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2025 Bc. Preslava Krasimirova Zheleva

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Low Melting Explosives

Master's Thesis

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Bc. Preslava Krasimirova
Zheleva

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ASSIGNMENT OF DIPLOMA THESIS

(project, art work, art performance)

Name and surname:	**Preslava Krasimirova Zheleva**
Personal number:	**C23492**
Study programme:	**N0711A130008 Engineering of Energetic Materials**
Work topic:	**Low melting explosives**
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Theses guidelines

1. Select appropriate criteria and make a literature search on the topic of low-melting explosives suitable as model compounds for additive manufacturing.
2. Based on the research done, select the appropriate compound for their preparation.
3. Prepare and characterize the selected substances.
4. Report the results in the form of a diploma thesis.

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Extent of graphics content:
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Recommended resources:

Supervisors of diploma thesis: **doc. Ing. Zdeněk Jalový, Ph.D.**
Institute of Energetic Materials

Consultant of diploma thesis: **Ing. Ondřej Zeman**
Institute of Energetic Materials

Reviewer of diploma thesis: **Mgr. Radovan Skácel, Ph.D.**

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L.S.

prof. Ing. Petr Němec, Ph.D.
Dean

doc. Ing. Jiří Pachman, Ph.D.
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ANOTACE

Tato práce studuje výbušniny s nízkou teplotou tání. Představuje komplexní přehled literatury a experimentální studii zaměřenou na perspektivní nízkotavitelné energetické materiály vhodné pro aditivní výrobu. Cílem bylo identifikovat a syntetizovat sloučeniny s dobrou tepelnou stabilitou v kapalné fázi, nízkou teplotou tání a snadnou přípravou. Sloučeniny byly charakterizovány fyzikálními vlastnostmi včetně hustoty, bodu tání, diferenciální tepelné analýzy, citlivosti na tření a nárazu. Práce navrhuje vhodné energetické materiály, které by mohly přispět do oblasti aditivní výroby výbušnin.

KLÍČOVÁ SLOVA

Aditivní výroba, nízkotající výbušniny, DTA

TITLE

Low melting explosives

ANNOTATION

This work studies low-melting explosives. It represents a comprehensive review of literature and an experimental study focused on promising low-melting energetic materials suitable for additive manufacturing. The aim was to identify and synthesise compounds with good thermal stability in the liquid phase, low melting point, and easy preparation. The compounds were characterised by physical properties that included density, melting point, differential thermal analysis, sensitivity to friction and impact. The thesis proposes suitable energetic materials that could contribute to the field of additive manufacturing of explosives.

KEYWORDS

Additive manufacturing, low melting explosives, DTA

CONTENT

LIST OF ILLUSTRATIONS AND TABLES

LIST OF ABBREVIATIONS AND SYMBOLS

A. G.	analytical grade
AFX-645	insensitive high explosive based on TNT, NTO, wax, and aluminium
AllNQ	allylnitroguanidine
AN	ammonium nitrate
ATR	attenuated total reflection
BuNQ	butylnitroguanidine
CAL	calculated axial lithography
CLIP	continuous liquid interface production
DEGN	diethyleneglycol dinitrate
DIW	direct ink writing
DLP	digital light processing
DNAN	2,4-dinitroanisole
DNB	1,3-dinitrobenzene
DNDA5	2,4-dinitro-2,4-diazapentane
DNDA6	2,4-dinitro-2,4-diazahexane
DNDA7	3,5-dinitro-3,5-diazaheptane
DTA	differential thermal analysis
FDM	fused deposition modelling
FTIR	Fourier-transform infrared spectroscopy
G. R.	guaranteed reagent
HeNQ	hexylnitroguanidine
HMX	1,3,5,7-tetranitro-1,3,5,7-tetrazocane (octogen)
iBuNQ	isobutylnitroguanidine
LOVA	low vulnerability ammunition
MNA	*N*-methyl-4-nitroaniline
M.p.	melting point
NDNAZ	1-nitroso-3,3-dinitroazetidine
NG	nitroglycerine
NQ	nitroguanidine
NTO	5-nitro-1,2-dihydro-3*H*-1,2,4-triazol-3-one (nitrotriazolone)
PeNQ	pentylnitroguanidine

PETN	pentaerythritol tetranitrate
Picryl azide	2-azido-1,3,5-trinitrobenzene
Picryl chloride	2,4,6-trinitrochlorobenzene
PrNQ	propylnitroguanidine
Py-NENA	2-nitratoethylamino-3,5-dinitropyridine
RDX	1,3,5-trinitroperhydro-1,3,5-triazine (hexogen)
RMSs	reactive microstructures
SLA	stereolithography
TLC	thin layer chromatography
TNAZ	1,3,3-trinitroazetidine
TNT	2,4,6-trinitrotoluene
TP	1*H*-1,2,4-triazolium perchlorate
UV	ultraviolet
4-ATN	4-amino-1,2,4-triazolium nitrate
4-ATP	4-amino-1,2,4-triazolium perchlorate
3D	three-dimensional

INTRODUCTION

The low-melting energetic materials are known as energetic fillers for ammunition because of their easy transfer in liquid state. This also allows the introduction of material in barely accessible geometries. The emerging area of additive manufacturing could utilise these compounds to design or modify promising energetic materials, which could then be applied within additive manufacturing technology (3D printing). Over the years, 3D printing has been used extensively in surgical operations, aerospace industry, and biochemical research. This technique can save raw materials, prepare products with high precision and complexity, as well as shorten the design period. Recently, the demand for ammunition products has been shifting towards reactive micro structures, high preparation efficiency, miniaturisation, and controllable energy release. 3D printing technology can break through the existing design and development mode by expanding explosives charging technology and, moreover, enabling the distribution of different types of explosives and varying the explosive density in a specific volume. Furthermore, the fabrication of ‘reactive microstructures’ (RMSs) can be done to better understand the phenomena of combustion and detonation at the micro and nanoscale [1]. Additive manufacturing can be used not only for the fabrication of materials with dimensions of submicrometres, but also for ones that can go up to several metres [2].

Key components in additive manufacturing of explosives are the energetic materials themselves and other adhesives or binders. Melt-cast explosives have a wide range of uses, especially as an explosive filler for mortars, grenades, artillery shells, warheads, and antipersonnel mines. Their development and optimisation have evolved, driven by advancements in chemistry, material science, and manufacturing methods. They are preferred for their ability to fill explosive charges of complicated shapes and of unconventionally large or small dimensions. Hence, these energetic materials should comply with some conditions such as low melting point, low vapour pressure, low inhalation toxicity, good thermal stability in the molten state, and considerable temperature gap between their melting point and decomposition.

The aim of this work is to present literature research for suitable low-melting explosive materials for 3D printing with specific requirements of good thermal stability in the liquid phase and their easy synthesis. The work also consists of evaluating and characterising the physical properties of the synthesised compounds.

1. Theoretical part

1.1. Melt-cast explosives

Through the years, two basic methods of filling the munition objects have been developed, with one being filling by casting under vacuum or under pressure (injection), and the other being filling by pressing, including screw-pressing (gradual pressing) and extrusion (extrusion into free space). Casting may be regarded as the most commonly used filling method of high explosives, mainly because it is the most universal one [3]. Melt-cast explosives consist of a carrier explosive, such as TNT or DNAN, and a solid high-energy explosive, such as RDX or HMX, and represent more than 90% of military composite explosives [4]. Melt-cast explosives should meet certain conditions. Taking into account their attribute of “low-melting”, they should have a melting point in the range of 50ºC to 120ºC, they should have low vapour pressure, and especially low inhalation toxicity, since they are being treated in the molten state. Furthermore, these substances should have a sufficient temperature gap between the melting point and the start of their decomposition (above 100ºC), for example, 2,4,6-trinitrotoluene or 2,4-dinitro-2,4-diazapentane (DNDA5) (**Figure 1**). In other words, they have to be thermally stable for safety reasons. When talking about the design of the ammunition as a whole, it should be kept in mind that these melt-cast explosives must not separate from the shell or casing and must not shrink or crack on cooling. Moreover, for safety reasons, premature detonation is highly undesirable. Greener, and simpler synthesis is preferred. More and more research is being done to find such compounds that have higher detonation parameters than the historical ones, but unfortunately, not all criteria can be met.

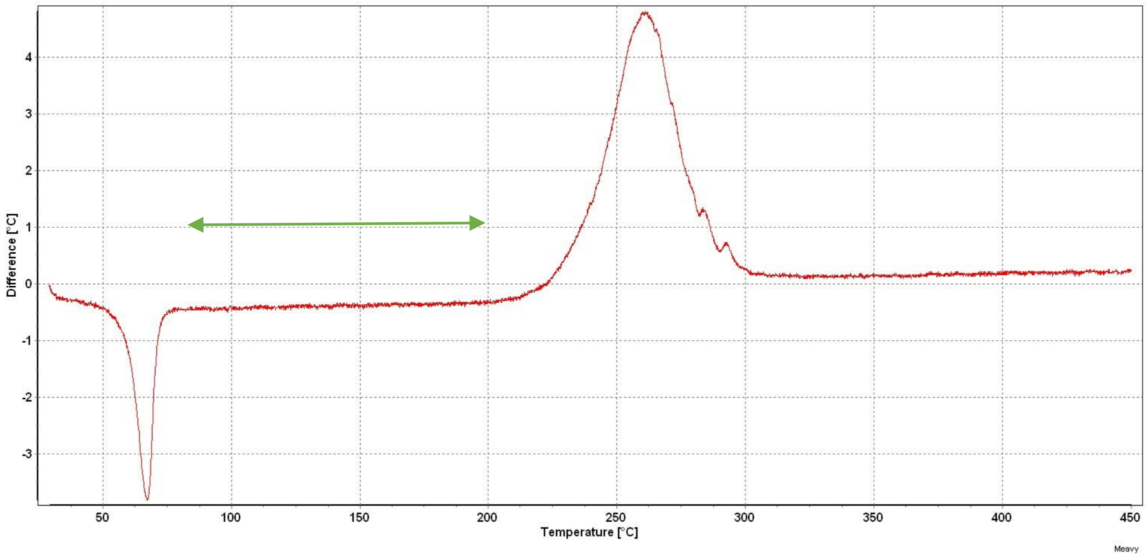


Figure 1: DTA thermogram of DNDA5

The process of melt-cast explosive production is carried out in large anchor melt-cast kettles that are heated in the temperature range of 80ºC to 120ºC with hot water or by steam, mixing the ingredients under low shear. After the first step, the molten explosive is ready to be poured into a mould or projectile, followed by cooling and solidification processes. In some cases, an energetic oxidiser (RDX, HMX, TNAZ, NTO) is added after the binder is molten. As easy as it sounds in theory, in practice, it is not easy to obtain an ideal melt-cast explosive [5].

The loading process of melt-cast explosives primarily depends on the phase transition of the carrier, specifically on its transformation from solid to liquid phase at high temperatures. In the explosive composition, the carrier must be present in more than 20%. This means that the physical, chemical, and mechanical properties, the detonation performance, and the stability of the carrier are of great importance with respect to overall performance.

TNT (2,4,6-trinitrotoluene) is a carrier that is traditionally used within melt-cast explosives due to its low manufacturing costs, its thermal stability, and its low sensitivity to mechanical stimuli. Some of the worldwide known compositions based on TNT are, for example: Composition B, AFX-645. These are widely used in both industrial and military applications. However, melt-cast explosives based on TNT face some substantial issues such as oil seepage, shrinkage, cavitation, and brittleness [6]. More importantly, TNT itself has drawbacks related to toxicity, biodegradation, and environmental pollution, and therefore, researchers are trying to find new low-melting explosives to replace it. Along with the other characteristics mentioned, the compound must have high density and good energetic performance. The challenge is that the melting point of energetic materials is unpredictable, and a relationship between structure and melting point cannot be found [7].

The traditional strategy of finding new high-energy and insensitive energetic materials is connected with heterocyclic rings like pyrazole, triazole, oxadiazole, furazan, and other high-nitrogen compounds, which are used as the backbone, to which another energetic group, like nitro, azide, and nitramino, is introduced [4]. These energetic groups are utilised to reduce the melting point of the energetic material and can also be nitroester, fluorine, and gem-nitro. The difficulty in synthesising novel melt-cast explosives is the design of the carrier [4, 7].

1.2. Additive manufacturing of EM

Additive manufacturing is a technology that can fabricate various energetic materials and enable the distribution of different types of explosives and explosive density in a specific volume. It can save raw materials, prepare products with high precision and complexity, as well as it shortens the design period. It can be used for the production of charges from submicrometers to several metres, which makes it a preferable technique.

Although it is considered to be new technology, 3D printing dates back to 1986, when Charles W. Hull patented (US4575330A) a technique for creating three-dimensional objects by curing photopolymer with light [8]. From this year until 2023, a lot changed, with another milestone from that year being the utilisation of pressure-assisted binder jetting 3D printing technology for the fabrication of solid propellants and analysis on the influence of printing parameters on the composition and performance of solid propellants in Iowa universities [9]. All this information leads to the fact that there has been a lot of development in this sphere, and a lot more is yet to come. This is mainly because 3D printing offers precise, rapid, controllable, and safe processing, thus overcoming the constraints of traditional manufacturing methods like melt casting, granulation, and pressing. Additionally, this technology can help overcome the limitations of previously impossible and difficult processes [10].

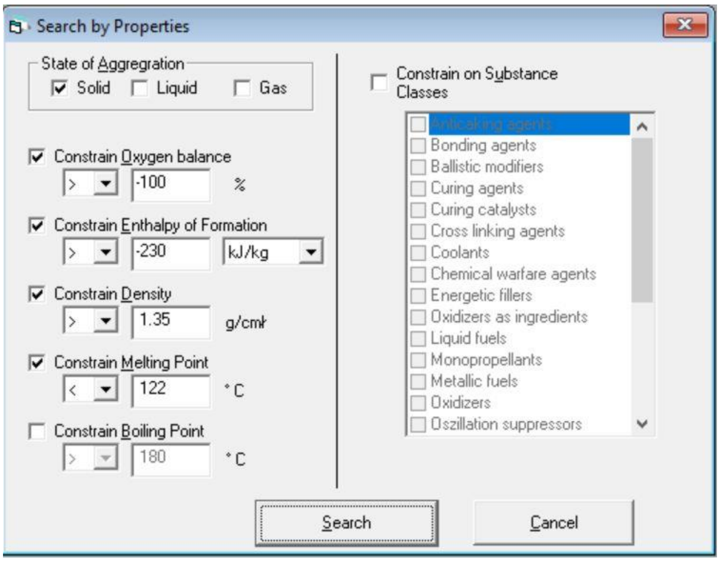
Additive manufacturing technology uses software and numerical control systems to extrude, melt, photocure, spray, or sinter raw materials based on digital model files. It has the potential to increase product diversity and innovate conventional manufacturing technologies. Some of the latter include casting, granulation, melt casting, and pressing, facing challenges in achieving high solid contents and complex cross-sectional shapes for explosives and propellant charges [10, 11]. For example, the 3D printing of melt-cast explosives can be divided into three areas, the first of which deals with the rheological parameters that include viscosity, yield stress, shear stress, and elastic/ viscous modulus of the raw materials. For the melt-cast energetic materials, the parameters are greatly affected by temperature, chemical additives, particle size, and solid contents. The next area quantifies the printing parameters according to the results of the experiment in order to obtain grains with higher density and accuracy. These printing parameters are temperature, nozzle diameter, printing velocity, and layer height. Last, but not least, is the characterisation of the printed grains' parameters like density, velocity of detonation, mechanical strength, sensitivity, or thermal behavior [11].

3D printing technologies used for printing and shaping of explosive materials can be different types: vat photopolymerization (including stereolithography (SLA), digital light processing (DLP), continuous liquid interface production (CLIP) and calculated axial lithography (CAL)); binder jetting; fused deposition modelling (FDM); direct ink writing (DIW). For all these types of additive manufacturing, adhesives are critical components that have strong bonding capabilities. This means that the design and precise control of the adhesive/ binder structure is of great importance regarding the stability and structural integrity of the energetic materials [10].

To conclude, the advantages of this procedure are the low cost, customisation, short timeframe, complex geometries, and technological diversity. On the other hand, the disadvantages are low energy density, high suspension viscosity, and so far, the lack of practical application [1].

1.3. Search for suitable substances

In particular, the thermochemical database ICT [12] and secondary literature Reaxys [13] were used to obtain suitable compounds. In the ICT database, target substances were determined by melting point, oxygen balance, and density (**Figure 2**).



Search by Properties

State of Aggregration

☑ Solid ☐ Liquid ☐ Gas

☑ Constrain Oxygen balance
> -100 %

☑ Constrain Enthalpy of Formation
> -230 kJ/kg

☑ Constrain Density
> 1.35 g/cm³

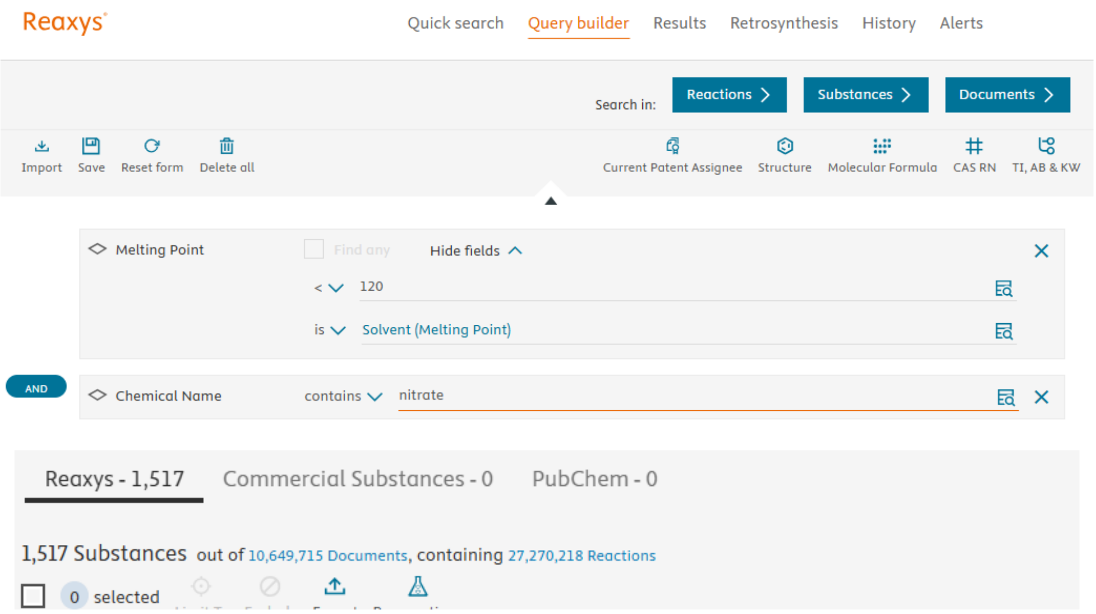
☑ Constrain Melting Point
< 122 °C

☐ Constrain Boiling Point
> 180 °C

☐ Constrain on Substance Classes

Figure 2: Sample search from the ICT database

In the case of Reaxys, the target substances were determined by melting point, and the search was completed with a chemical name segment, such as nitrate, perchlorate, picrate, acrylate, or allyl (**Figure 3**).



Melting Point < 120

is Solvent (Melting Point)

AND Chemical Name contains nitrate

Reaxys - 1,517

1,517 Substances out of 10,649,715 Documents, containing 27,270,218 Reactions

Figure 3: Sample search from Reaxys

In both cases, reasonable materials were selected from those found.

1.4. Dinitrobenzenes

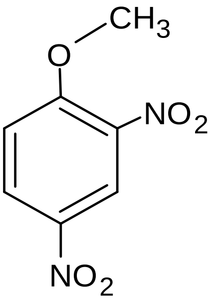


Figure 4: Structural formula of 1-methoxy-2,4-dinitrobenzene

1-Methoxy-2,4-dinitrobenzene (DNAN, 2,4-dinitroanisole) (**Figure 4**) has received considerable attention as a replacement of trinitrotoluene for the fabrication of melt-cast explosives mainly because of its low density, low shrinkage rate, and environmental friendliness [14]. It was first synthesised in 1869 and was historically used as a raw material for pesticides, synthetic dyes, and later in the Second World War, was used in the V-1 cruise missile charge Amatol-40 (20% DNAN, 35% ammonium nitrate (AN), 15% RDX) [15]. Since 1980, DNAN has again aroused strong attention. Some of the reasons for renewed interest are considered to be that it is a less sensitive melt-cast medium than TNT and that it is classified as a Class 4.1 flammable solid and, therefore, is subject to less stringent international transportation requirements than Class 1 materials [16]. DNAN is a slightly less powerful explosive than TNT, with a melting point of 94-95°C that can be easily reduced by several degrees with the addition of *N*-methyl-4-nitroaniline (MNA), for example [17]. The crystal structure of DNAN has two polymorph structures: H-DNAN and L-DNAN, with the former having a higher melting point of 94-97°C and the latter having a lower melting point of 86-89°C. Although the L-polymorph structure is more suitable as a carrier for melt-cast explosives, considering the melting point, it has been found that it possesses certain drawbacks. They include difficult direct synthesis and conversion into H-DNAN after a few months at room temperature. Therefore, the literature reports mainly the physical and chemical properties of H-DNAN [6].

DNAN is considered to be the main ingredient in low vulnerability munitions (LOVA) that are less sensitive to shock and high temperatures, and in this way minimise unintentional detonations. Researchers have found that DNAN exhibits greater kinetic inertness and thermal stability compared to TNT. Furthermore, the toxicity of 2,4-dinitroanisole has been found to be lower than that of TNT, which is in favour of its replacement as a carrier in melt-cast explosives [18, 19].

DNAN can form binary eutectic mixtures with 1,3-dinitrobenzene (DNB), which has a decreased melting point of 48°C, when the mass proportion of DNAN/ DNB is 1:1. This mixture is an irregular rough dendrite, which can easily generate hot spots under impact or friction and has an inferior spark sensitivity safety performance in comparison to pure DNAN [20]. DNAN and other dinitrobenzenes are described in **Table 1**.

Table 1: Selected physical properties of dinitrobenzenes

Compound	**Melting point [°C]**	**Boiling point [°C]**	**Density (ρ) [g/cm^3]**	**ΔH_f [kJ/mol]**	**Oxygen balance [%]**
1-Methoxy-2,4-dinitrobenzene	93-95 [21]	-	1.34 [22]	-	-96.90
1,3-Dinitrobenzene	89.9 [23]	301.9 [23]	1.58 (18°) [24]	-27.20 [25]	-95.17
1-Chloro-2,4-dinitrobenzene	53 [24]	315 [24]	1.7 [26]	-24.27 [27]	-71.09
1,3-Diazido-4,6-dinitrobenzene	99 [28]	-	1.65 [29]	569.02 [28]	-57.57

1.5. Trinitro aromatic compounds

TNT (**Figure 5**) is one of the most well-known representatives of this group. It was first synthesised in 1863, and it was by no means a high-performance explosive. Combining high chemical stability, moderate sensitivity to impact and friction, and a low melting point of 80.8ºC, it is ideal candidate for melt casting. [5].

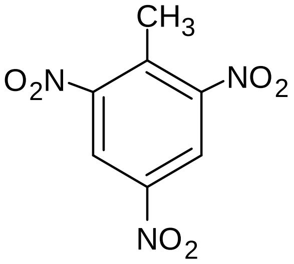


Figure 5: TNT structural formula

Nowadays, TNT-based melt-cast explosives are still widely used due to their properties that allow them to be molten with the addition of other explosives, and be poured into moulds of various shapes [30]. It is cast with considerable care, but the casting has some limitations, such as possible component segregation, non-uniform cast product, and the introduction of porosity and cavities [31]. Despite these drawbacks, some well-known melt-cast formulations are portrayed in **Table 2**, which are still used.

Table 2: TNT melt cast formulations

Name	Composition
Torpex	42% RDX, 40% TNT, 18% Al
Pentolite	50% PETN, 50% TNT
Ammonite	80% AN, 20% TNT
Octol	70–75% HMX, 25–30% TNT
TNTO	50% TNT, 50% NTO
Composition B	40% TNT, 60% RDX

However, such compositions are brittle, prone to cracking, and can exhibit dimensional instability in response to thermal cycling [5]. A widely used mixture is Composition B, which is the explosive composition in shaped charge and fragmentation-type warheads [30]. **Table 3** shows some parameters of TNT and other trinitro aromatic compounds. These include picryl chloride, picryl azide and several salts of picric acid with amines.

Table 3: Selected physical properties of trinitro aromatics

Compound	**Melting point [^{0}C]**	**DTA [^{0}C]**	**Density (ρ) [g/cm^3]**	**ΔH$_f$ [kJ/mol]**	**Oxygen balance [%]**
TNT	80.7 [32]	240*	1.65 [24]	-62.76 [33]	-73.96
Picryl azide	93 [28]	-	1.85 [29]	334.72 [28]	-44.07
Picryl chloride	83 [24]	260**	1.79 [24]	29.29 [34]	-42.01
Diethylamine picrate	74 [35]	-	1.36 [36]	-	-105.87
Dipropylamine picrate	97.5 [35]	-	1.36 (at 15^{0}C) [37]	-	-125.95
Diallylamine picrate	76 [38]	-	-	-	-117.69

*start of decompositiuon, ** start of boiling/decomposition

1.6. Trinitromethylbenzenes

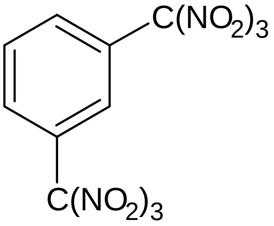


Figure 6: Structural formula of 1,3-bis-(trinitromethyl)benzene

Compounds with aromatic core and a nitro group bonded to the aliphatic carbon are represented by trinitromethylbenzenes. 1,3,5-Tris-(trinitromethyl)benzene has a high density and an oxygen balance close to zero. 1,3-Bis-(trinitromethyl)benzene (**Figure 6**) has a lower melting point and still a relatively high density. Trinitromethylbenzenes and their selected physical properties can be found in **Table 4**.

Table 4: Selected physical properties of trinitromethylbenzenes

Compound	**Melting point [^{0}C]**	**Density (ρ) [g/cm^3]**	**ΔH$_f$ [kJ/mol]**	**Oxygen balance [%]**
1,3,5-Tris-(trinitromethyl)benzene	113 [39]	1.90 [39]	355.22 [39]	-4.57
1,3-Bis-(trinitromethyl)benzene	65 [39]	1.73 [39]	147.28 [39]	-25.52

1.7. *N*-Alkyl-2,4,6-trinitroanilines and *N*-alkyl-*N*-nitro-2,4,6-trinitroanilines

In **Figure 7** are depicted the molecules of *N*-alkyl-2,4,6-trinitroaniline and *N*-alkyl-*N*-nitro-2,4,6-trinitroaniline, which properties are summarized in **Table 5**.

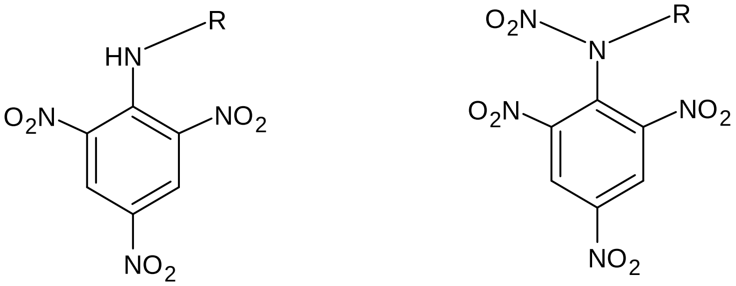


Figure 7: *N*-Alkyl-2,4,6-trinitroaniline and *N*-alkyl-*N*-nitro-2,4,6-trinitroaniline

Table 5: Selected physical properties of *N*-alkyl-2,4,6-trinitroanilines and *N*-alkyl-*N*-nitro-2,4,6-trinitroanilines

Compound	**R**	**Melting point [^{o}C]**	**Density (ρ) [g/cm^3]**	**ΔH_f [kJ/mol]**	**Oxygen balance [%]**
N-Allyl-2,4,6-trinitroaniline	Allyl	80 [40]	1.55 [41]	-	-95.46
N,2,4,6-Tetranitrobenzenamine	H	-	1.94 [41]	-	-
N-Ethyl-*N*-nitro-2,4,6-tetranitroaniline	Ethyl	95.8 [42]	1.63 [26]	-20.08 [33]	-61.09
N-Propyl-*N*-nitro-2,4,6-trinitroaniline	Propyl	98 [43]	1.64 [41]	-	-73.60
N-Isopropyl-*N*-nitro-2,4,6-trinitroaniline	Isopropyl	108 [40]	1.56 [40]	-	-
N-Butyl-*N*-nitro-2,4,6-trinitroaniline	Butyl	97.8-98 [44]	1.58 [41]	-	-85.05
N-Isobutyl-*N*-nitro-2,4,6-trinitroaniline	Isobutyl	110 [40]	1.57 [41]	-	-

1.8. Alkylnitroguanidines

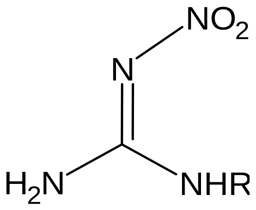


Figure 8: Alkylnitroguanidine

N-Alkyl-*N'*-nitroguanidines (**Figure 8**) were described in two papers in 1926 and 1927 by Davis, where they were obtained by heating nitroguanidine to 60-70ºC, which led to its decomposition reversibly to nitrocyanamide with the release of ammonia molecules [45, 46]. The alkyl-substituted nitroguanidine was a product of the introduction of the aliphatic amine to the reaction mixture.

The attachment of the alkyl chain to the nitroguanidine molecule introduces steric hindrance, which partially disrupts the interactions between the atoms involved in the formation of hydrogen bonds. This interaction leads to a reduction of the crystal lattice; therefore, the melting point becomes lower. The saturated alkyl chains tend to intensify the vibrations of the molecule under the influence of temperature increase, which additionally promotes the formation of liquid phase at low temperatures. The lowest melting point range is recorded for the *N*-butyl derivative (84-85ºC), however, *N*-propyl-nitroguanidine with a melting point of 98ºC, has a better oxygen balance, which leads to higher detonation parameters. Due to these properties, *N*-propyl-nitroguanidine is considered an ingredient of melt-cast explosive compositions that could replace Composition B [47]. Alkylnitroguanidines with melting points lower than 120ºC are shown in **Table 6**.

Table 6: Selected physical properties of alkylnitroguanidines

Compound	R	Melting point [°C]	DTA (start of decomposition [°C]	Density (ρ) [g/cm^3]	ΔH_f [kJ/mol]	Oxygen balance [%]
AllNQ	Allyl	105 [48]	183.2 [48]	1.19 [48]	-	-111.01
PrNQ	Propyl	96,5–99 [48]	188.7 [48]	1.35 [48]	-2882.00 [49]	-120.42
BuNQ	Butyl	81–83 [48]	195.9 [48]	1.31 [48]	-3535.00 [49]	-139.84
iBuNQ	Isobutyl	115–120 [48]	187.2 [48]	1.18 [48]	-	-139.84
PeNQ	Pentyl	95–99 [48]	191.6 [48]	1.19 [48]	-	-156.14
HeNQ	Hexyl	109–112.5 [48]	199.4 [48]	1.12 [48]	-	-170.01

1.9. DNDA compounds

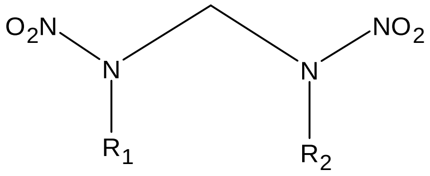


Figure 9: General formula of methylene dinitrodiaza compounds (DNDA)

Propellants typically include a polymeric binder as a structural base, which generally can be nitrocellulose. In the past, plasticizers only had the function to facilitate the propellant manufacturing, and the best-known and most employed plasticizers were nitroglycerine (NG) and diethylene glycol nitrate (DEGN). In the present day, studies are conducted to develop plasticizers that contribute to the combustion of propellants, which can be done by including a mixture of three dinitramines (DNDA57) in the nitrocellulose and RDX-based propellants (DNDA molecule, **Figure 9**). This mixture is composed of three different types of molecules: 2,4-dinitro-2,4-diazapentane (DNDA5, R_1, R_2=Me), 2,4-dinitro-2,4-diazahexane (DNDA6, R_1=Me, R_2=Et), and 3,5-dinitro-3,5-diazaheptane (DNDA7, R_1, R_2=Et), which are summarised in **Table 7** [50]. These linear nitramines can be used as plasticizing or filling agents for double base powders, solid rocket propellants, gas generating, and pyrotechnic compositions. DNDA5 has a low melting point, can plasticize nitrocellulose, and is soluble in nitroglycerine [51].

Table 7: Selected physical properties of methylene dinitrodiaza compounds

Compound	**R**	**Melting point [ºC]**	**Density (ρ) $[g/cm^3]$**	**ΔH_f [kJ/mol]**	**Oxygen balance [%]**
2,4-Dinitro-2,4-diazapentane (DNDA5)	$R_1=R_2=$ Methyl	54 [52]	1.48 [53]	-51.5 [54]	-58.49
3,5-Dinitro-3,5-diazaheptane (DNDA7)	$R_1=R_2=$ Ethyl	74-75 [52]	1.38 [55]	-135.10 [56]	-99.91
N-Ethyl-*N′*-methyl-*N,N′*-dinitromethanediamine	R_1=Methyl R_2=Ethyl	32-33 [52]	1.42 [55]	-	-80.8

1.10. Geminal dinitro compounds

Figure 10: Geminal dinitro structure and structural formula of 1,3,3-trinitroazetidine

Probably the most popular compound of the group, introduced in **Table 8**, is considered to be 1,3,3-trinitroazetidine (TNAZ) (**Figure 10**). With its geminal dinitro groups, TNAZ was anticipated to be an alternative melt-cast explosive to the well-known TNT. Its advantages are the low melting point of 101ºC and the good thermal stability to up to 252ºC. It was first synthesised by Archibald et al. in 1990, as he states it to be the simplest compound of its class [57]. The melting point of TNAZ enables the processing of formulations on modified production lines and has explosive performance approximately 30% greater than that of TNT. It is also reported that TNAZ is less vulnerable than most nitramines, is soluble in molten TNT, is compatible with different materials such as aluminium, steel, brass, and glass. TNAZ is attractive as a near-term candidate component for explosives or propellants with low sensitivity, good stability, and enhanced performance, although there are some challenges regarding its efficient and environmentally benign methods for large-scale production. It is suggested that TNAZ has great promise for technological advances in ammunition if the cost of production and the chemical volatility can be reduced to some extent [58].

Table 8: Selected physical properties of geminal dinitro compounds

Compound	**Melting point [^{0}C]**	**Boiling point [^{0}C]**	**Density (ρ) [g/cm^3]**	**ΔH$_f$ [kJ/mol]**	**Oxygen balance [%]**
1,7-Diazido-2,2,4,6,6-pentanitro-4-azaheptane	105.5 [59]	196.3 [60]	1.83 [59]	553.54 [60]	-23.52
1,9-Diazdio-2,2,8,8-tetranitro-4,6-dioxanonane	46.6 [61]	227.3 [60]	1.64 [62]	164.18 [60]	-35.53
1-*N*-nitramino-1'-carboimidoyl(3,3-dinitro)-1-azetidine	104 [63]	213 [63]	1.75 [63]	33.47 [63]	-34.17
1,3,3-Trinitroazetidine (TNAZ)	101 [64]	252 [65]	1.70 [66]	26.82 [67]	-16.66

1.11. Dinitroazido compounds

The azido group in the molecule increases the nitrogen content and enhances the explosive properties. Four aromatic azido-nitro compounds that meet the criteria are shown in **Table 9**.

Table 9: Selected physical properties of dinitroazido compounds

Compound	**Melting point [^{0}C]**	**Density (ρ) [g/cm^3]**	**ΔH$_f$ [kJ/mol]**	**Oxygen balance [%]**
1-Azido-2,4-dinitrobenzene	66 [28]	1.52 [29]	269.87 [28]	-72.68
2-Azido-1,3-dinitrobenzene	80 [28]	1.72 [29]	269.87 [28]	-72.68
1-Azido-3,5-dinitrobenzene	96 [28]	1.58 [29]	269.87 [28]	-72.68
2-Azido-4,6-dinitrophenol	64 [28]	1.65 [29]	40.17 [28]	-60.41

1.12. Nitroso compounds

1-Nitroso-3,3-dinitroazetidine (NDNAZ) is regarded to be the main condensed product of the decomposition of TNAZ. Moreover, Shukla et al. (2004) claim that the eutectic mixtures of the two compounds, TNAZ and NDNAZ, are considered as new energetic materials with high-energy contents, a possible replacement for HMX and TNT [68]. The group of TNAZ and cyclomethylene trinitrosamine is summarised in **Table 10**.

Table 10: Selected physical properties of nitroso compounds

Compound	**Melting point [⁰C]**	**Boiling point [⁰C]**	**Density (ρ) [g/cm^3]**	**ΔH$_f$ [kJ/mol]**	**Oxygen balance [%]**
1-Nitroso-3,3-dinitroazetidine	104 [63]	213 [63]	1.75 [63]	95.05 [63]	-27.26
Cyclotrimethylene trinitrosamine	105-107 [69]	-	1.50 [26]	285.85 [70]	-55.13

1.13. Pyridine derivatives

Six-membered heterocyclic compounds are represented by nitro-pyridine derivatives (**Table 11**).

Table 11: Selected physical properties of pyridine derivatives

Compound	**Melting point [⁰C]**	**Boiling point [⁰C]**	**Density (ρ) [g/cm^3]**	**ΔH$_f$ [kJ/mol]**	**Oxygen balance [%]**
2-(Methylnitramino)-3,5-dinitropyridine	121 [71]	190 [72]	1.70 [71]	93.93 [71]	-55.93
2-(Nitratoethylamino)-3,5-dinitropyridine	73 [73]	193 [73]	1.65 [73]	-26.36 [73]	-61.5
2-(Nitratoethylamino)-5-nitropyridine	103 [73]	204 [73]	1.55 [73]	-26.36 [73]	-91.16
Py-NENA	99 [73]	164 [74]	1.77 [75]	-6.28 [74]	-40.23
2-(Trinitromethyl)pyridine	72 [39]	-	1.62 [39]	-44.35 [39]	-56.11
4-(Methylnitramino)-3,5-dinitropyridine	103 [71]	210 [72]	1.68 [71]	114.27 [71]	-55.93

1.14. Triazoles and tetrazoles

The development of tetrazol, triazol (**Table 12**), pyrimidine, and other energetic heterocyclic compounds is an ongoing area of interest due to their vast possible application in civil and military areas. Tetrazoles combine high nitrogen content and good thermal stability because of their aromatic ring system. 5-Azido-1*H*-tetrazole is a member of this group that has extremely high and unpredictable explosive character. Despite that, it is said to have found application in effective precursors for carbon nanospheres and carbon nitride nanomaterials, in solid fuels in micropropulsion systems, in gas generators, and in smoke-free pyrotechnic fuels. The compound has high density, good thermal stability, and high positive heat of formation [76].

Table 12: Selected physical properties of triazoles and tetrazoles

Compound	**Melting point [^{o}C]**	**Boiling point [^{o}C]**	**Density (ρ) [g/cm^3]**	**ΔH_f [kJ/mol]**	**Oxygen balance [%]**
5-(4-Nitrofurazan-3-yl)-1,2,3-triazolo(4,5-c) furazan	35 [77]	160-165 [78]	1.87 [79]	842.66 [79]	-28.56
5-Cyano-1*H*-tetrazole	99 [80]	-	1.59 [29]	402.00 [70]	-75.74
5-Azido-1*H*-tetrazole	78 [81]	-	1.67 [82]	458.15 [82]	-36.01
2-Methyleneamine-5-nitrotetrazole	74 [29]	-	1.60 [29]	276.02 [29]	-44.41
2-(Dinitromethyl)-5-nitrotetrazole	105 [83]	-	1.90 [83]	302.00 [83]	10.95
5-Nitrotetrazole	101 [84]	-	1.75 [29]	26.66 [85]	-6.95

1.15. Furazan derivatives

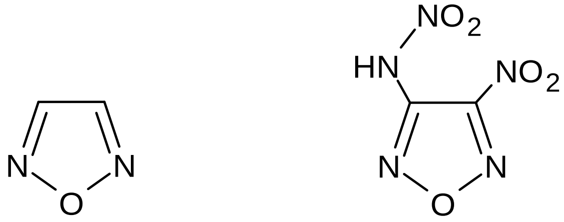


Figure 11: Furazan and 3-nitramino-4-nitrofurazan structures

Aminofurazans (**Figure 11**) are promising compounds that could be used as backbones for the synthesis of energetic materials. 3-Nitramino-4-nitrofurazan has improved energetic properties due to the introduction of the energetic nitramino group. It has good detonation performance, but unfortunately is hygroscopic, has low thermal stability, and high sensitivity to external stimuli. One suggested method to enhance the stability of this compound is to form energetic salts that exhibit high densities and can be used as ingredients in propellants, explosives, or pyrotechnic compositions [86]. 3-Nitramino-4-nitrofurazan and other suitable furazan derivatives are summarised in **Table 13**.

Table 13: Selected physical properties of furazan derivatives

Compound	Melting point [^{o}C]	Boiling point [^{o}C]	Density (ρ) [g/cm^3]	ΔH_f [kJ/mol]	Oxygen balance [%]
3-(4-Nitrofurazan-3-*NNO*-azoxy)-4-(4-nitrofurazan-3-azo)-furazan	70 [87]	-	1.79 [88]	1156.88 [88]	-17.38
3,4-Bis(4-nitrofurazan-3-*NNO*-azoxy)-furazan	85 [87]	-	1.89 [88]	1089.93 [88]	-12.49
3-Nitramino-4-nitrofurazan	60 [89]	101 [89]	1.93 [89]	251.04 [89]	4.57
Azo-bis(nitrofurazanylazo)furazan	85 [90]	-	1.76 [90]	1732.18 [90]	-28.56
Dinitro-difurazan	85 [91]	250 [91]	1.85 [88]	422.58 [79]	-14.03
Dinitroazofurazan	56 [77]	180 [90]	1.73 [88]	704.59 [92]	-12.49

1.16. Furoxan derivatives

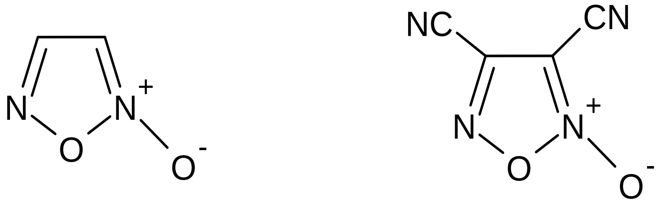


Figure 12: Structure of furoxan unit and 3,4-dicyanofuroxan

Furoxans (oxadiazoles) (**Figure 12**) exhibit a high enthalpy of formation and good thermal stability. The presence of active oxygen increases the energy capacity of the molecule, and the chemical properties of the compounds make it easy to introduce groups containing high-energy bonds that are able to increase the total energy of the molecule. 3,4-Dicyanofuroxan (**Figure 12**) represents an intermediate in the organic synthesis of energetic materials, and is used in chemical ignition systems, due to its ability to spontaneously ignite upon contact with rocket fuel components [93]. Furoxan derivatives are shown in **Table 14**.

Table 14: : Selected physical properties of furoxan derivatives

Compound	**Melting point [ºC]**	**Boiling point [ºC]**	**Density (ρ) [g/cm^3]**	**ΔH$_f$ [kJ/mol]**	**Oxygen balance [%]**
3,4-Dicyanofuroxan	42 [79]	200 [28]	1.58 [94]	465.26 [79]	-70.55
3-Methyl-4-nitrofuroxan	67.5 [26]	-	1.66 [95]	100.83 [85]	-38.6
4,4'-Dinitratomethyl-azoxyfuroxan	102 [79]	-	1.85 [79]	347.27 [96]	-13.18
4-Nitrofuroxan-3-carbonitrile	48 [79]	-	1.83 [79]	380.74 [79]	-20.5
Bis(4-nitrofurazan)-furoxan	108 [97]	-	1.88 [79]	642.24 [79]	-20.5
6-Nitro-5-azidobenzofuroxan	89 [28]	-	1.65 [29]	459.82 [28]	-64.83

1.17. Nitrates

The introduction of alkyl and nitro groups into the structure of different molecule skeletons like imidazole, tetrazole, or triazole ring can decrease the melting point and improve the oxygen balance, thus making suitable melt-cast explosives (**Table 15**). An example of such molecules are the 4-amino-1,2,4-triazolium nitrate (4-ATN) and 1-methylimidazolium nitrate, which are regarded as ionic liquids. Ionic liquids are low-melting salts that melt at or below 100ºC, normally composed of a large asymmetric organic cation and an inorganic or organic anion. They have some unique advantages like high thermal stability, non-toxicity, ionic conductivity, and low vapour pressure. The energetic ionic liquids are considered to be environmentally friendly, low-melting, and thermally stable, and have emerged as a new class of energetic materials in recent years [98]. Energetic ionic liquids based on azoles can store a large amount of energy in N=N and N-N bonds, and by introducing a *N*-amino group, the thermal stability of the triazole ring can be increased. 1-Methylimidazolium nitrate is of great industrial importance because it is one of the major green solvents. 4-Amino-1,2,4-triazolium nitrate is an energetic and non-sensitive ionic liquid which is stated to be a good candidate for the replacement of TNT in melt-cast explosives. 4-ATN is expected to be suitable for mixtures with RDX and HMX [99].

Besides the organic nitrates mentioned, some inorganic nitrates and tetraalkylammonium nitrates meet the criteria of the melting point below 120ºC.

Table 15: Selected physical properties of nitrates

Compound	**Melting point [^{0}C]**	**Boiling point [^{0}C]**	**Density (ρ) [g/cm^3]**	**ΔH_f [kJ/mol]**	**Oxygen balance [%]**
Magnesium nitrate hexahydrate	89 [100]	147 [100]	1.41 [101]	-790.65 [102]	53.94
Bismuth nitrate pentahydrate	75 [24]	-	2.83 [24]	-	24.74
Nickel nitrate hexahydrate	56.7 [103]	-	2.05 [104]	-415.09 [102]	43.79
Iron(III) nitrate nonahydrate	47 [103]	-	1.68 [105]	-	-
Aluminium(III) nitrate nonahydrate	73.5 [24]	150 [24]	-	-3757.06 [102]	31.99
1-Methylimidazolium nitrate	67 [106]	-	1.25 [107]	-	-93.71
N-Methyl-*N*-(2-nitroxyethyl)ammonium nitrate	73 [108]	-	-	-	-39.32
1,2,3-Trimethylimidazolium nitrate	63 [109]	-	-	-	-
4-Amino-1,2,4-triazolium nitrate	70 [110]	-	1.62 [110]	-41.84 [111]	-38.07
Formamidine nitrate	89 [112]	-	-	-	-22.42
Tetrabutylammonium nitrate	119 [113]	-	-	-	-
Tetrapentyammonium nitrate	114 [113]	-	-	-	-
Tetrahexylammonium nitrate	72 [113]	-	-	-	-
Heptyl(trihexyl)ammonium nitrate	72 [113]	-	-	-	-

1.18. Perchlorates

Perchlorates (**Table** *17*), as well as the nitrate anions, can be paired with nitroazoles to form low-melting energetic materials that are possible to be cast at moderate processing temperatures. The energetic salts have the advantage over non-ionic molecules because of their lower vapour pressure and higher densities [5]. 1,5-Diaminotetrazole is a compound with a very high content of nitrogen in its molecule that has a high enthalpy of formation and high density. It reacts with some acids, forming stable salts that are promising components of gas-generating compositions and solid propellants [114]. Its salt 1,5-diaminotetrazole perchlorate has a melting point of 113^{0}C and a reported density of 1.79 g/cm^3 [29]. Another energetic ionic liquid is the

4-amino-1,2,4-triazolium perchlorate (4-ATP), which possesses a high density and high heat of formation, as well as a melting point below 84°C, which is close to TNT. It can be used alone or like a eutectic or near eutectic mixture with other triazolium salts for melt-cast explosives. Other minor ingredients, like stabilisers, desensitisers, or traditional explosive compounds for further enhancement of the explosive performance, may also be incorporated. In **Table *16*** are shown several eutectic mixtures of 4-ATP.

Table 16: Eutectic mixtures with 4-ATP

Components	Ratio
4-ATP/ 4-ATN	70/ 30
4-ATP/ 4-ATN	30/ 70
4-ATP/ TP	30/ 70

The eutectic mixtures mentioned, 4-ATP/ 4-ATN (70/ 30) and 4-ATP/ 4-ATN (30/ 70), have significantly lower melting points, 67ºC and 66ºC, respectively, in comparison to the single salt 4-ATP with a melting point of 84ºC [115]. 4-ATN has an extremely low sensitivity while 4-ATP possesses high sensitivity and also high energy. 4-ATP/ 4-ATN (70/ 30) eutectic contains more triazolium perchlorate salt and has better detonation performance, which makes it better for potential substitution of TNT as a high-energy melt-cast explosive carrier [116].

Table 17: : Selected physical properties of perchlorates

Compound	**Melting point [^{0}C]**	**Boiling point [^{0}C]**	**Density (ρ) [g/cm^3]**	**ΔH_f [kJ/mol]**	**Oxygen balance [%]**
1,5-Diaminotetrazole perchlorate	113 [29]	-	1.79 [29]	137.99 [29]	0
2-Azidoethylamine perchlorate	90.2 [117]	225.2 [117]	1.68 [117]	45.56 [117]	-25.73
4-Amino-1,2,4-triazolium perchlorate	84 [110]	210 [110]	1.81 [110]	29.00 [29]	-17.34
Triaminoguanidine perchlorate	115 [118]	-	1.67 [118]	36.32 [118]	-15.64
Tetrahexylammonium perchlorate	110 [113]	-	-	-	-
Heptyl(trihexyl)ammonium perchlorate	103 [113]	-	-	-	-
Diheptyl(dihexyl)ammonium perchlorate	105 [113]	-	-	-	-
Tetraheptylammonium perchlorate	126 [113]	-	-	-	-

1.18. Fluorinated compounds

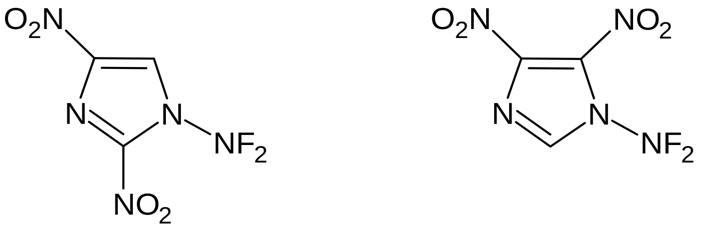


Figure 13: Structural formulas of 1-difluoroamino-2,4-dinitroimidazole and 1-difluoroamino-4,5-dinitroimidazole

Two difluoroamines with both nitro and difluoroamino groups (**Figure 13**) meet the criteria of this study. The compounds have high density and enthalpy of formation. In this case, hydrogen fluoride is present in the explosive reaction products. It is known that hydrogen fluoride is toxic and highly acidic, potentially causing harm to human health and the environment [49]. Fluorinated compounds are shown in **Table 18**.

Table 18: Selected physical properties of fluorinated compounds

Compound	Melting point [⁰C]	Boiling point [⁰C]	Density (ρ) [g/cm^3]	ΔH$_f$ [kJ/mol]	Oxygen balance [%]
1-Difluoroamino-2,4-dinitroimidazole	70 [119]	-	1.92 [119]	117.15 [119]	-11.48
1-Difluoroamino-4,5-dinitroimidazole	62 [119]	-	1.91 [119]	114.41 [119]	-11.48

1.19. Other compounds

In **Table *19***, other compounds with suitable parameters for this study are shown. Different nitrimines are of interest as explosives and components of propellants, with one such being 2-nitroguanidine, regarded as an insensitive high explosive. Its derivative 1-methyl-1,2-dinitroguanidine has higher energetic parameters due to the second nitro group in the molecule. Also, it has a low impact sensitivity level (on the level of TNT) and can be comparable to RDX detonation parameters [120].

Another suitable compound is considered to be triaminoguanidine dinitramide (TAGDN), which is a dinitramide salt with a high heat of formation. It is reported to have high sensitivity to friction and impact and thus considered too sensitive to be used in solid propellants [121].

Various hydrazinium azides are considered of general interest as a solid-fuel gas generator [122], [123]. The authors report good impact and friction sensitivity. A commonly used precursor is considered hydrazoic acid, which has the disadvantages of high toxicity and extreme sensitivity. Another mentioned energetic salt containing hydrazinium cation and dinitramide anion is the hydrazinium dinitramide, which has received attention for its high oxygen balance and high energy content. Moreover, it has high thermal stability and low hygroscopicity, which makes it suitable for the role of oxidiser in propellants [124].

Table 19: Selected physical properties of other suitable compounds

Compound	Melting point [⁰C]	Boiling point [⁰C]	Density (ρ) [g/cm^3]	ΔH$_f$ [kJ/mol]	Oxygen balance [%]
1-Methyl-1,2-dinitroguanidine	81 [120]	-	1.64 [120]	-6.61 [120]	-25.54
Triaminoguanidine dinitramide (TAGDN)	85 [125]	160 [125]	1.57 [125]	182.92 [79]	-18.94
Nitroguanyl azide	79 [126]	-	1.61 [29]	298.32 [70]	-12.3
Hydrazinium azide	75.4 [24]	-	1.42 [127]	246.96 [127]	-53.28
Hydrazinium dinitramide	83 [128]	-	1.83 [129]	-33.47 [129]	17.26
N,*N*-Bis(azidomethyl)-ethylenedinitramine	76 [130]	-	1.58 [130]	553.54 [131]	-49.2
2,4,6-Tris(methylnitramino)-1,3,5-triazine (TMNT)	114 [72]	210 [72]	1.64 [72]	275.10 [72]	-55.41
4,6-Bis(2-nitratoethylnitramino)-5-nitropyridine (Pm-NENA)	87 [132]	154 [132]	1.81 [132]	-8.33 [132]	-32.13
5,5'-Bis(azidomethyl)-3,3'bis(1,2,4-oxadiazole)	67 [133]	-	1.70 [133]	1011.69 [133]	-77.37

1.20. Compounds with allyl and vinyl groups

Compounds with allyl and vinyl groups have a double bond and may be used for 3D printing, followed by polymerisation, obtaining a solid material. The polymerisation can be initiated by UV light in the presence of a suitable catalyst. Some picrates, picryl allyl amine, allylnitroguanidine, reported in previous chapters, are included in **Table *20***.

Table 20: Selected physical properties of low melting monomers

Compound	Melting point [⁰C]	Boiling point [⁰C]	Density (ρ) [g/cm^3]	ΔH$_f$ [kJ/mol]	Oxygen balance [%]
1-Vinyl-3-methylimidazolium nitrate	70 [134]	155 [134]	1.41 [134]	-56 [134]	-
Allyl 3,5-dinitrobenzoate	49-50 [135]	-	1.41 [41]	-	-114.20
Diallylamine picrate	76 [38]	-	-	-	-117.69
N-Allyl-2,4,6-trinitroaniline	80 [40]	1.55 [41]	-	-	-95.46
Allylnitroguanidine	105 [48]	183.2 [48]	1.19 [48]	-	-111.01

2. Experimental part

2.1. Instruments and analytical methods used

2.1.1. Melting point

Melting points were measured on a Kofler block, manufactured by Nagema, GDR, without prior calibration.

2.1.2. Elemental analysis

Elemental analysis (C, H, N) was performed on an automatic elemental analyser Vario MICRO Cube from Elementar (Langenselbold, Germany). The operation was in CHNS mode with a basic calibration for sulfanilamide, sample weights were 1–2 mg.

The chlorine content was determined by titration with mercuric hydroxycyanide, according to Schöniger, at the Institute of Organic Chemistry and Technology, University of Pardubice.

2.1.3. Differential thermal analysis (DTA)

The differential thermal analysis (DTA) records were obtained by measuring on a DTA 550Ex instrument, manufactured by OZM Research. The samples were in limited contact with the air atmosphere, and the heating rate was 5°C.min^{-1}. Sample weights for analysis were 30 mg.

2.1.4. FTIR and Raman spectrometry

Infrared spectra (FTIR) were measured on a Nicolet iS50 FT-IR instrument (Thermo Scientific), using a single-reflection diamond ATR attachment. Measurements were performed in the range 4000–400 cm^{-1}, the number of scans was 64, and the resolution was 4 cm^{-1}. The Omnic 9 program (Thermo Scientific) was used to operate the instrument and work with the spectra.

Raman spectra were measured on a Nicolet iS50 instrument with a Raman iS50 attachment, resolution 4 cm^{-1}, number of scans 128. For the measurement of isotopically labeled substances, the resolution was 42 cm^{-1}, and the number of scans was 256. Laser power was in the range of 200–500 mW and wavelength λ=1064 nm. Omnic 9 (Thermo Scientific) was used to operate the instrument and work with spectra.

Abbreviations related to infrared and Raman spectra: s – strong, m – medium, w – weak, ν – stretching vibration, δ – deformation vibration, as/ asym – asymmetric, s/ sym – symmetric.

Characteristic bands are reported; their assignment was provided with the help of the Socrates handbook [136].

2.1.5. Density

A Micrometrics AccuPyc II 1340 gas helium pycnometer (MJ Micromeritics, Norcross, USA) was used to determine the density. Sample weights ranged from 0.2-2 g, weighed to four decimal places. After the sample temperature in the pycnometer stabilised, the density was measured, and the measurement temperature was recorded. For each substance, 10 measurement cycles were measured, and the resulting density is their average value.

2.1.6. Thin layer chromatography (TLC)

TLC glass plates (Adamant UV254) with silica-based fixed phase were used for thin layer chromatography. The mobile phase was hexane: acetone: chloroform 3:2:1. The substances were detected by UV radiation at a wavelength of 254 nm.

2.1.7. Vacuum stability test

A vacuum stability tester, provided by OZM, was used. The weight of the samples was 200 mg, and the temperature was 90°C.

2.1.8. Sensitivity to impact and friction

Sensitivity to impact was measured using the Kast fall hammer. The measurement apparatus and related supplies were manufactured by OZM Research (Hrochův Týnec, Czech Republic). A 5 kg hammer was used for the synthesised compounds, except for 4-amino-1,2,4-triazolium perchlorate, for which a 0.5 kg hammer was used. Testing sets comprised steel guide rings BFH-SR and steel cylinders BFH-SC. Method 0/6 was used for evaluation of the highest energy level, where no activation of the sample occurs [137].

Sensitivity to friction was determined using a BAM apparatus type FSA-12. Testing sets comprised porcelain BFST Pt 100 25x25 mm plates and porcelain BFST Pn 200 pegs. The measurement apparatus and related supplies were manufactured by OZM Research (Hrochův Týnec, Czech Republic). Method 0/6 was used for evaluation of the highest energy level, where no activation occurs [137].

2.2. Chemicals and starting materials

Acetone (G. R., Penta), allyl alcohol (for synthesis, Sigma-Aldrich), allylamine (98%, Aldrich), bismuth(III) nitrate pentahydrate (98%, Aldrich), butylamine (for synthesis, Sigma-Aldrich), chloroform (stabilized with ethanol A. G., Penta), diallylamine (99%, Sigma-Alrdich), dichloromethane (A. G., Penta), diethylamine (≥99.5%, Sigma-Aldrich), diethyl ether (A. G., Lach-Ner), dipropylamine (99%, Sigma-Aldrich), DNDA5 (IEM [138, 139]), ethylnitramine (IEM, [140]), formamidine acetate (99%, Alfa Aesar), hexane (99% A. G., Penta), hydroquinone (for synthesis, Sigma-Aldrich), iron(III) nitrate nonahydrate (A. G., Penta), magnesium(II) nitrate hexahydrate (A. G., Lach-Ner), magnesium sulfate (pure, Lach-Ner), methanol (A. G., Penta), *N*-Ethyl-*N*-nitro-2,4,6-trinitroaniline (IEM [141]), nickel(II) nitrate hexahydrate (99%, Acros organics), nitric acid (65+% A. G., Penta), nitric acid fuming (98%, Penta), paraformaldehyde (Chemanol), perchloric acid (70%, VWR Chemicals), picric acid (≥98%, Aldrich), potassium bicarbonate (A. G., Penta), propylamine (99+%, Thermo scientific), rubidium nitrate (99%, Alfa Aesar), sulfuric acid (96%, Lach-Ner), urea (pure, Lach-Ner), 1-chloro-2,4,6-trinitrobenzene (IEM [142, 143], m.p. 82ºC), 1-methylimidazole (≥99%, purified by redistillation, Sigma-Aldrich), 2-(methylamino)ethanol (≥98%, Sigma-Aldrich), 3,5-dinitrobenzoyl chloride (≥96.5%, Sigma-Aldrich), 4-amino-4*H*-1,2,4-triazole (for synthesis, Apollo Scientific).

2.3. Safety

The substances being prepared are explosives sensitive to impact, friction, and thermal stimuli. It is necessary to wear goggles or a safety shield, gloves, ear protection, and appropriate clothing when working in the laboratory. Efforts must be made to eliminate the formation of electrostatic sparks. Work with volatile, flammable, corrosive, toxic, or otherwise dangerous substances must be carried out in a ventilated fume hood. All reactions are carried out in an apparatus placed in a ventilated and closed fume hood.

2.4. *N*-Alkyl-*N*-nitro-2,4,6-trinitroanilines and *N*-alkyl-2,4,6-trinitroanilines

The preparation procedure was modified based on the description of the preparation of *N*-methyl-*N*-nitro-2,4,6-($^{15}N_3$)-trinitroaniline according to Franchimont and Jalovy et al [43, 144].

2.4.1. *N*-Propyl-2,4,6-trinitroaniline

The chemical equation of the preparation is shown in **Figure 14**.

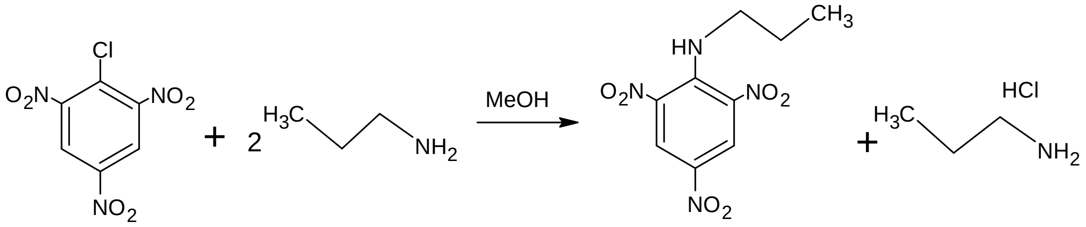


Figure 14: Reaction of 1-chloro-2,4,6-trinitrobenzene and propylamine to *N*-propyl-2,4,6-trinitroaniline

1-Chloro-2,4,6-trinitrobenzene (5.5 g, 0.02 mol) was dissolved in a 50 ml methanol and 5 ml water mixture. Propylamine (2.7 g, 0.04 mol) was added to the solution and stirred for 60 minutes with heating (40-50ºC) and reflux. The mixture was then cooled and filtered to yield 1.0 g (19%) of yellow solid.

2.4.2. *N*-Propyl-*N*-nitro-2,4,6-trinitroaniline

The chemical equation of the preparation is shown in **Figure 15**.

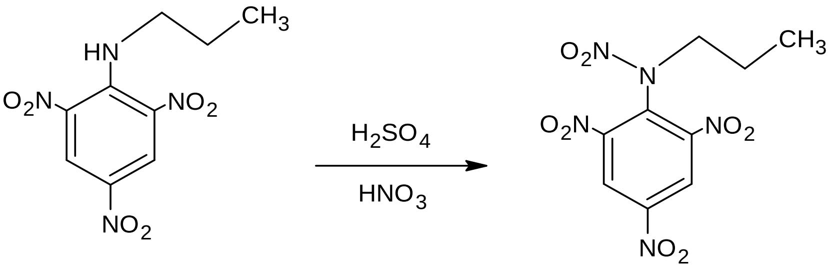


Figure 15: Nitration of *N*-propyl-2,4,6-trinitroaniline

N-Propyl-2,4,6-trinitroaniline (1.0 g, 0.0037 mol) was dissolved in 96% sulfuric acid (4.5 g, 0.0457 mol) at 5-10ºC and stirred for 15 minutes. Then, a mixture of nitric acid (0.47 g, 0.0074 mol) and sulfuric acid (2.0 g, 0.0203 mol) was slowly added. The temperature was kept 5-10ºC for 30 minutes. After that, the mixture was poured onto 33 ml of ice-water.

The product was filtered and washed with water to yield 0.85 g (73%) of the bright yellow solid. M.p. 97ºC (lit. 98ºC [43]). Anal. *Calc.* for $C_9H_9N_5O_8$ (%): C 34.29, H 2.88, N 22.22. *Found*: C 34.20, H 2.85, N 21.84. Density: 1.61 g/cm^3 (lit. 1.64 g/cm^3 [41]). FTIR (cm^{-1}): 3087m (ν CH arom.), 3069m-w (ν CH arom.), 3017w (ν CH arom.), 2965m-w (ν CH_2,CH_3), 2937m-w (ν CH_2,CH_3), 2877 (ν CH_2), 1607m (CC arom.), 1537s ($\nu_{as}$$NO_2$), 1466m-w ($\delta$ CH_2), 1381w (δ CH_3), 1337s (ν_s NO_2), 1314s (ν_s NO_2), 1273s (ν_s NNO_2). Raman (cm^{-1}): 3091m-w (ν CH arom.), 3068 m-w (ν CH arom.), 2984m (ν_{as} CH_3), 2969m (ν CH_2,CH_3), 2941m-w (ν CH_2,CH_3), 1617m ν_{as} (NNO_2), 1605 (ν_{as} NO_2), 1552m (ν_{as} NO_2), 1361s (ν_s NO_2), 1083w-m (propyl), 826m (δ NO_2).

The same procedure was done with temperatures around 40-50ºC, but a liquid oily phase resulted, and the crystallised product could not be obtained.

2.4.3. *N*-Butyl-2,4,6-trinitroaniline

The chemical equation of the preparation is shown in **Figure 16**.

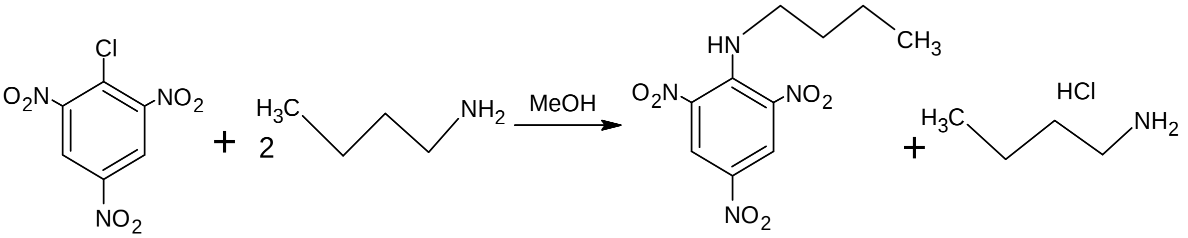


Figure 16: Reaction of 1-chloro-2,4,6-trinitrobenzene and butylamine to *N*-butyl-2,4,6-trinitroaniline

1-Chloro-2,4,6-trinitrobenzene (5.5 g, 0.02 mol) was dissolved in 50 ml methanol and 5 ml water mixture. Butylamine (2.9 g, 0.04 mol) was added to the solution and stirred for 60 minutes with heating under reflux. The mixture was then cooled and filtered to form solid and oily phases. The part with oily consistency was crystallised from methanol. Two yellow solid products were obtained – one filtered (0.70 g, 12%) and the oily crystallised from methanol (2.9 g, 51%).

2.4.4. *N*-Butyl-*N*-nitro-2,4,6-trinitroaniline

The chemical equation of the preparation is shown in **Figure 17**.

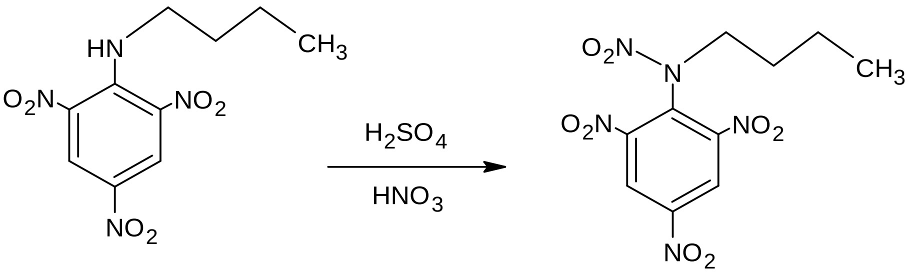


Figure 17: Nitration of *N*-butyl-2,4,6-trinitroaniline

N-Butyl-2,4,6-trinitroaniline (2.9 g, 0.01 mol) was dissolved in 96% sulfuric acid (14.8 g, 0.14 mol) at 5-10ºC and stirred for 15 minutes. Then, a mixture of nitric acid (1.29 g, 0.02 mol) and sulfuric acid (4.0 g, 0.04 mol) was slowly added. The temperature was kept 5-10ºC for 30 minutes. After that, the mixture was poured onto 94 ml of ice-water. The product was filtered and washed with water. A mixture of pasty consistency was formed at the end, which was washed with water, filtered, and washed again to a neutral pH reaction to yield 2.7 g (82%) of bright yellow solid. M.p. 97ºC (lit. 97.8-98ºC [44]). Anal. *Calc.* for $C_{10}H_{11}N_5O_8$ (%): C 36.48, H 3.37, N 21.28. *Found*: C 36.48, H 3.39, N 20.84. Density: 1.55 g/cm^3 (lit. 1.58 g/cm^3 [41]). FTIR (cm^{-1}): 3087m (ν CH arom.), 3069 (ν CH arom.), 2938m-w (ν CH_2,CH_3), 2878w-m (ν CH_2), 1607m (CC arom.), 1537s (ν_{as} NO_2), 1460m (δ CH_2), 1387 (δ CH_3), 1337s (ν_s NO_2), 1287 (ν_s NNO_2). Raman (cm^{-1}): 3088m (ν CH arom.), 2984m (ν CH_3), 2976m (ν CH_2,CH_3) 2943m (ν CH_2,CH_3), 2916m-w (ν CH_2,CH_3), 2879m (ν CH_2), 1617m (CC arom.),1552m (ν_{as} NO_2), 1459m (δ CH_2), 1386m-w (δ CH_3), 1361s (ν_s NO_2).

2.4.5. *N*-Allyl-2,4,6-trinitroaniline

The chemical equation of the preparation is shown in **Figure 18**.

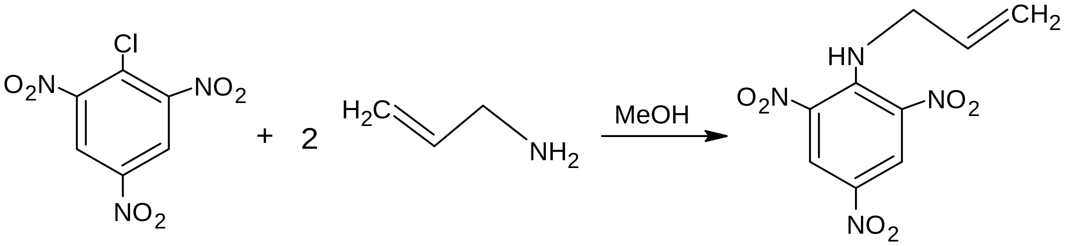


Figure 18: Reaction of 1-chloro-2,4,6-trinitrobenzene and allylamine to *N*-allyl-2,4,6-trinitroaniline

1-Chloro-2,4,6-trinitrobenzene (10 g, 0.04 mol) was dissolved in 91 ml methanol and 9 ml water mixture. Allylamine (4.6 g, 0.08 mol) was added to the solution and stirred for 60 minutes with heating at 40-50ºC and under reflux. The mixture was then cooled in an ice bath, and the precipitate formed was filtered; one part with oily consistency was crystallised from acetone and water with cooling. Two products were obtained, one filtered product (1) and one crystallised from acetone and water product (2). Yield (1): yellow crystalline solid (2.56 g, 24%). M.p. 78ºC (lit. 80ºC [40]). Anal. *Calc.* for $C_9H_8N_4O_6$ (%): C 40.30, H 3.01, N 20.89. *Found*: C 39.91, H 3.00, N 20.53. Density: 1.62 g/cm^3 (lit. 1.55 g/cm^3 [41]). FTIR (cm-^{1}): 3303m (ν NH), 3092mw (ν =CH$_2$), 3082mw (ν CH arom.), 3012m-w (ν CH arom.), 2933m-w (ν CH alif.), 1646 (ν C=C), 1613m (CC arom.), 1582m (CC arom.), 1552m-1525m-1505m (ν_{as} NO$_2$), 1361-1321 (ν_s NO$_2$). Raman (cm^{-1}): 3311w (ν NH), 3095-3085-3012 (ν CH unsat.), 2990m-2935m (ν CH sat.), 1646 (ν C=C), 1618m (CC arom.), 1585m (CC arom.), 1551m-w (ν_{as} NO$_2$), 1531m-w (ν_{as} NO$_2$), 1358-1344-1322m-s (CH2, CH), 1290 ($_{as}$ NO$_2$)
Yield (2): yellow solid (6.46 g, 60%). M.p. 76ºC (lit. 80ºC [40]). Anal. *Calc.* for $C_9H_8N_4O_6$ (%): C 40.30, H 3.01, N 20.89. *Found*: C 40.16, H 2.86, N 20.95. Density: 1.60 g/cm^3 (lit. 1.55 g/cm^3[41]).

2.5. 2,4-Dinitro-2,4-diazapentane (DNDA5)

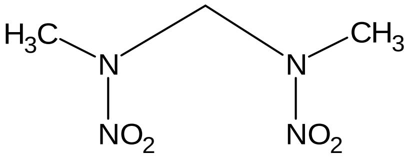


Figure 19: DNDA5 structure

The raw DNDA5 (**Figure 19**) [138, 139] was crystallised from methanol to give fine off-white crystals. M.p. 53ºC (lit. 54ºC [52]). Anal. *Calc.* for $C_3H_8N_4O_4$ (%): C 21.95, H 4.92, N 34.15. *Found*: C 22.28, H 4.93, N 33.89. Density: 1.48 g/cm^3 (lit. 1.48 g/cm^3 [53]). FTIR (cm^{-1}): 3037, 3025, 2992w-m (ν CH2, CH), 2925w-m (ν_s CH$_2$,CH$_3$), 1520, 1509m (ν_{as} NO$_2$), 1447m (δ CH$_2$), 1384w-m (δ CH$_3$), 1289s, 1242s (ν_s NO$_2$). Raman (cm^{-1}): 3038m (ν CH$_2$, CH$_3$), 2994, 2955m (ν CH$_3$), 2884w-m (ν CH$_2$), 1522s (ν_{as} NO$_2$), 1448m (δ CH$_2$), 1290m (ν_s NO$_2$).

2.6. 3,5-Dinitro-3,5-diazaheptane (DNDA7)

The chemical equation of the preparation is shown in **Figure 20**.

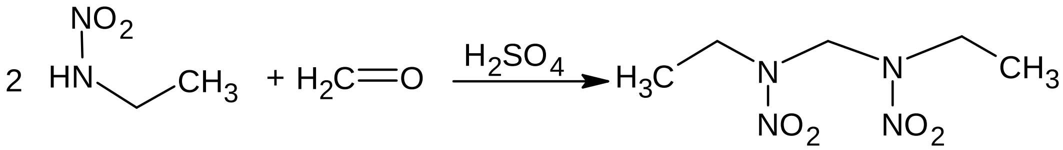


Figure 20: Preparation of 3,5-dinitro-3,5-diazaheptane

The preparation procedure was modified based on the description of Tartakovsky et al [139]. Paraformaldehyde (0.95 g, 0.0315 mol) was dissolved in 75% H_2SO_4 (15 ml) at 15-20°, and the reaction mixture was cooled to -4°C - 0°C. A mixture of ethylnitramine (5 g, 0.056 mol) and 2.5 ml CH_2Cl_2 was added slowly in small quantities to keep the temperature of the reaction mixture 0-5°C. After the addition, the reaction mixture was left to react for 30 minutes at temperatures below 5°C. The reaction mixture was then poured onto ice, filtered, and washed to neutral pH. The filtrate was extracted with dichloromethane (3 × 20 ml), the extract was washed with water (3 × 15 ml), dried with anhydrous magnesium sulfate, and the dichloromethane was allowed to evaporate overnight. The product was crystallised with a minimum quantity of methanol to yield 2.88 g (53%) of the fine white crystals. M.p. 74-75°C (lit. 74-75°C [50]). Anal. *Calc.* for $C_5H_{12}N_4O_4$ (%): C 31.25, H 6.3, N 29.16. *Found*: C 31.29, H 6.23, N 28.78. Density: 1.37 g/cm^3 (lit. 1.38 g/cm^3 [55]). FTIR (cm^{-1}): 3012, 2982-2968-2945-2853 (ν CH_2, CH_3), 2982w-m, 1525m (ν_{as} NO_2), 1460 (δ CH_2), 1444m (δ CH_2), 1384m-w (δ CH_3), 1295 (ν_s NO_2), 1274s (ν_s NO_2). Raman (cm^{-1}): 3012mw-2980-2941m-2880s (ν CH_3, CH_2), 1586w (νa_s NO_2), 1456m (δ CH_2), 1386m (δ CH_3), 1290m (ν_s NO_2).

2.7. Nitrates

2.7.1. Inorganic nitrates

For research purposes, the melting points and DTA thermograms were established for four suitable melt-cast inorganic nitrates.

$Fe(NO_3)_3.9H_2O$ M.p. 48°C (lit. 47°C [103]).

$Ni(NO_3)_2.6H_2O$ M.p. 55°C (lit. 56.7°C [103]).

$Bi(NO_3)_3.5H_2O$ M.p. 75°C (lit. 75°C [24]).

$Mg(NO_3)_2.6H_2O$ M.p. 89°C (lit. 89°C [100])

2.7.2. 1-Methylimidazolium nitrate

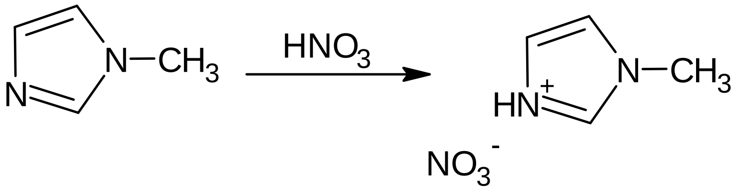


Figure 21: Preparation of 1-methylimidazolium nitrate

The preparation procedure was modified based on the description of the preparation of 1-methylimidazolium nitrate according to Bodor et al [145] (**Figure 21**).

Nitric acid (65%, 5.059 g, 0.08 mol) in 10 ml water was added to an aqueous solution of *N*-methylimidazole (4.089 g, 0.0498 mol) in 10 ml water at 0ºC. The reaction mixture was allowed to warm to room temperature. Water was then removed by rotary evaporator at 60ºC. Upon cooling the liquid down to room temperature, a white solid formed. It was washed with diethyl ether, filtered, and air-dried to yield 6.24 g (86%) of white crystalline solid. M.p. 65-66ºC (lit. 67ºC [106]). Anal. *Calc.* for $C_4H_7N_3O_3$ (%): C 33.10, H 4.87, N 28.96. *Found*: C 32.94, H 4.70, N 29.03. Density: 1.47 g/cm^3 (lit. 1.25 g/cm^3 [107]). FTIR (cm^{-1}): 3157m (ν NH), 3123m (ν NH), 3074-3030m (ν CH), 2822m (ν CH), 1623w (δ NH), 1380s-1341m-1323s-1284s ($\nu_{as.}$ NO_3^- and δ CH_3), 819m-s (δ NO_2) Raman (cm^{-1}): 3159m (ν NH^+), 3143m (ν NH^+), 2964m (ν CH_3), 2849m (ν CH_3), 1040s ($\nu_{s.}$ NO_3^-), 717m-w (δ NO_3^-).

2.7.3. *N*-Methyl-*N*-(2-nitroxyethyl)ammonium nitrate

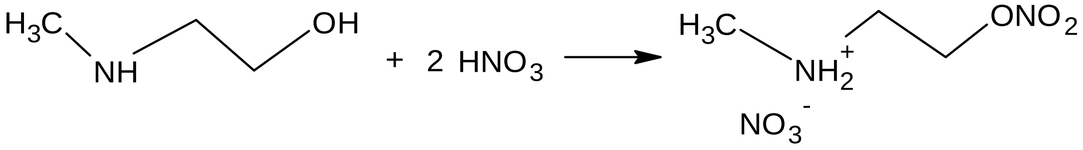


Figure 22: Preparation of 2-(methylamino)ethanol

The preparation procedure was based on the description of the preparation of *N*-methyl-*N*-(2-nitroxyethyl)ammonium nitrate according to Dániel Izsák and Thomas M. Klapötke [108] (**Figure 22**).

2-(Methylamino)ethanol (3.76 g, 0.05 mol) was added slowly to a 5ºC cold nitric acid (98%, 31.35 g, 0.5 mol) during which the temperature was maintained below 5ºC. After the addition, the solution was stirred for 20 minutes at 5ºC, then 1 hour at room temperature, and slowly, in parts, added to diethyl ether (250 ml). The colourless precipitate was filtered, washed well with diethyl ether and dried on air to yield 7.18 g (78%) colourless, fine crystalline solid M.p. 67-69ºC (lit. 73ºC [108]), Anal. *Calc.* for $C_3H_8N_4O_4$ (%): C 19.68, H 4.96, N 22.95. *Found*: C 19.52, H 4.94, N 21.42. Density: 1.51 g/cm^3. FTIR (cm^{-1}): 3053m (ν NH_2^+), 2921m (ν CH_3), 2841m (ν CH_2), 1642s (ν$_{as}$ NO_2), 1612m (δ NH_2^+), 1449m (δ CH_2), 1387m (δ CH_3), 1293s (ν$_s$ NO_2), 1280s (ν$_s$ NO_2). Raman (cm^{-1}): 3053w, 3039m (ν CH), 3015m (ν CH), 2974s (ν CH), 2837w-m (ν CH), 1648 (ν$_{as}$ NO_2), 1284m (ν$_s$ NO_2), 1046vs (ν$_s$ NO_3^-).

2.7.4. Formamidine nitrate

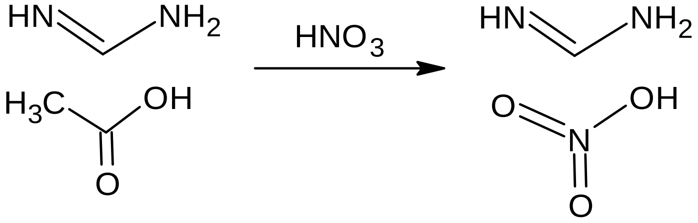


Figure 23: Preparation of formamidine acetate

The preparation procedure was modified based on the description of the preparation of *N*-methyl-*N*-(2-nitroxyethyl)ammonium nitrate according to Dániel Izsák and Thomas M. Klapötke [108] (**Figure 23**).

Formamidine acetate (10 g, 0.096 mol) was dissolved in 120 ml methanol, stirred, and cooled to a temperature of 5ºC. Nitric acid (98%, 6 g, 0.096 mol) was gradually added to the solution so that the temperature did not exceed 5ºC. The mixture was stirred for 30 minutes, and then it was left in a ventilated space so that the solvent could evaporate and crystals could be formed. The crystals obtained were diluted in 75 ml methanol and cooled to 5-10ºC. While stirring, 150 ml of diethyl ether was added in portions. The precipitated product was filtered to yield 6.86 g (67%) of the colourless, fine crystalline solid. M.p. 88ºC (lit. 89ºC [112]), Anal. *Calc.* For $CH_5N_3O_3$ (%): C 11.21, H 4.72, N 39.26. *Found*: C 11.33, H 4.79, N 39.16. Density: 1.41 g/cm^3. FTIR (cm^{-1}): 3316m-3288w-3238m-3145m-3125m (ν NH_2,NH_2^+), 3077w (ν CH), 2566 br (ν NH^+), 1640m (ν C=N), 1309m (ν$_{as.}$ NO_3^-), 823m (δ NO_3^-). Raman (cm^{-1}): 3234br (ν NH_2), 3097w-m (ν CH), 1049s (ν$_{s.}$ NO_3^-), 726m-w (δ NO_3^-).

2.7.5. 4-Amino-1,2,4-triazolium nitrate

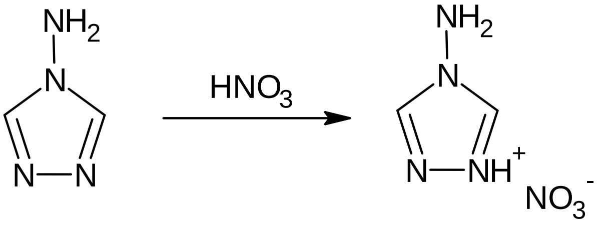


Figure 24: Preparation of 4-amino-4*H*-1,2,4-triazole

The preparation procedure was modified based on the description of the preparation of *N*-methyl-*N*-(2-nitroxyethyl)ammonium nitrate according to Dániel Izsák and Thomas M. Klapötke [108] (**Figure 24**).

4-Amino-4*H*-1,2,4-triazole (10 g, 0.12 mol) was dissolved in 100 ml methanol and cooled to 5ºC. Nitric acid (98%, 7.5 g, 0.12 mol) was slowly added to the solution, so the temperature did not exceed 5ºC. A white fine crystalline precipitate formed, to which was added 100 ml diethyl ether, and the mixture was filtered. Yield: white, fine crystalline solid (12.61 g, 71%). M.p. 65ºC (lit. 70ºC [110]), Anal. *Calc.* for $C_2H_5N_5O_3$ (%): C 16.33, H 3.43, N 47.62. *Found*: C 16.41, H 3.43, N 47.62. Density: 1.64 g/cm^3 (lit. 1.62 g/cm^3 [110]) FTIR (NO_3^-, cm^{-1}): 1383m-1363m-1348m-1310m ($\nu_{as.}$ NO_3^-), 823m (δ NO_3^-). Raman (cm^{-1}): 1039s (ν_s.NO_3^-), 726w (δ NO_3^-).

2.8. 4-Amino-1,2,4-triazolium perchlorate

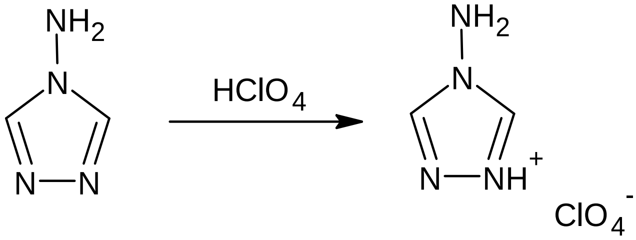


Figure 25: Preparation of 4-amino-1,2,4-triazolium perchlorate

The procedure for 4-amino-1,2,4-triazolium nitrate [108] was modified for perchlorate preparation (**Figure 25**).

4-Amino-4*H*-1,2,4-triazole (0.5 g, 0.006 mol) was dissolved in 5 ml methanol and cooled to 5-10ºC. Perchloric acid (70%, 0.9 g, 0.006 mol) was slowly added to the solution, so that the temperature did not exceed 20ºC. The solution was cooled and stirred for 30 minutes, then

200 ml diethyl ether was added. The precipitated product was filtered to yield 0.68 g (62%) of the white solid. M.p. 78ºC (lit. 84ºC [110]), Anal. *Calc*. for $C_2H_5N_4O_4Cl$ (%): C 13.02, H 2.74, N 30.37, Cl 19.21. *Found*: C 13.54, H 2.66, N 31.25, Cl 18.06. FTIR (ZnSe, ClO_4^-, cm^{-1}): 1075s-1051s-1031s ($\nu_{as}ClO_4^-$), 629s (δ ClO_4^-). Raman (cm^{-1}): 936s ($\nu_{s.}ClO_4^-$), 633m-627m (δ ClO_4^-), 464m-459m (δ ClO_4^-).

2.9. Allyl 3,5-dinitrobenzoate

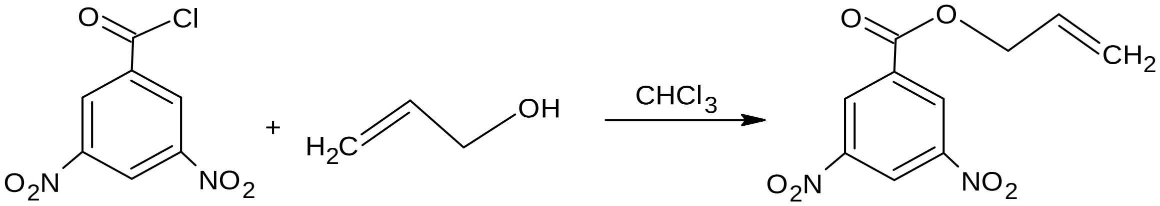


Figure 26: Preparation of allyl 3,5-dinitrobenzoate

The preparation procedure was modified based on the description of the preparation of allyl 3,5-dinitrobenzoate by Fairbourne and Foster [146] (**Figure 26**).

Hydroquinone (4.8 g, 0.043 mol) and 3,5-dinitrobenzoyl chloride (10 g, 0.043 mol) were dissolved in chloroform (33.5 g, 0.28 mol); then allyl alcohol (2.5 g, 0.043 mol) was added the mixture was left stand for two days After evaporation of chloroform, the solid was stirred with 100 ml of water, filtered, then stirred with 50 ml of water, filtered, and finally crystallised from 25ml ethanol. The product was washed with warm (40°C) water to yield 6.0 g (55%) of the off-white solid. M.p. 47ºC (lit. 49-50ºC [135]). Anal. *Calc*. for $C_{10}H_8N_2O_6$ (%): C 47.62, H 3.20, N 11.11. *Found*: C 47.53, H 3.10, N 11.04. Density: 1.44 g/cm^3 (lit. 1.41 g/cm^3 [41]). FTIR (cm^{-1}): 3089m (ν CH unsat.), 2987vw 3089m (ν CH sat.), 1728s (ν C=O), 1652w (ν C=C), 1629m (CC arom.), 1597 (arom.), 1550s (ν_{as} NO_2), 1538s, 1460 (ν CH_2), 1343s (ν_s NO_2), 1329s (ν_s NO_2). Raman (cm^{-1}): 3101w-m (ν CH usat., 3070 (ν CH unsat.) 3024w (ν CH arom.), 2991w (ν CH sat.), 2957w (ν CH sat.), 1739m (ν C=O), 1651m (ν C=C), 1629 (CC arom.), 1556m (ν_{as} NO_2), 1540m (ν_{as} NO_2), 1371s (ν_s NO_2), 1355s (ν_s NO_2), 1004s (δ *in plane* CH arom, 1,3,5-trisubst.).

2.10. Picrates

2.10.1. Dipropylamine picrate

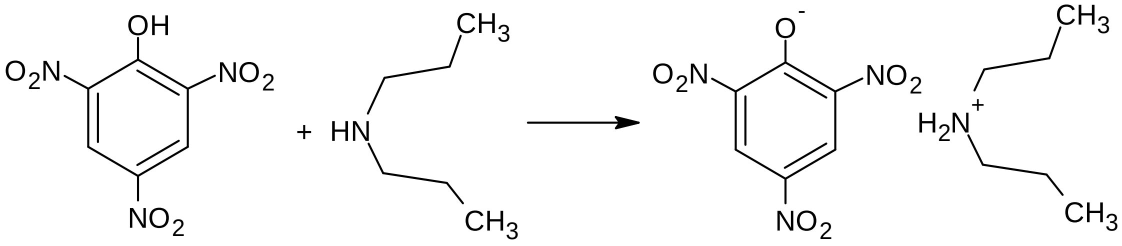


Figure 27: Preparation of dipropylamine picrate

The preparation procedure was modified based on the description of the preparation of ammonium picrate by Ernst Berl and Walter George Berl [147] (**Figure 27**).

2,4,6-Trinitrophenol (2 g, 0.0087 mol) was dissolved in 100 ml water and heated to 50-60°C while stirring. Dipropylamine (1.77 g, 0.0175 mol) was then added to the solution and stirred for 30 minutes, after which it was cooled to temperatures below 25°C. The precipitated product was filtered and air-dried to yield 0.39 g (13.4%) of the fine yellow crystals. M.p. 97°C (lit. 97.5°C [35]). Anal. *Calc.* for $C_{12}H_{18}N_4O_7$ (%): C 43.63, H 5.50, N 16.97. *Found*: C 43.99, H 5.56, N 16.88. Density: 1.33 g/cm^3 (lit. 1.36 g/cm^3 (at 15°C) [37]). FTIR (cm^{-1}): 3195 (ν CH arom.), 3098w-m (ν CH arom.), 2942(ν CH_3) 2971m (ν CH_2, CH_3), 2881m (ν$_s$ CH_2), 1632 (δ NH_2^+), 1615m (CC arom.), 1566 (ν$_{as}$ NO_2), 1552 (ν$_{as}$ NO_2), 1471m (δ CH_2, CH_3), 1432m (δ CH_2, CH_3), 1331s (ν$_s$ NO_2), 1309s (ν$_s$ NO_2). Raman (cm^{-1}): 3200w (ν NH_2), 3094w (ν CH arom.), 2943 (ν CH_2, CH_3), 2879m (ν CH_2), 1613 (CC arom.), 1560m (ν$_{as}$ NO_2), 1496w (CC arom.), 1362m (δ$_s$ CH_2, CH_3), 1333s (ν$_s$ NO_2), 1310s (ν$_s$ NO_2).

2.10.2. Diethylamine picrate

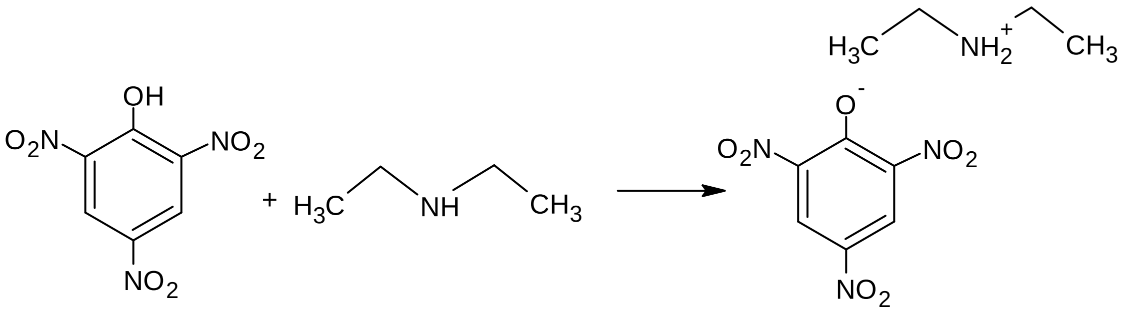


Figure 28: Preparation of diethylamine picrate

The preparation procedure was modified based on the description of the preparation of ethylamine picrate by Raman and Soundararajan [148] (**Figure 28**).

Diethylamine (1.28 g, 0.0175 mol) was dissolved in 4 ml ice-cold water, and picric acid (2 g, 0.0087 mol) was gradually added. The mixture was stirred in an ice bath for 30 minutes, and the precipitate was filtered and air-dried to yield 0.99 g (38%) of fine yellow crystals. M.p. 74ºC (lit. 74ºC [35]). Anal. *Calc*. for $C_{10}H_{14}N_4O_7$ (%): C 39.74, H 4.68, N 18.54. *Found*: C 39.93, H 4.69, N 18.43. Density: 1.46 g/cm^3 (lit. 1.36 g/cm^3 [36]). FTIR (cm^{-1}): 3074w-m (ν CC arom.), 2841m (ν CH_2), 2795m (ν NH_2^+), 1632w (δ NH_2^+), 1604m (CC arom.), 1574 (ν_{as} NO_2), 1497m (δ CH_2,CH_3), 1472m (δ CH_2,CH_3), 1429 (δ CH_2,CH_3), 1364m (ν_s NO_2), 1337m (ν_s NO_2), 1322m (ν_s NO_2). Raman (cm^{-1}): 3096vw (CC arom.), 2993 (ν CH_3), 2951w (ν CH_2, CH_3), 1611w (CC arom.), 1547m (ν_{as} NO_2), 1496w (CC arom.), 1362m (ν_s NO_2), 1337s (ν_s NO_2), 1321s (ν_s NO_2).

2.10.3. Diallylamine picrate

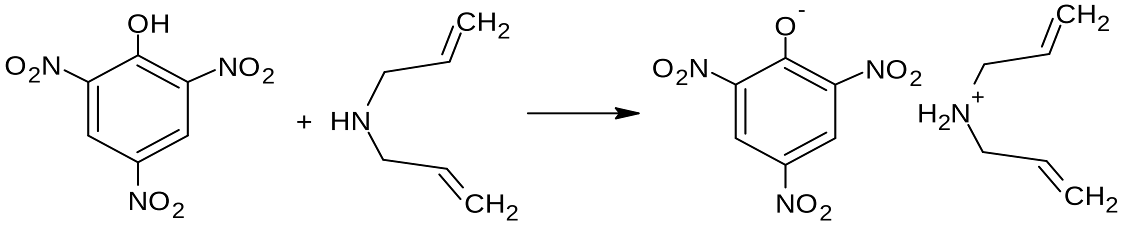


Figure 29: Preparation of diallylamine picrate

The preparation procedure was modified based on the description of the preparation of ammonium picrate by Ernst Berl and Walter George Berl [147] (**Figure 29**).

2,4,6-Trinitrophenol (2 g, 0.0087 mol) was dissolved in 100 ml water and heated to 50-60ºC and diallylamine (1.7 g, 0.0175 mol) was added. The reaction mixture was stirred for 30 minutes, then it was cooled to 25ºC and put in a deep fridge (-18°C) for 1 hour. The obtained crystals were filtered and air-dried to yield 1.43 g (51%) of fine yellow crystals. M.p. 75ºC (lit. 76ºC [38]). Anal. *Calc*. for $C_{12}H_{14}N_4O_7$ (%): C 44.17, H 4.33, N 17.17. *Found*: C 44.39, H 4.30, N 17.31. Density: 1.40 g/cm^3. FTIR (cm^{-1}): 3076m-w (ν_{as} CH unsat.), 3045m (ν_{as} CH arom.), 2997m (ν_s CH_2), 2985m (ν_s CH_2), 2956m (ν_s CH_2), 2831m (ν CH_2 or δ NH_2^+), 2781m (δ NH_2^+), 2706 (δ NH_2^+), 1602m (CC arom.), 1563m (ν_{as} NO_2), 1541m (ν_{as} NO_2), 1494m (δ CH, CH_2), 1453m (δ CH, CH_2), 1361 (ν_s NO_2), 1319m (ν_s NO_2). Raman (cm^{-1}): 3102w (ν $=CH_2$), 3032w (ν CH unsat.), 2991w (ν CH, CH_2), 2959w (ν CH, CH_2), 1653m (δ NH_2^+), 1611 (CC arom), 1546m (ν_{as} NO_2), 1364m (ν_s NO_2), 1333s (ν_s NO_2), 1318s (ν_s NO_2).

3. Results and discussion

3.1. Search of compounds, evaluation, and synthesis

The suitable compounds were searched mainly by the ICT thermochemical database and the Reaxys database. With the chosen characteristic values for the compounds, ICT found more than 300 molecules. In Reaxys, for nitrates, about 1,500 compounds were found, for perchlorates, about 1,900 compounds, and for picrates, approximately 5,000 compounds.

From these compounds, the suitable ones were selected especially from the point of view of ease of preparation. The compounds and their properties were summarised in the theoretical part. The described groups included benzenes with different substituent groups, alkylnitroguanidines, methylene dinitrodiaza compounds, germinal dinitro compounds, nitroso compounds, pyridine, furazan, and furoxan derivatives, triazoles, and tetrazoles, different salts, such as nitrates, perchlorates, and picrates, fluorinated compounds, and acrylates. From the vast number of suggested molecules, toxic groups like nitroso or fluorinated compounds were excluded for synthesis, as well as those with tedious or multistep synthesis. The special class is those compounds that contain double bonds that may theoretically polymerise after printing, using UV hardening.

Potentially promising candidates were selected for the preparation and evaluation of physical properties. These included the following: *N*-alkyl-*N*-nitro-2,4,6-trinitroanilines and *N*-alkyl-2,4,6-trinitroanilines, methylene dinitrodiaza compounds, some nitrates, picrates, one representative of the perchlorate salts, and an acrylate.

The preparation of *N*-propyl-*N*-nitro-2,4,6-trinitroaniline, *N*-butyl-*N*-nitro-2,4,6-trinitroaniline, and *N*-allyl-2,4,6-trinitroaniline resulted in a precipitate and an oily phase. The oily phase would be crystallised with a suitable solvent to solid product.

The synthesised nitrates were obtained with relatively high yields (from about 60% to more than 80%), and their synthesis was unproblematic. One candidate from the perchlorate group, 4-amino-1,2,4-triazolium perchlorate, was synthesised, resulting in a relatively high yield of 62%.

The preparation of 3,5-dinitro-3,5-diazaheptane was quick and easy, unfortunately with greater losses, with a practical yield of only 53%. Despite that, the physical characteristics were almost identical to those in the literature.

Diethylamine, dipropylamine, and diallylamine picrates were difficult to obtain because of their solubility in organic solvents. Different procedures were applied, which resulted in low practical yields (from 13% to approximately 50%).

The special class compounds were those with double bonds. The energetic properties in the molecule are welcome because the traditional matrix based on acrylate is not energetic. The compound 3-(nitroxy)-2,2-bis[(nitroxy)methyl]propyl acrylate (**Figure 30**) was suggested [149], [150]. However, the main limitation of the synthesis of the compound was the tedious preparation, the toxic starting material acryloyl chloride, the poor accessibility of the starting material Petrin, and the low yield [151].

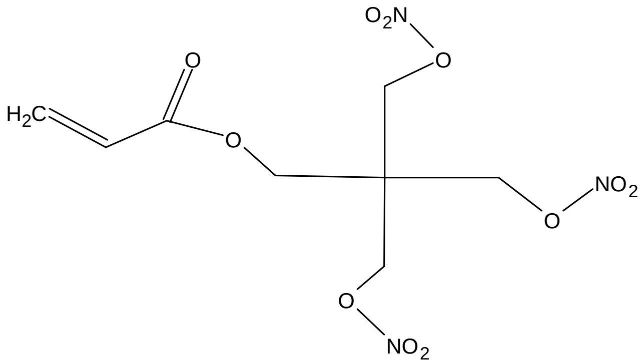


Figure 30: 3-(Nitroxy)-2,2-bis[(nitroxy)methyl]propyl acrylate

The solution was the suggestion of another compound: allyl 3,5-dinitrobenzoate (**Figure 31**). The energetic group in it is represented by the 3,5-dinitrobenzoate moiety, and the double bond by the allyl group. The advantage of this compound is that the preparation was easier than 3-(nitroxy)-2,2-bis[(nitroxy)methyl]propyl acrylate (**Figure 32**).

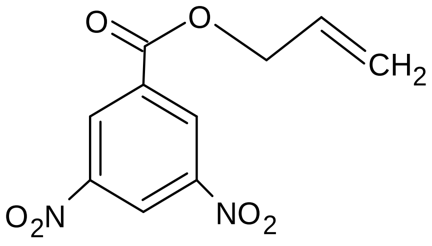


Figure 31: Allyl 3,5-dinitrobenzoate

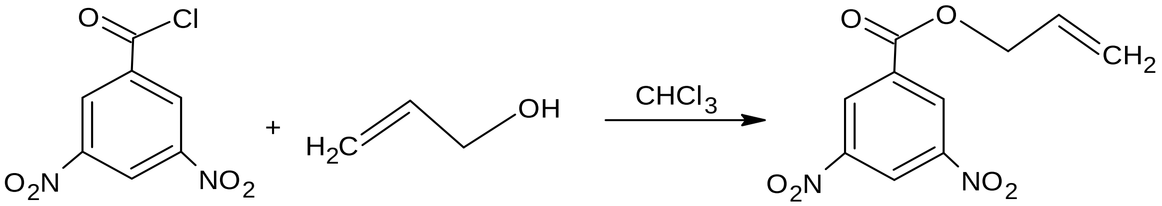


Figure 32: Preparation of allyl 3,5-dinitrobenzoate

The other synthesised compounds that could be regarded as low-melting monomers included diallylamine picrate and *N*-allyl-2,4,6-trinitroaniline (**Figure *33***).

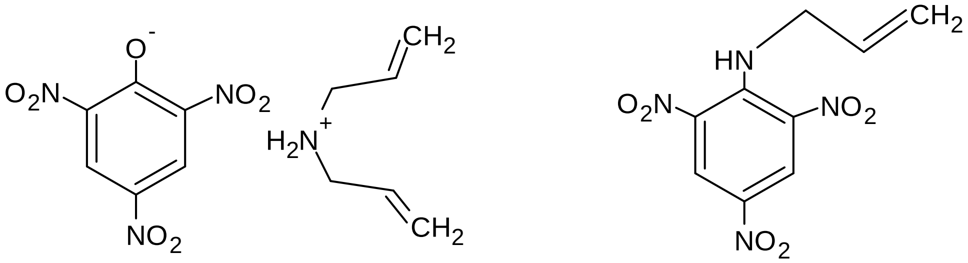


Figure 33: Diallylamine picrate and *N*-allyl-2,4,6-trinitroaniline

3.2. Density, melting point, and DTA onset of endotherm

The synthesised compounds were characterised by density, melting point, and oxygen balance (**Table 21**). All compounds had a melting point below 100°C and a negative oxygen balance.

Table 21: Selected properties of synthesised compounds

Compound	**Molecular formula**	**Melting point [°C]**	**Density [g/cm^3]**	**Oxygen balance [%]**
N-Propyl-*N*-nitro-2,4,6-trinitroaniline	$C_9H_9N_5O_8$	97	1.61	-73.60
N-Butyl-*N*-nitro-2,4,6-trinitroaniline	$C_{10}H_{11}N_5O_8$	97	1.55	-85.05
N-Allyl-2,4,6-trinitroaniline (1)	$C_9H_8N_4O_6$	78	1.62	-95.46
N-Allyl-2,4,6-trinitroaniline (2)	$C_9H_8N_4O_6$	76	1.60	-95.46
DNDA5	$C_3H_8N_4O_4$	53	1.48	-58.49
DNDA7	$C_5H_{12}N_4O_4$	74-75	1.37	-99.91
1-Methylimidazolium nitrate	$C_4H_7N_3O_3$	65-66	1.47	-93.72
N-Methyl-*N*-(2-nitroxyethyl)ammonium nitrate	$C_3H_9N_3O_6$	67-69	1.51	-39.32
4-Amino-1,2,4-triazolium nitrate	$C_2H_5N_5O_3$	65	1.64	-38.07
Formamidine nitrate	$CH_5N_3O_3$	88	1.41	-22.42
4-Amino-1,2,4-triazolium perchlorate	$C_2H_5N_4O_4Cl$	78	1.81 [110]	-17.34
Allyl 3,5-dinitrobenzoate	$C_{10}H_8N_2O_6$	47	1.44	-114.20
Dipropylamine picrate	$C_{12}H_{18}N_4O_7$	97	1.33	-125.95
Diethylamine picrate	$C_{10}H_{14}N_4O_7$	74	1.46	-105.87
Diallylamine picrate	$C_{12}H_{14}N_4O_7$	75	1.40	-117.69

Table 23 illustrates the behaviour of the synthesised compounds when exposed to rising temperatures from 25ºC to 500ºC. The endothermic onset temperature is possibly the melting temperature, and the exothermic start is presumably the start of decomposition of the synthesised organic compounds. All compounds exhibit an endothermic onset temperature between 45ºC and 100ºC and a start of the exotherm above 100ºC. Not all synthesised compounds have been selected as promising, due to their temperature gap (Interval 1). DTA analysis has been done on inorganic nitrates as well. They appear to have presumably endothermic decomposition (**Table 22**).

3.3. Suitable compounds according to DTA

The suitable candidates for low-melting explosives are presented in **Table 24**, where their physical characteristics are shown. DNDA5, DNDA7, 4-amino-1,2,4-triazolium nitrate, formamidine nitrate, 1-methylimidazolium nitrate, 4-amino-1,2,4-triazolium perchlorate, allyl 3,5-dinitrobenzoate and diethylamine, dipropylamine, and diallylamine picrates have been selected as promising. The selection was based on their low melting point and their thermal stability interval between endothermic onset and exothermic start from the DTA analysis (Interval 1 from **Table 23**). The compounds had to be thermally stable in the liquid phase and therefore have a temperature interval greater than 90ºC. The density, melting point, vacuum stability test, and sensitivity to impact and friction were found for these compounds. Yet, there are still more tests to be done for the full characterisation of the energetic materials on their stability and sensitivity.

3.4. Sensitivity to impact and friction

The sensitivity to impact and friction can be seen in **Table 24**. It was briefly examined according to the Czech regulation [137]. The simple method 0/6 aimed to find the highest energy level, where the sample is not activated. Generally, the synthesised compounds were not sensitive, except for 4-amino-1,2,4-triazolium perchlorate. 4-ATP resulted in 2 J (0.5 kg, 40 cm), the highest energy level of impact, where zero out of six trials no initiation of the sample occurred. Sensitivity tests for the other compounds did not show initiation at 50 J (5 kg, 100 cm). The results on friction sensitivity were no different: having the highest energy level, where no initiation occurs for 4-ATP to be 30 N. For the other synthesised compounds, the value was established to be 360 N. In comparison to the other compounds, 4-ATP showed to be rather sensitive when it comes to friction and impact, and for additive manufacturing testing as for now. Apart from the 4-ATP, the other synthesised compounds showed to be insensitive to impact and friction. The method used in this work is rather simple in comparison to other methods like Probit or Up and Down. They would be suitable for deeper sensitivity characteristics for future work.

Table 22: DTA results for inorganic nitrates

Compound	**Endotherm**	**Endothermic decomposition**			**Interval 1 [ºC]**	**Interval 2 [ºC]**
	Onset [ºC]	**Start [ºC]**	**Onset [ºC]**	**Maximum [ºC]**		
$Fe(NO_3)_3.9H_2O$	48.7	102.4	110.2	139.9	54	62
$Ni(NO_3)_2.6H_2O$	56.0	285.8	305.1	327.2	230	249
$Mg(NO_3)_2.6H_2O$	88.6	409.8	422.3	428.6	321	334
$Bi(NO_3)_3.5H_2O$	72.5	106.6	130.7	143.0	34	58

Interval 1: temperature interval between onset (endotherm) and start (exotherm)

Interval 2: temperature interval between onset (endotherm) and onset (exotherm)

Table 23: DTA results from synthesised compounds

Compound	**Endotherm**	**Exotherm**			**Interval 1 [ºC]**	**Interval 2 [ºC]**
	Onset [ºC]	**Start [ºC]**	**Onset [ºC]**	**Maximum [ºC]**		
N-Ethyl-*N*-nitro-2,4,6-trinitroaniline	90.7	133.6	163.2	164.3	43	72.5
N-Propyl-*N*-nitro-2,4,6-trinitroaniline	96.3	126.6	151.0	163.2	30	55
N-Butyl-*N*-nitro-2,4,6-trinitroaniline MeOH	91.9	101.3	146.3	161.0	9	54
N-Allyl-2,4,6-trinitroaniline (1)	74.9	135.5	189.4	200.6	61	115
N-Allyl-2,4,6-trinitroaniline (2)	74.6	145.6	182.9	199.3	71	108
DNDA5	52.4	210.2	222.4	252.2	158	170
DNDA7	73.5	201.5	224.0	250.7	128	151
1-Methylimidazolium nitrate	65.4	156.0*	162.2	219.5	91	97
N-Methyl-*N*-(2-nitroxyethyl)ammonium nitrate	65.8	127.7	149.6	151.2	62	84
4-Amino-1,2,4-triazolium nitrate	67.1	168.7*	192.4	259.0	102	125
Formamidine nitrate	84.3	209.2*	225.0	278.0	125	141
4-Amino-1,2,4-triazolium perchlorate	68.2	253.4*	264.8	406.5	185	197
Allyl 3,5-dinitrobenzoate	47.9	182.3	229.9	271.3	134	182
Dipropylamine picrate	95.9	187.5*	237.4	250.6	92	142
Diethylamine picrate	73.3	216.7	247.9	259.3	143	175
Diallylamine picrate	74.6	175.3*	209.3	230.2	101	135

*Values were found manually

Interval 1: temperature interval between onset (endotherm) and start (exotherm)

Interval 2: temperature interval between onset (endotherm) and onset (exotherm)

Table 24: Characteristics of promising compounds

Compound	**Melting point [ºC]**	**DTA onset (endotherm) [ºC]**	**Start of decomposition [ºC]**	**Oxygen balance [%]**	**Density (ρ) [g/cm^3]**	**Friction sensitivity [N]***	**Impact sensitivity [J]***
DNDA5	53	52.4	210.2	-58.49	1.48	360	50
DNDA7	74-75	73.5	201.5	-99.91	1.37	360	50
4-Amino-1,2,4-triazolium nitrate	65	67.1	168.7	-38.07	1.64	360	50
Formamidine nitrate	88	84.3	209.2	-22.42	1.41	360	50
1-Methylimidazolium nitrate	65-66	65.4	156.0	-93.72	1.47	360	50
4-Amino-1,2,4-triazolium perchlorate	78	68.2	253.4	-17.34	1.81 [110]	30	2
Diethylamine picrate	74	73.3	216.7	-105.87	1.46	360	50
Dipropylamine picrate	97	95.9	187.5	-125.95	1.33	360	50
Diallylamine picrate	75	74.6	175.3	-117.69	1.40	360	50
Allyl 3,5-dinitrobenzoate	47	47.9	182.3	-114.20	1.44	360	50

* Friction sensitivity and impact sensitivity are presented by the maximum energy level where no initiation occurs

3.5. Preliminary tests and suggestions

The synthesised special group of compounds, consisting of allyl 3,5-dinitrobenzoate, diallylamine picrate, and *N*-allyl-2,4,6-trinitroaniline, was subjected to polymerisation experiments. Wavelengths of 365, 395, and 405 nm were used to harden the molten compounds, but they were not affected and remained in the liquid phase. The molten allyl 3,5-dinitrobenzoate was added to a commercial resin, resulting in a homogenous, viscous liquid. The mixture was kept for several days, and there was no precipitate. This observation may suggest the use of these compounds as additives to different resins to enhance their properties. Future work is needed to evaluate these properties and observe the behavior of these mixtures. Moreover, the accessible catalyst used was designed for polyesters, so there is a need for an appropriate polymerisation catalyst in future work.

A preliminary stability test using Stabil was provided to measure the volume of gases at 90°C. The data are summarised in **Table 25**.

Table 25: Vacuum stability test results

Compound	Volume of gases [ml/ g]
TNT	0.322
RDX	0.073
DNDA7	1.292
DNDA5	2.0885
1-Methylimidazolium nitrate	0.658
Allyl 3,5-dinitrobenzoate	0.43
Diethylamine picrate	0.05

Heat of formation is an essential parameter for energetic compounds, especially for calculating the explosive properties. Literature data can be obtained or should be measured experimentally for many of the compounds. Further studies on this topic are recommended.

To fully characterise the synthesised compounds, hygroscopicity and sensitivity to electrostatic discharge should be determined as well.

CONCLUSION

The current work aimed to present a literature search for low-melting energetic materials, which could be suitable for additive manufacturing. The compounds had to comply with specific thermal stability and synthesis requirements. The purpose was to find compounds that were easy to synthesise and had good thermal stability in the liquid phase. The second objective of the work was to evaluate and characterise the physical properties of the synthesised compounds.

The low-melting energetic compounds have the advantage of easy transportation in the liquid state. This allows them to be introduced in small geometries and used as energetic fillers for ammunition. These compounds can be used in additive manufacturing technology to modify and design promising energetic materials. The selected explosives have a low melting temperature and good thermal stability, with a considerable temperature interval between melting and decomposition temperature. The compounds suggested in this work have been selected to have a melting point below 120ºC and a temperature interval (stability in liquid state by DTA) of 100ºC or more. Most of the compounds have a low sensitivity to mechanical stimuli. Their selected physical properties were described, and fourteen compounds were synthesised. Ten of the synthesised compounds exhibited the desired interval of stability at DTA and were then chosen as promising low-melting energetic materials for 3D printing. They were distributed in different groups: *N*-alkyl-*N*-nitro-2,4,6-trinitroanilines and *N*-alkyl-2,4,6-trinitroanilines, methylene dinitrodiaza compounds, nitrate and perchlorate salts, picrates, and acrylates. The compounds were characterised by density, melting point, DTA, friction and impact sensitivity. Further experimental investigations are needed to estimate the heat of formation and, therefore, the explosive parameters. More broadly, the sensitivity to electrostatic discharge and the hygroscopicity of the compounds should be assessed. The vacuum stability test would be worth completing for fully characterising the synthesised energetic materials. The compounds consisting of an allyl group could produce interesting findings regarding their polymerisation. The syntesised and characterised low-melting energetic materials are regarded as promising compounds for the field of additive manufacturing.

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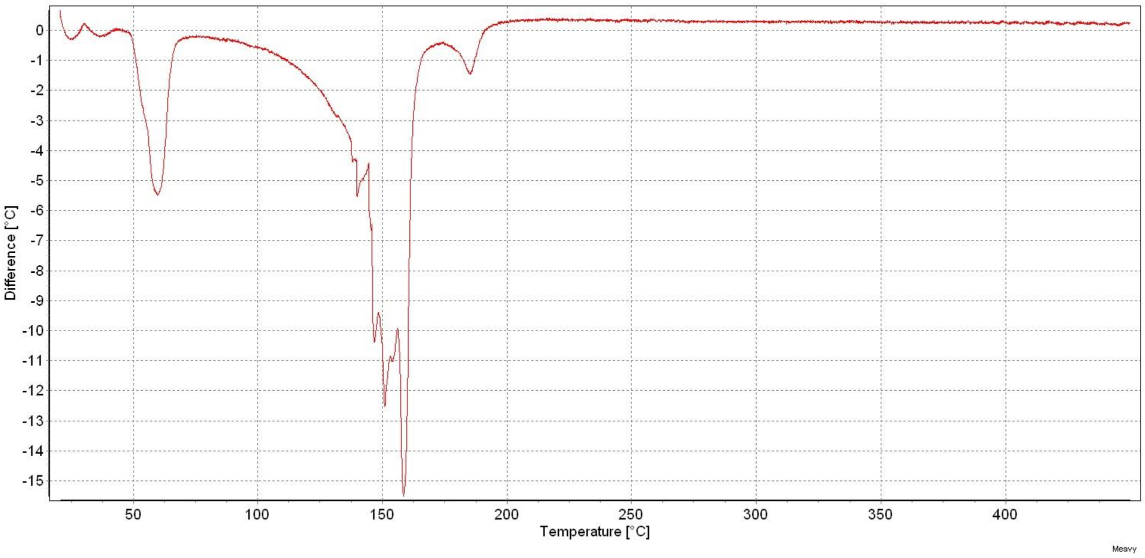
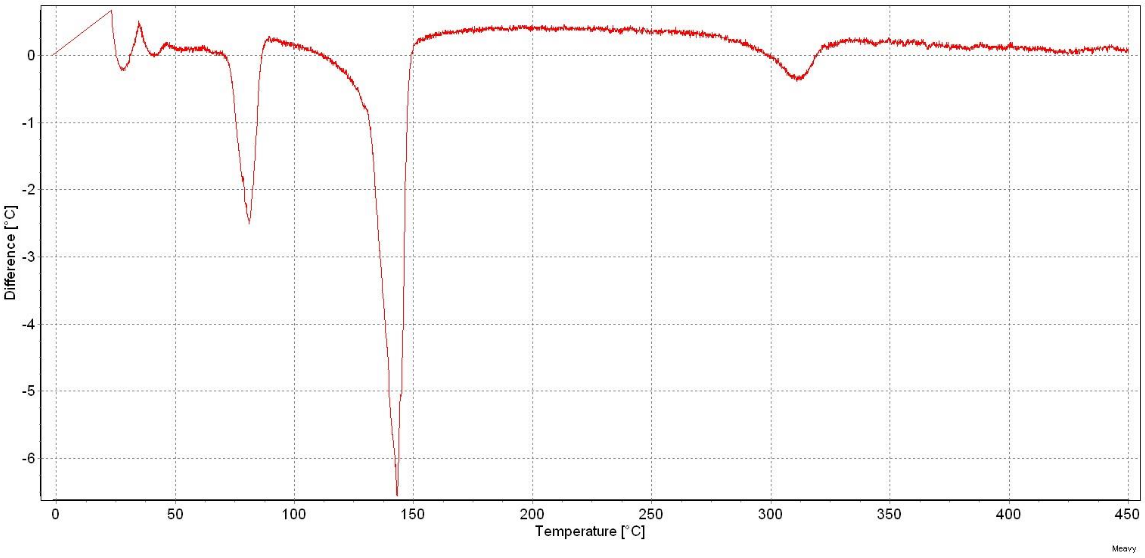
ANNEX

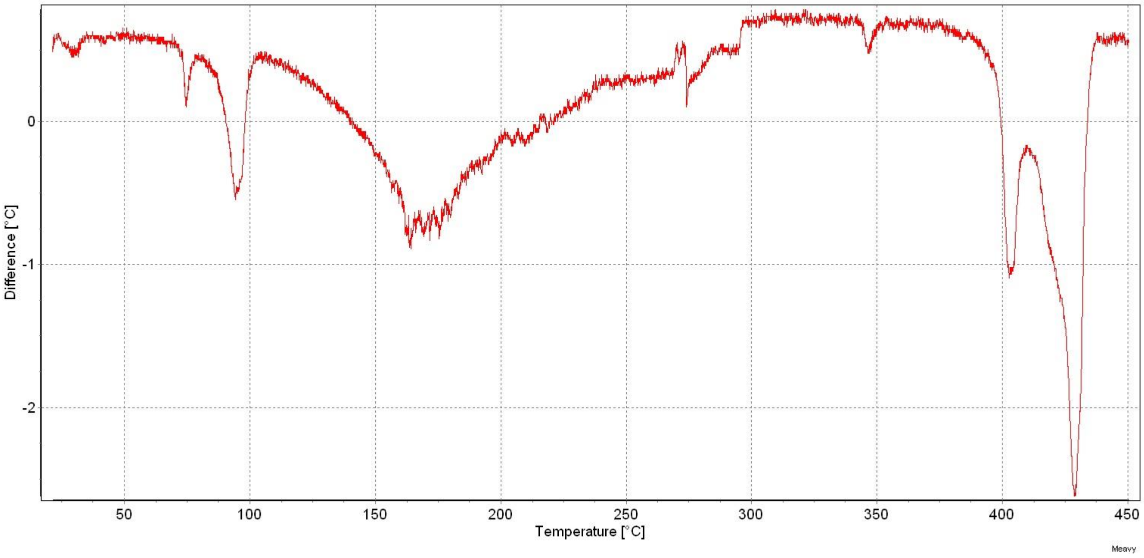
DTA thermograms:



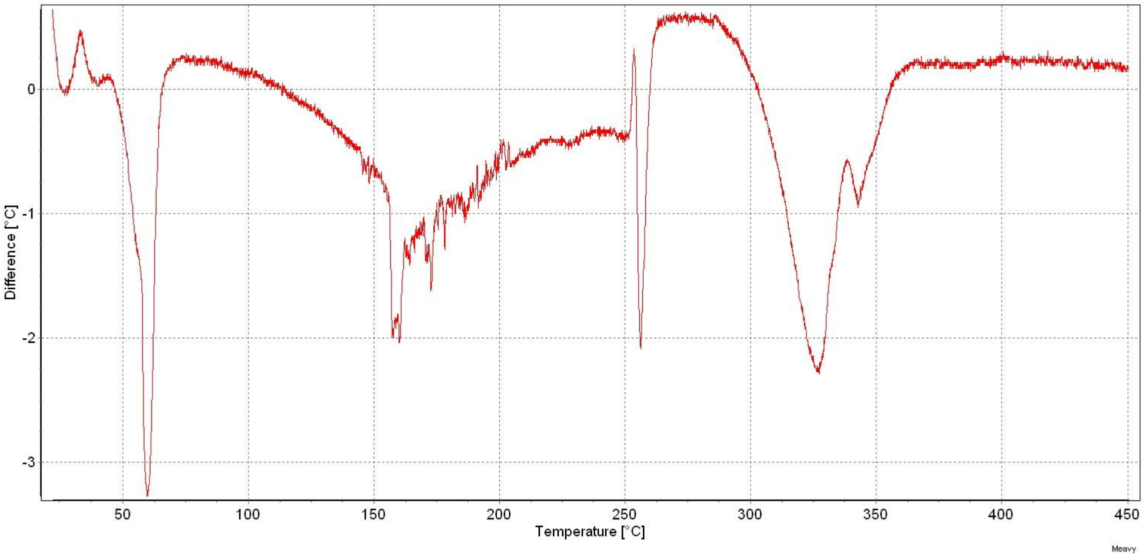
Annex 1: Iron nitrate nonahydrate



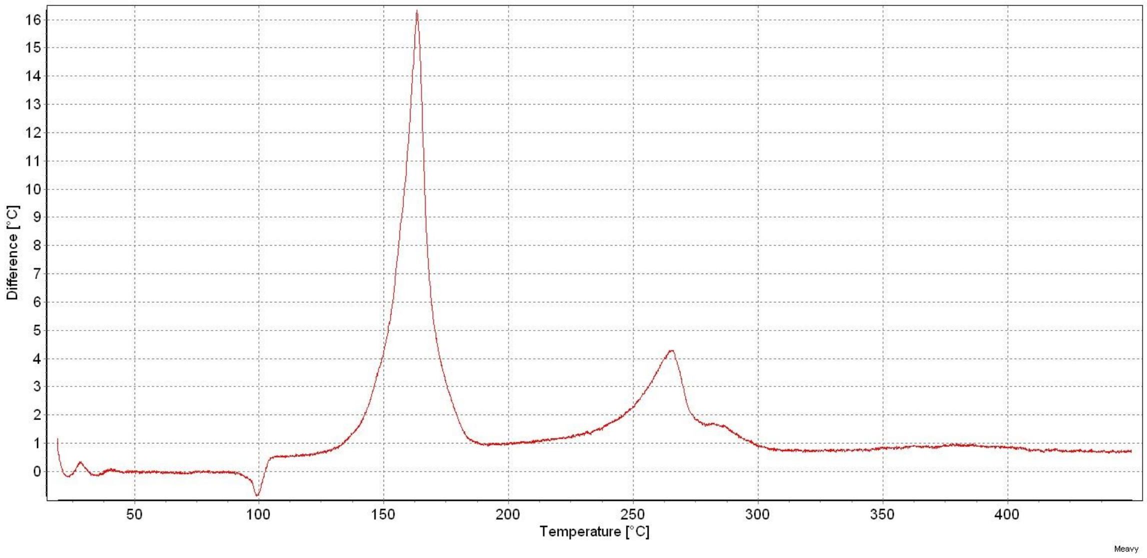
Annex 2: Bismuth nitrate pentahydrate



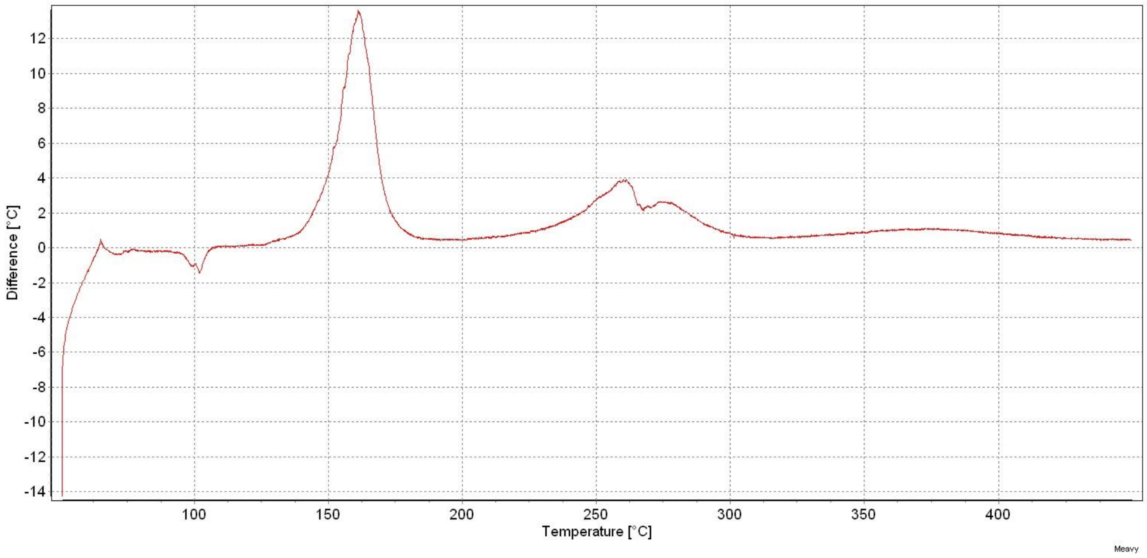
Annex 3: Magnesium nitrate hexahydrate



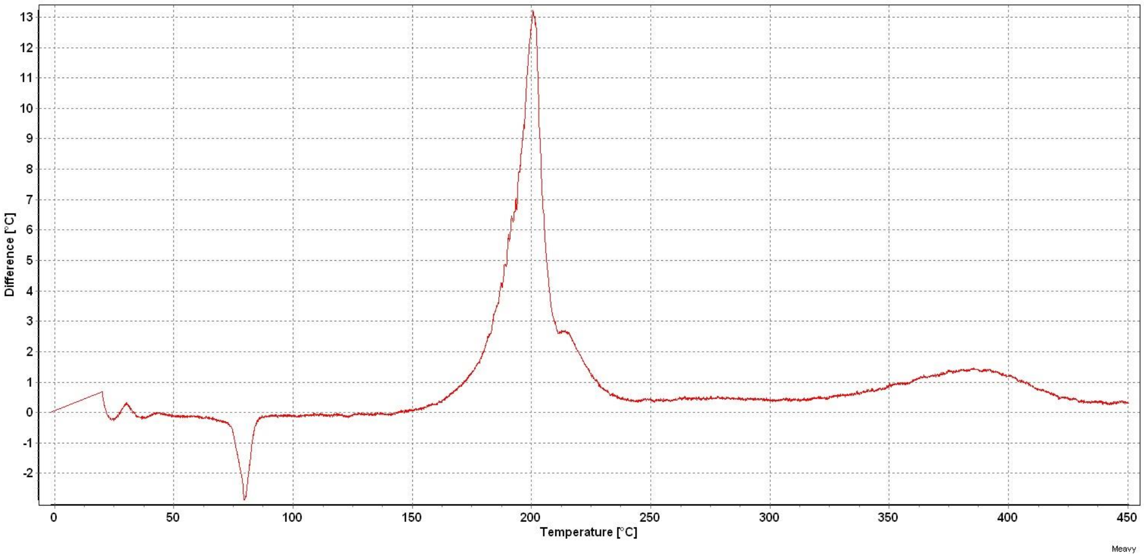
Annex 4: Nickel nitrate hexahydrate



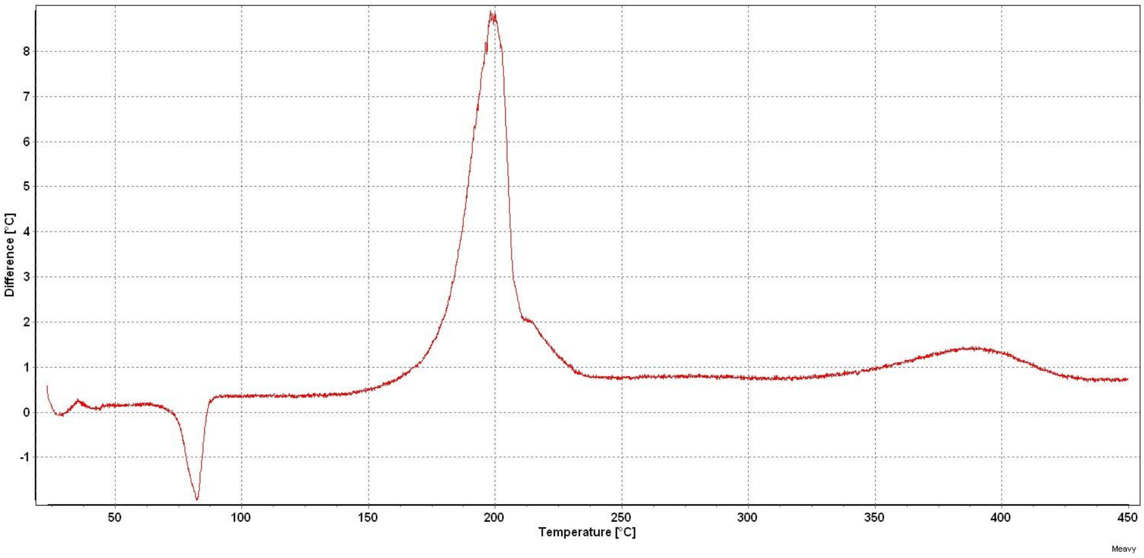
Annex 5: *N*-Propyl-*N*-nitro-2,4,6-trinitroaniline



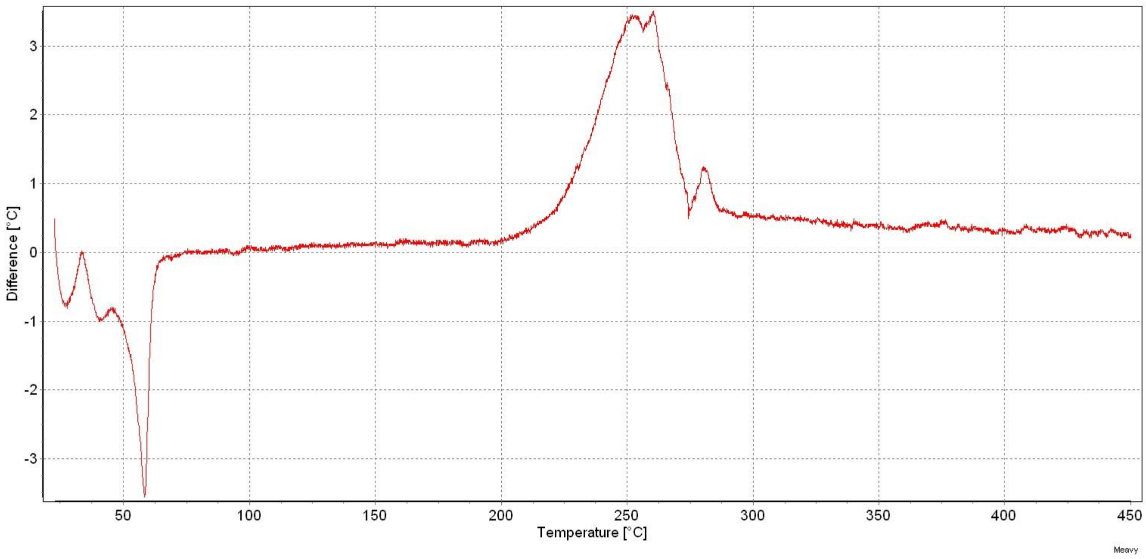
Annex 6: *N*-Butyl-*N*-nitro-2,4,6-trinitroaniline



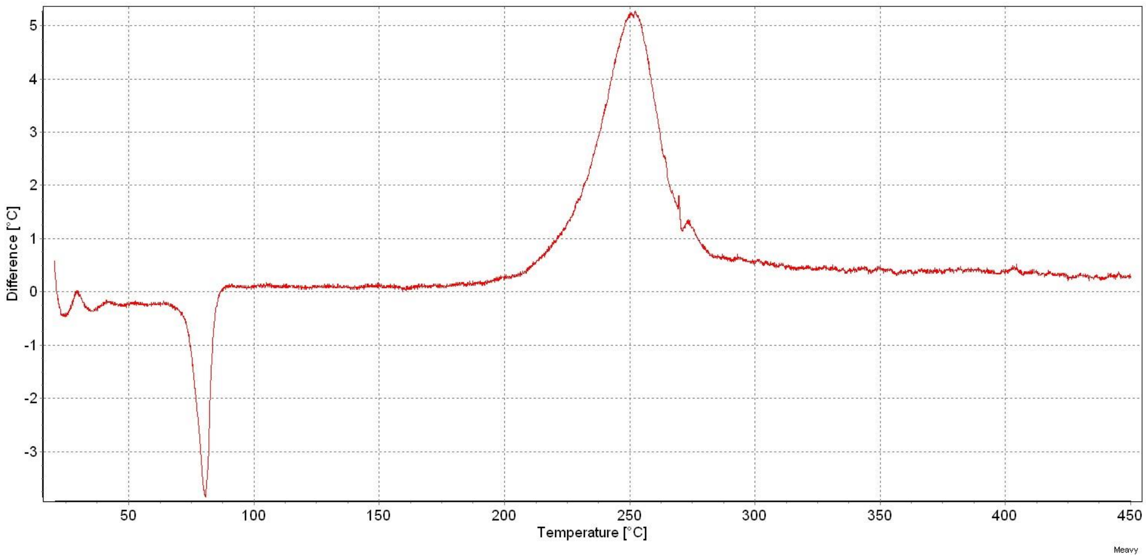
Annex 7: *N*-Allyl-2,4,6-trinitroaniline (1)



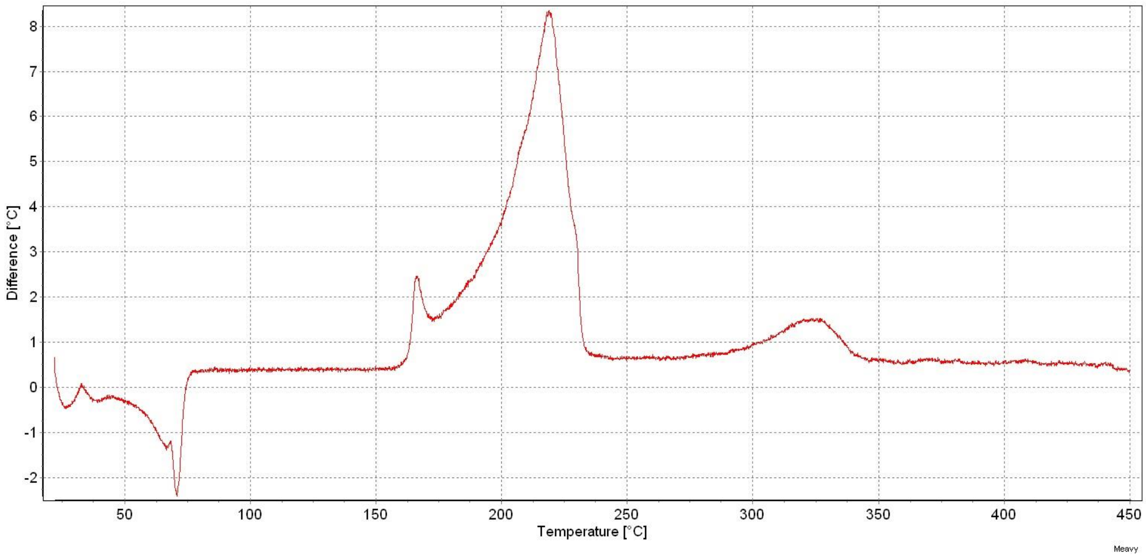
Annex 8: *N*-Allyl-2,4,6-trinitroaniline (2)



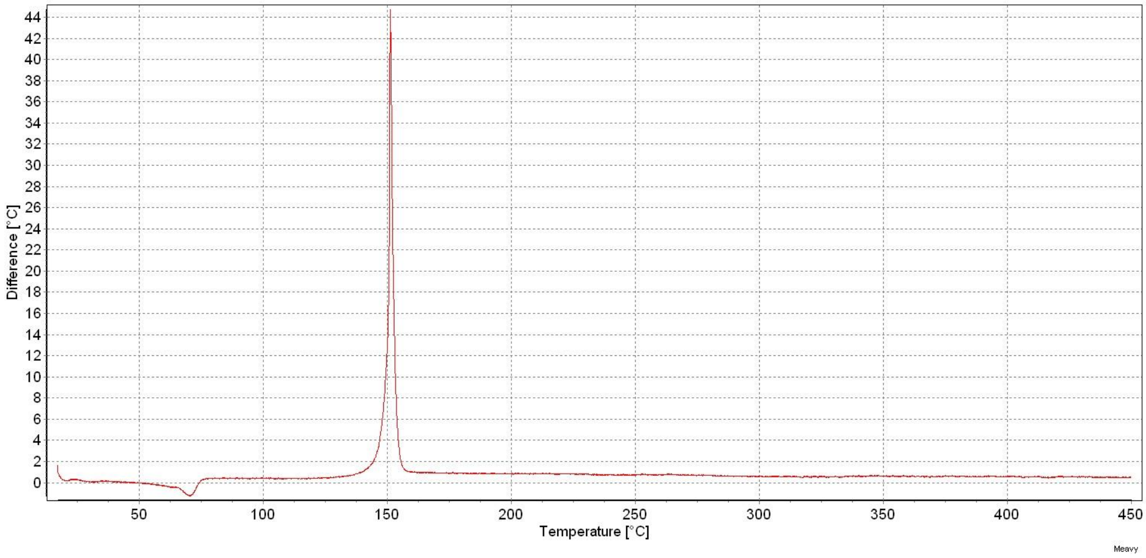
Annex 9: DNDA5



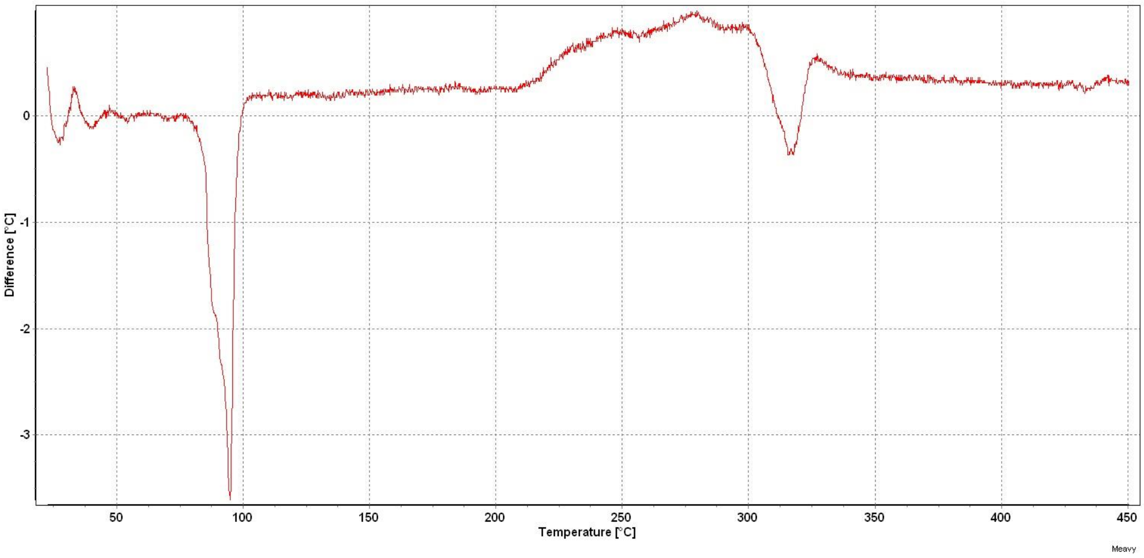
Annex 10: DNDA7



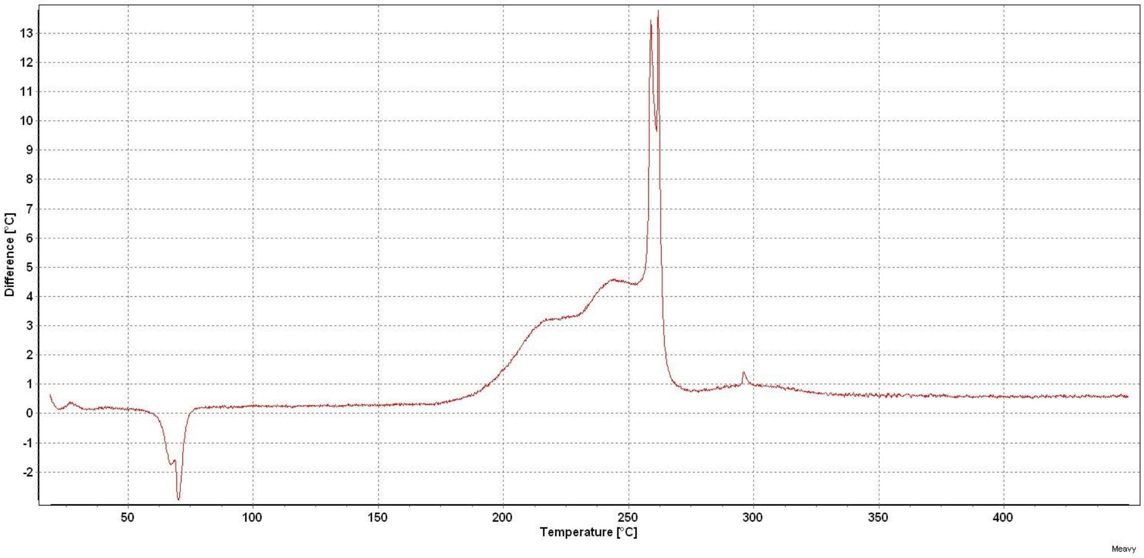
Annex 11: 1-Methylimidazolium nitrate



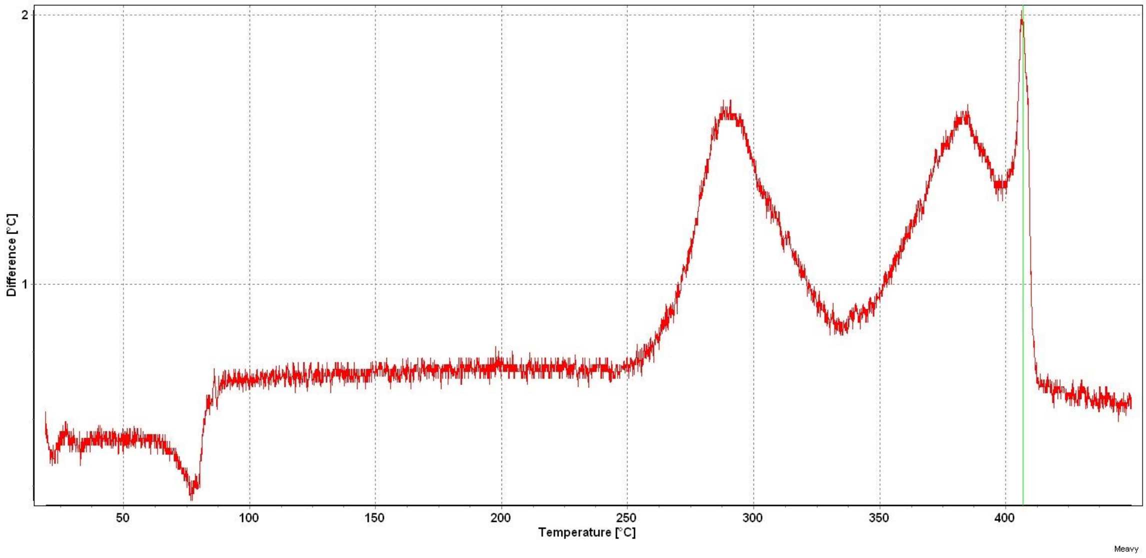
Annex 12: *N*-Methyl-*N*-(2-nitroxyethyl)ammonium nitrate



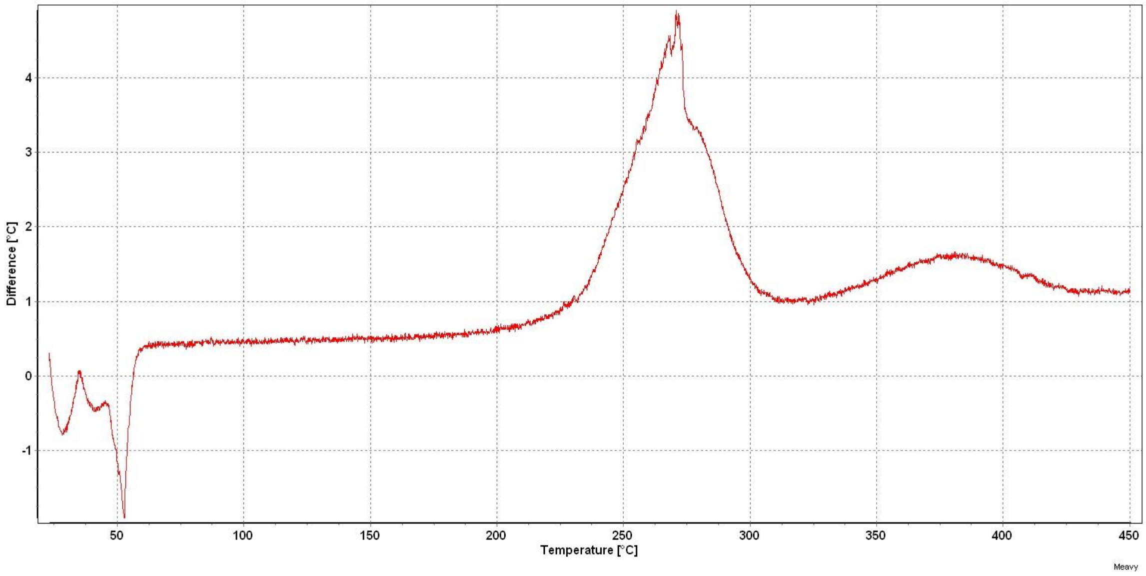
Annex 13: Formamidine nitrate



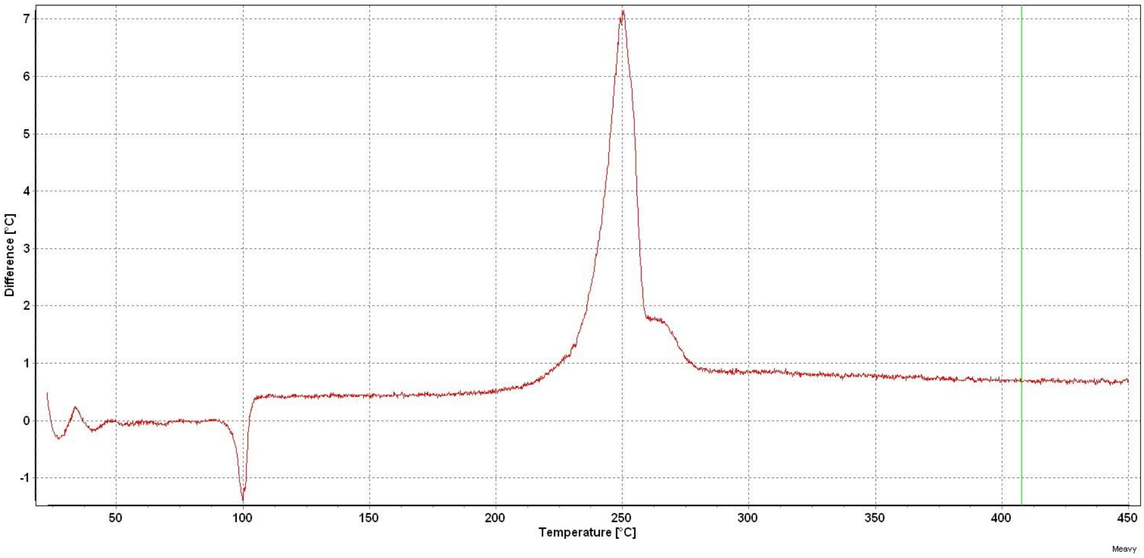
Annex 14: 4-Amino-1,2,4-triazolium nitrate



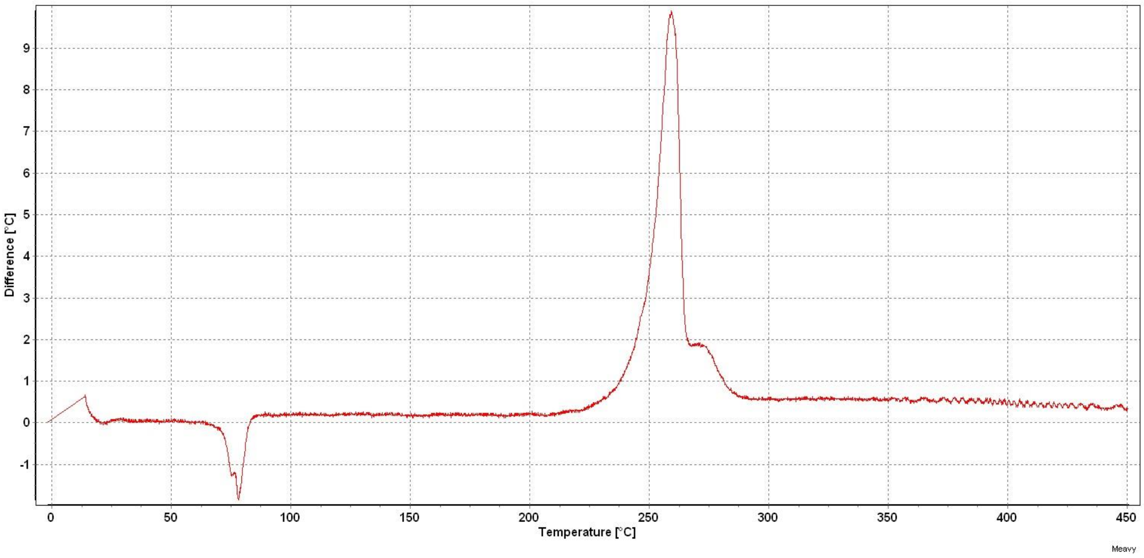
Annex 15: 4-Amino-1,2,4-triazolium perchlorate



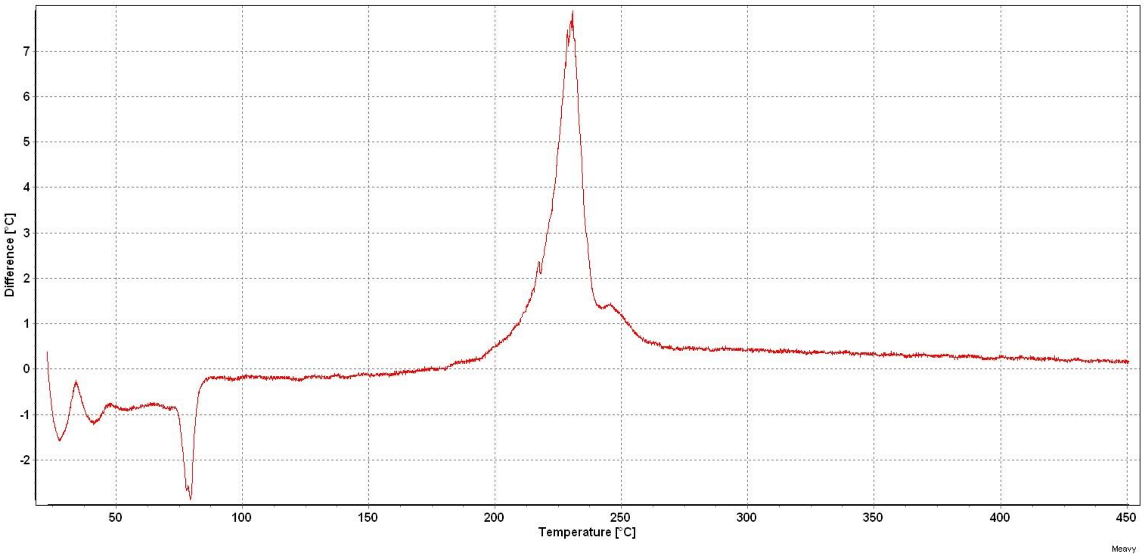
Annex 16: Allyl 3,5-dinitrobenzoate



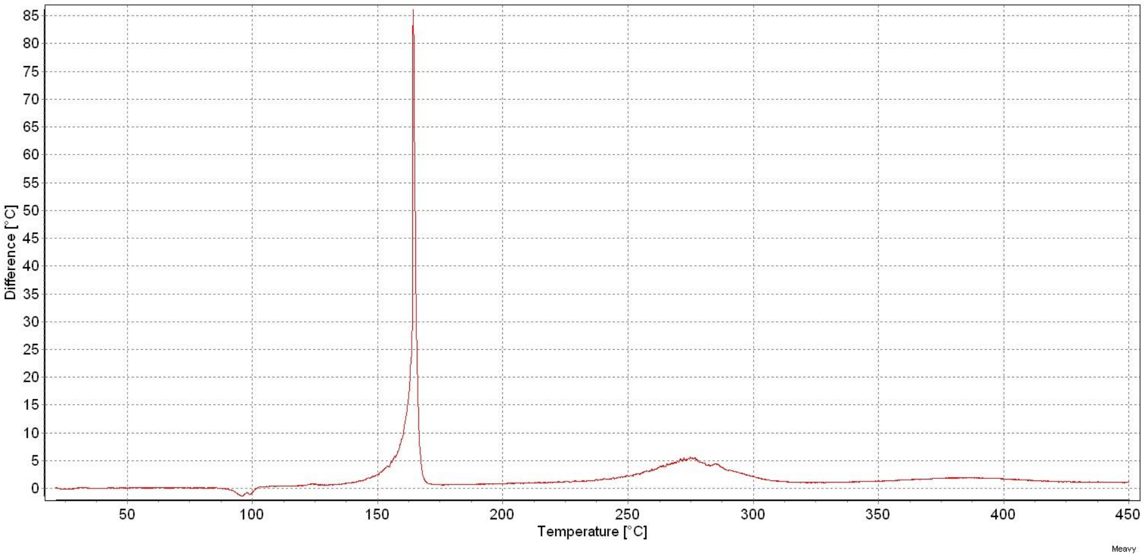
Annex 17: Dipropylamine picrate



Annex 18: Diethylamine picrate



Annex 19: Diallylamine picrate



Annex 20: *N*-Ethyl-*N*-nitro-2,4,6-trinitroaniline