МИНИСТЕРСТВО НА ОТБРАНАТА

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„RESEARCH AND EVALUATION MODEL OF ENERGETIC MATERIALS WITH LOW ECOTOXICOLOGY”

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1. INTRODUCTION

The recent decades have been marked by rapid technological advancements and their integration into all areas of societal life. Scientific research is increasingly focused on fundamental discoveries capable of reshaping existing paradigms and paving the way for innovative solutions. Industry and the economy are closely intertwined with the scientific community, decisively investing in research and development and adopting new technologies to enhance efficiency and economic performance.

Modern warfare significantly differs from classical military operations of the past, owing to the global war on terrorism and the deployment of cutting-edge technologies. The changing nature of warfare requires a different approach to targeted objectives, identification and monitoring. Response times have been significantly reduced, demanding exceptionally high operational efficiency.

There remains a strong scientific interest in insensitive munitions. This area of energetic materials research continues to be a key direction in contemporary studies. The development and utilisation of smokeless propellants and charges represents a broad field with considerable potential for advancements in synthetic chemistry, with particular focus on increasing energy density.

The relevance of the present research is underscored by the growing scientific emphasis on replacing toxic explosives with environmentally benign compounds. This trend is driven by increasing societal pressure and increasingly stringent legislative frameworks. Unlike conventional chemical syntheses and processes, current research is directed towards fundamental breakthroughs at the molecular level, with the potential to deliver more radical and powerful solutions offering significant benefits.

Notable progress in modern high-energy materials has been achieved through the development of nitrogen-rich compounds. This dissertation focuses on the theoretical and experimental investigation of such high-nitrogen compounds, which exhibit remarkable properties. The robust covalent bonding between nitrogen atoms

facilitates increased material density, which, in turn, enhances detonation velocity and heat of formation. Poly-nitrogen heterocycles are particularly promising, offering high density, improved performance, reduced carbon content, and improved oxygen balance. A distinct advantage of nitrogen-rich chemical structures is their compliance with stringent requirements for non-toxic impacts on ecosystems and human health, as their primary decomposition product is nitrogen gas.

The objective of this dissertation is to assess the suitability of innovative high-nitrogen compounds as alternatives to conventional energetic materials, to systematise the main research directions and future applications, and to propose a reliable, sufficiently precise methodology for evaluating their environmental impact.

Given the advantages, recent years have witnessed the development of numerous new poly-nitrogen structures by research teams worldwide. A substantial body of scientific work with valuable results and insights is currently emerging, necessitating the introduction of systematic approaches to consolidate knowledge, delineate key research directions, and enhance the efficiency of investigative processes.

The central hypothesis of this dissertation is to evaluate the potential of fundamental high-nitrogen compounds to replace toxic contemporary explosives and to identify the principal trends for assessment and development of the next generation of innovative energetic materials.

Accordingly*, the scope of this dissertation* is concentrated on the physico-chemical and environmental properties of poly-nitrogen compounds, based on experimental studies and quantum chemical calculations.

Since its inception, the concept of “Green Chemistry” has evolved from a theoretical construct into a comprehensive framework, driven by coordinated efforts within the European Union and the United States [1]. Contemporary scientific research is predominantly oriented towards substances, products, and processes that can be

categorised as “green.” Mukesh Doble and Anil Kumar define five primary directions derived from the principles of green chemistry:

➢ Reduction – Minimising the use of chemicals, energy, and solvents.

➢ Safety – Employing safe raw materials, solvents, and processes.

➢ Process-Oriented Design – Creating efficient processes with minimal waste and by-products, using catalysts.

➢ Waste Reduction – Monitoring waste generation in real-time, with an emphasis on biodegradable waste.

➢ Sustainability – Ensuring all chemicals, materials, energy sources, and solvents are renewable or sustainable [2].

At no point in history have the production and utilisation of energetic materials been subjected to such stringent environmental restrictions and requirements. In addition to standard demands for improved performance and safety, strict environmental protection standards have been imposed. The principles of green chemistry provide general developmental guidelines, but they lack specific recommendations for achieving sustainability within specific chemicals or manufacturing processes. Various proposals exist to introduce greater structure to these efforts; however, there remains no universally adopted, robust framework for the evaluation of green materials and environmentally sound manufacturing processes.

Encouraging progress has been made in the scientific development of innovative energetic materials, with the following key research directions emerging [3]:

•Quantum chemical methods for the design of green energetic materials with targeted properties (identifying substances with enhanced performance).

•Electrochemical synthesis methods for energetic materials and wastewater purification processes associated with their production.

•Reducing detonation sensitivity through molecular-level research to identify molecular and crystalline structures capable of mitigating the risk of unintended detonations.

•Pyrotechnic materials – Eliminating perchlorates, toxic heavy metals (e.g., lead, chromium), and harmful organic compounds.

•Primary explosives – Ongoing efforts to replace lead azide and lead styphnate.

•Secondary explosives – Development of green alternatives to the widely used military explosive RDX (1,3,5-trinitro-1,3,5-triazacyclohexane).

•Green oxidisers – Enhancing the stability and compatibility of ammonium dinitramide.

Practical experience demonstrates that the development of innovative energetic materials contributes not only to improved safety and operational sustainability but also to reduced ecotoxicity and enhanced economic performance. Comprehensive lifecycle assessment, encompassing the entire chain from research and development to field deployment, represents an exceptionally effective approach to achieving these goals

2. CONCLUSIONS FROM THE LITERATURE REVIEW

The analysis of the presented information regarding the current state of the research topic leads to the following conclusions:

1.Energetic materials have played a significant role in the advancement of human civilisation, evolving from early gunpowder for firearms to rocket propellants, explosives, pyrotechnic devices, and gas generators, which are now utilised not only in military applications but also in numerous civilian sectors such as construction, infrastructure development, mining, oil extraction, and entertainment.

2.Their widespread use necessitates continuous improvement of their physic-chemical properties, including detonation velocity, detonation pressure, heat of explosion, thermal stability, sensitivity, chemical stability, water solubility, and smokeless combustion.

3.Societal expectations for the environmental sustainability of modern energetic materials are steadily increasing. These expectations are being formalised through environmental legislation, strict adherence to established standards, and the imposition of economic sanctions and restrictions.

4.A strategic roadmap has been developed for the advancement of green chemistry and, by extension, green energetic materials. This roadmap advocates for a holistic approach to evaluating an energetic material, encompassing the entire life cycle: raw materials, synthesis, production, utilisation, storage, decomposition products, and environmental remediation.

5.The principles of green chemistry create a necessity for interdisciplinary collaboration within research teams developing innovative energetic materials. Beyond chemists, specialists from fields such as information technologies, environmental science, toxicology, and economics must be actively involved.

6.Environmental risk assessment of a given energetic material is becoming a standard criterion for authorising its use, transport, and storage.

7.The design and synthesis of poly-nitrogen compounds constitute a vital research direction, driven by their favourable detonation and combustion characteristics, desirable thermochemical properties, oxygen balance, advantageous environmental performance, and safety profile.

8.The requirements imposed on next-generation energetic materials necessitate a fundamentally new approach to the development of poly-nitrogen compounds, incorporating new knowledge and practices related to synthesis, testing methodologies, and computational modelling.

9.Existing data concerning the properties of high-nitrogen compounds indicate that their future development—particularly of high-nitrogen heterocyclic structures—holds significant scientific potential, warranting increased research efforts in this field.

10.A highly relevant research direction involves the modification of existing or novel compounds using nitrogen-rich

cations and anions. Nitrogen-rich functional groups are employed in the design and synthesis of poly-nitrogen energetic salts to enhance properties such as density, detonation performance, and thermal stability.

11.High-nitrogen fuel components exhibit a de-oxidising effect on flame behaviour in pyrotechnic devices, resulting in reduced combustion temperatures. This concept has been successfully applied to smoke-generating pyrotechnics, including both coloured and white smoke formulations. Efforts to fully replace chlorine-based products with high-nitrogen molecules are ongoing.

12.To align scientific research with contemporary demands for low-toxicity, cost-effective, efficient, and environmentally responsible materials, strategies for sustainable development and practical implementation of green chemistry principles are being introduced. The advancement of high-nitrogen structures encompasses both the optimisation of existing synthesis and research methods and the development of fundamentally novel approaches and methodologies.

3. GOAL AND OBJECTIVES

The primary goal of this dissertation is to investigate the suitability of innovative high-nitrogen compounds as alternatives to contemporary energetic materials, to systematise the main directions in their research and potential future applications, and to propose a reliable and sufficiently precise methodology for assessing their environmental impact.

To achieve this goal, the following specific objectives have been set:

1.To analyse the conditions that necessitate the improvement of energetic materials through the development of environmentally friendly and sustainable alternatives:

1.1. To examine the necessity for the development of eco-friendly energetic materials.
1.2. To review the international legislative framework regulating the environmental requirements for chemical substances.
1.3. To explore the challenges associated with the creation and advancement of green energetic materials.
1.4. To outline current trends in the research and development of environmentally responsible energetic materials.

2.To investigate the potential and feasibility of advancing high-nitrogen energetic materials:

2.1. To conduct a comprehensive review of scientific developments aimed at discovering high-nitrogen compounds with desirable characteristics.
2.2. To analyse and compare the physic-chemical properties of these compounds.
2.3. To define the target properties for the development of high-nitrogen compounds.

3.To develop a conceptual framework for the evaluation of high-nitrogen energetic materials:

3.1. To propose a classification scheme for the systematisation of scientific research related to poly-nitrogen compounds.
3.2. To assess the integration of green chemistry principles across the entire life cycle of high-nitrogen materials.
3.3. To present a methodology for the measurement, analysis, and prediction of the environmental impact associated with novel high-nitrogen chemical structures.

4. NEED FOR THE DEVELOPMENT OF ENVIRONMENTALLY ORIENTED ENERGETIC MATERIALS

4.1. Limitations of Contemporary Energetic Materials

Modern energetic materials, including secondary explosives, pyrotechnic compositions, and propellants, exhibit considerable limitations that necessitate the development of a new generation of explosives. The high toxicity and sensitivity of many existing formulations are incompatible with contemporary safety standards and environmental regulations, directing scientific efforts towards the development of alternative, environmentally improved compounds and production processes.

Primary explosives continue to rely heavily on lead azide and other toxic heavy metals such as cadmium and mercury. Lead, cadmium, and mercury are highly toxic to humans and other living organisms, primarily due to their inhibition of vital enzymatic processes, resulting in multi-organ failure.

Lead styphnate, also known as 2,4,6-trinitroresorcinol lead salt ($C_6H_3N_3O_8 \cdot Pb$), is another energetic material containing toxic heavy metal salts, prompting increasing restrictions on its use. Lead styphnate is insoluble in water and most organic solvents, and numerous incidents have been reported during its manufacture, often triggered by static electricity [4].

According to Jacqueline Akhavan [5], lead styphnate is regarded as a relatively weak primary explosive due to its high metal content (44.5%) and is generally not used as a stand-alone initiator charge in detonators. Instead, it is incorporated into ignition capsules in combination with lead styphnate, lead azide, and aluminium powder.

The widespread use of lead-containing compounds across both military and civilian sectors—including batteries, electrical wiring, pipelines, tanks, paints, pigments, and X-ray equipment—has resulted in significant environmental contamination. Human exposure occurs

primarily through inhalation of airborne lead particles and the consumption of leafy vegetables cultivated in contaminated soils.

Efforts to reduce lead contamination are multi-faceted, involving not only the reduction of lead usage but also the remediation of polluted soils and water sources. Decontamination processes are costly, often amounting to millions of pounds depending on the scale of the site.

Another toxic compound historically used in explosives is mercury fulminate ($C_2N_2O_2Hg$). Mercury fulminate is highly sensitive to shock, friction, and heat, and can be readily detonated by sparks or flames. Consequently, it has been utilised as a primary explosive, typically stored underwater and protected from light exposure.

Upon detonation, mercury fulminate decomposes into stable products according to the following reaction (Equation 1):

$$(CNO)_2Hg \rightarrow 2CO + N_2 + Hg \quad (1)$$

On 1 January 2018, the European Parliament Regulation 852/2017 concerning mercury entered into force, following its publication on 17 May 2017 [6]. Mercury is classified as highly toxic and a global threat to human health, ecosystems, and biodiversity. The associated Convention mandates that member states develop strategies for the identification and remediation of mercury-contaminated sites.

Over the past fifty years, ammonium perchlorate has been extensively employed as a solid oxidiser, prized for its reliable performance, relatively low handling risk, and broad spectrum of ballistic properties. Despite its benefits, ammonium perchlorate poses significant environmental and human health risks. The perchlorate anion (ClO_4^-) has been detected in numerous global drinking water sources.

Although perchlorate is considered chemically inert under certain conditions, it can exhibit explosive behaviour when combined with oxidisable materials such as organic compounds or ammonium ions. This behaviour is attributed to the release of small gaseous

molecules that undergo rapid thermal expansion, creating fast, unpredictable reactions.

The most common form, ammonium perchlorate, is utilised as a solid rocket oxidiser and ignition source in munitions and fireworks. Potassium perchlorate is found in highway flares, airbag inflation systems, and, since the 1950s, in the treatment of Graves' disease (hyperthyroidism). Militarily, ammonium perchlorate serves as an oxidiser in explosive formulations, rocket propellants, and artillery shells. Without the addition of fuel, tertiary explosives based on pure ammonium perchlorate exhibit detonation energies roughly one-third that of TNT. In terms of transport and storage regulations, ammonium perchlorate is classified as an oxidiser rather than an explosive. Nevertheless, tertiary explosives have been responsible for some of the most catastrophic accidents in history.

The environmental concerns associated with perchlorates arise from their high chlorine content, which is converted into hydrochloric acid during combustion. During burning, these boosters emit large volumes of exhaust gases containing hydrochloric acid and other chlorine-containing by-products. These emissions are highly toxic and corrosive, with the release of hydrochloric acid contributing to acid rain formation [7]. Laboratory studies on animals and humans suggest that exposure to perchlorates may cause irreversible effects on thyroid function.

In recent decades, heavy metals such as barium, lead, and hexavalent chromium have been widely used in various pyrotechnic compositions and medium-calibre munitions. One common method for generating green light in pyrotechnics involves the use of barium nitrate in the presence of chlorinated organic compounds, forming stable barium chloride as the luminous emitter. Historically, many incendiary charges have contained significant quantities of metal-based fuels in the form of barium nitrate as the oxidiser. The high combustion temperatures produced generate metal oxides, such as barium oxide (BaO), which emit across a broad molecular spectrum and serve as intense white light generators [3]. Barium chromate

($BaCrO_4$) has traditionally been used as a delay composition in pyrotechnic devices.

Numerous barium compounds and their combustion products are considered carcinogenic [8]and are regarded as hazardous in occupational settings.

Due to the relatively high environmental mobility of explosives and their by-products, energetic materials developed since World War II have contaminated air, water, and soil with toxic substances. Many of these compounds bioaccumulate, necessitating their restriction or outright bans because of regulatory action.

4.2. Requirements for Modern Energetic Materials

The search for innovative explosives with enhanced thermal stability (decomposition temperatures exceeding 320°C) and superior performance characteristics has become a central goal in current research. High thermal stability correlates with reduced sensitivity, thereby improving the safety of handling and storage.

Research objectives for the next generation of energetic materials focus on the development of compounds that are less sensitive, more compatible, more stable, and more efficient, while simultaneously providing greater safety and reduced eco-toxicity.

According to Agrawal [7], energetic materials with high thermal stability can be achieved through:

- Formation of salts.
- Incorporation of nitro groups.
- Introduction of conjugated systems.
- Condensation with triazole rings.

In the theoretical design of new compounds, target parameters are established, including detonation velocities exceeding 9000 $m \cdot s^{-1}$, detonation pressures above 380 kBar, and explosion heats surpassing that of RDX (6200 $kJ \cdot kg^{-1}$). The thermal stability of newly synthesised materials should exceed 180°C, ensuring safe handling of munitions

subjected to prolonged exposure to direct sunlight and elevated ambient temperatures.

In addition to these factors, the safe storage of explosives requires sustained high thermal stability under elevated temperatures without observable decomposition. The sensitivity of RDX to external stimuli such as impact (7 J), friction (120 N), and electrostatic discharge (0.20 J) serves as the benchmark for comparison [9].

4.3. Novel Approaches for the Development of Innovative Energetic Materials. Advantages of High-Nitrogen Compounds over Carbon-Based Structures.

The primary objective in achieving high-performance energetic materials lies in the development of compounds with high density. The energy content of such materials is introduced through ring systems in combination with nitro or nitramine functional groups, which contribute to an optimised oxygen balance and increased nitrogen content.

Various approaches exist for the design and synthesis of such molecular structures. Selected examples of these approaches are presented in Table 1. [10] [11]

Table 1

Strategies for the synthesis of high-energy materials.

Type	Example	Specifics
Oxidation of the carbon skeleton, aliphatic compounds	TNT, Nitropenta, Hexogen	Compounds may be exothermic or endothermic, covalent or ionic
Ring (cyclic) chains	Hexanitrohexaaziisowurtzitane (Cl-20), Octanitrocubane (ONC)	Most are endothermic and covalent

Nitrogen-rich molecules	Hydrazinium azotetrazolate (HZT), Triamino-guanidinium azotetrazolate (TAGZT)	They are always endothermic compounds, they can be covalent or ionic

4.4. Conclusions from Chapter Four

There is a clear understanding regarding the toxic constituents of energetic materials, as well as extensive research addressing their detrimental impact on ecosystems. Improvements in toxicity and sensitivity of existing energetic materials have been precisely defined as critical characteristics in the search for innovative alternatives. Enhancements in detonation performance are achieved primarily through increasing the material density, which directs scientific efforts towards quantum chemical solutions. The robust covalent triple bond between nitrogen atoms proves to be a key factor in achieving excellent performance while simultaneously reducing harmful environmental effects. This underscores the importance of in-depth investigations into nitrogen-based molecular structures and high-nitrogen compounds.

5. RESEARCH AND DEVELOPMENT OF POLY-NITROGEN COMPOUNDS

5.1. Contemporary Investigations into Pure Nitrogen Compounds

In recent years, theoretical quantum chemical calculations have been conducted to predict the high enthalpies of formation and densities achievable through the construction of strained structures composed almost entirely of nitrogen atoms or nitrogen-oxygen assemblies, which utilise the stabilising properties of oxygen. From a theoretical perspective, the application of poly-nitrogen compounds

has the potential to deliver specific impulses in the range of 350 to 500 seconds, with material densities between 2.0-3.9 g/cm^3. [12]

A major challenge in the study of new high-nitrogen energetic compounds lies in the unsatisfactory accuracy of energy potential analyses for specific representatives within this group. Existing assessments often overlook the fact that, in addition to the primary energy carrier within the molecule, additional energy contributions are provided by structural fragments incorporated to optimise other performance parameters beyond energetic output.

Figure 1 illustrates the molecular structures of several hypothetical poly-nitrogen compounds that are currently the subject of ongoing scientific investigation.

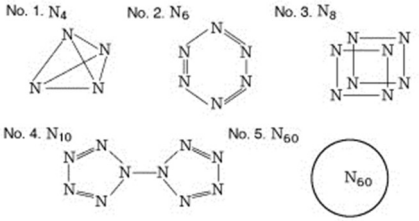

Figure 1. Hypothetical poly-nitrogen compounds

For these novel compounds to have practical applications, they must not only release large amounts of energy when required but also demonstrate sufficient chemical stability to allow for safe production, handling, and storage. This implies that poly-nitrogen systems should possess both a high decomposition energy and a relatively elevated activation barrier for degradation. Quantum mechanical calculations suggest that N_4, N_5, N_8, and N_{10} are viable molecular species. [13]

Poly-nitrogen structures can generally be categorised as linear, cyclic, or cage-like frameworks. The latest research trends in this field focus on maximising the formation of single covalent bonds between nitrogen atoms, as these contribute to the release of significant amounts of energy upon decomposition. Most scientific investigations to date have concentrated on the synthesis and characterisation of

linear or cyclic structures containing up to ten nitrogen atoms, including both neutral and ionic forms. [14]

For neutral poly-nitrogen species, several covalent, allotrope-like nitrogen structures have been identified, including a cubic arrangement, polymeric nitrogen with a structure analogous to black phosphorus, and the molecular form of N_8. [15]. In recent years, several ionic nitrogen species have also been discovered, such as the pentazole anion, the pentazenium cation, and metal pentazolate hydrate complexes. Larger nitrogen-based anions have been identified, including tungsten hexanitride and the N_8^- anion, which has been synthesised on the sidewalls of multi-walled carbon nanotubes and stabilised on boron-doped graphene surfaces [14]

While several theoretical studies have proposed that species such as N_3, N_4, N_5^+, N_5^-, N_6, N_8, N_{10}, and even N_{60} have potential as high-energy-density materials, only a limited number of these species have been successfully synthesised to date. Experimentally producing poly-nitrogen compounds under standard atmospheric conditions remains extremely challenging. Typically, their synthesis requires high pressures and cryogenic temperatures (below -153°C). Moreover, there is still no universal synthetic methodology for producing pure nitrogen compounds, largely due to their highly endothermic nature.

Among nitrogen-containing heterocycles, tetrazoles—containing approximately 80% nitrogen by mass—rank second in terms of nitrogen content, surpassed only by pentazoles, which contain 92.3% nitrogen. Pentazoles are noted for their remarkable stability and significant electron-donating capabilities. Tetrazoles, however, are more frequently employed in the synthesis of novel energetic materials. The high thermal stability of tetrazoles, coupled with their substantial heat of formation (+237 $kJ \cdot mol^{-1}$), makes them a reliable structural foundation for the development of new energetic compounds. [16]

At present, scientific efforts are focused on exploring the possibility of combining N_{10} and N_3^- ions to form a neutral N_8 species, either as an ionic salt (N_5^+ N_3^-) or as a covalently bonded azido pentazole structure. Should such a compound be successfully

synthesised in a stable form, its energy content is projected to exceed that of hydrazine—a commonly used rocket propellant—by over 200%. [13]

The Table 2 below summarises the calculated performance parameters of poly-nitrogen compounds in comparison to conventional high-energy materials. [13]

Table 2

Performance Parameters of Poly-Nitrogen Compounds Compared to Conventional High-Energy Materials.

Compound	**Formula**	**Density, g/cm^3**	**Enthalpy of formation, ккал/mol**	**Detonation speed, км/s**	**Detonation pressure, GPa**
Octogen	$C_4H_8N_8O_8$	1.90	28.00	9.10	39.00
Hexanitrohexaazoisowurtzitane	$C_6H_6N_{12}O_{12}$	2.00	109.80	9.40	42.00
Dinitroazoxyfurazan	$C_4N_8O_8$	1.91	159.10	10.00	50.00
Octanitrocubane	$C_8N_8O_{16}$	2.10	111.00	10.10	50.00
N_4	N_4	1.75	268.70	13.24	77.02
N_5^{1+}	N_5^{1+}	1.85	350.00	12.51	73.95
N_6	N_6	1.97	345.58	14.04	93.32
N_8	N_8	2.15	406.69	14.86	108.39
N_{10}	N_{10}	2.21	473.42	12.08	58.05
N_{12}	N_{12}	2.28	579.82	12.53	64.07
N_{60}	N_{60}	2.67	546.00	17.31	196.00

Based on theoretical calculations, poly-nitrogen compounds are characterised by exceptionally high enthalpies of formation, ranging from 2000 to 5000 $kcal \cdot kg^{-1}$, and high densities in the condensed phase, between 2.0 and 4.0 $g \cdot cm^{-3}$. [17] If large-scale production of poly-nitrogen materials can be achieved, they could significantly transform technologies within the high-energy materials sector.

5.2. Contemporary Research on other Poly-Nitrogen Compounds

A notable breakthrough has been made in the development of energetic poly-nitrogen salts. Compared to their atomic or non-ionic counterparts, these salts exhibit lower vapour pressures, higher densities, and enhanced thermal stability. Furthermore, the extensive nitrogen-nitrogen bonding contributes to high heats of formation, while their low carbon and hydrogen content improves oxygen balance.

A crucial advantage of poly-nitrogen salts is their classification as environmentally friendly "green" materials, as nitrogen gas is the primary decomposition product. Their properties can be further enhanced by combining different cations and anions or through independent modifications of the ionic components. Progress has been made in the development of high-performance poly-nitrogen salts with improved sensitivity profiles.

5.2.1. Ammonia-Based Salts

This group of poly-nitrogen salts is distinguished by exceptionally high nitrogen content. Examples include hydrazoic acid (HN_3, nitrogen content: 97.7%), tetraazidomethane ($C(N_3)_4$), hydrazinium azide ($N_2H_5N_3$, empirical formula N_5H_5), obtained by neutralising unstable hydrazoic acid with hydrazine hydrate,

ammonium azide (NH_4N_3, empirical tetrazene, N_4H_4), and diazene (N_2H_2), all with nitrogen contents of approximately 93.3%.

Pure liquid hydrazoic acid can detonate spontaneously, while hydrazinium azide is highly sensitive to accidental initiation. [18] The sensitivity of hydrazinium azide can be reduced by crystallising it in the presence of excess hydrazine during its preparation; however, this reduces the nitrogen content to 91.5%. [19]

5.2.2. Dinitramide-Based Salts

The application of dinitramide salts in composite solid propellants mitigates the formation of chlorine-containing waste products during combustion. These salts exhibit high heats of formation and favourable densities, making them promising candidates for high-energy materials with broad military and civilian applications. Key advantages include high specific impulse, fast burn rates, low gas emissions, and competitive production costs.

Ammonium dinitramide (ADN) is the best-known dinitramide salt, widely studied for its excellent performance in composite solid propellants. ADN represents an environmentally acceptable alternative to ammonium perchlorate. Although ADN has a lower oxygen balance and heat of formation compared to perchlorate, it offers superior specific impulse and produces combustion gases free from hydrogen chloride. The current use of ADN remains limited due to its high hygroscopicity, although significant research efforts are underway to address this drawback.

Silver dinitramide ($AgN(NO_2)_2$) is also under investigation as a green alternative to ammonium perchlorate [20], primarily serving as a reagent for dinitramide transfer.

5.2.3. Nitrogen Fluoride-Based Salts

Despite extensive research, there is still no clear consensus regarding the practical viability of nitrogen fluorides. Nitrogen forms

four binary fluorides: nitrogen trifluoride (NF_3), diazo tetrafluoride (N_2F_4), difluorodiazene (N_2F_2), and azido fluoride (FN_3).

Numerous other nitrogen-fluorine compounds exist, the most notable being nitrosyl fluoride and nitrile fluoride; however, only NF_3 and N_2F_4 are currently of interest as oxidisers for rocket propulsion.

When employing nitrogen trifluoride in military applications, rigorous purity analyses are required, as impurities may interfere with the performance of heterocyclic molecular structures, particularly in laser fuel. [21]

5.2.4. High-Nitrogen Heterocycles

Heterocyclic molecular compounds are frequently preferred over carbocyclic analogues due to their higher heats of formation, increased densities, and improved oxygen balance. High-energy salts in which both the cation and anion are nitrogen-rich offer distinct advantages over non-ionic molecules, including lower vapour pressures and higher densities.

Although high-nitrogen compounds tend to be more expensive to produce, their benefits such as low flame temperatures (resulting in reduced barrel corrosion in firearms), suitability for tactical missiles, and low detection signatures are indisputable.

5.2.5. Ionic Liquids

Ionic liquids exhibit properties distinct from those of conventional molecular liquids. To increase melting points, ionic salts incorporating small ions such as lithium cations, protons, or chloride anions are often synthesised. Halogen-free ionic salts represent an intriguing class of environmentally responsible materials.

The introduction of functional groups into the ionic structure can enhance melting points and/or viscosity, enabling the design of novel ionic liquids with targeted energetic properties.

5.3. Conclusions from Chapter Five

Ionic liquids exhibit properties distinct from those of conventional molecular liquids. To increase melting points, ionic salts incorporating small ions such as lithium cations, protons, or chloride anions are often synthesised. Halogen-free ionic salts represent an intriguing class of environmentally responsible materials. The introduction of functional groups into the ionic structure can enhance melting points and/or viscosity, enabling the design of novel ionic liquids with targeted energetic properties.

6. RESULTS AND DISCUSSIONS. FRAMEWORK MODEL FOR EVALUATION.

The demonstrated advantages of high-nitrogen molecular systems have resulted in a substantial body of scientific discoveries, which must be systematically organised to enable more accurate evaluation and to define clear directions for further development. The present study does not aim to encompass the entirety of existing research on high-nitrogen energetic materials, but rather focuses on those studies that, to date, have shown the most promising results. It is essential to maintain systematic monitoring of the continuously evolving requirements, regulations, and societal factors to ensure an objective assessment of progress in this field. This dissertation develops a framework model for the evaluation, comparison, and projection of high-nitrogen compounds. The structural framework defines the stages and individual elements within the complex process of designing, producing, and applying a given poly-nitrogen compound.

6.1. Classification of Developed High-Nitrogen Compounds

The comprehensive research presented herein focuses on the nomenclature and categorisation of the poly-nitrogen compounds discussed. The proposed classification, illustrated in Figure 2, is based on the structural principles underlying both hypothetical and experimentally confirmed poly-nitrogen building blocks, the synthesis processes, and the comparison of key detonation parameters.

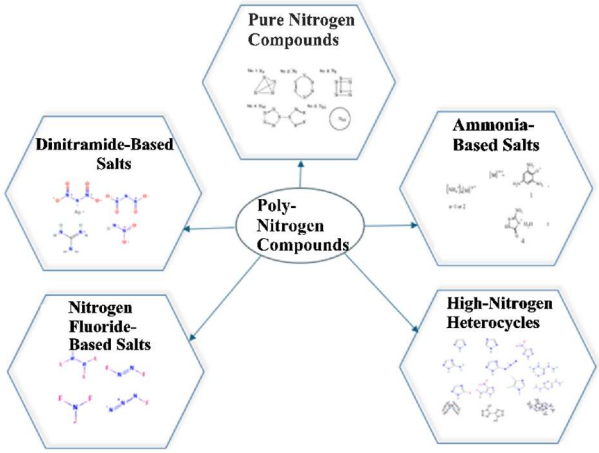

Figure 2. Classification of High-Nitrogen Energetic Materials Based on Their Molecular Building Structures

High-nitrogen compounds have demonstrated diverse applications in defence technologies and aerospace engineering. The nitrogen-containing compounds identified in this research represent a promising alternative to currently used energetic materials. Building upon the established classification framework for energetic materials, Figure 3 presents an extended qualification scheme for newly discovered poly-nitrogen compounds, based on their application within the defence sector.

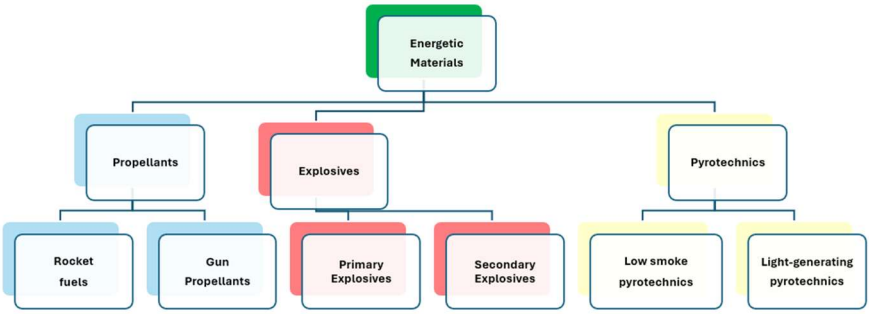

Figure 3. Classification of Poly-Nitrogen Compounds by Defence Application.

6.1.1. Propellants

The primary oxidiser in composite propellants is ammonium perchlorate (AP), discussed in Section 4.1, which poses significant toxicity risks to living organisms. Ammonium dinitramide (ADN) has emerged as an effective replacement for AP, offering superior performance and improved environmental characteristics. Ongoing research focuses on enhancing the sensitivity and stability of ADN. [7] Applying polymer coatings to composite propellants, such as octogen (HMX), as exemplified by polymer-bonded explosives PBX-9501 and PBX-9011, reduces sensitivity. This technology embeds newly synthesised explosive crystals within rubber-like polymer matrices. The use of suitable polymers, such as hydroxyl-terminated polybutadiene (HTPB), significantly improves the safety of these formulations for both composite solid propellants and polymer-bonded explosives. [22]

Compounds such as ammonium azotetrazolate (AAT), guanidinium azotetrazolate (GAT), and triaminoguanidinium azotetrazolate (TAGAT) are suitable for low-emission propellants. Ammonium and triaminoguanidinium salts also show potential as replacements for HMX in propellant formulations.

6.1.2. Primary Explosives

A key characteristic of primary explosives is their rapid deflagration-to-detonation transition (DDT), which describes the progression from deflagration at approximately 100 $m \cdot s^{-1}$ to detonation speeds exceeding the speed of sound, generating a shock wave capable of initiating less sensitive secondary explosives. Primary explosives are predominantly used as initiators in detonators and blasting caps. Their toxicity is largely attributed to the presence of heavy metals. Promising alternatives include high-nitrogen compounds free from heavy metals, such as tetrazine or dipotassium 1,1-dinitramino-5,5-bistetrazole (KDNABT) [23],], as well as salts incorporating less toxic metals like copper or cobalt—for example, copper 5-nitrotetrazolate (CuNT) or pentamine-1,5-cyclopentamethylenetetrazole cobalt perchlorate (PMTCP). [24]

6.1.3. Secondary Explosives

Compared to primary explosives, secondary explosives must demonstrate superior detonation performance while maintaining low sensitivity to external stimuli, with impact sensitivity above 7 J and friction sensitivity above 120 N. [10] Current mainstream energetic materials in this category include TNT, RDX, HMX, and PETN, widely used due to their relatively simple, cost-effective synthesis and satisfactory performance. Nevertheless, significant opportunities exist for advancement in this area. Recent research focuses on various strategies for improving secondary explosive molecules, with high-nitrogen heterocycles, particularly azoles and azines, identified as promising candidates for high-performance green energetic materials. [7] Their elevated nitrogen content contributes to high heats of formation and predominantly non-toxic decomposition products, such as nitrogen gas, carbon dioxide, and water. Azoles are noted for their high densities, excellent thermal stability, and structural flexibility, allowing functional modifications. A notable example is TATB, offering exceptional thermal stability with a decomposition

temperature of 350°C, although its synthesis is costly and the material is highly insensitive, thus primarily reserved for nuclear applications.

A new explosive reported by J.P. Agrawal's team is 1,3-bis(1,2,4-triazol-3-yl)amino-2,4,6-trinitrobenzene (BTAATNB). [25] Its properties indicate excellent thermal stability (320°C) and improved insensitivity to impact and friction compared to 1,3,5-tris(2-nitroxyethyl)nitramino-2,4,6-trinitrobenzene (TNOENTNB), proposed as a potential PETN replacement.

Agrawal also synthesised bis(1,2,4-triazol-3-yl)-4,4-diamino-2,2,3,3,5,5,6,6-octanitroazobenzene (BTDAONAB), which has an unprecedented decomposition point above 550°C and a detonation velocity of 8300 $m \cdot s^{-1}$, currently the most thermally stable energetic material compared to established alternatives.

Further development of BTDAONAB focuses on optimising synthesis and conducting comprehensive assessments before potential industrial application. A similar material has been reported by Keshavarz, in which triazole groups are substituted with more endothermic tetrazole units. [26] However, both compounds remain compatible with existing primary explosives, such as lead azide or lead styphnate.

A recently identified secondary explosive is 5,5-bis(2,4,6-trinitroethyl)-2,2-bis(1,3,4-oxadiazole) (TKX-55), synthesised from demilitarised TNT. It exhibits promising detonation properties, with a velocity of 8030 $m \cdot s^{-1}$ and detonation pressure of 273 kBar. [27] [28]

6.1.4. Pyrotechnic Formulations

Military pyrotechnics primarily include signal flares, smoke ammunition, and delay compositions. Modern research focuses on replacing perchlorates, halogens, and heavy metals known to be harmful to living organisms. High-nitrogen compounds offer potential as fuels and colourants, especially when combined with less toxic metal ions, such as substituting barium with copper. "Green" pyrotechnic formulations exclude perchlorates and heavy metals, and should rely on low-cost, easily synthesised, non-hygroscopic

compounds. High nitrogen content is desirable to minimise smoke and mechanical residues. [29]

Tetrazoles, aromatic compounds with nitrogen content approaching 80%, exhibit good stability. A recent candidate for low-smoke coloured ammunition is strontium ditetrazolate pentahydrate, which produces a bright red colour derived from strontium hydroxide. The compound and its decomposition products are insensitive to impact, friction, or electrostatic discharge.

Protonating bistetrazole with amines, metal carbonates, or hydroxides produces nanoporous metal foams, which serve as precursors for poly-nitrogen salts utilised in gas generators, automotive airbags, and propellant additives. The addition of copper sulphate yields copper bistetrazole complexes, which emit coloured light and exhibit low sensitivity, making them attractive for pyrotechnic applications due to their affordability.

Ammonium, guanidinium, and triaminoguanidinium azotetrazolate salts have been synthesised and evaluated for pyrotechnic use, confirming their suitability for smokeless gas generators and propellant additives.

Recently, the properties and crystal structures of several alkali metal salts of the aminotetrazole anion have been published. These salts are inexpensive to produce, chemically stable up to 350°C, and exhibit melt behaviour without decomposition. Sodium salts produce flame colours ranging from red, orange, purple, lavender to pink, while lithium salts produce a red flame without perchlorate content. Despite their high nitrogen content, these compounds display low sensitivity to impact and friction.

One of the most promising materials for smokeless coloured fireworks is 3,6-dihydrazino-1,2,4,5-tetrazine (DHTz). Although not new (first synthesised in 1963), its production process has recently been optimised. DHTz burns at higher rates than traditional fuels like HMX, with reduced gas-phase luminosity and significantly lower combustion temperatures. When ground with oxidisers (AP or ADN) and small quantities of colourants, including sodium (yellow), strontium (red), barium nitrate (green), copper oxide or sulphide

(blue), and antimony (white), DHTz produces star compositions for fireworks. These mixtures are binder-free, pressed into desired shapes after moistening with water or ethanol, then air-dried. DHTz is also considered for use in propellant and rocket fuel applications.

6.2. Application of Green Chemistry Principles Across the Life Cycle of Poly-Nitrogen Compounds

Technological advancements continuously reveal new evidence of environmental pollution and the associated health risks to living organisms. These discoveries inevitably influence public opinion, which, in turn, drives increasingly restrictive legislation. Such developments intensify scrutiny of the environmental impact of munitions and their decomposition products. Given the complexity and multidimensional nature of this challenge, an integrated approach is essential, involving experts from diverse disciplines and financial stakeholders. Linking environmental impact assessments to cost reduction strategies enhances the attractiveness of investments in this area. A preventative approach is preferable to merely managing the consequences. Consequently, evaluating novel high-nitrogen formulations must extend beyond laboratory and scientific assessments to incorporate systematic, interdisciplinary analyses encompassing manufacturing feasibility, economic efficiency, and risk management.

The core detonation properties of innovative high-nitrogen formulations suitable for industrial production and practical application are summarised in Figure 4.

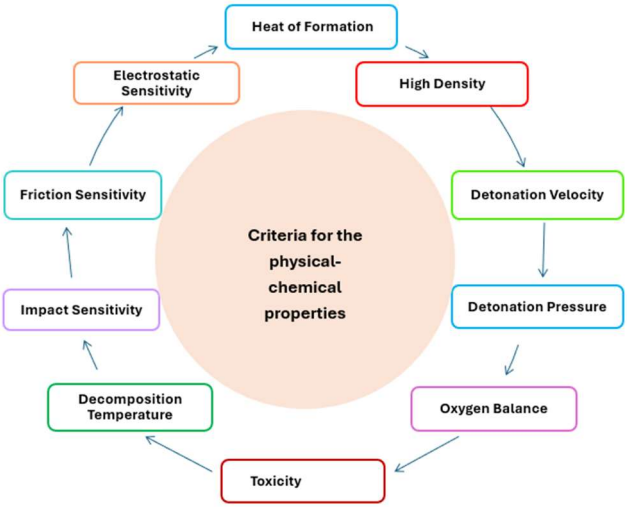

Figure 4. Criteria for the physical-chemical properties of novel high-nitrogen compounds.

The properties of high-nitrogen energetic materials presented in Figure 4 provide a critical assessment of their suitability for use in ammunition and weapon systems. However, this evaluation does not encompass the entire production process, environmental impact, economic costs, and associated risks. Research and development departments must adopt a more systematic approach and cultivate a culture of collaboration with other professional fields. When developing a new energetic material, the ultimate goal is its large-scale production and practical application. While the discovery of a new molecular formula with promising performance and stability properties is undoubtedly a significant scientific achievement, this does not automatically imply that the material is feasible for industrial production and operational use. The journey from laboratory discovery to manufacturing implementation is long and filled with numerous challenges that must be addressed.

Considering the principles of Green Chemistry, a structured roadmap has been developed to guide the selection process for

advancing a new high-nitrogen compound towards production. This roadmap is illustrated in Figure 5.

Figure 5. Roadmap for Assessing the Feasibility of Producing High-Nitrogen Energetic Materials.

Based on these analyses, it can be summarised that the development of high-nitrogen energetic materials should focus on the following key aspects:

- A simple and efficient synthesis process.
- The production and utilisation of environmentally benign compounds, precursors, and decomposition products, with consideration for their toxicity to the environment and living organisms.
- Strong detonation performance.
- Long-term stability

6.3. Methodology for Toxicity Assessment of High-Nitrogen Energetic Materials

6.3.1. Goals and Objectives

The objective is to establish a simplified yet reliable methodology for measuring and analysing the toxicity of high-nitrogen energetic materials.

To achieve this objective, the following tasks have been outlined:

1. To select an appropriate parameter for evaluating environmental risk, which effectively and accurately reflects the toxicity level of a given high-nitrogen compound.
2. To define a measurement method for determining the toxicity of energetic materials.
3. To develop a software platform for compiling and evaluating a toxicity database for poly-nitrogen materials.
4. To implement machine learning techniques for the prediction of toxicity in energetic compounds.

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6.3.2. Results and Discussions

Currently, environmental and human health impacts are considered as important as the detonation performance of explosives. In order to make informed decisions regarding environmental safety, modern analytical methods for predicting toxicity must align with the latest scientific advancements in this field.

A key parameter for environmental risk assessments is the EC_{50} value, which measures acute, short-term toxicity. EC_{50} is defined by both the European REACH Regulation and the United States Environmental Protection Agency (EPA). [30] [31] [32] It represents the concentration of a contaminant that causes adverse effects in 50% of test organisms.

The determination of EC_{50} considers factors such as observable biological effects, exposure duration, the selected test organisms, and experimental conditions. EC_{50} is a point-specific measure, for which variability coefficients can also be calculated. Detailed guidelines and algorithms for EC_{50} calculations are provided in [33]. In the context of energetic materials, EC_{50} is applied during the early stages of compound discovery to evaluate whether the molecular structure exhibits the desired properties.

The EPA recommends selecting test organisms that can tolerate typical environmental conditions but are sensitive to the contaminants under investigation. For energetic materials, the luminescent bacterium *Aliivibrio fischeri* has been identified as a suitable test organism for determining the aquatic toxicity of water-soluble chemicals. This method is rapid, cost-effective, and avoids animal testing . [34]

Professor Klapötke's research group, recognised for their work on high-nitrogen compound synthesis, recently published a study on the toxicity of several new energetic materials using Aliivibrio fischeri. [35]. Their research not only quantifies the toxicity of individual explosives but also identifies toxicity trends across various high-nitrogen structural groups. The findings indicate that tetrazoles exhibit low toxicity towards Aliivibrio fischeri, with disubstituted tetrazoles being more toxic than monosubstituted analogues. The introduction of azo groups increases toxicity, particularly in furazan derivatives. Nitroamine functionalities show minimal toxicity, especially in potassium salts. Covalent azides demonstrate lower toxicity compared to their ionic counterparts, while pyrazoles, trinitroalkyl groups, and fluorodinitroethyl groups are associated with significant toxicity.

Klapötke's group has announced ongoing research into the suitability of Aliivibrio fischeri for evaluating the toxicity of energetic materials. This is not their only study employing this methodology. In 2012, they used the same bacterium to assess the aquatic toxicity of TKX-50, a high-nitrogen alternative to RDX [36]

As early as 1994, German researchers identified Aliivibrio fischeri as an effective tool for assessing the toxicity of 24 explosives and related compounds. Based on toxicity data for aquatic organisms, explosives were classified as highly toxic, moderately toxic, or less toxic. [37]

Further innovation in the use of bioluminescent bacteria has been reported by Chinese scientists, who have developed biosensors combining Aliivibrio fischeri with magnetic nanoparticles. Preliminary tests suggest these biosensors could be promising tools for monitoring soil contamination, although the technology remains in its infancy and requires further research and development. [38]

The discovery of novel, environmentally acceptable energetic materials necessitate advancements in toxicity measurement and assessment methodologies. While systematic databases exist for the physico-chemical properties of energetic materials, including high-nitrogen compounds, comprehensive toxicity data remain limited. To reduce reliance on animal testing and accelerate toxicity assessments for nitrogen-rich compounds, predictive computational models have been proposed. One such approach is the development of in silico models, such as Quantitative Structure-Activity Relationship (QSAR) models.

QSAR was introduced by Corwin Hansch in 1962 for virtual drug screening. [39]. Over the past five decades, QSAR has evolved from a simple regression-based tool for structurally similar compounds into a sophisticated, machine-learning-driven methodology capable of analysing extensive molecular datasets. QSAR models are widely used to predict the biophysical properties of chemicals and assess their potential impact on human health and ecosystems. Their application has expanded to the field of energetic materials. In 2012, South Korean researchers presented an advanced, online QSAR model designed to evaluate new high-energy molecules [40] The model integrates three core functions: management, calculation, and search.

The management module provides a user-friendly interface for storing and managing molecular structures and properties of energetic

materials. The system automatically computes numerous compositional and topological molecular descriptors upon the entry of a new energetic formula into the database.

Physicochemical properties, such as heat of formation, density, and impact sensitivity, can be calculated using group contribution methods. For example, impact sensitivity can be estimated based on established empirical data using built-in predictive algorithms.

The search function enables users to locate specific energetic materials and their properties by sketching 2D chemical structures or inputting a set of desired compound characteristics.

QSAR models can be successfully applied to the prediction and assessment of toxicity in high-nitrogen molecules and compounds.

In this context, a schematic algorithm for toxicity evaluation is presented in Figure 6. The proposed computational model has the potential to become a powerful tool for developing promising new energetic materials. Establishing a comprehensive chemical database is of utmost importance, serving as a valuable resource for identifying potential new molecular candidates. Quantum-mechanically derived virtual structures can be utilised by theoretical researchers to synthesise new compounds with targeted properties.

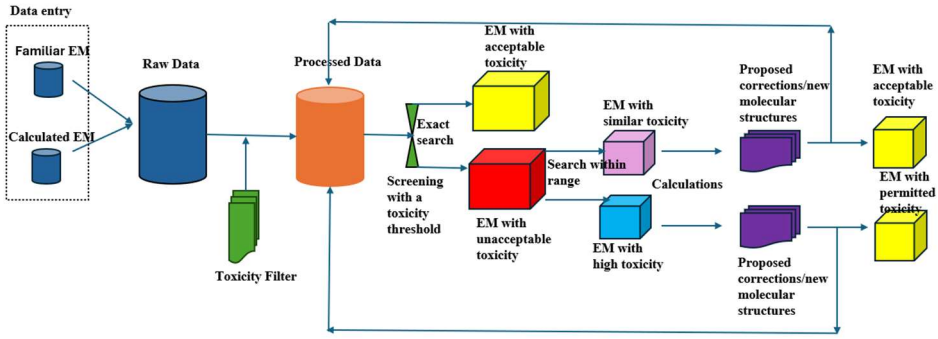

Figure 6. Schematic Algorithm for the Management of a Toxicity Database for Real and Virtual Energetic Materials (EM)

QSAR models are currently used for computational toxicity prediction of chemical compounds. These models estimate biological properties based on the presence of specific functional groups within a given structure. While they enable a meaningful mechanistic interpretation of toxicity predictions, such models often struggle to process heterogeneous or randomised datasets.

One of the widely discussed challenges in machine learning relates to the models' inability to produce user-interpretable results, especially when employing more complex algorithms. These models are often described as "black boxes." Nevertheless, advanced algorithms generally perform well when applied to large and complex datasets. A key advantage of such models is their flexibility in integrating new data blocks, which contributes to improved predictive performance. This characteristic necessitates the regular updating of the data sources used for model training. In addition to incorporating pre-structured data blocks, modern models can extract information directly from scientific reports, facilitating the collection of relevant and processable data.

A notable feature of toxicity data is its inherent imbalance, often containing disproportionate distributions of positive and negative cases. Machine learning approaches are well-suited to handling such imbalanced datasets and can deliver conformal, reliable toxicity predictions. [41] [42] Interpreting results generated by machine learning models remains an active area of research and ongoing methodological improvement.

In this context, the integration of machine learning techniques with existing toxicity databases for energetic materials could significantly enhance the reliability of toxicity predictions for high-nitrogen explosives. To support the framework model proposed in this research, a machine learning-based toxicity prediction model for poly-nitrogen compounds has been developed, as illustrated in Figure 7.

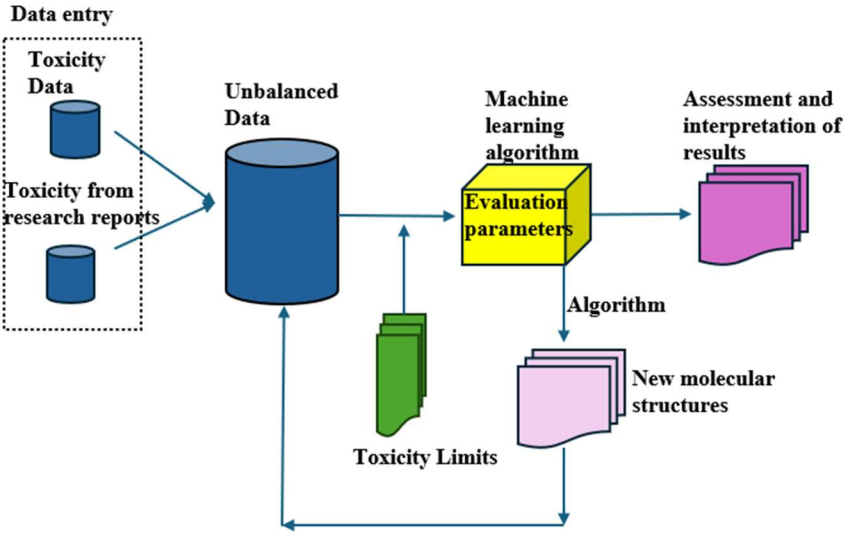

Figure 7. Machine learning model for the toxicity of polynitrogen compounds.

At the beginning of 2023, a group of young researchers from France published information on a computational method they developed for predicting the toxicity of energetic materials. [43] The method, which applies in silico techniques, serves as an alternative to traditional in vitro and in vivo laboratory methods, which are time-consuming, resource-intensive, and often require animal testing.

The primary goal of the research is to enable rapid assessment of the potential hazardous effects of specific compounds on the environment and living organisms. The method focuses on substances registered under REACH as genotoxic or carcinogenic—two key toxicity parameters considered by the European Chemicals Agency (ECHA) during the registration of chemical substances.

Experimental assessments for genotoxicity and carcinogenicity during the development of new compounds are typically lengthy and costly. Consequently, in silico methods address these limitations by reducing the time and resources required during the early stages of

scientific research. During the development of their methodology, the research group compared the performance and accuracy of their toxicity prediction model, based on the Extra Trees algorithm, with other established models such as Percepta and ToxTrees. Their model achieved 85.13% accuracy in tenfold cross-validation, which corresponds to the theoretical maximum for Ames test prediction models. These results provide a strong rationale to suggest that toxicity prediction models can be effectively applied to datasets containing energetic materials.

Computational toxicity prediction is particularly suitable for the early stages of discovering high-density compounds. One of its key advantages is its ability to model and forecast complex problems, such as those encountered in the application of energetic materials.

To achieve reliable results, such models require significant computational power and access to extensive toxicity databases from which artificial intelligence systems can learn and improve.

7. CONCLUSIONS AND SUMMARY

MAIN FINDINGS

1.The conducted research has demonstrated that the investigation of toxicity in energetic materials remains underdeveloped, with a lack of consistent, reliable datasets. The analysis within this dissertation reveals considerable progress in the discovery and development of high-nitrogen compounds, with these new materials exhibiting improved performance and superior environmental profiles. This progress underpins the growing scientific interest in high-nitrogen compounds as a potential new generation of energetic materials.

2.The conducted analysis confirms significant improvements in both performance and environmental impact of newly synthesised compounds, establishing them as promising alternatives to conventional carbon-based analogues. However, a key challenge remains the insufficient investigation and regulation regarding the

environmental aspects associated with high-nitrogen compounds. The environmental impact across the entire life cycle—from synthesis to disposal—must become an integral part of research and development activities.

3.Current literature lacks comprehensive research and regulatory standards concerning the environmental effects of high-nitrogen compounds, necessitating further scientific studies. Implementing the principles of “Green Chemistry” requires an integrated approach encompassing the full life cycle of poly-nitrogen explosives, from synthesis to final disposal.

4.Existing methods for the synthesis of high-nitrogen compounds do not yet offer economically viable production processes. Nonetheless, ongoing efforts in this field are driven by the superior detonation characteristics, low flame temperatures, and improved environmental performance of these compounds compared to carbon-based analogues.

5.Given the complexity of energetic materials, quantum-chemical calculations are increasingly essential for predicting properties and optimising new structures. This approach contributes to achieving high statistical accuracy in results while significantly reducing the duration of the theoretical research phase.

6.The utilisation of computational models supports the development of more precise toxicity testing strategies throughout the life cycle of these compounds. Furthermore, the more extensive the collection of toxicological data, the more accurate and efficient toxicity prediction models will become.

7.Computational modelling combined with machine learning establishes a robust scientific foundation for assessing environmental risks associated with energetic materials. This enables the application of Green Chemistry principles. The developed framework for ecotoxicological assessment of high-nitrogen compounds provides a structured foundation for guiding scientific progress, supported by a system of key factors and decision-making rules.

8.To date, the available literature does not present a clearly structured process for evaluating the production viability of high-

nitrogen compounds. The proposed roadmap for selecting innovative high-nitrogen compounds for production integrates a complex set of analytical factors. These factors facilitate the comprehensive evaluation of poly-nitrogen compounds across their life cycle, from development to disposal. The roadmap includes criteria relating to raw material supply, synthesis methods, production safety, economic feasibility, regulatory compliance, environmental impact, and storage.

9.The developed toxicity assessment methodology integrates environmental impact considerations at the earliest research stages for poly-nitrogen compounds. The discovery of new, high-performance poly-nitrogen materials that meet modern requirements also demands improvements in measurement and evaluation methods. The selected parameter for environmental risk, EC_{50}, combined with the use of bioluminescent bacteria, enables sufficiently accurate early-stage toxicity assessments.

CONCLUSIONS

This dissertation investigates the scientific development of high-nitrogen energetic compounds. The analysis confirms considerable advancements in both performance and environmental profiles of these materials, establishing them as a promising alternative to conventional carbon-based energetic compounds. The advantages of high-nitrogen compounds are largely attributable to innovative approaches in molecular design and the utilisation of quantum-chemical calculations.

Nevertheless, significant challenges persist, particularly the insufficient research and regulation concerning the environmental aspects of high-nitrogen compounds. Their environmental impact throughout the entire life cycle—from synthesis to disposal—must be a consistent focus of research. Furthermore, available literature reveals a lack of systematic, high-quality toxicological data for energetic materials.

There is a clear need for an integrated, multidisciplinary approach that considers not only the performance and applicability of

these compounds but also their operational safety and environmental impact.

The framework for ecotoxicological assessment of high-nitrogen compounds, developed in Chapter 5, aims to provide a structured foundation to support and guide scientific research. The framework presents a systematic set of factors and decision-making rules.

The proposed assessment model incorporates two classifications, presented in Figures 5.1.1 and 5.1.2. These classifications structure poly-nitrogen compounds according to their molecular building blocks and their application within the defence sector. Using these classifications, promising scientific achievements in the field of high-nitrogen research can be systematically evaluated and organised.

Section 5.2 introduces a roadmap for evaluating the production feasibility of innovative high-nitrogen compounds. This model addresses a complex array of analytical factors across the entire life cycle—from development to disposal. The roadmap encompasses factors such as raw material availability, synthesis methods, production safety, economic assessments, regulatory requirements, environmental impact, and storage.

The methodology for toxicity assessment outlined in Section 5.3 ensures that toxicity is integrated as a core parameter in the evaluation of poly-nitrogen compounds. The discovery of innovative, high-performance poly-nitrogen compounds demands continued advancements in measurement and evaluation methods. The selected EC_{50} parameter and the application of bioluminescent bacteria provide accurate early-stage toxicity assessments.

To facilitate the creation of a toxicity database for high-nitrogen materials, a management algorithm for real and virtual energetic materials has been designed (Figure 5.3.1). The proposed QSAR-based computational model streamlines the toxicological process and provides reliable data on environmental risks.

To further enhance computational toxicity models, a machine learning-based predictive model has been developed (Figure 5.3.3).

Although relatively new, this approach demonstrates high reliability for predicting toxicity at early stages of research. Long-term success with this method depends on the continuous enrichment of high-quality, reliable toxicological data.

The research presented in this dissertation can serve as a foundation for further analysis and assessment regarding the future development of energetic materials. The advancement of high-nitrogen energetic compounds represents an innovative and promising field that requires the careful integration of scientific progress, technological innovation, and environmental responsibility. Only through a comprehensive, interdisciplinary approach can sustainable development and the safe implementation of these materials in practical applications be ensured.

SCIENTIFIC AND PRACTICAL CONTRIBUTIONS

Based on the conducted research, analysis, and the conclusions drawn, the following contributions can be identified:

SCIENTIFIC AND APPLIED CONTRIBUTIONS:

1. A comprehensive system of key parameters for analysing new high-nitrogen compounds has been developed, incorporating toxicity as a critical factor.
2. A roadmap for assessing the life cycle of new energetic materials has been constructed, covering production, transportation, storage, and operational use.
3. Classifications for innovative poly-nitrogen compounds have been developed, based on both their molecular structures and their potential defence applications.
4. A framework model for measuring and analysing the toxicity of high-nitrogen energetic materials has been proposed.
5. A methodology for toxicity measurement and analysis of high-nitrogen compounds has been designed.

6. An algorithm for toxicity assessment based on QSAR models has been developed.
7. An algorithm incorporating machine learning for toxicity prediction of high-nitrogen compounds has been created.

PRACTICAL CONTRIBUTIONS

1. The research confirms that toxicity assessment of energetic materials can be reliably conducted using bioluminescent bacteria.
2. The analysis results validate that the significant improvements in both performance and environmental footprint of new high-nitrogen compounds position them as promising alternatives to carbon-based energetic materials.
3. The findings summarise current trends in the development of green energetic materials.
4. The evaluation of QSAR models confirms their reliability for computational toxicity predictions of energetic materials.
5. The optimisation of detonation properties demonstrates the effectiveness of quantum-chemical methods for increasing the density of energetic materials.
6. The application of machine learning, despite being a relatively new approach, shows high reliability for early-stage toxicity prediction of high-nitrogen compounds.

PUBLICATIONS ON THE SUBJECT OF THE DISSERTATION

1. Nadejda Jeleva, **"Concept of Green Energetic Materials and Trends in Their Research and Development."** *'Modern Research and Technologies for Defence* (International Conference Advanced Research and Technology for Defence – ARTDef), 29 - 30 юни, Варна, ISSN 2815-2581, (2021) I-43.

2. Nadejda Jeleva, **Assessment of perchlorate properties, associated benefits and risks, and recommended remediation strategies**., *12th International Scientific Conference HEMUS 2024: 'Scientific Research, Innovation, and Industrial Cooperation – A Paradigm for Effective Defence', Plovdiv, ISSN 1312–2916, (2024), (под печат).*

3. Nadejda Jeleva, **International regulations governing the use of lead-based munitions,** *12th International Scientific Conference HEMUS 2024: 'Scientific Research, Innovation, and Industrial Cooperation – A Paradigm for Effective Defence', Plovdiv ISSN 1312–2916, (2024), (под печат).*

4. Nadejda Jeleva, Petia Gencheva, **Innovative in situ technologies for Remediation of Energetics**, *16th International Scientific and Practical Conference ENVIRONMENT. TECHNOLOGY. RESOURCES, June 19-20, 2025, Rezekne Academy of Technologies, Rezekne, Latvia. Print ISSN 1691-5402, Online ISSN 2256-070X Published by Rezekne Academy of Technologies, 2024 (in print).*

5. Nadejda Jeleva, Petia Gencheva, **Aapproaches towards improving the safety of dinitramides as energetic materials**, *16th International Scientific and Practical Conference ENVIRONMENT. TECHNOLOGY. RESOURCES, June 19-20, 2025, Rezekne Academy of Technologies, Rezekne, Latvia. Print ISSN 1691-5402, Online ISSN 2256-070X Published by Rezekne Academy of Technologies, 2024, (in print).*

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