* **1996**, *104*, 2598-2619;

b) J. A. M. Jr., M. J. Frisch, J. W. Ochterski, G. A. Petersson, *The Journal of Chemical Physics* **2000**, *112*, 6532-6542.

[148]   M. S. Westwell, M. S. Searle, D. J. Wales, D. H. Williams, *Journal of the American Chemical Society* **1995**, *117*, 5013-5015.

[149]   J. Köhler, R. Meyer, A. Homburg, *Explosivstoffe*, Wiley-VCH: Berlin, **2008**.

[150]   T. A. K. Roy Dennington, and John M. Millam, GaussView *Vol. Version 6.1*, Shawnee Mission: KS, **2016**.

[151]   S. Gordon and B. J. McBride, Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications, NASA Reference Publication 1311, **1996**.

[152]   R. L. Schwartz, A., in *18. IMEKO-TC3-Konferenz*, Celle, **2003**.

[153]   M. W. J. Chase, *NIST-JANAF Themochemical Tables, Vol. Monograph 9*, Journal of Physical and Chemical Reference Data Monographs **1998**.

[154]   J. K. Niemeier, D. P. Kjell, *Organic Process Research & Development* **2013**, *17*, 1580-1590.

[155]   L. G. Cole, E. C. Gilbert, *Journal of the American Chemical Society* **1951**, *73*, 5423-5427.

[156]   R. C. Ahlert, C. J. Shimalla, *Journal of Chemical & Engineering Data* **1968**, *13*, 108-109.

[157]   T. M. Donovan, C. H. Shomate, W. R. McBride, *The Journal of Physical Chemistry* **1960**, *64*, 281-282.

[158]   Y. Wang, S. Huang, W. Zhang, T. Liu, X. Qi, Q. Zhang, *Chemistry – A European Journal* **2017**, *23*, 12502-12509.

[159]   a) B. V. S. Jyoti, M. S. Naseem, S. W. Baek, H. J. Lee, S. J. Cho, *Combustion and Flame* **2017**, *183*, 102-112;
         b) B. Melof, M. Grubelich, in *37th Joint Propulsion Conference and Exhibit*.

[160]   S. Aldrich, https://www.sigmaaldrich.com/germany.html.

[161]   G. R. Rarata, K. Surmacz, P. , *Central European Journal of Energetic Materials* **2016**, *13*, 778-790.

[162]   S. Guseinov, S. Fedorov, V. Kosykh, P. Storozhenko, *Russian Chemical Bulletin* **2018**, *67*, 1943-1954.

[163]   G. Rarata, W. Florczuk, *Journal of KONES. Powertrain and Transport* **2016**, *23*, 271-278.

[164]   a) P. Wardman, L. P. Candeias, *Radiation research* **1996**, *145*, 523-531;
         b) H. J. H. Fenton, *Journal of the Chemical Society, Transactions* **1894**, *65*, 899-910.

[165]   V. K. Bhosale, J. Jeong, S. Kwon, *Fuel* **2019**, *255*, 115729.