



High Energy Density Materials (HEDM): Overview, Theory and Synthetic Efforts at FOI*

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Abstract: This paper presents a literature overview of HEDM. A number of potential HEDMs with performances theoretically up to more than 10 times HMX have been identified, ranging from ionic all-nitrogen compounds like N_5^- and N_5^+ with suitable counter ions ($N_5^+N_5^-$ gives a performance of ~1.6 times HMX) to polymeric nitrogen (10 times HMX) and metallic hydrogen. In between there are for example metastable nitrogen “clusters” (N_x , $x \approx 4$ to 60). Calculations show that N_4 has approximately 3.2 times the performance of HMX. Both metallic hydrogen and polymeric nitrogen are high-pressure compounds (several Mbar) and thus probably hard to synthesize in larger amounts. The nitrogen clusters offer an interesting alternative or complement in that they are all “normal” chemical compounds and they all have high heat of explosion, and probably also high density (2.0-2.7 g/cm³).

This overview covers conventional chemistry, novel chemistry (all-nitrogen compounds, new oxidizers in the form of N_xO_y compounds) and exotic physics (eg. metallic hydrogen, cold fusion and anti-matter). The time in which these concepts can be realised ranges from near future to many years ahead and some may possibly never be made at all or perhaps only in lab scale. The overview is complemented with theoretical and experimental results from our institute in our effort to synthesize new all nitrogen compounds, e.g. pentazolate ion (N_5^-) and tetraazatetrahydrodrane ($N_4(T_d)$).

Keywords: HEDM, synthesis, QM, performance, all nitrogen compounds

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Introduction

The three most important reasons for the development of energetic materials for military purposes today are the needs for increased performance, increased safety and certain tailored properties. This is important for warhead, propulsion and launch applications. Several factors influence the development directly or indirectly. The most important are increased use of insensitive munitions (IM), the need for more precise weapons effects, higher performance, weapon specific properties, environmental concerns, internationalisation, standardisation, and increased system integration.

In this paper we will discuss the possibilities to develop materials with performance considerably better than what is used today, commonly referred to as High Energy Density Materials (HEDM). The aim of this paper, which is based on the available literature and on work done at our institute, is to give an overview of the area, to see the possibilities of what could be achieved with different concepts, soon or in a longer time perspective.

When dealing with new energetic materials a term that has been used in the Energetic Material community is High Energy Density Materials (HEDM). The limit between conventional energetic materials and HEDM has never been defined and may therefore differ between research groups. In the first European Workshop on High Energy Density Materials, held at FOI in October 2005, the participants agreed on a common definition for HEDM as “*energetic materials better than the best that are in use in systems today*”. The baseline will vary with the application and we end up with different reference substances for different applications. The European definition gives the following baselines; HEDMs are explosives with higher performance than HMX, solid rocket propellants with higher performance than AP/Al/HTPB and gun propellants better than JA2 (NC/NG) propellants.

Computational modelling, using mainly quantum chemical methods (numerically solving the Schrödinger equation at different level of approximation), plays an integral part in the development of new high energy density materials. This is the case both for the synthesis, detection and characterization of new all-nitrogen compounds, and in the design and synthesis of conventional type explosives.

The performance of a substance is readily calculated from its heat of formation and density; two properties that can be estimated by means of quantum chemical computations. Apart from performance, some practical aspects such as stability, sensitivity and state of aggregation are important. In order to make experimental work meaningful it is also essential to calculate properties that make it possible to detect and identify the material once it has been made. It is also very useful to use quantum mechanics to evaluate synthesis routes.

This paper is mainly based on a more comprehensive overview of HEDM research, including chapters on QM and performance calculations “*High Energy Density Materials (HEDM) – A Literature Survey*” [1]. This report was a joint effort by many people whose contribution is hereby acknowledged.

Historic Review

Yesterday, today ...

The earliest known energetic material was black powder and Greek fire, both with origins held in some mystery but probably invented about 2000 years ago, Greek fire in ancient Greece and black powder in China. Black powder was first used only for fireworks and mainly not for war. The first real use for warfare was probably in the 14th century as propellant for guns and firearms. It was then in use until the “little revolution” of the mid-nineteenth century when the black powder era ended, and when modern-day propellants and high explosives came into use. The development of energetic materials has since then proceeded relatively slowly. Most of the explosives found in today’s weapons systems are still TNT, PETN, HMX or RDX, i.e. energetic materials developed in the 19th century or, in one case, the 1940’s (HMX).

Table 1 shows an overview of the history of energetic materials development. The column for Performance gives values relative to the performance of HMX. The performance increases about 70% from picric acid (60) to HMX (100) between World War One and today. This can be compared to the threefold increase at the end of the black powder era.

The slow development during the greater part of the 20th century was partly due to a lack of understanding of energetic molecular structures rather than a poorly developed synthesis technique. For instance, scientists believed for a long time that HNB, hexanitrobenzene, was the optimal high explosive. The relative performance of HNB vs. RDX is 1.23. After Russian scientists first reported the successful synthesis of this compound, US researchers spent 10 years trying to find the synthetic path. This was finally achieved, after which it became apparent that the substance was unstable and highly sensitive to light.

... tomorrow

During the last decade, the development of computers and thus the increased capability for quantum chemical calculations, as well as a broadened view of the characteristics of energetic molecules and their applications, have yielded new opportunities for the development of energetic materials. It was generally

believed that useful energetic materials would be CHNO-substances, with molecules containing carbon, hydrogen, nitrogen and oxygen. Today, several completely different types of compounds have been added to the list of possible energetic materials. Among these are caged molecules that contain more energy per unit of mass and volume, molecular composites where fuel and oxidizer are mixed at a molecular level, nano-systems of reactive materials and meta-stable compounds. Even very extreme forms of energy storage, such as nuclear isomers and anti-matter are investigated.

In other words, the last decade has seen an "explosive" development in the number of theoretical candidates for useful energetic materials. Some of these have already been synthesised and produced in useful quantities.

Today, the development of energetic materials follows two distinct lines, one evolutionary and one revolutionary. There is also the development of reactive materials that combined with energetic materials can increase the performance of future weapons systems.

Table 1. Historical overview of development of energetic materials

Invented	In application	Energetic material	Energy (MJ/kg)	Density (kg/m ³)	Performance (relative to HMX=100)
1000?	1600-1870	Black Powder	3	1	20
1847	1870-2010	Nitroglycerine	6.5	1.6	70
1867	Not in weapons	Dynamite	5	1.45	50
1771	WW1	Picric Acid	5	1.6	60
1863	1900-2020	TNT	5	1.55	60
1899	WW2	RDX	6.6	1.8	90
1894	WW2	PETN	6.3	1.8	80
1940's	1960-	HMX	6.5	1.9	100
1986	<i>2005</i>	CL-20	7.5	2.1	120
2006-	?	?			?

HEDM Possible by the Use of Conventional Chemistry

The evolutionary development of new energetic materials concerns CHNO-substances prepared by conventional chemistry. The two main driving forces for the development of explosives are lower sensitivity and increased performance. Until now, new energetic materials have either been less sensitive with retained performance compared to current materials or more powerful but

also more sensitive (Figure 1). A long-term objective is of course to merge these two qualities and produce energetic molecules that are both more powerful and less sensitive than current materials. Compounds with the performance of CL-20 and the sensitivity of TATB would be desirable long-term goals.

To increase performance compared to current explosives the molecules need to contain particularly energetic structures that give a high heat of formation (e.g. caged molecules, strained rings, nitramines, furazanes, tetrazines) and/or have high-density functional groups (e.g. fluorine, cage, urea, guanidine). Computational methods allow quite accurate prediction of density and heat of formation, which makes it possible to evaluate large numbers of candidate molecules before their preparation is attempted.

It is more difficult to predict the sensitivity of new energetic materials, which leads to a more qualitative analysis of the proposed target molecules. Factors that influence sensitivity are for instance functional groups (e.g. nitrate esters), crystal structure and hydrogen bonding. It is also possible to influence the sensitivity of explosives by perfecting their crystal shape. Round, flawless crystals are desired, both because of their easier processability and their decreased sensitivity. Recently the long studied crystallization of RDX yielded the product I-RDX [2] which is equal to normal RDX performance-wise, but has improved sensitivity characteristics towards shock. This breakthrough has sparked an interest for the preparation of I-HMX [3] and perhaps even I-CL-20.

The most promising new candidate molecules are CL-20, ADN, and FOX-7, which have all been produced in sufficient quantities to allow them to be used for various applications. TATB and NTO are two low sensitivity energetic materials that are already in use.

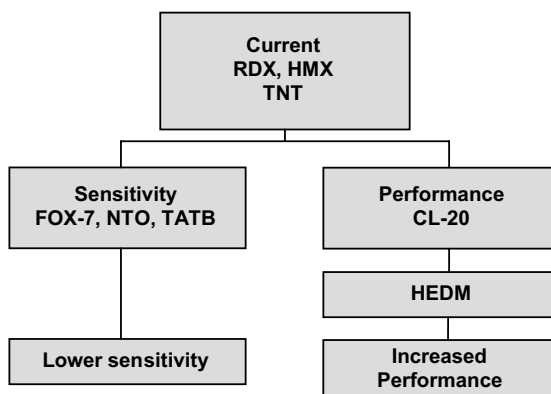


Figure 1. Lines of development of energetic materials.

A number of potential HEDM molecules have been theoretical or experimental investigated. Some of the most promising or interesting are shown. A short description of each is also given below.

CL-20 or Hexanitrohexaazaisowurtzitan contains more energy than earlier high performance energetic materials, e.g. HMX. The purely chemical theoretical increase in performance is 20%. In shaped charges, because of the higher energy content in the explosive charge, different materials can be used in the liner yielding an increase in performance of about 60%. CL-20 is, however, as sensitive as PETN regarding impact and friction. As for HMX there are several polymorphs of the substance adding further complexity to its handling. Due to a difficult synthesis the price is also quite high.

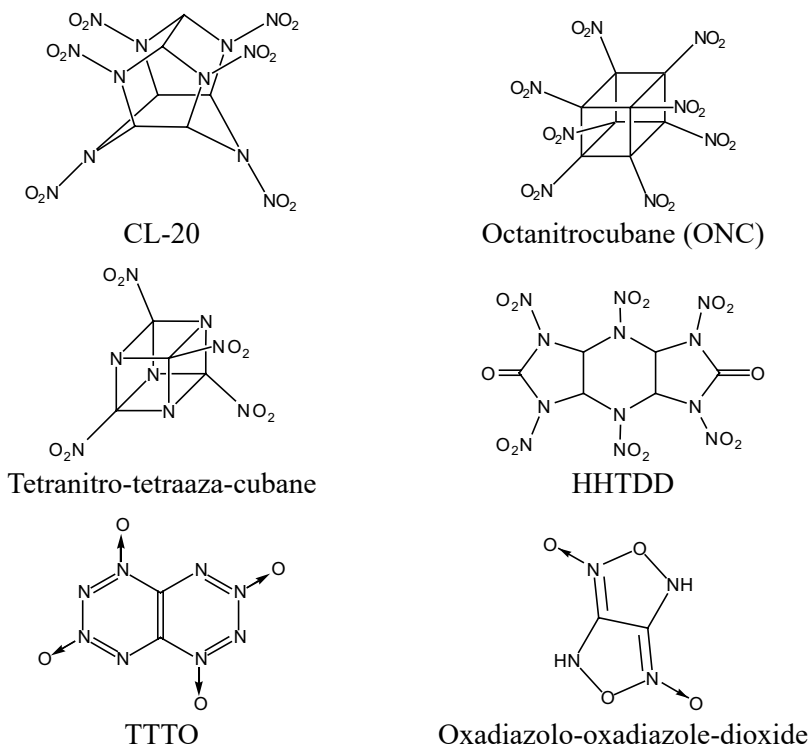


Figure 2. HEDM molecules possible by the use of conventional chemistry.

Octanitrocubane or ONC was first envisioned by Gilbert in the beginning of the 1980s as a compound with a perfect oxygen balance and exceptionally high heat of formation and density [4]. As the compound was a C-Nitro explosive

with good sensitivity properties was also expected [4]. These predictions were also supported by advanced calculations. The compound was finally prepared in the year 2000 after a very long and laborious synthesis but proved to be a disappointment with a lower than expected density [4]. It turned out that the heptanitrocubane was a superior explosive due to its higher density, there are however hopes to find a higher density polymorph of ONC which might live up to the predictions.

2,4,6,8-Tetranitro-1,3,5,7-tetraaza-cubane a proposed compound with a structure similar to that of ONC. The proposed high density is derived from the cubane structure which also contributes to its heat of formation. The compound would also be perfectly oxygen balanced. The calculated performance is 1.4 times that of HMX.

HHTDD or *cis-syn-cis-2,6-dioxo-1,3,4,5,7,8-hexanitrodecahydro-1H, 5H-diimidazo[4,5-b:4',5'-e] pyrazine*. The dinitrourea moiety confers high density to molecules containing it. A property, which has been realized and utilized in a whole series of experimental energetic materials. HHTDD [5] is supposed to be the explosive with the best performance ever prepared, it lacks however both in sensitivity and hydrolytic stability something it shares with its close analogue Sorguyl (TNGU) [6]. Our calculations based on experimental density and heat of formation implies a performance slightly below that for CL-20.

TTTO or [1,2,3,4]tetrazino[5,6-e][1,2,3,4]tetrazine 1,3,5,7-tetraoxide is a compound that has not been prepared but which has been evaluated by computational techniques and found to be extremely interesting. Calculations propose a density of 2.38 g/cm³ and a heat of formation of 190 kcal/mole, leading to a relative performance of 2.2 times HMX. This compound can be seen as a possible performance limit to normal explosives and what could be achieved by a focused, well funded research program.

1H,4H-[1,2,5] Oxadiazolo[3,4-c][1,2,5]oxadiazole 3,6-dioxide is another proposed bicyclic heterocycle similar to TTTO. The two nitrogen atoms are N-oxidized and the compound has a proposed high density (2.3 g/cm³) which would give it excellent performance as a high explosive (1.7 times HMX).

In Table 2 the calculated densities, heats of formation and performances of the described compounds are compiled. Data were calculated by the methods described in Reference 1. The values for ONC were taken directly from the Cheetah 2.0 database.

Table 2. Calculated performance of HEDM prepared or possible to prepare by ordinary chemistry

Energetic material	Density (g/cc)	Heat of formation (kJ/mol)	Detonation velocity (mm/ μ s)	Detonation pressure (GPa)	Energy (HMX=100, $V=2.2 V_0$)
CL-20	2.04*	393*	10.0	47.8	121
ONC	1.92	381	9.2	37.1	105
Tetranitrotetraaza-cubane	2.02	912.4	10.5	50.1	137
HHTDD	2.07*	153.4*	10.2	46.1	118
TTTO	2.38	794.6	10.9	131	220
Oxadiazolooxadiazole dioxide	2.30	263.8	11.3	71.3	167

* Experimental data

In conclusion, the evolutionary development of energetic materials during the last decade gives a potential for future increase in systems performance of up to 100%. The foundation has been laid, but more applied research is needed in order to fill the requirements of specific weapons systems. This would also make it possible to tailor energetic materials and high explosives for various applications.

All-Nitrogen Compounds

Polynitrogen compounds have received considerable attention in recent years as potential candidates for high energy density materials (HEDMs). The fact that most of these have a very high calculated energy content is a consequence of the large bond energy of 228 kcal/mol of the triple bond in molecular nitrogen (N_2) compared to the bond energies of nitrogen-nitrogen single and double bonds, which typically amounts to 39 and 100 kcal/mol, respectively. In addition to the favorable energetics of the polynitrogen compounds, they also have the advantage that the energy releasing decomposition into N_2 leads to no deposition of harmful substances. This makes them particularly suitable for propulsion of spacecrafts, since the commonly used propellants of today results in large depositions of harmful substances in the atmosphere. The special properties

of polynitrogen compounds also make them of great interest for energy storage. The high heat of formation and large density makes polynitrogens nearly ideal for use as high explosives.

Even though theoretical studies have identified a number of potentially stable structures, the experimentally observed nitrogen compounds are still few. The azide anion, N_3^- , was first synthesized in 1890 by Curtius. Christe and co-workers have since 1999 reported the preparation and isolation of N_5^+ together with several different counter ions [7]. A few other species, such as N_3 , N_3^+ and N_4^+ , have been observed only as gaseous or matrix-isolated ions or radicals. The formation of N_5^- from arylpentazoles in mass spectrometry experiments has recently been reported from our lab [8, 9] and from Air Force Research Laboratory (Edwards Air Force Bas) in the US [10]. The detection of HN_5 and a zinc pentazolate salt in solution has also been reported [11]. These results have however been questioned [12].

Quantum mechanical studies of stability and energy content have been carried out on a number of nitrogen compounds. For a recent review on the structure and stability of N_4 and N_5 systems (see Nguyen [13] and references therein). An overview of some calculated structures and stabilities of N_2 to N_{10} species as well as their spectroscopic characteristics can be found in a report by Bartlett [14]. Many all-nitrogen structures have also been treated by Glukhovtsev et al. [15]. Theoretical calculations lay the foundation for ongoing attempts to synthesise such compounds and increases the possibility of successfully producing one or a few useful substances and formulations. A possible development in this field is substances allowing an increase in performance as high explosives of 2-5 times the values of today. The impulse of, for example, N_4 is comparable to H_2/O_2 but has the enormous advantage of a much higher density which would allow for smaller and thereby lighter rockets.

Quantum mechanical calculations to determine the heat of formation for a number of poly-nitrogen molecules (Figure 3) have been made at FOI using Gaussian 98 at B3LYP/6-31G(d) level of theory.

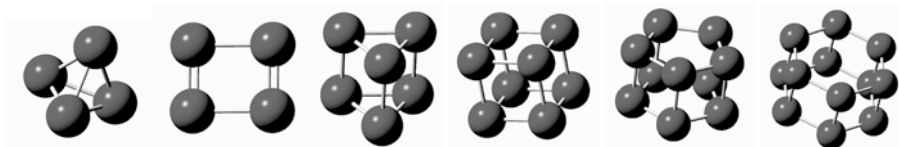


Figure 3. Calculated structures of $N_4(D_{2h})$, $N_4(T_d)$, $N_6(D_{3h})$, $N_8(O_h)$, $N_{10}(D_{5h})$ and $N_{12}(D_{6h})$.

The difference between $\Delta H_f(g)$ and $\Delta H_f(s)$ is the sublimation energy, i.e. the energy gained by the molecules by forming a solid or liquid instead of gas. The size of this difference is one indication of a substance's inclination to be in solid phase.

Table 3. Heats of formation from QM calculations (Gaussian 98, hs95fo), densities calculated with MOLPAK and detonation velocities, pressures and performances (except I_{sp}) calculated with Cheetah 2.0 (BKWC), I_{sp} calculated with NASA CEA

Molecule	$\Delta H_f(g)$ (kcal/mol) ^a	$\Delta H_f(s)$ (kcal/mol) ^a	Sublimation energy (kcal/mol)	Density (g/cm ³)	Detonation velocity (km/s)	Detonation Pressure (GPa)	Boiling point (K) ^c	Energy (HMX=100, V/V ₀ =2.2)	Impulse (sec)	T _c (K)	Force (J/g)
N₄(D_{2h})	194	189	5	2.2	15.5	121	289	313	408	7563	3932
N₄(T_d)	202	201	1 ^b	2.3	15.7	125	200	327	422	7795	4212
N₆(D_{3h})	346	342	4	2.5	17.6	169	285	428	439	8079	5193
N₈(O_h)	480	473	7	2.7	19.0	206	331	498	444	8162	-
N₁₀(D_{5h})	551	544	7	2.7	19.2	208	364	484	433	7971	4628
N₁₂(D_{6h})	712	703	9	2.8	19.7	224	407	526	443	8140	-

^a Heat of formation is calculated at B3LYP/6-31G(d) level of theory. This level has been chosen for comparative purposes and does not give the most accurate values calculated. The differences to heats of formation calculated at higher levels of theory are however small and do not affect the calculated performance in an important way.

^b Results by Karle [17] indicate a higher sublimation energy for N₄(T_d) (5 kcal/mol) which would of course mean a higher boiling point.

^c The boiling point has been calculated using a lower level of theory, STO-5 using the method described in ref.

The estimation of the state of aggregation for a substance from calculations is a difficult task. In Table 3 one can see that very little is gained for N₄(T_d) so this may not be expected to be in solid state at ambient temperature and pressure. Absolute estimations are very difficult to make. Use of the methods described by Murray [16] give boiling points. The accuracy of these calculations varies with

substance. For comparison, the calculated boiling point for hydrazine is 338 K (exp 386 K) and for tetrazole 434 K (exp 429 K mp sublimates). The trend is clear; N_8 , N_{10} and N_{12} are liquids at room temperature, N_{10} and N_{12} may even be solids. N_4 is a gas at room temperature, but would be a liquid or even probably solid at liquid nitrogen temperature.

Interesting from a point of view of usefulness of new materials are properties such as energy content (ΔH), density, energy barrier towards dissociation, *i.e.* stability and aggregation form. Some of these properties such as aggregation form are more difficult to estimate than others. From an experimentalists point of view in trying to make these molecules it is also necessary to have reasonable synthesis routes, something that can often also be studied with quantum mechanics. One of the most important questions for an experimentalist to answer is how to detect the successful synthesis of the molecule. Quantum chemistry is very useful in supplying answers.

There are many papers describing quantum mechanical calculations on various all-nitrogen molecules. Calculations on larger nitrogen molecules are mainly focused on geometry and finding stable forms. Little has been done on determining chemical or thermal stability and performance. For any of these molecules to be of experimental interest, there must also exist ideas on synthesis routes. All of these compounds have high energies (based on the number of single or double bonds), but in order to assess their performance, their density must also be calculated. Only a few, such as N_4 and N_5^- , have been extensively studied with quantum mechanics and other calculations. In this paper $N_4(T_d)$ and N_5^- will serve as example on how to proceed towards the synthesis of HEDM with the aid of QM calculations.

Tetraazatetrahedrane, $N_4(T_d)$

One of the most interesting candidates for a HEDM among the polynitrogen compounds is tetraazatetrahedrane, $N_4(T_d)$. Phosphorous (below nitrogen in the periodic table) exists in, among other forms, the form of P_2 as well as $P_4(T_d)$ (white phosphorous) whereas nitrogen is only known in the form of a dimer (N_2).

Energy content and stability

In 1990, Francl and Chesick [18] calculated the energy of formation of N_4 (814 kJ/mol) as well as its dissociation barrier (315 kJ/mol). They concluded that the calculated barrier was “*large enough to suggest a significant lifetime and metastability if N_4 could be made and trapped*”. The energy release involved

(heat of reaction) in the dissociation of $N_4(T_d)$ into N_2 has been calculated in many studies, giving similar results. Lee and Martin [19] give a value of 763 ± 2 kJ/mol.

The dissociation barrier has also been discussed in many studies with results ranging from 118 to 315 kJ/mol. The height of the dissociation barrier, *i.e.* the activation energy, can be calculated with much higher accuracy now than only ten years ago. The first studies used very simple approximations to estimate the height. Francl and Chesick [18] used the lowest energy point on the ridge of intersection between the potential energy surface (PES) of ground state N_4 and the PES of two N_2 molecules, giving the high value of 315 kJ/mol. Yarkony [20] used a much more refined method taking into account that the potential energy surfaces of other states may cross the investigated PES (Figure 4). This resulted in the low value of 118 kJ/mol. A later study taking in more information about the system but essentially using the same principle has given a higher value of 214 kJ/mol [21]. Despite the incredibly high energy content, this computed dissociation barrier indicates that it is sufficiently stable for most potential applications.

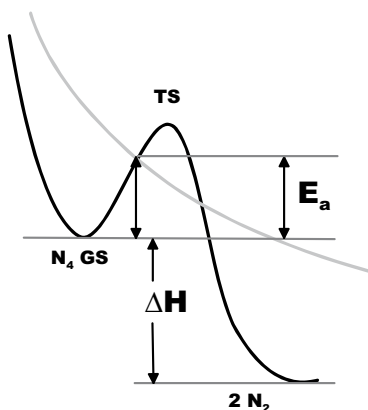


Figure 4. Schematic picture of a potential energy curve (blue) for the dissociation of a substance via a transition state (TS) releasing the energy ΔH . A potential energy curve (green) from a different state crosses it, effectively lowering the activation energy E_a .

The high energy content of $N_4(T_d)$ makes it hard to make by traditional methods in chemical synthesis. All attempts of experimental preparation and detection of $N_4(T_d)$ have so far been unsuccessful. Radziszewski and co-workers reported to have detected $N_4(T_d)$ in 2000 [22], but it was later shown that the

reported isotope effect on the observed IR-band is not compatible with $N_4(T_d)$ [19]. An open chain N_4 isomer in the triplet state was recently detected in mass-spectrometry experiments [23-25]. However, this species is expected to be too unstable and also too low in energy to be of any interest as a HEDM.

Suggested synthesis routes

A number of synthesis routes have been suggested, mainly by our institute, and in some cases the chances of success using these routes have been assessed by quantum chemical calculations. Francl and Chesick [18] suggested that “*prolonged irradiation of liquid nitrogen with radiation of wavelength less than 140 nm might yield evidence of N_4 formation*”. (Note that the calculated wavelength here is too high. The energy of the barrier has to be added to the photon energy which gives ~106 nm.) This suggestion was of course based purely on an energetic basis. In order to increase the chances of success, more refined arguments and investigations can be made. In Figure 5 an overview of possible synthetic routes to $N_4(T_d)$ is shown.

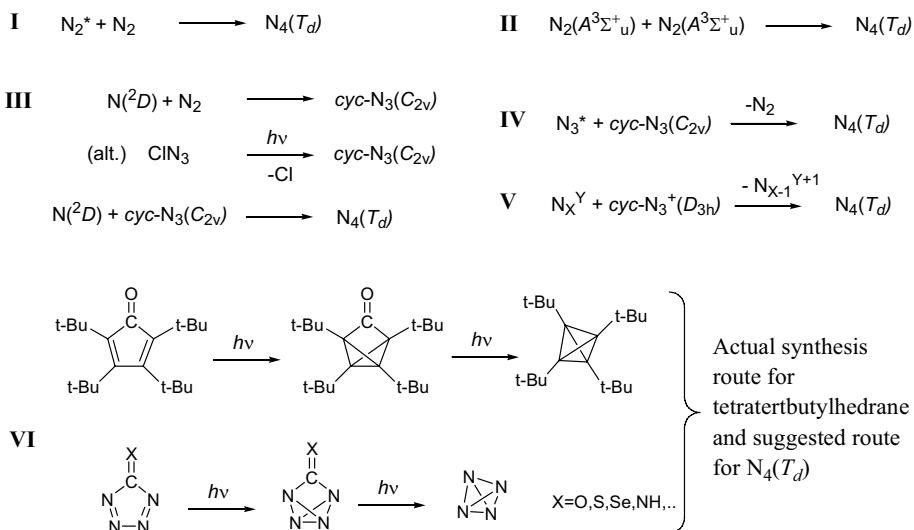


Figure 5. Proposed routes for synthesis of $N_4(T_d)$. Excited states are marked by *.

- I. The collision of a ground-state N_2 with an excited-state N_2 to form N_4 requires that their total energy is high enough to form the molecule and reach over its dissociation barrier. The triplet excited states generally have longer lifetimes than the singlet excited states and are therefore most interesting for this

- type of reaction. The result would be a N_4 molecule of triplet character. Calculations [26] show that metastable excited triplet states exist, which increases the chances of success. However, the electronic structure of ground-state N_2 is not optimal for formation of new N-N bonds. The required excited states can be produced by excitation of nitrogen in liquid or solid form. Excited nitrogen molecules can also be obtained by RF (microwave cavity) or electrical discharges (hollow cathode or pulsed nozzle discharge), and the reaction products can be trapped on a cold surface. Ion bombardment of solid nitrogen or nitrogen in rare gas matrices is another possibility.
- II. Another suggested route is $N_2(A^3\Sigma_u^+) + N_2(A^3\Sigma_u^+) \rightarrow N_4(T_d)$. This reaction has the advantages that the orbital occupancy of $N_2(A^3\Sigma_u^+)$ is favorable for formation of new N-N bonds, and that this state has a long life time (1.9s). The collision of two molecules in an excited state is generally very difficult to achieve but there are ideas on how to succeed. Ion or α -particle bombardment of solid nitrogen in argon has been shown to excite nitrogen to the $A^3\Sigma_u^+$ state [27]. It is likely that molecules are excited primarily along the trajectory of the ions or α -particles through the matrix. This enhances the chances of two molecules next to each other being excited to the correct state.
 - III. On the basis of quantum chemical calculations we have suggested that $N_4(T_d)$ may be synthesized from molecular nitrogen and atomic nitrogen in the 2D state in a two step process [28]. In the first step a cyclic N_3 isomer, *cyc*- $N_3(C_{2v})$ is formed by the addition of N_2 to $N(^1D)$. Addition of a second $N(^1D)$ to N can lead to the formation of $N_4(T_d)$. Nitrogen atoms in the 2D state have a long lifetime in cryogenic matrices (37 s) and can be generated at high concentrations. The main drawback of this route seems to be side reactions. Linear N_3 , $N_3(D_\infty)$ can be formed in the first step and $2 N_2$ in the second step. The existence of *cyc*- $N_3(C_{2v})$ has been confirmed in a recent experimental study, where it was produced by photolysis of ClN_3 [29]. An experiment could be setup where the photolysis products are deposited in a nitrogen matrix with a high concentration of $N(^2D)$. In addition, recent unpublished computations from our group indicate that a cyclic N_3^+ isomer, *cyc*- $N_3^+(D_{3h})$, exists, which can be obtained directly by ionization of *cyc*- $N_3(C_{2v})$. These two new species opens up new potential pathways for synthesis of $N_4(T_d)$ and other polynitrogen allotropes.
 - IV. It can be noted that both the production of N_3 from $N(^2D) + N_2$ and ClN_3 is likely to lead to a mixture of $N_3(D_\infty)$ and *cyc*- $N_3(C_{2v})$. (A 0.8/0.2 mixture was obtained from ClN_3 .) The reaction between $N_3(D_\infty)$ and *cyc*- $N_3(C_{2v})$ to form $N_4(T_d)$ and N_2 should be considered. Preliminary calculations indicate

that this reaction could have a too high barrier to be feasible. However, the reaction between *cyc*-N₃(C_{2v}) and an excited state of N₃ may be barrierless. This could be achieved experimentally by simultaneous application of two laser sources, one tuned for photolysis of ClN₃ and the other to the proper excitation wavelength.

- V. Unpublished calculations show that a stable cyclic N₃⁺ isomer, *cyc*-N₃⁺(D_{3h}), can be formed by ionization of *cyc*-N₃(C_{2v}). Although it is higher in energy than ground state linear N₃⁺, it is very stable towards unimolecular decomposition. The reaction between *cyc*-N₃⁺(D_{3h}) and N₃⁻ should be investigated. It may be possible to deposit both ions into a matrix. Also reactions between *cyc*-N₃⁺(D_{3h}) and other neutral and ionic states of N and N₃ should be explored by computations to find possible pathways for formation of N₄(T_d).
- VI. Tetratertbutyltetrahedrane can be formed by photolysis of tetratertbutyl-cyclopentadienone in argon matrices [30]. It may be possible to form tetraazetetrahedrane (N₄(T_d)) by a similar method starting from tetrazole-5-one. This starting material is not known from the literature and low level (B3LYP/6-311G) calculations indicate that it is not stable, but higher level calculations should be performed to test the stability of this and alternative starting materials. Another option is to use arylpentazoles as starting material. This type reaction is suitable for mass spectrometric studies with laser-induced decomposition of suitable precursors.

Detection

The symmetric nature of N₄(T_d) means that IR spectroscopy alone is insufficient. The only line available gives no identification capabilities. The difficulties are clearly illustrated by the questionable assignment of the origin of an IR line as N₄(T_d) [22], made by Radziszewski et al. Lee and Martin showed that the experimental isotopic shift upon ¹⁵N-labeling unfortunately does not match the theoretical predictions for N₄(T_d) [19].

Raman spectroscopy is a much better choice of detection method for N₄(T_d). It gives a fingerprint of the molecule with three lines. The detection limit in a matrix has been determined by combining experimental signal strength and noise levels of N₂ in solid nitrogen with *ab initio* quantum mechanical calculations of Raman intensities of N₂ and N₄(T_d) [31]. Using that particular experimental setup 80 ppm is necessary for detection using 8 h measurement time and 1W laser power. This detection limit is too high considering that no optimization of a signal can be made during the measurement. An improvement of the experimental setup, for example by using a Raman probe, could lower the detection limit rendering Raman spectrometry a feasible detection method.

A more sensitive Raman method, Surface Enhanced Raman Spectroscopy (SERS), has been evaluated for the purpose of N_4 detection using white phosphorous, $P_4(T_d)$ as a model substance [32, 33]. No SERS effect was observed for P_4 which may indicate that SERS is not a promising detection method for N_4 .

Detection with Laser-Induced Fluorescence (LIF) would be ideal due to its sensitivity. However, accurate calculations of excitation energies and geometry optimizations of the excited states are necessary to determine laser and fluorescence wavelengths. An excited state of $N_4(T_d)$ has been identified by EOM-CCSD theory which is 10.89 eV above the ground state, and which is optically active for one and two-photon absorption [34]. However, it has not yet been possible to optimize the excited state geometry. A similar study of rectangular N_4 , $N_4(D_{2h})$, has successfully given a useful route for LIF detection [35]. The vertical absorption and emission energies for the first excited state were determined to 1.58 and 1.55 eV respectively (laser and detection wavelengths 785 and 800 nm respectively).

It may be possible to use the previously discussed state at 10.89 eV to detect $N_4(T_d)$ by UV absorption at around 114 nm. This is just outside the relatively easily accessed range where PM-tubes, MgF_2 windows and deuterium lamps work so extra attention to the experimental setup would be necessary.

Mass spectroscopy is another option for N_4 detection, but it is difficult to tell whether an m/z 56 fragment is due to a bound D_{2h} or T_d structure or is the result of a weakly bound $(N_2)_2$ complex. There is also a need for calculations to determine whether ionized $N_4(T_d)$ is bound and stable enough to detect in a mass spectrometer.

Isotopic labeling can be used in conjunction with the above techniques to confirm or rule out certain origins of spectral lines and mass spectrometric fragments.

Roadmap to Pentaaza HEDM:s ($N_5^+/N_5^-/N_5^+N_5^-$)

The making of High Energy Density Materials with fivemembered nitrogen compounds starts with the synthesis N_5^+ or N_5^- . Recently the novel homoleptic polynitrogen ion, N_5^+ (Figure 6) was synthesized [7]. This is the first new stable all nitrogen ion in more than 100 years. So far no useful counter ion has been found. It has been suggested that *cyclo*- N_5^- (Figure 7) may be combined with N_5^+ to form a N_{10} salt.

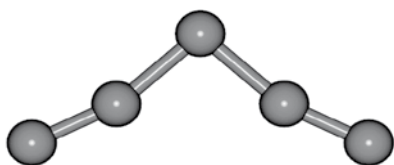


Figure 6. N_5^+ the first new all-nitrogen compound in 100 years.

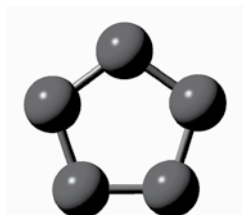


Figure 7. Pentazolate anion, $cyclo-N_5^-$.

The nitrogen pentazole ring system has been studied since 1903, when Hantzsch made the first attempts to prepare phenylpentazole [36]. The first preparation of substituted pentazoles was however achieved by Huisgen and Ugi [37] in 1956. The making of pentazolate compounds starts with decomposition of arylpentazoles (Figure 8). A breakthrough was achieved when the feasibility of this process was confirmed in a laser induced mass spectrometry experiment at our institute [8], in which the pentazolate anion was detected from selective cleavage of p-dimethylaminophenylpentazole.

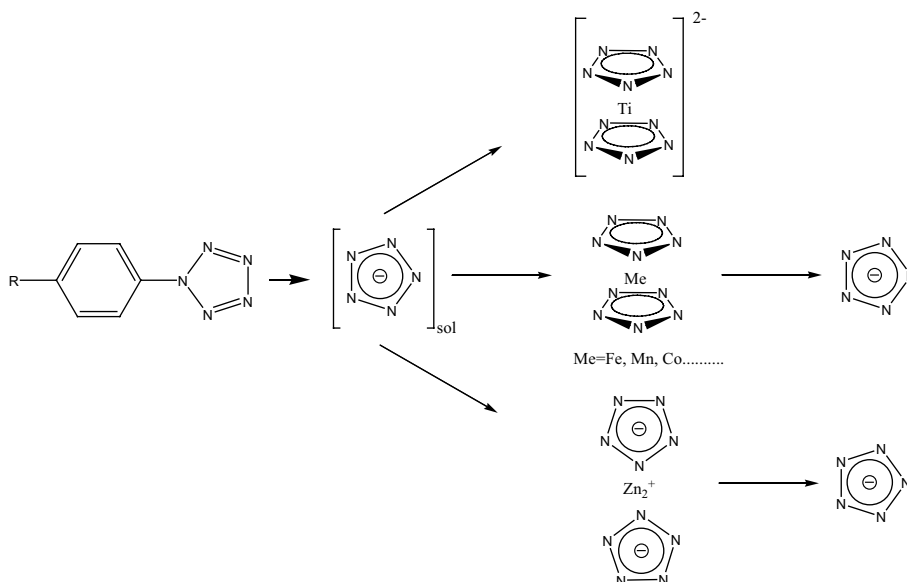


Figure 8. How to make pentazolate HEDM's.

Calculations have shown that the aromatic pentazole anion (N_5^-) should be stable enough to isolate, especially if trapped as a metal complex [38-43].

This complex could, if a suitable metal were used as the complexing agent, be highly energetic. More important, it could serve as a N_5^- -containing compound, stable enough for an ion exchange to be performed. Some metals are believed to stabilize the pentazole ring, both in the arylpentazole and in pure ionic form. In a recent study [44] to investigate if amination of halobenzenes is a viable way to isolate the pentazolate anion, the reactivities of halobenzenes were compared to phenylpentazole. The reaction energetics for phenylpentazole became favorable after complexation with Zn^{2+} . The study indicated that addition of Zn^{2+} lowers the free energy of activation by more than 6 kcal/mol, which may be sufficient to make the reaction useful for synthesis.

Once a stable complex with N_5^- has been made, an ion exchange can be attempted in order to find a suitable counter ion that makes a good HEDM. Calculations show that a salt with the recently discovered [7] N_5^+ ion would be highly energetic, with a performance as an explosive about 1.6 times that of HMX [45], provided of course that it is stable. QM calculations on the stability of $N_5^+N_5^-$ are not conclusive. There are three studies of its stability, two of which predict that $N_5^+N_5^-$ is stable and one that predicts its instability.

The first publication, by Fau et al. [46, 47], concludes that $N_5^+N_5^-$ is a stable compound with a dissociation barrier of 19 kcal/mol and high density (1.9 g/cm³) and heat of formation (296 kcal/mol, 1239 kJ/mol). They conclude that its performance as a rocket propellant is about the same as that of hydrazine but that its high density (about twice that of hydrazine) will allow for smaller and lighter rockets.

The second publication, by Evangelisti et al. [48], concludes that $N_5^+N_5^-$ is stable and that $(N_5^+N_5^-)_2$ is even more stable. They also conclude that the dimer stability suggests the possibility of a $N_5^+N_5^-$ crystal. Worth noticing here is that even though no crystal structure is calculated, calculations indicate that $(N_5^+N_5^-)_2$ has a planar, layered structure. This is very interesting since it is believed that such structures give less sensitive energetic materials.

The third publication, by Dixon et al. [50], concludes that both $N_5^+N_5^-$ and $N_5^+N_3^-$ are unstable. They have also experimentally confirmed that $N_5^+N_3^-$ really is unstable. Interestingly enough, despite their negative results, they state that “a hypothetical polynitrogen compound, such as $N_5^+N_5^-$, would be an excellent monopropellant for rocket propulsion or explosives, if it could be synthesized in a stable form”.

The fourth publication by Gagliardi et al. [51] concludes that the reaction to form a bicyclic form of N_{10} from free ions proceeds without a barrier. “*If we, however, allow the two ions to approach each other along the energetically most favourable path, an ion pair can be formed that is bound with 117 kcal/mol with*

respect to the free ions.” The ion pair is 24 kcal/mol higher in energy than the bicyclic form.

Calculations using Cheetah 2.0 give $I_{sp}=281$ s for a HTPB/ $N_5^+N_5^-$ mixture with 70 vol% solids.

Metastable States: Polymeric Nitrogen

The natural state (low energy form) of the elements nitrogen and hydrogen is as diatomic molecules, N_2 (triple bond) and H_2 (single bond). Much energy can therefore be stored in nitrogen molecules with single or double bonds. A form of nitrogen with all single bonds and therefore high energy content is polymeric nitrogen. It also has high density (compare with carbon in the form of graphite versus diamonds). Theory suggests that if a volume of fluid N_2 is sufficiently squeezed, the nitrogen will give up its diatomic structure and form a continuous network of single covalent bonds [52]. This chemical structure is similar to that of its chemically similar group V neighbour’s phosphorus and arsenic. The energy released when the densely packed polymeric nitrogen is released to the diatomic state would be pollution free and enough to qualify it as an interesting future HEDM. Theoretical calculations first predicted the existence of a metastable polymeric nitrogen phase at the pressure 65 GPa [52]. In high pressure experiments several new phases of nitrogen have been found, among them a non-molecular phase that could be recovered to ambient pressure [53]. The most promising cubic gauge structure (cg-N) was predicted to have high energy and high density compared to α - N_2 .

The theoretically estimated performance is I_{sp} 516s, density 3.9 g/cm³, and the performance as an explosive is 10.6 times the performance of HMX. This is based on thermochemical calculations with Cheetah 2.0 made with BKWC equations of state and with data from Mailhiot [52]. Notice that the equation of state used (BKWC) only is calibrated up to 40 GPa so this is a very large extrapolation.

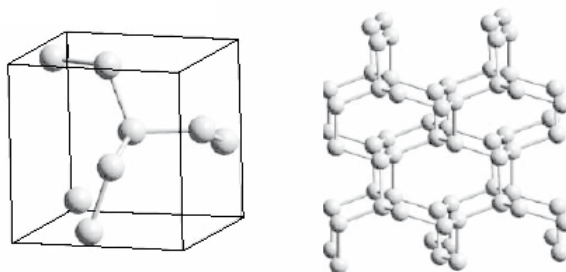


Figure 9. Polymeric cg-N-structure: Each nitrogen atom is connected to three neighbours by three single covalent bonds [54].

A group under Mikhail Eremets has managed to prove its existence [55]. To synthesize it, a diamond anvil cell was used (Figure 10). It is a robust device with a small ($\sim 20 \mu\text{m}$ diameter) sample chamber within which pressures exceeding that at the centre of the earth ($\sim 350 \text{ GPa}$) have been reached. In this experiment 110 GPa at temperatures above 2000 K was reached by heating of a laser. The existence of cubic gauge structure was experimentally verified by X-ray and Raman measurements.

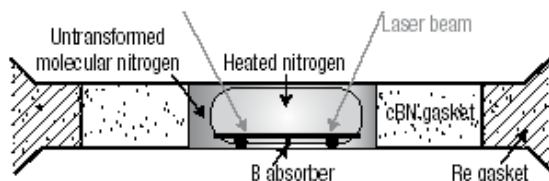


Figure 10. A cross-section of the sample arrangement. The heated nitrogen sample is coloured blue and untransformed molecular nitrogen is red. The laser beam is absorbed by a black, thin, boron plate resting on c-BN pieces that thermally insulate the plate from the bottom anvil. The sample squeezed between the anvils is surrounded by the c-BN/epoxy gasket followed by the metallic (Re) supporting ring [55].

To get a useful substance it needs to have a huge hysteresis enabling it to be recovered to ambient pressures. In the experiment above the structure was stable down to 42 GPa at room temperature. At low temperatures the pressure could be further released, at 140 K it reached 25 GPa before the gasket ruptured. It is a typical problem of the current technique and a novel method of recovering

the sample to ambient pressure needs to be developed. Theory predicts that this structure is metastable at atmospheric pressures [52, 56]. It would then be an analogue to carbon that is stable as graphite at atmospheric pressure but also metastable as diamond created at very high pressures and temperature. If cg-N is not metastable at ambient pressure, it can perhaps be stabilized in compounds with other elements or by introducing impurities [54].

Conclusions

The available energy in exotic materials such as nuclear isomers and antimatter is orders of magnitude larger than the energy of HMX (Figure 11). These have very high potential but the risk of failing is also very high. On a more intermediate level, materials such as all-nitrogen compounds have high potential and lower (but still high) risk. Other materials such as reactive materials based on nanotechnology and HEDM by conventional chemistry have good potential, will probably be accessible in shorter time and involve much less risk of failure. In Table 4 a summary of potential HEDM is given. An increase of performance of three to six times the performance of HMX would revolutionize warfare. This can be compared to the performance increase of three times at the end of the black powder era which is known to have changed the battlefield enormously.

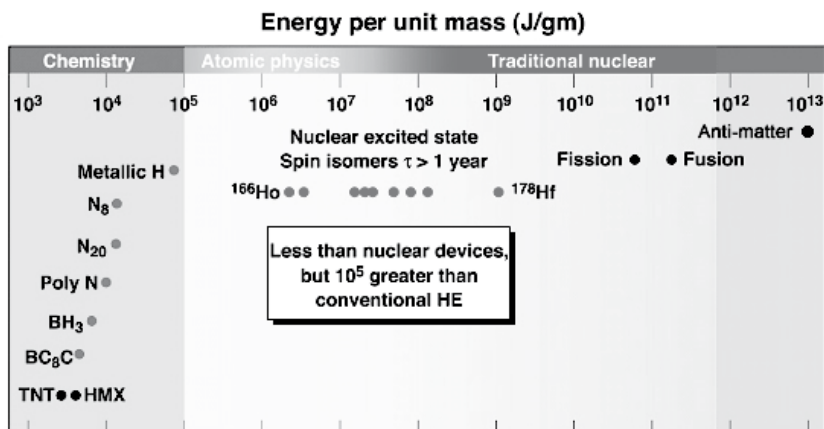
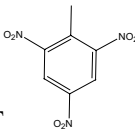
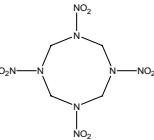
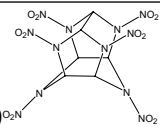
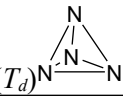
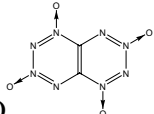


Figure 11. Energy content of some HEDM's. The figure is from LLNL (internet). The point for "Anti-matter" has been added to the figure. The comment in the figure refers to nuclear isomers.

Table 4. Comparison of performance for common high explosives, high nitrogen compounds and some theoretical HEDMs, calculations using Cheetah 2.0 with BKWC EOS

Energetic material	Density (g/cc)	Heat of formation (kJ/mol)	Detonation velocity (mm/ μ s)	Detonation pressure (GPa)	Energy (HMX=100, V=2.2 V ₀)	Energy (HMX=100, V=40 V ₀)	Impulse (s)	Force (J/g)
<i>Reference compounds:</i>								
NC, Nitrocellulose	1.65	-708	7.3	21.2	60	65	226	992
 TNT	1.65	-63	6.9	19.6	55	63	210	897
 HMX	1.905	74.75	9.1	38.5	105	103	266	1397
 CL-20	2.04	393	10	47.8	121	116	273	1380
<i>HEDM:</i>								
$N_5^+N_5^-$	1.9	1239	12.1	62	162	156	347	~2000
 $N_4(T_d)$	2.3	761	15.5	121	308	288	422	3700
N_{60}	1.97	6780	12.3	65	161	150	331	2296
Polymeric nitrogen	3.9	290	30	660	1060	- ^a	513	- ^a
 TTTO	2.38	795	10.9	131	220	- ^a	288	- ^a

^a Calculations do not converge.

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