Alexandre Coelho Rodrigues Gomes

# Computational prediction of the stability and decomposition barriers of neutral molecular polynitrogens

Belo Horizonte (MG)

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Master's defense presented as partial requirement for obtaining the title of master in Chemistry, sub-area Physical-Chemistry. Supervisor: Prof. Dr. Breno Rodrigues Lamaghere Galvão, Co-supervisor: Prof. Dr. Mateus Xavier Silva

#### CENTRO FEDERAL DE EDUCAÇÃO TECNOLÓGICA DE MINAS GERAIS (CEFET-MG)

Departamento de Química

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Belo Horizonte (MG) 2021 Alexandre Coelho Rodrigues Gomes

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To my family.

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### Abstract

This work presents a broad study on the stabilities of several neutral molecular polynitrogens (polyN), with sizes six, eight and ten, focusing in theoretically predicting their usability as high-energy-density materials (HEDMs). If stable enough to be synthesized and stored, these systems may be used as a green source of energy. However, it is very difficult to obtain these structures under mild experimental conditions. One of the main factors that can help this sort of analysis is the predicition of the activation energy barriers of these structures towards unimolecular decomposition. The latter was the basis of the discussions presented throughtout the text. The calculation methodology applied for all the polyN was based on density functional theory (DFT), using exchange and correlation functionals that are known for their high accuracy in predicting energy barriers heights (M06-2X and SOGGA11-X). This made possible a direct and fair comparison between all molecules analysed. The path taken towards achieving this goal started with the search for transition states (TSs) that connected the initial structures to unimolecular decomposition. After finding the TSs, an intrinsic reaction coordinate calculation was carried out for each polyN in order to confirm the decomposition mechanism found. For the most promising structures, a reaction dynamics study was made, in order to check other possible decomposition routes. For this initial and exploratory part of the work, the SOGGA11-X/def2-SVP level of theory was used. A refinement of the results was then performed at the M06-2X, SOGGA11-X/def2-TZVPP levels, being the energies zero point energy corrected. For a structural and electronic analysis of the systems the average bond lengths, average bond orders, HOMO-LUMO gaps and asphericities were calculated. From this analysis, it was possible to classify the structures in chains, rings, cages and prismatic cages ones and achieve a correlation between the systems and their energy content. However, it was not possible to assess a clear correlation between the activation energy barriers of the structures with their structural and electronic properties. The results indicate that the prismatic caged polyN can be expected to present higher energy densities and be more stable with respect to unimolecular decomposition. And finally, specific structures could be selected as potential candidates for use as HEDMs.

Key-words: Clusters; Decomposition barriers; DFT; Polynitrogens; Stability

## Resumo

Este trabalho apresenta um amplo estudo da estabilidade de vários polinitrogênios (poliN) moleculares neutros, com nuclearidades seis, oito e dez, tendo como enfoque a predição teórica do potencial que essas estruturas possuem em atuar como materiais de alta densidade de energia (HEDMs, da sigla em inglês, *High-energy-density materials*). Se suficientemente estáveis para serem sintetizados e armazenados, esses sistemas podem ser utilizados como fontes verdes de energia. No entanto, é muito difícil obter essas estruturas em condições experimentais brandas. Um dos principais fatores que podem ajudar esse tipo de análise é a previsão das barreiras de ativação que essas estruturas possuem em direção à decomposição unimolecular. Esse fator foi a base das discussões apresentadas ao longo do texto. A metodologia de cálculo baseou-se na teoria do funcional da densidade (DFT, da sigla em inglês, *Density Functional Theory*) utilizando funcionais de troca e correlação conhecidos pelas suas altas precisões no cálculo de barreiras de energia (M06-2X e SOGGA11-X). Isso tornou possível uma comparação direta e justa entre todas as moléculas analisadas. O caminho escolhido para alcançar os objetivos do presente trabalho teve início com a busca dos estados de transição (TSs, da sigla em inglês, Transition states) que conectam as estruturas iniciais com os seus produtos de decomposição unimolecular. Depois de encontrados, cálculos dos caminhos intrínsecos de reação (IRC, da sigla em inglês, Intrinsic reaction coordinate) para cada sistema foram realizados, a fim de confirmar os mecanismos de decomposição obtidos. Para as estruturas que apresentaram os resultados mais promissores, um estudo das dinâmicas das reações foi feito, a fim de checar outras possíveis rotas de decomposição. Para essa parte inicial e exploratória, o nível de cálculo SOGGA11-X/def2-SVP foi utilizado. Um refinamento dos resultados foi então realizado utilizando dos níveis de cálculo M06-2X,SOGGA11-X/def2-TZVPP, sendo nesse ponto, as energias corrigidas com as suas respectivas energias de ponto zero. Para uma análise estrutural e eletrônica dos poliN, foram calculados os tamanhos médios de ligação, as ordens médias de ligação, os qaps HOMO-LUMO e as esfericidades de cada estrutura. A partir desses cálculos, foi possível classificar estruturalmente os sistemas em cadeias, anéis, "jaulas" e "jaulas prismáticas" e obter uma correlação entre os seus conteúdos energéticos. No entanto, não foi possível obter uma correlação clara entre as barreiras de decomposição com as propriedades estruturais e eletrônicas calculadas. Os resultados indicaram que os poliN que possuem estruturas do tipo "jaulas prismáticas" são os mais prováveis de possuírem altas densidades de energia e serem mais estáveis em condições ambientes. Por fim, pôde-se selecionar estruturas específicas como potenciais candidatos para uso como HEDMs.

Palavras-chaves: Barreiras de decomposição; Clusters; DFT; Estabilidade; Polinitrogênios

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# List of abbreviations and acronyms

ABL	Average bond lengths
ABO	Average bond orders
AE	Activation energy
AS	Asphericity
B3LYP	Hybrid exchange and correlation functional Becke, three-parameter, Lee-Yang-Parr
CASSCF	Complete Active Space Self-Consistent Field
CC	Coupled Cluster
cc- $pV(N)Z$	Correlation-Consistent Polarized Valence N-Zeta basis set (Dunning $et \ al.)$
CCSD	Coupled Cluster with Single and Double Substitutions
$\operatorname{CCSD}(\mathrm{T})$	Coupled Cluster with Single and Double Excitations and Perturbative Triples
CI	Configuration Interaction
DE	Dissociation energy
DE/n	Dissociation energy per nitrogen atom
de2-SVP	def2 family of basis sets - split valence polarized
def2-TZVPP	def2 family of basis sets - triple zeta valence plus polarization
DFT	Density-functional theory
GA	Genetic Algorithm
GTOs	Gaussian type orbitals
GGA	Generalized Gradient Approximation
HF	Hartree-Fock
HL	HOMO-LUMO gap
HP	Hartree-product

- HEDMs High-energy density materials
- HOMO Highest Occupied Molecular Orbital
- IRC Intrinsic reaction coordinate
- KS Kohn-Sham
- LCAO Linear Combination of Atomic Orbitals
- LUMO Lowest Unoccupied Molecular Orbital
- M06-2X Hybrid meta-GGA minnesota exchange and correlation functional 06
- MP2 Second Order Møller-Plesset Perturbation Theory
- MRCI Multireference Configuration Interaction
- MUE Mean unsigned error
- NHTBH Non-hydrogen transfer barrier height
- PES Potential energy surface
- PolyN Polynitrogens
- QCISD(T) Quadratic Configuration Interaction with Single and Double Excitations and Perturbative Triples
- RHF Restricted Hartree-Fock
- STOs Slater Type Orbitals
- SCF Self-Consistent Field
- SOGGA11-X SOGGA11 exchange-correlation hybrid GGA functional
- TS Transition state

# List of symbols

$\Psi$	Time-dependent wave function
$\psi$	Time-independent wave function
$ \Psi ^2$	Probability density or Born's interpretation of the wave function
$\hbar$	Reduced Planck's constante
m	Mass
V(x)	Total potential energy of a system
E	Allowed value of energy, or, eigenvalue of Schrödinger's Equation
$\hat{H}$	Hamiltonian operator
$ abla^2$	Laplacian operator
Ζ	Atomic number
$N_e$	Total number of electrons
ρ	Electron density
n	Number of nitrogen atoms
$\chi(x)$	Spin-orbital wave function
f(i)	Fock-operator
ε	Eigenvalue of the Hartree-Fock Equation
$C_{\mu i}$	Coefficients of the linear combination of atomic orbitals
$m_s$	Electron spin
$I_x, I_y, I_z$	Moments of inertia

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# 1 Introduction

Clusters can be defined as an aggregate of a countable number of particles, which can consist of identical molecules, atoms or ions or different species. The interest in the study of these aggregates arises, in part, from the fact that they constitute a new type of material, with unique and diverse properties, often different from analogous materials on a macroscopic scale, in the called bulk regime. Much of current research includes uses and applications in catalysis, in the semiconductor industry, in nanotechnology science and in the development of clean energy materials. Polynitrogens systems (PolyN) are included in this context of clusters studies, being, therefore, an aggregate of a countable number of nitrogen atoms (AKUTSU et al., 2017; FERRANDO; JELLINEK; JOHNSTON, 2008; SAMARTZIS; WODTKE, 2006; TAM et al., 2013).

PolyN have been the subject of a vast number of studies in the past decades, both in neutral and ionic forms, due to the fact that they are candidates for clean energy sources. This comes from the nature of their structures, built by single and/or double N-N bonds. The triple bond of molecular nitrogen is highly stable <sup>1</sup>, and therefore these polyN tend to decompose, dissociating into gaseous N<sub>2</sub> molecules and releasing large amounts of energy. As the product of this dissociation is the major component of atmospheric air, this process occurs without the formation of polluting compounds or greenhouse gases, such as carbon dioxide (HIRSHBERG; GERBER; KRYLOV, 2014; MANAA, 2000; SAMARTZIS; WODTKE, 2006; ZARKO, 2010).

Because of their high potential energy content, polyN are part of a group of substances called high energy density materials (HEDMs). For practical usage, nevertheless, the material must not only be able to release a large amount of energy, but also must be reasonably inert at ambient conditions in order to be produced and stored. For polyN systems, this means a high dissociation energy coupled with a sufficiently high unimolecular decomposition barrier (SAMARTZIS; WODTKE, 2006).

PolyN species can be sub-categorized in chain, ring or caged structures. The latter tend to present more single bonds between nitrogen atoms, and thus may be expected to release a larger amount of energy when several new triple  $N_2$  bonds are formed upon its dissociation. As this process may involve the breaking of several chemical bonds simultaneously, its decomposition barrier is also expected to be higher (BRINCK; RAHM, 2014). Therefore, cage-like structures are possibly the most suitable ones HEDM use.

<sup>&</sup>lt;sup>1</sup> The triple bond of molecular nitrogen possesses an energy of 226.1 kcal.mol<sup>-1</sup>, which is stronger than the sum of three simple N-N bonds (116.9 kcal.mol<sup>-1</sup>) and almost one and a half times higher than a double bond (146.6 kcal.mol<sup>-1</sup>)(ATKINS; PAULA, 2015).

#### 1.1 Motivation

Experimentally, it is very hard to synthesize polyN at ambient conditions. Usually, extreme pressures and temperatures are necessary (GIMALDINOVA et al., 2020; NGUYEN, 2003). In the field of neutral polyN (see Figure 1), it has already been experimentally reported a covalent allotropic form of nitrogen in which the atoms are rearranged in a cubic gauche structure (cg-N) (EREMETS et al., 2004), a polymeric nitrogen with the black phosphorus structure (bp-N) (LANIEL et al., 2020) and a molecular form of N<sub>8</sub> (DUWAL et al., 2018). When it comes to ions, an allotropic form of the N<sub>8</sub><sup>-</sup> anion has been synthesized on the sidewalls of multi-walled carbon nanotubes and have also been stabilized on boron-doped graphene (WU et al., 2014; YAO et al., 2019). Ionic clusters, mainly involving the pentazole anion (N<sub>5</sub><sup>-</sup>), have also been reported in the form of salts with metal cations (LANIEL et al., 2018; STEELE et al., 2016; WANG et al., 2018; ZHOU et al., 2020).

Figure 1 – Cubic gauche form of nitrogen (cg-N),(a) and polymeric nitrogen with the black phosphorus structure (bp-N),(b)



Sources: Eremets et al.(2004), (a), and Laniel et al.(2020), (b).

Theoretically, several studies involving polyN (mainly up to 10 atoms) have been reported over the past decades, regarding their structures and thermodynamic properties, both in neutral and ionic forms at gas phase. Stable molecular crystals of  $N_6$ ,  $N_8$  and  $N_{10}$ (GRESCHNER et al., 2016; HIRSHBERG; GERBER; KRYLOV, 2014; LIU et al., 2020; BONDARCHUK, 2020) have also been proposed. However, less attention has been given to their decomposition barriers, which is one of the most important aspects to predict which isomeric forms may actually be stable at ordinary temperatures, which is important for storage. Most of previous research that has been published on this topic focused on chain or ring structures with up to 10 atoms for neutral (mainly  $N_6$ ,  $N_8$  and  $N_{10}$ ) and ionic forms. The dissociation (and/or isomerization) barriers of neutral caged structures have been, up until now, little exploited (GAGLIARDI et al., 1997; LI; LIU, 2002; SCHMIDT; GORDON; BOATZ, 2000; TÜRKER, 2019), and most of these studies employed symmetry constraints in the search for transition state structures.

Considering the perspective of creating materials that could provide large amount

of clean energy, it is important to elucidate and find which, among the theoretically predicted isomeric forms most found in the literature (and some others that are not so commonly found), are the most suitable for HEDMs use. For that purpose it is important to take into account the respective activation energies of each structure especially for caged ones, since it is expected that these will present higher decomposition barriers and release larger amounts of energy.

#### 1.2 Objectives

#### 1.2.1 Main

For the reasons mentioned above, this work has as main objective the theoretical prediction and broad study of the decomposition barriers (i.e. activation energies) of several neutral molecular polyN reported in the literature, among other structures that are not well explored, focusing in the nuclearities six, eight and ten, and using the same calculation method for all structures. The latter aims for a direct comparison between the polyN studied. In this research, ionic systems will not be regarded.

#### 1.2.2 Specifics

The specific objective of this work is the prediction of the stability and reactivity of polyN molecules, and therefore, infer about their HEDMs usability. In order to achieve that, this work will try to find the respective transition state structures that connect the initial structures to their decomposition products; calculate the intrinsic reactions paths (IRC) to corroborate the decomposition mechanisms found; perform reaction dynamics studies in the most promising structures found for each nuclearity; compare the electronic and structural differences relatively to caged geometries with the other shapes (rings and chains); and try to correlate some molecular parameters with the decomposition barriers obtained.

# 2 Literature review

#### 2.1 Polynitrogens (PolyN)

#### 2.1.1 The element nitrogen

Nitrogen, as all elements of the fifteenth group of the periodic table, possesses five valence electrons. It can present several oxidation numbers and, although being the most present element in atmospheric air, it is not abundant on the Earth's crust. In the gas phase, molecular nitrogen  $(N_2)$  is widely used to produce an inert atmosphere, for experimental purposes (LEE, 1999).

It is important to mention that nitrogen differs from the other elements of the same group and neighbors of other groups, especially when it comes to the form that is usually found (gas and not solid, at room temperature) and the fact that it does not present natural allotropic forms, such as phosphorus, oxygen and carbon (LEE, 1999; SHRIVER et al., 2008).

Allotropes can be defined as different 3D arrangements of the same element. They can present differents chemical bondings between the atoms and different discrete molecular units (SHARMA, 1987). The absence of allotropic forms of nitrogen can be explained due to the existence of a very stable triple bond between both atoms, and therefore, the dissociation of substances constituted of nitrogen atoms into molecular nitrogen is very energetically favorable. Therefore, allotropic forms of nitrogen tend to be unstable and reactive, easily decomposing into N<sub>2</sub> (LEE, 1999; SHRIVER et al., 2008).

At the same time, analysing the great stability of the triple bond present in molecular nitrogen, this fact opens the perspective that, if allotropic forms of nitrogen could be formed, namely polynitrogens (polyN), these substances would release a large amount of clean energy, since the products of decomposition would lead to gaseous molecular nitrogen. Figure 2 shows a schematic representation of the decomposition process of polyN structures. These polyN would be cathegorized, therefore, in a class of materials called high energy density materials (HEDMs) (SAMARTZIS; WODTKE, 2006). This topic and perspective have been widely studied over the past decades, considering substances both in ionic and neutral forms, and will be briefily reviewed in the next section, focusing on the neutral studies, which are the main topic of this work.



Figure 2 – Decomposition process of polyN structures

#### 2.1.2 Review on polyN-neutral systems

The structures and energies of several  $N_6$ ,  $N_8$  and  $N_{10}$  polyN have already been well detailed in previous works using all sort of different theoretical methodologies. A common label used in the literature is based upon the symmetries of each system, while their names come from the most similar carbon built structures. The prefix "aza", which comes from the word azote, is used in this context to indicate that the carbon atoms have been substituted for nitrogen ones. The subsections that follow present a review on the neutral allotropic forms of polyN found in the literature, focusing on the nuclearities studied in this work.

Since there are many works using several different methodologies, they will be summarized regarding the most common structures found and reported. When necessary, these researches will be quoted on the *Results and discussion* chapter in order to compare the results found in this present work with others that were previously reported.

#### 2.1.2.1 N<sub>6</sub> systems

Regarding the N<sub>6</sub> isomers, the most commonly found in the literature are the hexaazadewarbenzene ( $C_{2v}$ -A), hexaazabenzvale ( $C_{2v}$ -B), hexaazaprismane ( $D_{3h}$ ) and diazide ( $C_{2h}$ ). Figure 3 presents their structures next to their analogous carbon built ones.





It is well known from the literature that the potential energy surface (PES) of these isomers is highly dependent on the level of theory used, especially regarding correlation effects (SAMARTZIS; WODTKE, 2006). For instance, depending on the calculation method employed, the benzene-like structure (hexaazabenzene) can be a stable minimum and can possess one or two imaginary frequencies (ENGELKE; STINE, 1990; GLUKHOVTSEV; SCHLEYER, 1992; LAUDERDALE; STANTON; BARTLETT, 1992). The isomers shown in Figure 3 are all true minima in all types of calculation methods. Among these, the open chain diazide is almost unanimously considered the most thermodinamically stable isomer (GLUKHOVTSEV; SCHLEYER, 1992; GLUKHOVTSEV; JIAO; SCHLEYER, 1996; TOBITA; BARTLETT, 2001). As it will be noted in the sub section *Decomposition barriers*, great efforts have already been put into the discovery of the decomposition path of this structure.

The majority of works also agree with the fact that, if synthetized, isomer  $N_6(D_{3h})$  would carry a large energy content, and therefore constitutes a good HEDM candidate. Nevertheless, its decomposition pathway has not been fully understood yet (LI; LIU, 2002).

#### 2.1.2.2 N<sub>8</sub> systems

When it comes to the polyN structures with eight atoms, the most commonly found isomers in previous reports are the octaazacyclooctatetraene  $(D_{2d})$ , octaazacuneane  $(C_{2v}-A)$ , octaazatryciclooctadiene  $(C_{2v}-B)$  and octaazacubane  $(O_h)$ . Figure 4 shows their structures next to their analogous carbon built ones.

Figure 4 – Most common  $N_8$  isomers found in the literature and their name-giving organic counterparts (white is for hydrogen atoms).



For N<sub>8</sub> isomers, as in the case of N<sub>6</sub>, correlation effects demonstrated to be very significant (SAMARTZIS; WODTKE, 2006). All these isomers, in different levels of theory, were demonstrated to be true minima on the N<sub>8</sub> PES (GLUKHOVTSEV; JIAO; SCHLEYER, 1996; TÜRKER, 2018). The most considered isomer is octaazacubane (CHEN; SHYU, 1999; GAGLIARDI et al., 1998; LAUDERDALE; STANTON; BARTLETT, 1992; LEININGER; SHERRILL; SCHAEFER, 1995; MIKHAILOV; CHACHKOV, 2020; TIAN et al., 1997) and, probably because of its caged and highly strained structure, it is reported as being one of the most energetic HEDM that could be proposed. In general, most works agree that this would be a good candidate for HEDM use, with some exceptions (SCHMIDT; GORDON; BOATZ, 2000). The results of these papers will be addressed and discussed along this dissertation.

Another point of agreement that exists in the literature is that isomer azidopentazole (Figure 5, symmetry  $C_s$ ) is, probably, the most stable of this nuclearity (NGUYEN; HA, 1996). The existence of N<sub>5</sub> and N<sub>3</sub> ions is well known in the literature (FAU; BARTLETT, 2001; FAU; WILSON; BARTLETT, 2002; GAGLIARDI et al., 2001; XU et al., 2020). Many studies try to elucidate the polyN that would be formed experimentally by using these ions. In fact, azidopentazole is formed by a N<sub>5</sub><sup>+</sup> cation and the azide ion (N<sub>3</sub><sup>-</sup>) (Figure 6). The approximation of these two ions, following the reaction path, turns the system into azidopentazole. Nevertheless, although being considered the most stable within these isomers, it has been already shown that it possesses a small barrier towards decomposition, making it not suitable for HEDM use. The byciclic azapentalene (Figure 5, symmetry)

 $D_{2h}$ ) was also studied, but it demonstrated low activation barrier heights, although being considered stable (CHUNG; SCHMIDT; GORDON, 2000; GAGLIARDI et al., 2001).





Figure 6 – Most common  $N_5$  and  $N_3$  ions found in the literature



For this nuclearity, octaazacubane and other cage-like structures, such as octaazacuneane, still remain a hope in the search for polyN with possible HEDM usability.

#### 2.1.2.3 $N_{10}$ systems

When it comes to  $N_{10}$  isomers, previous studies are less frequent, especially for cage-like structures. The mostly found cage-like structures are the ones with  $C_{3v}$  and  $D_{5h}$ symmetries (CHEN; SHYU, 1999; CHEN; SUN; SHYU, 1999; REN et al., 2001; TÜRKER, 2019; ZHOU et al., 2005). Their structures are shown in Figure 7. There is not a common nomenclature used for  $N_{10}$  isomers, apart from their symmetries. Since there may be a great amount of stable  $N_{10}$  structures yet to be discovered, one can conclude that there is still a great gap regarding the study of this nuclearity, especially when it comes to activation energies calculations (SAMARTZIS; WODTKE, 2006).

The great majority of  $N_{10}$  isomers considered and found in the literature are those constituded of pentazole units (LIANG et al., 2012). The structure constituted of two pentazole units (symmetry  $D_{2h}$ , Figure 7) is considered, up until now, to be the lowest  $N_{10}$ minimum (BONDARCHUK, 2020; CHEN; SUN; SHYU, 1999; GLUKHOVTSEV; JIAO; SCHLEYER, 1996; LIU et al., 2020) and it has been theoretically proposed as a molecular



Figure 7 – Most common  $N_{10}$  isomers found in the literature.

crystal (BONDARCHUK, 2020; LIU et al., 2020). It is also possible to find studies that try to achieve stable isomers combining the v-shaped cation of  $N_5$  with pentazoles units (Figure 6) (XU et al., 2020). However, the study of the decomposition pathways of isomers with this nuclearity is still scarce in the literature.

#### 2.1.2.4 Decomposition barriers

Unlike the study of energies and geometries of  $N_6$ ,  $N_8$  and  $N_{10}$  isomers, their decomposition and isomerization barriers have been little explored. Since the main objective of this present work is to infer stability and HEDM usability through decomposition barriers calculations, the main results mentioned below, will also be discussed later in the *Results and Discussion* section.

Within N<sub>6</sub> isomers the focus was given to the lowest energy one, as mentioned before, the diazide (N<sub>6</sub>( $C_{2h}$ )) (GAGLIARDI et al., 2000a; HIRSHBERG; GERBER, 2012; NGUYEN; HA, 2001). The decomposition of N<sub>6</sub>( $C_{2v}$ )-A was also addressed (HIRSHBERG; GERBER, 2012). Li *et al.* (2002) tried to calculate activation and isomerization barriers of several different isomers, including one of the best HEDM candidates so far, the hexaazaprismane (LI; LIU, 2002). However, they could not find a direct decomposition barrier of N<sub>6</sub>( $D_{3h}$ ). The authors reported an isomerization path, which in fact, showed a high decomposition barrier, and mentioned that a direct decomposition path, if found, would possibly possess a likewise high activation energy.

Regarding N<sub>8</sub> isomers, great effort has been given into octaazacubane. Some studies developed a symmetry forbbiden decomposition pathway (ENGELKE; STINE, 1990; EVANGELISTI; GAGLIARDI, 1996), while others proposed a less symmetric path, which is more likely to occur (SCHMIDT; GORDON; BOATZ, 2000). Dynamics calculations were also proposed (GIMALDINOVA et al., 2020). It has been found that N<sub>8</sub>( $C_{2v}$ )-B is an intermediate in the decomposition of N<sub>8</sub>( $O_h$ ), and this result has been discussed in previous works (GAGLIARDI et al., 1997; SCHMIDT; GORDON; BOATZ, 2000). As mentioned before, azidopentazole and azapentale (Figure 5) were also studied, but it was demonstrated that they possess low barriers towards decomposition or isomerization (CHUNG; SCHMIDT; GORDON, 2000; GAGLIARDI et al., 2000b; GAGLIARDI et al., 2001; NGUYEN; HA, 1996). Open chain isomers of  $N_8$  were also approached, leading to the conclusion that these systems easily decompose (CHUNG; SCHMIDT; GORDON, 2000; FAU; BARTLETT, 2001).

As for  $N_{10}$  isomers, the majority of previous works focused on pentazole based units and open chains of  $N_{10}$  (KLAPÖTKE; HARCOURT, 2001; MANAA, 2000; STROUT, 2002; WANG; MEZEY; ZGIERSKI, 2004). As already mentioned, the decomposition pathways of cage-like  $N_{10}$  isomers have been, up until now, little approached, and therefore, still remain an open prospect of research.

#### 2.1.3 Other nuclearities

Apart from neutral and ionic molecular polyN with less than ten atoms, there are a few theoretical studies regarding even bigger structures, such as the ions of  $N_{11}^-$ ,  $N_{11}^+$ ,  $N_{15}^-$  and the neutrals  $N_{12}$ ,  $N_{18}$ ,  $N_{20}$ ,  $N_{24}$ ,  $N_{30}$ ,  $N_{36}$  and even a fullerene-like structure of  $N_{60}$ . However, the experimental production of such large allotropes is still out of sight (MANAA, 2000; SAMARTZIS; WODTKE, 2006). Besides that, a recent paper reported that only small nitrogen cages with single N-N bonds tend to be stable. Nitrogen cages larger than  $N_{10}$  are expected to be very unstable (KATIN et al., 2020).

#### 2.2 Quantum chemistry

#### 2.2.1 Wave functions and Schrödinger's Equation

When classical Newtonian mechanics was applied to very small particles, such as electrons, in the early twentieth century, it demonstrated flaws and contradictions when the results were compared with available experimental data. It became clear that a new mechanics needed to be developed in order to explain the behavior of these particles, in a microscopic way. In this context, quantum chemistry arrived to explain and be applied to solve problems in chemistry, that deal with molecules, ions, atoms and electrons (ATKINS; PAULA, 2015; LEVINE, 2000).

Quantum mechanics takes into account the quantization of energy and the duality of matter (wave-particle), in which, instead of moving along a defined trajectory, particles are distributed in space, in a manner similar to a wave. At first, this may seem unsual, but the solutions and applications of this discovery were (and still are) undoubtedly extremely relevant and important for Science, in many different aspects. The mathematical representation of these waves is called the wave function ( $\Psi$ )(ATKINS; PAULA, 2015). The austrian physicist Erwin Schrödinger suggested in 1926, an equation to determine the wave function of any system, which is shown in Equation 2.1, in its time-dependent form, one-dimensional and for one particle. Equation 2.2 is the time-independent form for which the lower case  $\psi$  is used, also one-dimensional and for one particle (LEVINE, 2000). This Equation is considered one of the postulates of quantum mechanics, and it is the basis to rationalize and solve problems that involve small particles.

$$-\frac{\hbar}{i}\frac{\partial\Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + V(x,t)\Psi(x,t)$$
(2.1)

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x)$$
(2.2)

One can say that the wave function contains all information about the dynamic properties of a particle, such as position and momentum and, if the potential energy of the system is time-independent, Equation 2.2 can be used (ATKINS; PAULA, 2015; GRIFFITHS, 1995). It is important to mention that the wave function itself does not have a proper physical interpretation, since, as it can be imaginary or negative. The value of  $|\Psi|^2$ , in fact, provides this necessary interpretation. Considering the fact that the concept of trajectory is left behind, and a probabilistic approach is adopted, the probability of finding a particle, characterized by a specific wave function, in a small volume centered at a given point and at a given moment is proportional to the value of  $|\Psi|^2$  at this point. This interpretation of the wave function is called the Born interpretation (ATKINS; PAULA, 2015; LEVINE, 2000).

Schrödinger's equation can also be written in the form of operators. Considering the problem time-independent, and writing Equation 2.2 in the form of Equation 2.3, the terms in brackets are an operator, and  $\psi(x)$  is an eigenfunction, being E the respective eigenvalue ( $\hat{H}\psi = E\psi$ ). This operator is called Hamiltonian ( $\hat{H}$ ) and it contains the terms related to the kinetic and potential energy of the system, that is, its total energy (ATKINS; PAULA, 2015; LEVINE, 2000).

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi(x) = E\psi(x)$$
(2.3)

Basically, although not easy and many times analitically impossible, in order to to solve a problem in quantum mechanics, one must consider the Hamiltonian (taking into account the total energy of the system), solve Schrödinger's equation applying the boundaries conditions of the problem in particular and normalize  $|\psi|^2$ . To solve problems of chemical interest, which involve a large number of particles, it is necessary to make approximations.

#### 2.2.2 The Born-Oppenheimer approximation for polyatomic systems

The wave function of multielectronic systems is much more complicated and complex than the one for systems that have only one electron. This results from the interaction between all particles (electrons and nuclei), that the system contains. In order to demonstrate this complexity, Equation 2.4 presents the full Hamiltonian of Schrödinger's equation of a system with N electrons and M nuclei (GRIFFITHS, 1995; SZABO; OSTLUND, 1989). Atomic units are used, differently from Equations 2.1, 2.2 and 2.3 for a simpler notation.

$$\hat{H} = -\sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 - \sum_{A=1}^{M} \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} + \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_A Z_B}{R_{AB}}$$
(2.4)

In which *i* and *j* are electrons; *A* and *B* are nuclei; *Z* stands for the atomic numbers of each nucleus; *r* and *R* are the distances between electrons and nuclei, being *r* relative to the position of the electrons and *R* of the nuclei;  $\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}$  and  $\nabla_A^2 = \frac{\partial^2}{\partial x_A^2} + \frac{\partial^2}{\partial y_A^2} + \frac{\partial^2}{\partial z_A^2}$ 

In Equation 2.4, the first term is the operator of the electron kinetic energy; the second term is the operator of the kinetic energy of the nuclei; the third term represents the Coulombian attraction between electrons and nuclei; the fourth and fifth terms represent, respectively, the repulsion between electrons and between nuclei (SZABO; OSTLUND, 1989).

Thus, in more complex systems, it is necessary to develop and apply approximations, such as the Born-Oppenheimer one. This approach considers that the nuclei are fixed in well-defined positions and Schrödinger's equation is solved for the electrons separately. The nuclei of the system are admitted to be much heavier than the electrons, i.e., they are considered stationary (no kinetic energy and mutual repulsions constant), while the electrons move in the field that these create (ATKINS; PAULA, 2015; LEVINE, 2000; SZABO; OSTLUND, 1989).

In this approach the total Hamiltonian is separated in nuclear and electronic parts. Equation 2.5 presents the electronic Hamiltonian, being the problem minimized, although not necessarily easy to solve. The last term of Equation 2.5 is the repulsion between the nuclei, but this is a constant. The effects of this constant will be briefly discussed below (JENSEN, 2007; SZABO; OSTLUND, 1989).

$$\hat{H}_{elec} = -\sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} + \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_A Z_B}{R_{AB}}$$
(2.5)

The solution of the electronic Equation  $(\hat{H}_{elec}\psi_{elec} = E_{elec}\psi_{elec})$  is the electronic

wave function:

$$\psi_{elec} = \psi_{elec}(r_i; R_A) \tag{2.6}$$

which demonstrates that the motion of the electrons depends on the electrons coordinates, but also, depends parametrically on the nuclear ones. Thus, the electronic energy also depends parametrically on the nuclei coordinates:

$$E_{elec} = E_{elec}(R_A) \tag{2.7}$$

Therefore, the total electronic energy for a certain arrangement of the nuclei must possess the constant nuclear repulsion, as it is demonstrated on Equation 2.5(SZABO; OSTLUND, 1989).

However, since the electrons move much faster than the nuclei, the electronic coordinates can be replaced, approximately, by their average values, resulting on a nuclear Hamiltonian, analogous to the electronic one:

$$\hat{H}_{nuc} = -\sum_{A=1}^{M} \frac{1}{2M_A} \nabla_A^2 + E_{elec}(R_A)$$
(2.8)

The total energy, given by the sum of the electronic energy with the nuclear repulsion, provides a potential for the motion of the nuclei. Therefore, the nuclei in the Born-Oppenheimer approximation move on a potential energy surface that arrives from the solution of the electronic problem.

The solutions of the nuclear equation describes the vibration, rotation and translation of a molecule. The total energy, therefore, in the context of the Born-Oppenheimer approximation, takes into account the energies of these motions adding the electronic energy. Usually, unless it is necessary, the vibration-rotation-translation problem is disconsidered, and only electronic wave functions are analysed (SZABO; OSTLUND, 1989).

After finding the electronic wavefunction and the electronic energy (taking into account the Born-Oppenheimer approximation), considering the Hamiltonian in the form of Equation 2.5 in order to solve Schrödinger's equation, several properties can be extracted, such as the equilibrium geommetry, ionization potential, electron affinity, and so on. Transition states structures, which are the key to the present work, can also be determined (ATKINS; FRIEDMAN, 2005).

After considering this, computational electronic structure calculations can be performed. This will be considered in the next section.

#### 2.3 Electronic structure

The basis of electronic structure calculation is the Hartree-Fock (HF) method. All other more advanced methodologies, such as the Density-functional theory (DFT), start, in some way, from the HF procedure. This method will be regarded in the next section, followed by the calculation method used in this work, DFT.

#### 2.3.1 Ab initio approach: The Hartree-Fock (HF) method

In order to make the computation of electronic energies more feasible, for systems with more than one electron, the best way to start is finding a well behaved wave function. The first step is based on calculating an approximate one using the Hartree-Fock procedure. This approximation is the basis for calculations of electronic structure that involve atomic and molecular orbitals in polyelectronic systems and it is an *ab initio* approach, since it is based on first principles. Approximation because it considers that the electronic repulsion of the various electrons that constitute the system is an average potential (mean field). This approximation allows each electron to be solved individually. Therefore, it is important to observe that the HF procedure does not consider the electron correlation (ATKINS; FRIEDMAN, 2005; LEVINE, 2000).

In order to fully describe one electron, besides its spatial distribution, it is necessary to specify its spin. The combination of these two elements leads to the spin-orbital wave functions  $(\chi(x))$ . Considering this fact, and the fact that each electron is solved individually, the total wave function will be the product of these one electron spin-orbitals (Equation 2.9) (LEVINE, 2000; SZABO; OSTLUND, 1989).

$$\psi^{HP}(x_1, x_2, \dots x_N) = \chi_i(x_1)\chi_j(x_2)\dots\chi_k(x_N)$$
(2.9)

Here, HP is the Hartree product and N is the last electron of the system. It is important to mention that this approach disconsiders the inherent instantaneous electronic repulsion, as mentioned before.

Another aspect that must be considered is that this resulting wave function does not obbey Pauli's principle, i.e., the Hartree product is not antisymmetric, and the interchange between two electrons does not change the sign of the wave function. To solve this problem, Slater determinants are used, like the one that is shown in Equation 2.10.

$$\psi(x_1, x_2, \dots, x_N) = (N_e!^{-1/2}) \begin{vmatrix} \chi_i(x_1) & \chi_j(x_1) & \dots & \chi_k(x_1) \\ \chi_i(x_2) & \chi_j(x_2) & \dots & \chi_k(x_2) \\ \vdots & \vdots & \vdots \\ \chi_i(x_N) & \chi_j(x_N) & \dots & \chi_k(x_N) \end{vmatrix}$$
(2.10)

In which  $N_e!^{-1/2}$  is a normalization factor and  $N_e$  is the total number of electrons.

To obtain the most realistic spin-orbitals, an initial guess function must be variationally optimized such as to yield the lowest total energy of the system. This optimization is constrained to the fact that the spin-orbitals must be orthonormal (ATKINS; FRIEDMAN, 2005; LEVINE, 2000). After applying the variational principle, taking into account the orthonormality constraint, the HF Equation (Equation 2.11) is obtained.

$$f(i)\chi(r_i) = \varepsilon\chi(r_i) \tag{2.11}$$

In Equation 2.11, the term  $f_{(i)}$  is called Fock operator. This operator, analogous to the Hamiltonian  $(\hat{H})$ , contains terms that express mathematically the electron kinetic energy, the potential energy between this electron and the nuclei of the system, the mean field created by the other electrons, and the effects of spin correlation between the electrons of the system. The Fock operator considers the average repulsion among electrons, mentioned previously, unlike the Hamiltonian, which considers this potential more broadly.

Since the Fock operator depends on all electrons, its detailed shape depends on all the individual wave functions of the electrons, so that it is necessary to provide an initial shape for these wave functions in order for them to be used in  $f_{(i)}$  and the equation can be solved. So it is a numerical and iterative method. The process is repeated using the newly found wave functions, until the moment when the energies and wave functions stop changing, reaching a so-called self-consisted field (SCF), within a convergence criteria previously established (ATKINS; FRIEDMAN, 2005; ATKINS; PAULA, 2015).

The Hartree-Fock procedure can be used to solve numerically the problem of atoms. However, for molecules, this would be very computationally expensive. Therefore, a modification of this method needed to be applied. In 1951, C. C. J. Roothaan and G. G. Hall suggested, independently, that the spin-orbitals can be expanded in a linear combination of known basis functions, like shown in Equation 2.12, in order to achieve an electronic total energy that is closer to the minimum of energy (ATKINS; FRIEDMAN, 2005; LEVINE, 2000).

$$\chi(r_i) = \sum_{\mu=1} C_{\mu i} \chi_{\mu}$$
 (2.12)

The basis functions are chosen to be "atomic orbitals" that will provide the respective molecular orbitals. This procedure, therefore is called linear combination of atomic orbitals (LCAO). With this procedure, the problem of calculating the wave functions is reduced in finding the coefficients  $C_{\mu i}$ . Again, this needs to be done iteratively, since the

Fock operator depends on the yet unknow coefficients, that will be optimized (ATKINS; FRIEDMAN, 2005; LEVINE, 2000).

If a complete set of basis is chosen the HF energy would be equal to the lowest energy given by the variational theory. Nevertheless, an infinite set of basis is computationally not feasible. In general, the selected basis functions are gaussian-type, since this type of functions generate integrals that are more easily solved. One can say that, if a sufficiently large enough basis set is chosen, the better the results will be (ATKINS; FRIEDMAN, 2005).

Like mentioned before, although the HF method, combined with the Roothaan-Hall contribution, is extremely important for quantum calculation, it does not take into account the instantaneous Coulombic interactions between electrons, i.e., it does not consider electron correlation. This means that the HF energy can, and should, be improved by using post-HF methodologies which take into account this inherent correlation that the chemical systems possess.

Nowadays, there are several post-HF methods that aim to improve the electronic energy by adding the effects of electron correlation. These methodologies are not in the scope of this present work though. However, one can mention Configuration interaction (CI); Multiconfiguration and multireference methods (MCSCF); the Møller-Plesset manybody perturbation theory (MP); and Coupled-Cluster (CC). Details of these approaches can be found in several references (ATKINS; FRIEDMAN, 2005; LEVINE, 2000; SZABO; OSTLUND, 1989).

#### 2.3.2 Density Functional Theory (DFT)

Another approach to calculate electronic energies and properties of quantum systems, especially those with many atoms and using larger basis sets, is the Density Functional Theory (DFT). Differently from the wave-function based methods mentioned in the previous section, DFT does not try to achieve the molecular wave function. Insted, it tries to obtain the electron density ( $\rho$ ) and from this, it calculates the molecular electronic energy (ATKINS; FRIEDMAN, 2005; LEVINE, 2000).

A question that arises is: How  $\rho$  can be calculated? i.e., what is the probability of finding an electron (any electron of the system) in a certain volume element in space? To answer these questions one must remember that electrons are indistinguishable. Therefore, the probability density for finding an electron near a point (x, y, z) is given by Equation 2.13. In this Equation the fact that  $\psi$  is antisymmetric with respect to electron exchange is taken into account (LEVINE, 2000).

$$\rho(r) = N_e \sum_{allspins} \int \dots \int |\psi(r, r_2, \dots, r_N, m_{s1}, m_{sN})|^2 dr_2 \dots dr_N$$
(2.13)

In which dr = dxdydz,  $N_e$  is the total number of electrons and  $m_s$  are their respective spins.

When integrated over all space this electron density provides the total number of electrons,  $N_e$ , i.e., how many electrons are there (Equation 2.14) (CRAMER, 2004; LEVINE, 2000).

$$N_e = \int \rho(r) dr \tag{2.14}$$

In this method, the electronic energy is obtained as a functional of the electron density  $(E[\rho])$ , which means that a number (the energy) is associated to a function. A functional, therefore, is a mathematical rule that associates a number for each function. For a given density, it only exists one corresponding energy (ATKINS; FRIEDMAN, 2005; LEVINE, 2000).

In 1964, P. Hohenberg and W. Kohn proved that the fundamental ground state energy can be determined by the electron density (The Hohenberg–Kohn Existence Theorem, (HOHENBERG; KOHN, 1964)). They proved that the ground state electron probability density determines the external potential, and therefore, determines the number of electrons (Equation 2.14). However, they did not provide the proper shape of the functional. The external potential mentioned before defines one problem, i.e., defines the system being analysed (ATKINS; FRIEDMAN, 2005; CRAMER, 2004; LEVINE, 2000).

Later, W. Kohn and L. J. Sham demonstrated that the exact ground state electronic energy can be written in the form of Equation 2.15 (Kohn–Sham Self-consistent Field Methodology (KOHN; SHAM, 1965)),

$$E[\rho] = -\frac{\hbar^2}{2m_e} \sum_{i=1}^N \int \chi_i^*(r_1) \nabla_1^2 \chi_i(r_1) dr_1 - j_0 \sum_{I=1}^M \frac{Z_I}{r_{I1}} \rho(r_1) dr_1 + \frac{1}{2} j_0 \int \frac{\rho(r_1)\rho(r_2)}{r_{12}} dr_1 dr_2 + E_{XC}[\rho]$$
(2.15)

in which  $E[\rho]$  is the exact ground state electronic energy of an N-electron system, and the Kohn-Sham (KS) orbitals are the one-electron spatial orbitals  $\chi_i (i = 1, 2, ..., N)$ . M is for the nuclei with atomic number  $Z_I$  and  $j_0 = \frac{e^2}{4\pi\varepsilon_0}$  (ATKINS; FRIEDMAN, 2005).

The first term on the right of Equation 2.15 represents the kinectic energy of electrons; the second is the electron-nucleus attraction; the third represents the Coulomb interaction between the total charge distribution at  $r_1$  and  $r_2$  and finally, the last term is the exchange-correlation energy of the system. Of all these terms,  $E_{XC}$  is the only that does not possess an exact known form. This is also a functional of the electronic density and contains all the unknown quantities that emerged during the process of calculation (ATKINS; FRIEDMAN, 2005).

In DFT theory, therefore, theoretical chemists and physicists try to achieve better and more specific exchange and correlation functionals, in order to make the calculations of molecular properties, such as barrier heights, more accurate.

Although not technically considered a variational methodology, a sort of variation theory can be applied in the electronic energy in order to solve the KS equations and find the respective KS orbitals. In a way analogous to the variational principle used for HF calculations, the true ground state electron density minimizes  $E[\rho]$ . This variational theorem used in DFT theory was proved by Hohenberg and Kohn in 1965 (The Hohenberg–Kohn Variational Theorem). As in the HF method, the KS equations are solved in a self-consistent way. These orbitals can also be found by being expressed in terms of a known set of basis functions. Gaussian functions can also be used in this case (ATKINS; FRIEDMAN, 2005; LEVINE, 2000).

Besides the fact of being less computationally demanding than other post-HF methods, especially for larger systems, DFT takes into account electron correlation, differently from pure HF methodology, and decreases significantly the number of variables needed to perform quantum calculations. This latter comes from the fact that the potential energy (or in DFT theory, the external potential) of one electron and the nuclei depends only on the three spin spatial coordinates (x, y, z) of this electron, regardless of the total number of electrons. It is worth remembering that the nuclei are considered fixed, so their coordinates are not variables (JENSEN, 2007).

#### 2.3.3 A parallel between HF and KS

After considering these two methodologies (HF and KS), a parallel can be made. First and foremost, DFT optimizes an electron density while molecular orbital theory optimizes a wave function. Therefore, in order to calculate a certain molecular property using DFT, one must find how this property depends on the electron density. Unlike wave-function based methods, in which the correct quantum mechanical operator needs to be known (CRAMER, 2004).

In the HF method, the molecular orbitals are written in terms of a linear combination of atomic orbitals, and these are varied in order to minimize the electronic energy, restricted to the orthonormality condition. The minimization of a single Slater determinant in the HF procedure leads to the HF equation. In DFT, the KS orbitals are defined, and the electronic density is minimized, restricted to the fact that, if integrated all over the space, it must be equal to the number of existing electrons. This minimization leads to an equation that is analogous to the HF one.

#### 2.3.4 Most common basis functions

As mentioned in previous sections, one of the most important steps in performing electronic structures calculations is the proper selection of basis sets. This is one of the inherent approximations needed to be done, including for *ab initio* methods. The accuracy of the calculations is highly dependent on the set of basis functions selected in a way that the larger the ammount of atomic orbitals used as functions, more closely the system will be to the real molecular orbitals. This section aims to cite the most common ones used in this context (JENSEN, 2007). It is important to recall the fact that the unknown coefficients of Equation 2.12 are determined iterativelly.

There are, basically, two types of basis functions (atomic orbitals): Slater and Gaussian types orbitals. Slater Type Orbitals (STOs) are constructed with the use of spherical harmonics functions and with an exponential dependence on the distance between the nucleus and electrons (exact orbitals for the hydrogen atom). STOs are mainly used for atomic and diatomic systems. In polyatomic molecules, the STOs are centered on each of the atoms. Therefore, the bigger the molecule, more complex integrals need to be evaluated, and more time consuming is the process. Gaussian type orbitals (GTOs) are less computationally demanding since the increase of these basis functions leads to integrals that are more easily solved, when compared to the STOs ones (the product of two Gaussian functions gives just one Gaussian) (JENSEN, 2007; LEVINE, 2000).

Improvements of these basis sets can be achieved by doubling all basis functions, leading to a Double Zeta (DZ) type. A variation of this basis is to double only the number of valence orbitals (split valence basis, or VDZ - valence double zeta). This is important because it focuses on the valence electrons, i.e., those that in fact participate in chemical reactions. The increase of these basis leads to the triple zeta (TZ) and valence triple zeta basis functions (VTZ), and so on. There are also correlation-consistent polarized valence (double, triple, and so on) basis sets, which can be used for calculations that require the addition of electron correlation (JENSEN, 2007).

Several chemists and physicists developed (and still develop) basis functions sets for all different sorts of calculations, i.e., depending on the problem that needs to evaluated. In this work, the Turbomole def2 family of basis sets (Split Valence Polarized (SVP) and Triple Zeta Valence plus Polarization (TZVPP))developed by Ahlrichs and co-workers were chosen, since they are known to perform well for density-functionals calculations, which was the method chosen in this work. The def2-SVP basis set is used in this work for exploratory calculations, while the def2-TZVPP ones are used for the reported results (WEIGEND; AHLRICHS, 2005).

# 3 Methodology

#### 3.1 PolyN selection

The initial structures of the polyN selected for a broad study of stability and decomposition barriers were taken from the work of Silva *et al.* (2018). The major goal was to choose structures that could provide a diverse set of geometrical classes, such as chains, rings and cages. In a recent work, Katin et al. (KATIN et al., 2020) reported that nitrogen cages larger than 10 atoms tend to be very unstable. Therefore, for the present work, only neutral structures with sizes six, eight and ten were selected for further study of their stabilities and decomposition barriers. For each nuclearity, four different structures were selected. By this selection, it was expected to assess which structures and nuclearities are more kinetically stable towards unimolecular decomposition, and from that, analyse their potential as HEDMs.

In the 2018 work (SILVA et al., 2018), the potential energy surfaces of polyN up to 10 atoms were explored by means of the use of a genetic algorithm (GA). In this initial approach, the systems were studied at the DFT level of theory, using the 6-31G basis set, and then, the obtained structures were reoptimized using second order Møller-Plesset Perturbation Theory (MP2) and coupled cluster with single and double excitations and perturbative triples (CCSD(T)) levels, and employing larger basis sets.

The only structure considered in the present work that was not taken from the above mentioned work was the octaazacubane one. The latter initial structure was taken from the work of Mikhailov and Chachkov (2020). In this work, the authors achieved the optimized structure by means of the quadratic configuration interaction with single and double excitations and perturbative triples (QCISD(T)). Figure 8 presents the initial structures of all the twelve polyN that were explored in this work.


Figure 8 – Initial structures of the neutral systems

## 3.2 Functionals selection

Since one of the main objectives of this work is to infer kinetic stability towards unimolecular decomposition of polyN systems, the exchange and correlation functionals used must be adequate and suitable for this type of analysis. The M06-2X and SOGGA11-X were chosen due to their known accuracy for predicting energy barrier heights (ZHAO; TRUHLAR, 2008; MARDIROSSIAN; HEAD-GORDON, 2016). In fact, it has been shown by Peverati and Truhlar (2012), that the mean unsigned error (MUE) for non-hydrogentransfer barrier heights (NHTBH <sup>1</sup>) for the hybrid SOGGA11-X functional and of M06-2X are respectively 1.16 kcal.mol<sup>-1</sup> and 1.22 kcal.mol<sup>-1</sup>. Therefore both functionals show chemical accuracy for potential energy barriers and are expected to provide reliable results for the purposes of this research.

All of the initial structures were reoptimized using the calculation method employed in this work. Vibrational analysis was also performed in all structures, in order to confirm that they were true minima within the M06-2X and SOGGA11-X/def2(SVP and TZVPP) (WEIGEND; AHLRICHS, 2005) approaches. All electronic structure calculations reported here were performed using the GAMESS-US (SCHMIDT et al., 1993) and MOLPRO (WERNER et al., 2015) packages.

# 3.3 Preliminary approach

As a first step, the smaller def2-SVP basis set was used for an initial exploration of possible dissociation and isomerization paths associated with each studied polyN, regarding their respective transition states. For this approach, only the SOGGA11-X functional was employed. After finding the TSs, intrinsic reaction coordinate (IRC) calculations were performed with this basis set for all TSs found to ensure they were connected to the decomposition or isomerization products.

The methodology of finding the TSs, the IRC calculations and the energy refinement approach, regarding both functionals, will be detailed in the next sections.

### 3.3.1 Transition states (TSs) search and IRC calculations

The knowledge of the energies and structures of the minima and TSs, associated with the respective value of the barrier height may provide good insight on reaction mechanisms. The point of maximum potential energy on the respective minimum energy path is the transition state, i.e. the structure that connects reactants and products. These must possess only one imaginary vibrational frequency. The energy difference between the

<sup>&</sup>lt;sup>1</sup> The NHTBH are a part of the Minnesota database group that includes several types of benchmark barrier heights calculations (ZHENG; ZHAO; TRUHLAR, 2009).

TS and the reactants is the barrier height of the respective reaction, i.e. the activation energy barrier (LEVINE, 2000).

Two approaches were employed in order to search for the transition states. For some structures, a possible decomposition coordinate was assumed, and incremental steps were performed in this coordinate, while optimizing all others. After that, a graph was plotted and a TS was searched on the maximum of the obtained curves. For cases in which this approach demonstrated to be very time consuming and/or difficult, it was decided to follow the 3N - 6 vibrational modes of the polyN structures. This latter approach provided a guess possibility for the TS, which had to be further optimized. This approach demonstrated to be very efficient on the search for the transition states, since one (or more than one) vibrational mode, when followed, would eventually lead to the decomposition of the polyN.

An intrinsic reaction coordinate (IRC) path is a calculation that can provide the minimum-energy path of one reaction. The IRC leads to the minimum-energy path steepest descent from the TS (LEVINE, 2000). In this work, the Gonzalez-Schlegel second-order algorithm (GONZALEZ; SCHLEGEL, 1990), as implemented in the GAMESS package (SCHMIDT et al., 1993) was employed.

Vibrational analysis was carried out to confirm the minima and transition states (TSs) found within the employed levels of theory. The wxmacmolplt program was used for graphic visualization and representation of the molecular geometries (BODE; GORDON, 1998).

#### 3.3.2 Reaction dynamics studies

For the structures with largest decomposition barriers found in this research, which demonstrated promising results, an additional effort was made in order to check if there existed other possible decomposition routes with smaller activation energies than the ones reported. For these cases, classical trajectories on the DFT PES were integrated for over 10 ps, as implemented in GAMESS (SCHMIDT et al., 1993; GORDON; CHABAN; TAKETSUGU, 1996), to check if the trajectories would lead to new decomposition routes. These studies were performed using the def2-SVP approach. The relevant graphs obtained can be found in Appendix B.

Two trajectories were calculated for each of the molecules. No attempt was made to integrate a batch of trajectories to simulate a fixed temperature. The nuclei were treated classically, following Newton's mechanics. Both trajectories started with fixed kinectic and potential energies, and allowed to proceed with a time step of 0.1 fs.

The first trajectory started without any initial velocity, at a geometry close to the transition state. If there were unexplored reaction paths with lower energy barriers than

those predicted, it was expected that the trajectory would eventually escape through this path. Otherwise, if the trajectory was "locked", one can consider that no other potential barrier was available and the minimum activation energy for decomposing the structure was found. In the second, the trajectory started at the optimal geometry of each polyN (with zero potential energy), and the kinetic energy given was two times higher than that necessary for dissociation to occur via the TSs obtained here. This initial kinetic energy was distributed evenly among all normal modes.

# 3.4 Energy refinement

After optimizing the structures, finding their respective TSs towards unimolecular decomposition and calculating the intrinsic reaction coordinates, all the minima and TSs found were reoptimized employing the larger def2-TZVPP basis set. The energies of all minima and TSs were zero point energy corrected within this approach and no symmetry restrictions were imposed in any case.

The results obtained from this energy refinement are the ones presented on the tables discussed throughout the text.

#### 3.4.1 Dissociation energies (DEs) and activation energies (AEs) calculation

The dissociation energies (DE) were calculated according to Equation 3.1.

$$DE = E_{PolyN} + ZPE_{PolyN} - \frac{n}{2}[E_{N_2} + ZPE_{N_2}]$$
(3.1)

where  $E_{PolyN}$  and  $E_{N_2}$  stand for the total energies of the initial polyN and a nitrogen molecule, respectively.  $ZPE_{PolyN}$  and  $ZPE_{N_2}$  are the corresponding zero-point energies of these species and n is the total number of N atoms of the polyN.

One can say that the DEs give the amount of energy released in the processess of unimolecular decomposition, and therefore, are directly related to the energetic content of the HEDMs.

The activation energies (AE) were calculated according to Equation 3.2.

$$AE = E_{TS} + ZPE_{TS} - [E_{PolyN} + ZPE_{PolyN}]$$

$$(3.2)$$

where  $E_{TS}$  and  $E_{PolyN}$  stand for the total energies of the transition state and initial polyN.  $ZPE_{TS}$  and  $ZPE_{PolyN}$  are the corresponding zero-point energies of these species.

In the calculation of AE, only the lowest lying TS was considered. One can say that the AEs are a measure of how difficult it is to break the polyN structure in an unimolecular decomposition.

#### 3.4.2 Selected molecular parameters of the structures

For all structures, some molecular parameters were calculated in order to summarize and rationalize the results obtained. These parameters were the average bond lenghts, the average bond orders, the HOMO-LUMO gaps and the asphericities.

The average bond lengths and average bond orders were calculated as a simple arithmetic average. The first data set was taken from the values provided by the Wxmac-molph program (BODE; GORDON, 1998), while the second from the outputs archives of each structure. The HOMO-LUMO gaps were calculated by the energy difference between both orbitals.

In order to try to correlate the results with some shape factor, the asphericities (AS) were calculated according to Equation 3.3, in a way similar to Theodorou (1985),

$$AS = I_z^2 - \frac{1}{2}(I_x^2 + I_y^2)$$
(3.3)

in which  $I_x$ ,  $I_y$  and  $I_z$  are the moments of inertia.

The flowchart presented in Figure 9 summarizes the methodology employed on this work.



Figure 9 – Flowchart of the methodology employed

# 4 Results and discussion

The results and discussion of the dissociation and/or isomerization processes are presented in subsections for each nuclearity. According to Peverati and Truhlar (2012), the mean unsigned error (MUE) of the hybrid SOGGA11-X functional is a little bit smaller than that of the M06-2X one, when it comes to non-hydrogen-transfer barrier heights (NHTBH) calculations. Therefore, the energies mentioned in the text are at the SOGGA11-X/def2-TZVPP level.

The reaction pathways in the IRC plots are displayed with black circles (at the SOGGA11-X/def2-SVP level). The horizontal lines in these graphs correspond to the ZPE corrected energies at M06-2X/def2-TZVPP (orange) and SOGGA11-X/def2-TZVPP (black) levels. In the IRC graphics, the energies are given relatively to the  $nN_2$  dissociation limit.

# 4.1 N<sub>6</sub>

Four isomers of N<sub>6</sub> have been considered in the present work. Figures 10, 11, 12 and 13 present the results of the IRC calculations for structures N<sub>6</sub>( $C_{2v}$ )-A, N<sub>6</sub>( $C_{2v}$ )-B, N<sub>6</sub>( $C_{2h}$ ) and N<sub>6</sub>( $D_{3h}$ ) respectively. Table 1 gathers their AE, DE and DE/n values.

As can be noted, isomers  $N_6(C_{2v})$ -A and  $N_6(C_{2v})$ -B possess small dissociation barriers (*AE* of 7.33 and 4.23 kcal.mol<sup>-1</sup>, respectively), indicating that they are kinetically unstable at ambient conditions. These isomers decompose in a stepwise process, being the first the elimination of a N<sub>2</sub> molecule, followed by the dissociation of the well known  $D_{2h}$ form of N<sub>4</sub> (NGUYEN, 2003; ELESIN et al., 2009), which has a very small dissociation barrier (around 6.45 kcal.mol<sup>-1</sup> above the N<sub>4</sub> well(NGUYEN, 2003)).

Table 1 – Activation energy barriers (AE), Dissociation energies (DE) and Dissociation energies per nitrogen atoms (DE/n) in kcal.mol<sup>-1</sup> for the N<sub>6</sub> isomers employing the def2-TZVPP basis set.

Structure	Functional	AE	DE	DE/n
$N_6(C_{2v})$ -A	M06-2X	5.59	240.30	40.05
	SOGGA11-X	7.33	231.53	38.59
$N_6(C_{2v})$ -B	M06-2X	1.94	247.00	41.17
	SOGGA11-X	4.23	239.69	39.95
$N_6(C_{2h})$	M06-2X	18.42	178.13	29.69
	SOGGA11-X	19.23	173.20	28.87
$N_6(D_{3h})$	M06-2X	40.53	319.89	53.32
	SOGGA11-X	40.96	309.90	51.65

Figure 10 – Decomposition path of  $N_6(C_{2v})$ -A isomer obtained from IRC calculation at SOGGA11-X/def2-SVP level. The bars correspond to the zero-point corrected energies of the structures relative to the fully dissociated system at M06-2X/def2-TZVPP (orange) and SOGGA11-X/def2-TZVPP (black) levels.



Figure 11 – Decomposition path of  $N_6(C_{2v})$ -B isomer with IRC calculation following the scheme of Fig.10



The diazide isomer  $(N_6(C_{2h}))$  presents a considerably higher decomposition barrier (19.23 kcal.mol<sup>-1</sup>) when compared to the previous two, although possessing a chain configuration. Nevertheless, it may not be sufficient to ensure its stability at ambient conditions, as it has been suggested in the literature that an energy barrier of approximately (or above) 30 kcal.mol<sup>-1</sup> is desirable for a structure to be considered a good HEDM (CHUNG; SCHMIDT; GORDON, 2000; LI; LIU, 2002). In agreement with previous studies (GAGLIARDI et al., 2000a; NGUYEN; HA, 2001; LI; LIU, 2002; HIRSHBERG; GERBER, 2012), it was found a concerted dissociation mechanism in which N<sub>6</sub>( $C_{2h}$ ) breaks directly into three N<sub>2</sub> molecules. It is worth mentioning that Greschner *et al.* (2016) recently predicted a stable molecular crystal composed of N<sub>6</sub>( $C_{2h}$ ) chains. Their molecular dynamics simulations suggest reasonable thermal stability.

Figure 12 – Decomposition path of  $N_6(C_{2h})$  isomer obtained from IRC calculation following the scheme of Fig.10



Differently from the other three,  $N_6(D_{3h})$  (hexaazaprismane) demonstrated more promising results. In this research, it was found a TS that connects prismane directly into  $N_4(D_{2h}) + N_2$ , with an energy barrier of 40.96 kcal.mol<sup>-1</sup> (upper panel in Figure 13). Li and Liu (2002) found instead a considerable isomerization energy barrier towards the  $N_6(C_{2v})$ -B structure (34.4 kcal.mol<sup>-1</sup>) at CCSD/6-311G(d)(energies)//B3LYP/6-311G(d)(geometries) level. This isomerization path connecting these two isomers (lower panel in Figure 13) was also found within the methodology employed in this work, and an energy barrier of 40.84 kcal.mol<sup>-1</sup> was obtained. Within the accuracy of the calculations performed, both isomerization and dissociation processes can be considered as energetically equivalent. These barriers are a good indicative of practical use of  $N_6(D_{3h})$  as HEDM, and the unraveling of the direct decomposition pathway is relevant to the understanding of the energy landscape associated with prismane.

Exploratory trajectories were performed for this structure, following the approaches mentioned in section 3.3.2, in order to try to locate possible TSs with lower energies that were not previously found. As can be seen in Figures A13 and A14 of Appendix B, the first trajectory was integrated for 10 ps, without any initial kinetic energy, and it did not leave this energy basin, which indicates that there is no other route available. In the second, with higher kinetic energy, the polyN decomposed in less than 2 ps, through the mechanism proposed here.

Within the N<sub>6</sub> size, prismane releases the largest amount of energy considering its dissociation into three N<sub>2</sub> molecules, being 78% more exothermic than the chain isomer  $(N_6(C_{2h}))$ . Its *AE* is also more than two times higher than that of N<sub>6</sub>( $C_{2h}$ ), indicating that it may be stable on higher temperatures. This can be partially attributed to its caged geometry. Although, as it will be pointed out along this work, not all caged structures follow this trend.

Figure 13 – Direct decomposition path of  $N_6(D_{3h})$  isomer into  $N_4(D_{2h}) + N_2$  (upper panel) and an alternative path to the same products passing through an intermediate (lower panel). Following the scheme of Fig.10



# 4.2 N<sub>8</sub>

Four allotropes of N<sub>8</sub> have been considered in the present work. Figs. 14, 15, 16 and 17 present the results of the IRC calculations for isomers N<sub>8</sub>( $C_{2v}$ )-A, N<sub>8</sub>( $C_s$ ), N<sub>8</sub>( $C_{2v}$ )-B and N<sub>8</sub>( $O_h$ ), respectively. Table 2 gathers the values of their AEs, DEs and DEs/n.

Regarding the N<sub>8</sub>( $C_{2v}$ )-A isomer, a decomposition path that leads to N<sub>6</sub>( $C_{2v}$ )-A + N<sub>2</sub> was found (Figure 14). It passes through an intermediate resulting from the opening of a triangular ring of the initial structure. The isomerization barrier that is determinant to the decomposition process was found to be 23.72 kcal mol<sup>-1</sup> (AE). Although not as high as that of prismane, this isomer might be a good candidate for production. The N<sub>8</sub>( $C_s$ ) isomer did not present promising results, as its predicted barrier for decomposition into N<sub>6</sub>( $C_{2v}$ )-A + N<sub>2</sub> is only 4.53 kcal.mol<sup>-1</sup> (Figure 15).

Table 2 – Activation energy barriers (AE), Dissociation energies (DE) and Dissociation energies per nitrogen atoms (DE/n) in kcal.mol<sup>-1</sup> for the N<sub>8</sub> isomers employing the def2-TZVPP basis set.

Structure	Functional	AE	DE	DE/n
$N_8(C_{2v})$ -A	M06-2X	22.26	375.47	46.93
	SOGGA11-X	23.72	363.13	45.39
$N_8(C_{2v})$ -B	M06-2X	31.65	352.27	44.03
	SOGGA11-X	29.34	341.44	42.68
$N_8(C_s)$	M06-2X	3.33	350.60	43.83
	SOGGA11-X	4.53	339.09	42.39
$N_8(O_h)$	M06-2X	24.11	450.31	56.29
	SOGGA11-X	24.06	436.51	54.56

Figure 14 – Decomposition path of  $N_8(C_{2v})$ -A isomer obtained from IRC calculation following the scheme of Fig.10



More promising results were achieved for the  $N_8(C_{2v})$ -B isomer. At the preliminary exploration using the def2-SVP basis set, only one barrier was found to be relevant. However, when the minima and TSs were reoptimized using the def2-TZVPP basis set, another barrier presented a similar and promising result. Both barriers are reported here.

First, a mechanism that leads to a  $D_{2d}$  structure followed by decomposition to  $N_6(C_{2h}) + N_2$  with an activation energy of 30.84 kcal.mol<sup>-1</sup> (upper panel in Figure 16). Second, a direct decomposition path through an opening transition state structure led to an activation energy of 29.34 kcal mol<sup>-1</sup>, arriving into an open chain  $N_8(C_1)$  isomer (lower panel in Figure 16). Both barriers are high and show similar values, and thus  $N_8(C_{2v})$ -B may be another promising HEDM candidate. Fau and Bartlett (2001) reported that isolated open chains of N<sub>8</sub> possess a relatively low decomposition barrier. In their work, this  $C_1$  structure is easily decomposed to  $N_6 + N_2$  (FAU; BARTLETT, 2001). Thus, considering the second decomposition mentioned, after surpassing the isomerization barrier to the  $C_1$  symmetry structure, the decomposition would be easily achieved.

Figure 15 – Decomposition path of  $N_8(C_s)$  isomer obtained from IRC calculation following the scheme of Fig.10



Still regarding  $N_8(C_{2v})$ -B, it should be noted that a TS directly connecting it to full dissociation, was obtained by Schmidt *et al.* (2000) at the MP2/6-31G(d) level, with an AE of 20 kcal mol<sup>-1</sup>, but could not be reproduced within the methodology employed in this work. Gagliardi *et al.* (1997) found (employing B3LYP/cc-pVTZ calculations) two pathways for this structure: one similar to that shown in the upper panel of Figure 16, with a barrier of 43.3 kcal mol<sup>-1</sup>, and another for isomerization of  $N_8(C_{2v})$ -B into another structure of 28.2 kcal mol<sup>-1</sup>. In summary, the final AE value reported by Gagliardi *et al.* is similar to the one reported here.

A dynamics simulation was also carried out for this structure. However, 10 ps, even with higher kinetic energy, were not sufficient to get a conclusive analyses. A greater computational effort would be necessary to obtain a more elucidative response, but, unfortunately, this greater effort was not possible to be done due to the computational resources available for this research. In fact, as it will be noted along the text, the dynamics studies were only conclusive for the prismane case, due to the lower number of degrees of freedom. For the other most promising structures, that possess a greater number of degrees of freedom, it would be necessary a considerably longer simulation time.

Extensive research has been performed regarding the octaazacubane allotrope (ENGELKE; STINE, 1990; EVANGELISTI; GAGLIARDI, 1996; GAGLIARDI et al., 1997; SCHMIDT; GORDON; BOATZ, 2000; TÜRKER, 2019; GIMALDINOVA et al., 2020),  $N_8(O_h)$ . Engelke and Stine (1990) studied the concerted symmetry forbidden  $D_{4h}$ dissociation path  $N_8(O_h) \rightarrow 4N_2$  and found a 162 kcal.mol<sup>-1</sup> energy barrier at RHF/4-31G\* level, in good agreement with the work of Evangelisti and Gagliardi (1996) (159 kcal.mol<sup>-1</sup> at CASSCF/VDZP level) considering the same constrained  $D_{4h}$  path. These high decomposition barriers have arisen due to the fact that this path is symmetry forbidden. However, both studies agree that octaazacubane dissociation should occur in a



Figure 16 – The two possible paths for  $N_8(C_{2v})$ -B with energicatly equivalent barriers as indicated in the text. Following the scheme of Fig.10

less symmetric path.

Gimaldinova *et al.* (2020) made a study of the kinetic stability of octaazacubane inside a fullerene carbon cage, using tight-binding molecular dynamics simulations. They found a barrier of only 2.54 kcal.mol<sup>-1</sup> for the total decomposition of the isolated  $(O_h)$  into  $4N_2$ . It was concluded that the carbon cage increases the kinetic stability of the structure, but due to the method of calculation used for the isolated cluster, it is not possible to compare their results with the ones obtained here. The lowest energy TS linked to  $N_8(O_h)$ that this research was able to find lies 24.06 kcal.mol<sup>-1</sup> above it. According to the IRC calculations, this TS, as a matter of fact, connects  $N_8(O_h)$  to the  $N_8(C_{2v})$ -B isomer.

The proposed isomerization pathway agrees with the results of Gagliardi *et al.* (1997) and Schmidt *et al.* (2000) for octaazacubane. After isomerization,  $N_8(O_h)$  may follow the  $N_8(C_{2v})$ -B decomposition path already discussed. Therefore, analogously to the  $N_8(C_{2v})$ -B isomer, octaazacubane may also be of experimental relevance, but with the advantage of generating 28% more energy upon full dissociation.

Octaazacubane,  $N_8(O_h)$ , presents the highest DE/n ratio among all polyN studied



Figure 17 – Isomerization path of  $N_8(O_h)$  into  $N_8(C_{2v})$ -B. Following the scheme of Fig.10

here, which can be attributed to its strained prismatic structure where each N atom makes 3 single bonds. On the other hand, surprisingly,  $N_8(C_{2v})$ -B (which does not possess a caged structure) shows the highest activation energy for the 8 atoms polyN. From this result, although it is possible to find correlations between the geometric shape and *DE* values, a similar analysis often fails to explain the calculated *AEs*. Finally, the relatively small difference between the dissociation barriers of  $N_8(C_{2v})$ -B and  $N_8(O_h)$  (5.3 kcal mol<sup>-1</sup>) compared to the significant difference between their *DEs* (95 kcal.mol<sup>-1</sup>) should be taken into consideration, for future work.

# **4.3** N<sub>10</sub>

Four allotropes of  $N_{10}$  have been considered. Figures 18, 19, 20 and 21 present the results of the IRC calculations for isomers  $N_{10}(C_s)$ ,  $N_{10}(D_{5h})$ ,  $N_{10}(C_1)$  and  $N_{10}(C_{3v})$ , respectively. The numerical results are gathered in Table 3. The difference between the two exchange correlation functionals employed in the case of the  $N_{10}$  structures follows the same trend observed for the previous structures: both functionals predict very similar *AEs*, but M06-2X predicts larger *DEs*.

The chain isomer  $N_{10}(C_s)$  possesses a small decomposition barrier (7.73 kcal.mol<sup>-1</sup>) and may not be a good candidate for HEDM. Together with the other chain isomer explored in this work ( $N_6(C_{2h})$ ), they represent the lowest DE/n ratio. Interestingly,  $N_6(C_{2h})$  has a decomposition barrier 2.5 times larger than  $N_{10}(C_s)$ , despite the analogous structure, which again indicates the difficulty in correlating the AE value with molecular shape.

The prismatic  $N_{10}(D_{5h})$  isomer decomposes in a stepwise process, passing through two different intermediates, to reach a chain isomer (Figure 19). As reported by Strout (2002), such acyclic forms of  $N_{10}$  tend to possess low decomposition barriers towards Table 3 – Activation energy barriers (AE), Dissociation energies (DE) and Dissociation energies per nitrogen atoms (DE/n) in kcal.mol<sup>-1</sup> for the  $N_{10}$  isomers employing the def2-TZVPP basis set.

Structure	Functional	AE	DE	DE/n
$N_{10}(C_s)$	M06-2X	7.14	305.30	30.53
	SOGGA11-X	7.73	299.23	29.92
$N_{10}(D_{5h})$	M06-2X	23.97	513.39	51.34
	SOGGA11-X	25.81	498.12	49.81
$N_{10}(C_1)$	M06-2X	9.02	463.42	46.34
	SOGGA11-X	9.55	449.47	44.95
$\mathcal{N}_{10}(C_{3v})$	M06-2X	7.24	471.95	47.19
	SOGGA11-X	8.22	457.24	45.72

dissociation, and thus, one can conclude that the system will easily dissociate from this acyclic form. Therefore, if there is available energy for  $N_{10}(D_{5h})$  to surpass the first isomerization barrier (25.81 kcal.mol<sup>-1</sup>), it will promptly undergo dissociation. This barrier is comparable to those presented by  $N_8(C_{2v})$ -B and  $N_8(O_h)$  isomers which, together with a large energy released upon full dissociation (*DE*), makes  $N_{10}(D_{5h})$  the most attractive polyN within the  $N_{10}$  structures for possible HEDM application.

Figure 18 – Decomposition path of  $N_{10}(C_s)$  isomer obtained from IRC calculation following the scheme of Fig.10



Even though  $N_{10}(C_1)$  and  $N_{10}(C_{3v})$  possess cage-like structures and high energy content (high DE/n), their rather small decomposition energy barriers (AE) make them not suitable for HEDM application. This is also the case for smaller polyN such as  $N_8(C_s)$ and  $N_6(C_{2v})$ -B, although all of them present significant DEs. Isomer  $N_{10}(C_{3v})$  decomposes into  $N_8(C_s) + N_2$  and  $N_{10}(C_1)$  to  $N_4(D_{2h}) + 3N_2$ .

Therefore, despite caged structures are consistently related to higher DEs, this is not the determining factor regarding their decomposition barriers. Symmetry seems to play an important role, as specific prismatic structures with peripheral N<sub>4</sub>(D<sub>2h</sub>) rings presented

Figure 19 – Decomposition path of  $N_{10}(D_{5h})$  isomer obtained from IRC calculation following the scheme of Fig.10



higher kinetic stability, as well as DEs. Like the other prismatic structures approached here,  $N_{10}(D_{5h})$  is the isomer that releases the greatest amount of energy towards full decomposition into N<sub>2</sub> molecules.

The  $N_{10}(D_{5h})$  barrier is rather high, when compared to the others structures studied in the present work and can lead to the conclusion that prismatic caged forms of polyN, indeed, posses greater decomposition and/or isomerization barriers and could be the most stable forms of these structures, regarding synthetic and experimental use.

Figure 20 – Decomposition path of  $N_{10}(C_1)$  isomer obtained from IRC calculation following the scheme of Fig.10



Figure 21 – Decomposition path of  $N_{10}(C_{3v})$  isomer obtained from IRC calculation following the scheme of Fig.10



## 4.4 Selected molecular parameters

## 4.4.1 Activation energies X dissociation energies

For an initial attempt of summarizing the results, a graph relating activation energy with dissociation energy is presented (Figure 22, page 38). For a better visualization, the structures were labeled according to their geometric shapes, i.e., chains, rings, cages and caged prisms. It will become clear from the discussions that follows, that this classification is quite useful.

Although no clear correlation between AE and DE is observed, this graph can give some insight in a broader way. First of all, the two graphs show that both functionals are in good agreement and the exact same conclusions can be achieved from both. From the analysis of this graph, it becomes easy to notice that  $N_6(D_{3h})$  is the polyN that stands out, regarding its high AE. It possesses a smaller DE when compared to the sizes eight and ten, however, it is expected that the larger the structure, the higher will be its dissociation energy, since more bonds will be broken.

At the same time, it can be noted that the systems  $N_8(C_{2v})$ -B,  $N_8(C_{2v})$ -A,  $N_8(O_h)$ and  $N_{10}(D_{5h})$  possess relatively high AEs and high DEs, being possible candidates for HEDM production. All other structures would not be good candidates, since, even the ones that possess high DEs, are very kinetically unstable. The chain structure of  $N_6(C_{2h})$ , although possessing a comparable AE with  $N_8(C_{2v})$ -A,  $N_8(O_h)$  and  $N_{10}(D_{5h})$ , would release much less energy, when decomposing to nitrogen molecules. The visual analysis of this graph reinforces the discussions and conclusions made in the previous sections.

It is important to highlight that although all prismatic structures are possible HEDM candidates, being caged does not necessarily mean a high activation energy. All caged structures present a high energy content (DE) but for some reason it is relatively easy to break some of them (small AE). Ring structures often have low activation energy, and are easier to break, with N<sub>8</sub>( $C_{2v}$ )-B being an important exception.

Figure 22 – Calculated activation energies as a function of the dissociation energies using the def2-TZVPP basis set. The M06-2X functional is shown in the upper panel, while the SOGGA11-X one is on the lower panel.



For a global analysis of all results given in the previous section, and also aiming to find correlations between the energetic properties with electronic or structural ones (since no direct correlation could be found regarding AEs and DEs), several molecular parameters, i.e., average bond length, average bond order, HOMO-LUMO gap and asphericity were calculated for all polyN structures. The subsections below present the discussion of these results. For a better understanding, Table 4 gathers all the numerical values of these properties. The graphs of the DEs, DEs/n and AEs as a function of these properties can all be found in Appendix A.

Table 4 – Average bond lengths (ABL), Average bond orders (ABO), HOMO-LUMO gap (HL) and Asphericities  $(\log_{10}(AS))$  of all the polyN employing the def2-TZVPP basis set.

Structure	Functional	ABL (Angstrons)	ABO	HL $(eV)$	$\log_{10}(AS)$
$N_6(C_{2v})$ -A	M06-2X	1.39	1.12	9.06	5.00
	SOGGA11-X	1.39	1.14	8.05	5.00
$N_6(C_{2v})$ -B	M06-2X	1.43	0.99	9.04	4.93
	SOGGA11-X	1.42	1.02	7.90	4.93
$N_6(C_{2h})$	M06-2X	1.23	1.19	7.12	5.76
	SOGGA11-X	1.23	1.15	6.23	5.76
$N_6(D_{3h})$	M06-2X	1.47	0.89	9.83	4.18
	SOGGA11-X	1.46	0.90	8.97	4.17
$N_8(C_{2v})$ -A	M06-2X	1.46	0.88	9.35	4.98
	SOGGA11-X	1.45	0.90	8.44	4.97
$N_8(C_{2v})$ -B	M06-2X	1.42	1.01	7.97	5.15
	SOGGA11-X	1.41	1.03	7.02	5.15
$N_8(C_s)$	M06-2X	1.44	0.95	8.93	5.25
	SOGGA11-X	1.44	0.97	7.89	5.24
$N_8(O_h)$	M06-2X	1.50	0.84	8.31	1.23
	SOGGA11-X	1.49	0.87	7.43	0.61
$N_{10}(C_s)$	M06-2X	1.27	1.16	7.83	6.61
	SOGGA11-X	1.27	1.13	6.87	6.61
$N_{10}(D_{5h})$	M06-2X	1.48	0.84	8.41	5.22
	SOGGA11-X	1.48	0.88	7.53	5.22
$N_{10}(C_1)$	M06-2X	1.46	0.87	9.68	5.45
	SOGGA11-X	1.45	0.89	8.82	5.45
$N_{10}(C_{3v})$	M06-2X	1.47	0.85	9.47	5.08
. ,	SOGGA11-X	1.47	0.88	8.58	5.08

#### 4.4.2 Average bond lengths and average bond orders

From the analysis of the data gathered in Table 4 and Figures A1, A2 and A3, it can be noted that, the larger the energy content of the structures (DE/n), the greater is the average bond lengths. This fact becomes even clearer when the prismatic cages are taken into account. This is expected, since cage structures tend to have more distant bonds, and therefore, more single bonds. When the average bond orders are considered

(Figures A4, A5 and A6) this conclusion is reinforced. Longer bonds lead to smaller bond orders.

The classification of the structures into chains, rings, cages and prismatic cages becomes more clear from this analysis. While chain structures tend to possess smaller bond lengths, their bonds possess a more double character like (higher bond orders). Ring structures are between the other two classes (chains and cages), while the prismatic caged ones are the ones that possess a stronger single-bonded structure. One structure that can be considered as deviating slightly point from the ring structures is the N<sub>8</sub>( $C_{2v}$ )-A one, since it possesses average bond lengths and average bond orders similar to the ones found from chain structures. However, by visual inspection, it becomes clear that this polyN is neither a chain or a cage.

Therefore, a correlation between the average bond lengths and the average bond orders can be drawn. Nevertheless, no clear correlation could be achieved regarding these structural properties with the AEs, as it can be noted in Figures A3 and A6.

#### 4.4.3 HOMO-LUMO-gaps

When it comes to the HOMO-LUMO gaps, a correlation could almost be found. However, no conclusive affirmative can be made. Analysing Table 4 and Figure A7, it can be noted that some structures are indeed stable, at least towards reactions with oxygen molecules, considering their higher HOMO-LUMO gaps. For instance, structures  $N_{10}(C_{3v})$ ,  $N_{10}(C_1)$ ,  $N_8(C_s)$ ,  $N_6(C_{2v})$ -A and  $N_6(C_{2v})$ -B possess considerably high HOMO-LUMO gaps. This could mean that they might be stable under an oxidizing atmosphere, but due to their low AEs, synthesis would be very difficuly and they would easily decompose.

More interesting remarks can be made for  $N_6(D_{3h})$ ,  $N_8(O_h)$ ,  $N_8(C_{2v})$ -A and  $N_{10}(D_{5h})$ . Besides the fact that these structures possess high AEs, they present relatively high HOMO-LUMO gaps. Meaning that, apart from being kinetically stable towards unimolecular decomposition, they can be considered more inert, than the others structures. This could make storage more feasible, if these structures were to be experimentally produced. On the other hand,  $N_8(C_{2v})$ -B, that demonstrated a high AE, possesses a considerably lower HOMO-LUMO gap. This fact means that its production might be easy, but it would not be sufficiently inert under an oxidizing atmosphere.

A similar but not so consistent analysis could be made regarding the DEs (Figure A8). However, since the DEs/n are more related to the energy content of the structures, the discussions and conclusions mentioned above gave good insights regarding the reactivity of the structures towards oxidation reactions.

Although not as clear as the graphs of ABL and ABO, it can be noted a separation between chained, rings and caged structures. But then again, no direct correlation could be achieved regarding the HOMO-LUMO gaps with the AEs (Figure A9).

#### 4.4.4 Asphericities

Regarding the last structural property calculated, some considerations can be made. A closer to zero value of asphericity, the more the molecule can be treated as a sphere. From that, it is no surprise that octaazacubane is the structure with the lowest value of asphericity. The chain structures, on the other hand, are the ones with highest asphericities. This was also expected due to their open nature and the fact that they present a two dimensional nature.

That being said, this property was the one that led to the most inconclusive correlation with the AEs, and the other energetic properties (DEs and DEs/n). It was an atemptive to find a shape factor that correlated with the decomposition barriers. But instead, the conclusion is that, pretty much all the structures, except those mentioned before, possess similar asphericities, regardless of their more promising (or not) potential as being HEDMs.

As a final conclusion of this section, one can say that, apart from some correlations with the DEs/n and the ABLs and ABOs, none of the molecular parameters explored here were found to correlate with AE. A recent paper, exploring other properties, such as chemical potential, hardness and softness, also came to the conclusion that it is very difficult to find a property that directly correlate with decomposition barriers of polyN (KATIN et al., 2020). If such correlation existed, it would be very useful for predicting the dissociation barriers of new polyN structures obtained in the future, since exploring their high dimensional PES in the search for the lowest TS is a very difficult and consuming task.

# 5 Final considerations

After the conclusion of this work, it is possible to say that the proposed objectives were satisfactorily accomplished. It was possible to theoretically predict the decomposition barriers of several neutral molecular polyN with nuclearities six, eight and ten. Available data was used to compare the results previously reported in the literature, at the same time that new results were obtained. Besides that, it was possible to perform a consistent study using the same calculation method (SOGGA11-X/def2-TZVPP and M06-2X/def2-TZVPP levels of theory), allowing for a direct comparison between all the structures analysed. These two methods were shown to yield similar results.

Regarding the specific objectives, it was possible to assess computationally the stabilities and reactivities of the polyN studied and infer about their respective usability as high-energy density materials, by means of theirs activation energy barriers and dissociation energies. For all structures, a transition state towards the products of unimolecular decomposition was found, being these results confirmed through the calculation of the intrinsic reaction coordinates for each polyN. Unfortunately, the reaction dynamics studies were only conclusive for prismane  $N_6(D_{3h})$ , due to its lower number of degrees of freedom. These dynamics studies employing expensive electronic structure calculations are very time consuming and unfeasible for usage in many trajectories or longer simulation times.

Besides that, selected molecular parameters, i.e., average bond lenghts, average bond orders, HOMO-LUMO gaps and asphericities were calculated, aiding the structural and electronic analysis of the molecules. A clear difference between chains, rings, cages and prismatic cages could be observed, especially regarding their average bond lenghts, average bond orders and energy content (DE/n, which may be released if these substancesare used as energy sources).

However, it was not possible to correlate these properties with their corresponding activation energies, and therefore, to presume based on these molecular parameters new structures that would lead to a more successful HEDM (high AE), with higher kinetic stability at ambient conditions.

More especifically, it was possible to conclude that prismatic caged structures of  $N_6$ ,  $N_8$  and  $N_{10}$  are more likely to be stable at room conditions. For each nuclearity, they presented the greater activation barriers and considerable HOMO-LUMO gaps, with the exception of the  $N_8$  systems, in which a boat-like structure, with  $C_{2v}$  symmetry, showed a little higher barrier than the prismatic caged allotropic form. However, the latter structure may be reactive towards oxidation, considering its comparably low HOMO-LUMO gap.

Regarding the dissociation energies, the prismatic caged structures also show the

greater values. Therefore, being caged does not necessarily imply a high activation energy. Symmetry factors seem to be important for the stability of these structures.

Comparing between individual structures, it was found that prismane  $(N_6(D_{3h}))$ shows a very high dissociation barrier and, if it could be synthesized, would be very stable, perhaps allowing its storage at room conditions. Upon triggering its dissociation reaction, it would deliver a very large amount of energy, without producing any pollutant products.

A paper regarding the results obtained in this work was published on the RSC Advances journal, of The Royal Society of Chemistry. In the paper, the dissociation energies presented here are benchmarked with CCSD(T)-F12 calculations, being the results in good agreement with the DFT ones. The full text can be found on Appendix C.

As future perspectives, it can be mentioned: the computational prediction of the stability and decomposition barriers of ionic polynitrogens, with nuclearities five, seven and nine; and the study of the formation and practical viability of solid nitrogen phases, only for the most stable polyN found at gas phase. Solid allotropes and salts of polyN are an important and current topic of research (BONDARCHUK, 2020; GRESCHNER et al., 2016; HIRSHBERG; GERBER; KRYLOV, 2014; LANIEL et al., 2018; LIU et al., 2020; STEELE et al., 2016; WANG et al., 2018; ZHOU et al., 2020).

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# APPENDIX A – Graphs of selected molecular parameters against DE/n, DE and AE

Figure A1 – Calculated dissociation energies per nitrogen atom as a function of the average bond lengths using the def2-TZVPP basis set. The M06-2X functional is shown in the upper panel, while the SOGGA11-X one is on the lower panel.



Figure A2 – Calculated dissociation energies as a function of the average bond lengths using the def2-TZVPP basis set. The M06-2X functional is shown in the upper panel, while the SOGGA11-X one is on the lower panel.



Figure A3 – Calculated activation energies as a function of the average bond lengths using the def2-TZVPP basis set. The M06-2X functional is shown in the upper panel, while the SOGGA11-X one is on the lower panel.



Figure A4 – Calculated dissociation energies per nitrogen atom as a function of the average bond orders using the def2-TZVPP basis set. The M06-2X functional is shown in the upper panel, while the SOGGA11-X one is on the lower panel.



Figure A5 – Calculated dissociation energies as a function of the average bond orders using the def2-TZVPP basis set. The M06-2X functional is shown in the upper panel, while the SOGGA11-X one is on the lower panel.



Figure A6 – Calculated activation energies as a function of the average bond orders using the def2-TZVPP basis set. The M06-2X functional is shown in the upper panel, while the SOGGA11-X one is on the lower panel.



Figure A7 – Calculated dissociation energies per nitrogen atom as a function of the HOMO-LUMO gaps using the def2-TZVPP basis set. The M06-2X functional is shown in the upper panel, while the SOGGA11-X one is on the lower panel.


Figure A8 – Calculated dissociation energies as a function of the HOMO-LUMO gaps using the def2-TZVPP basis set. The M06-2X functional is shown in the upper panel, while the SOGGA11-X one is on the lower panel.



Figure A9 – Calculated activation energies as a function of the HOMO-LUMO gaps using the def2-TZVPP basis set. The M06-2X functional is shown in the upper panel, while the SOGGA11-X one is on the lower panel.



Figure A10 – Calculated dissociation energies per nitrogen atom as a function of the asphericities using the def2-TZVPP basis set. The M06-2X functional is shown in the upper panel, while the SOGGA11-X one is on the lower panel.



Figure A11 – Calculated dissociation energies as a function of the asphericities using the def2-TZVPP basis set. The M06-2X functional is shown in the upper panel, while the SOGGA11-X one is on the lower panel.



Figure A12 – Calculated activation energies as a function of the asphericities using the def2-TZVPP basis set. The M06-2X functional is shown in the upper panel, while the SOGGA11-X one is on the lower panel.



# APPENDIX B – Results of classical trajectories for $N_6(D_{3h})$ .



Figure A13 – Potential energy as a function of time in a classical trajectory inside the  $N_6(D_{3h})$  basin of attraction. Without initial kinetic energy.

The energy is given relative to the optimized value for the polyN minimum (the zero of energy), and the energy of the proposed transition state (that will lead to unimolecular decomposition) is marked with a red bar. The trajectory started with zero kinetic energy, in a geometry close to the transition state that was obtained by a small displacement along the imaginary mode such as to show a potential energy 1 kcal.mol<sup>-1</sup> below the transition state. It is seen that the trajectory could not leave the polyN basin, indicating that no other TS with lower energy is available.



Figure A14 – Potential energy as a function of time in a classical trajectory inside the  $N_6(D_{3h})$  basin of attraction. Initial kinetic energy two times higher than necessary for decomposition.

The energy is given relative to the optimized value for the polyN minimum (the zero of energy), and the energy of the proposed transition state (that will lead to unimolecular decomposition) is marked with a red bar. This trajectory started at the  $N_6(D_{3h})$  optimal geometry (with zero potential energy), and the kinetic energy given was two times higher than that necessary for dissociation to occur via the TS obtained here. This initial kinetic energy was distributed evenly among all normal modes. It can be seen that dissociation occured in less than 2 ps, which occurred through the proposed mechanism.

# APPENDIX C – Published work-RSC Advances

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# PAPER

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# 1 Introduction

Polynitrogen systems (polyN) have been the subject of a vast number of studies in the past decades, both in neutral and ionic forms, due to the fact that they are candidates for clean energy sources. This comes from the nature of their structures, built by single and/or double N–N bonds. The triple bond of molecular nitrogen is highly thermodynamically stable, and therefore these systems tend to decompose, dissociating into N<sub>2</sub> molecules and releasing large amounts of energy. As the product of this dissociation is the major component of atmospheric air, this process occurs without the formation of polluting compounds or greenhouse gases, such as carbon dioxide.<sup>1-4</sup>

Because of their high potential energy content, polyN are part of a group of substances called high energy density materials (HEDMs). For practical usage, the material must not only be able to release a large amount of energy on demand, but also must have a reasonable chemical stability in order to be

# Stability of neutral molecular polynitrogens: energy content and decomposition mechanisms<sup>†</sup>

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The potential application of all-nitrogen molecules as high energy density materials (HEDMs) has been attracting considerable scientific effort. If stable enough to be synthesized and stored, these systems may be used as a green source of energy. However, it is very difficult to obtain these structures under mild experimental conditions. Theoretical chemistry may aid in the search for polynitrogens that are more likely to have experimental usability. The barriers towards decomposition are an effective way to assess their stability, but these have not been thoroughly studied. Most of the previous effort in this direction focus on a single  $N_x$  case, each employing different accuracy levels, and the decomposition of caged structures has been little explored. Here we explore the stability and decomposition of several neutral molecular polynitrogens of different sizes and shapes using a common and accurate theoretical framework in order to compare among them, search for patterns and identify potential candidates for synthesis. We focus especially on new caged geometries, and our results indicate that the prismatic ones can be expected to present higher energy densities and be very stable with respect to unimolecular decomposition. It is shown that the energy content can be clearly stratified between chain, ring, cage and prismatic cage structures.

produced and stored. For polyN systems, this means a high dissociation energy coupled with a relatively high decomposition barrier.<sup>1</sup>

PolyN species can be sub-categorized in chain, ring or caged structures. The latter tend to show more single bonds between nitrogen atoms, and thus may be expected to release a larger amount of energy when several new triple  $N_2$  bonds are formed upon its dissociation. As this process may involve the breaking of several chemical bonds simultaneously, its decomposition barrier is also expected to be higher.<sup>5</sup> Therefore, cage-like structures are possibly the most suitable ones for HEDM use.

Experimentally, it is very hard to synthesize polyN at ambient conditions. Usually, extremely high pressures and cryogenic temperatures are necessary.<sup>6,7</sup> In the field of neutral polyN, it has already been reported a covalent allotropic form of nitrogen in which the atoms are arranged in a cubic gauche structure (cg-N),<sup>8</sup> a polymeric nitrogen with the black phosphorus structure (bp-N)<sup>9</sup> and a molecular form of N<sub>8</sub>.<sup>10</sup> On the ionic front, on the other hand, many species have been obtained over the past few years, such as the pentazolate anion,<sup>11</sup> the pentazenium cation<sup>12,13</sup> and metal pentazolate hydrate complexes.<sup>14</sup> Slightly larger anions have also been recently reported, such as a tungsten hexanitride<sup>15</sup> and the N<sub>8</sub><sup>-</sup> anion, which has been synthesized on the sidewalls of multi-walled carbon nanotubes<sup>16</sup> and also stabilized on boron-doped graphene.<sup>17</sup>

Theoretically, several studies involving polyN (especially up to 10 atoms) have been reported over the past decades, regarding their structures and thermodynamic properties, both

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<sup>†</sup> Electronic supplementary information (ESI) available: Structures and frequencies obtained at the M06-2X and SOGGA11-X/def2-TZVPP levels; graphs of selected molecular parameters against AE, DE and DE/n. See DOI: 10.1039/d1ra03259c

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in neutral<sup>18-36</sup> and ionic forms at gas phase.<sup>22,37-40</sup> Stable molecular crystals of N<sub>6</sub>, N<sub>8</sub> and N<sub>10</sub><sup>2,41-43</sup> have also been proposed. However, less attention has been given to their dissociation and isomerization barriers, which is a key aspect to predict what isomeric forms may actually be stable at ordinary temperatures, which is a major advantage for storage. Most of previous research that has been published on this property focused on chain or ring structures with up to 10 atoms for neutral<sup>4,6,7,44-60</sup> and ionic forms.<sup>7,52,54,59,61-65</sup> To the best of our knowledge, the dissociation and isomerization barriers of neutral caged structures have been, up until now, little exploited,<sup>66-69</sup> and most of these studies employed symmetry constraints in the search for transition state structures.

For the reasons mentioned above, this work is focused on providing a systematic study on the decomposition mechanisms for several polyN neutral molecules, in order to provide insights into what type of structure might be best suitable for HEDMs. The various isomers are compared by their calculated dissociation barriers and dissociation energies using the same theoretical level for all structures and without symmetry constraints in the decomposition pathways, allowing for a fair comparison between all structures. We focus on caged geometries, but for each polyN size, other relevant structures are always included for a direct analysis between the different classes.

### 2 Methodology

All electronic structure calculations reported here were performed using the GAMESS-US70 and MOLPRO71 packages. The calculations were based on density functional theory (DFT)72 using the def2 (SVP and TZVPP) basis sets.73 The M06-2X74 and SOGGA11-X75,76 exchange and correlation functionals were chosen due to their known accuracy for predicting energy barrier heights.<sup>77,78</sup> In fact, it has been shown by Peverati and Truhlar,76 that the mean unsigned error (MUE) for nonhydrogen-transfer barrier heights (NHTBH) for the hybrid SOGGA11-X functional and of M06-2X are respectively 1.16 kcal mol<sup>-1</sup> and 1.22 kcal mol<sup>-1</sup>. Therefore both functionals show chemical accuracy for potential energy barriers and are expected to provide reliable results for our purposes. Vibrational analysis was carried out to confirm the minima and transition states (TSs) found within the employed levels of theory. The wxMacMolPlt program was used for graphic visualization and representation of the molecular geometries.79

The initial structures selected (shown in Fig. 1) were taken from ref. 36 and 80 and were chosen such as to provide four different structures for each molecular size, and to present a diverse set of all geometrical classes of structures. This work provides the first account on the unconstrained dissociation paths of six nitrogen allotropic forms:  $N_8(C_{2\nu})$ -A,  $N_8(C_S)$ , and all four  $N_{10}$  isomers including the prismatic one.

As a first step, the smaller def2-SVP basis set was used for an initial exploration of possible dissociation and isomerization paths associated with each studied polyN. Intrinsic reaction coordinate (IRC) calculations were performed with this basis set using the Gonzalez–Schlegel second-order algorithm<sup>81</sup> for all



ig. 1 Initial structures.

TSs found to ensure their connection to decomposition or isomerization products. After that, reoptimization employing the larger def2-TZVPP basis set was carried out for all stationary points found. The energies of all minima and TSs were zero-

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point energy (ZPE) corrected within the def2-TZVPP approach and no symmetry restrictions were imposed in any case.

To assess the performance of our DFT results, we have also performed geometry optimizations and frequencies calculations at the coupled cluster singles and doubles and perturbative triples (CCSD(T)) level,<sup>82-84</sup> using the cc-pVDZ basis set.<sup>85,86</sup> This was followed by a single point energy refinement using the explicitly correlated coupled cluster method (CCSD(T)-F12) method,<sup>87,88</sup> using the aug-cc-pVTZ basis set. Such calculations were considered as benchmark and the results were directly compared to the DFT ones.

# 3 Results

In the results presented throughout this work, the energies in all graphs are given relatively to the  $nN_2$  dissociation limit. The reaction pathways in the IRC plots are displayed with black circles (at the SOGGA11-X/def2-SVP level). The horizontal lines in these graphs correspond to the ZPE corrected energies at M06-2X/def2-TZVPP (orange) and SOGGA11-X/def2-TZVPP (black) levels.

For a summary of the results, the tables in this section show the numerical values of the activation energy (AE) and dissociation energies (DE), which are positively defined as

$$AE = E_{TS} + ZPE_{TS} - [E_{polyN} + ZPE_{polyN}]$$
(1)

and

$$DE = E_{polyN} + ZPE_{polyN} - \frac{n}{2}[E_{N_2} + ZPE_{N_2}]$$
(2)

where  $E_{\rm TS}$ ,  $E_{\rm polyN}$  and  $E_{\rm N_2}$  stand for the total energies of the transition state, the initial polyN and a nitrogen molecule, respectively.  $\rm ZPE_{TS}$ ,  $\rm ZPE_{polyN}$  and  $\rm ZPE_{N_2}$  are the corresponding zero-point energies of these species and *n* is the total number of atoms of the polyN. In the calculation of AE, only the lowest lying TS is considered. In summary, AE is a measure of how



**Fig. 3** Decomposition path of  $N_6(C_{2v})$ -B isomer with IRC calculation following the scheme of Fig. 2.

difficult it is to break the polyN structure in an unimolecular decomposition, while DE gives the amount of energy released in the process. We also report the values of dissociation energy per atom (DE/n), since this is more related to the energy content of the HEDM.

The Cartesian coordinates and frequencies of all minima and transition states reported in this section are given in the ESI† for both DFT functionals. Although the results of both functionals are given in the figures and tables, the energies discussed in the text are given only at the SOGGA11-X/def2-TZVPP level for simplicity.

#### 3.1 N<sub>6</sub>

Four isomers of N<sub>6</sub> have been considered in the present work. Fig. 2–5 present the results of the IRC calculations for structures N<sub>6</sub>( $C_{2v}$ )-A, N<sub>6</sub>( $C_{2v}$ )-B, N<sub>6</sub>( $C_{2h}$ ) and N<sub>6</sub>( $D_{3h}$ ) respectively. Table 1 gathers their AE and DE values. All three different calculation methods predict the same energetic ordering between the four structures, and both DFT functionals are in fairly good agreement with the CCSD(T)-F12/aug-cc-pVTZ//CCSD(T)/cc-pVDZ



Fig. 2 Decomposition path of  $N_6(C_{2v})$ -A isomer obtained from IRC calculation at SOGGA11-X/def2-SVP level. The bars correspond to the zero-point corrected energies at M06-2X/def2-TZVPP (orange) and SOGGA11-X/def2-TZVPP (black) levels. The zero of energy is set as the fully dissociated system ( $nN_2$ ).



Fig. 4 Decomposition path of  $N_6(C_{2h})$  isomer obtained from IRC calculation following the scheme of Fig. 2.



(upper panel) and an alternative path to the same products passing through an intermediate (lower panel). Following the scheme of Fig. 2.

IRC-SOGGA11-X

SOGGA11-X

M06-2X

15

SOGGA11-X

20

M06-2X

IRC-SOGGA11-X

20

25

10

15

results for DE. The mean absolute difference between the benchmark results and the M06-2X one is only 2.0%, with a standard error of the mean (SEM) of 0.2%. A similar comparison is obtained for the SOGGA11-X functional, with a mean absolute difference of 2.2%. This good agreement between the methods reinforces the conclusions of this work

Table 1 Activation energy barriers (AE), dissociation energies (DE) and dissociation energies per nitrogen atoms (DE/n) in kcal mol<sup>-1</sup> for the N<sub>6</sub> isomers

Structure	Method	AE	DE	$\mathrm{DE}/n$
N <sub>6</sub> (C <sub>2v</sub> )-A	M06-2X	5.59	240.30	40.05
	SOGGA11-X	7.33	231.53	38.59
	CCSD(T)-F12		235.12	39.19
	M06-2X	1.94	247.00	41.17
$N_6(C_{2v})$ -B	SOGGA11-X	4.23	239.69	39.95
	CCSD(T)-F12		243.65	40.61
	M06-2X	18.42	178.13	29.69
$N_6(C_{2h})$	SOGGA11-X	19.23	173.20	28.87
	CCSD(T)-F12		181.77	30.29
	M06-2X	40.53	319.89	53.32
$N_6(D_{3h})$	SOGGA11-X	40.96	309.90	51.65
	CCSD(T)-F12		312.61	52.10



Fig. 6 Decomposition path of  $N_8(C_{2y})$ -A isomer obtained from IRC calculation following the scheme of Fig. 2.

regarding which structure is more stable towards unimolecular decomposition. A broader comparison between the methods and their accuracy will be given in the discussion section.

As it can be seen, isomers  $N_6(C_{2v})$ -A (which shows a Dewar benzene structure) and  $N_6(C_{2v})$ -B possess small dissociation barriers (AE of 7.33 and 4.23 kcal mol<sup>-1</sup>, respectively), indicating that they are kinetically unstable at ambient conditions. These isomers decompose in a stepwise process, being the first the elimination of a N2 molecule, followed by the dissociation of the well known D<sub>2h</sub> form of N<sub>4</sub>,<sup>7,58</sup> which has a very small dissociation barrier (around 6.45 kcal mol<sup>-1</sup> above the N<sub>4</sub> well<sup>7</sup>).

The  $N_6(C_{2h})$  isomer, also named as diazide, presents a considerably higher decomposition barrier (19.23 kcal  $mol^{-1}$ ) when compared to the previous two, in spite of its chain configuration. Nevertheless, it may not be sufficient to confirm its stability at room temperature, as it has been suggested that an energy barrier of approximately 30 kcal  $mol^{-1}$  is desirable.50,67 In agreement with previous studies,48,52,60,67 we found a concerted dissociation mechanism in which  $N_6(C_{2h})$  breaks directly into three N2 molecules. It is worth mentioning that Greschner et al.41 recently predicted a stable molecular crystal



Fig. 7 Decomposition path of  $N_8(C_s)$  isomer obtained from IRC calculation following the scheme of Fig. 2.



Fig. 8 The two possible paths for  $N_8(C_{2\nu})$ -B with energetically equivalent barriers as indicated in the text. Following the scheme of Fig. 2.

composed of  $N_6(C_{2h})$  chains. Their molecular dynamics simulations suggest reasonable thermal stability.

Differently from the other three,  $N_6(D_{3h})$  (or prismane) shows more promising results. In our study, we found a new TS that connects prismane directly to  $N_4(D_{2h}) + N_2$ , with an energy barrier of 40.96 kcal mol<sup>-1</sup> (upper panel in Fig. 5). Li and Liu<sup>67</sup> found instead a considerable isomerization energy barrier towards the N<sub>6</sub>( $C_{2v}$ )-B structure (34.4 kcal mol<sup>-1</sup>) at CCSD/6-311G(d)(energies)//B3LYP/6-311G(d)(geometries) level. We could also find the isomerization path connecting these two isomers (lower panel in Fig. 5), and an energy barrier of 40.84 kcal mol<sup>-1</sup> was obtained. Within the accuracy of our calculations, both isomerization and dissociation processes can be considered as energetically equivalent. The N<sub>6</sub>( $C_{2v}$ )-B isomer, in turn, will easily dissociate as illustrated in Fig. 3. These barriers are a good indicative of practical use of N<sub>6</sub>( $D_{3h}$ ) as HEDM, and the unraveling of the direct decomposition pathway is relevant to the understanding of the energy landscape associated with prismane.

Within the N<sub>6</sub> size, prismane releases the largest amount of energy considering its dissociation into three N<sub>2</sub> molecules, being 78% more exothermic than the chain isomer (N<sub>6</sub>( $C_{2h}$ )). Its AE is also more than two times higher than that of N<sub>6</sub>( $C_{2h}$ ), indicating that it may be stable on higher temperatures. This can be partially attributed to its caged geometry, but as will be explored later in section 4, not all caged structures follow this pattern, and there are other features involved.

#### 3.2 N<sub>8</sub>

Four allotropes of N<sub>8</sub> have been considered in the present work. Fig. 6–9 present the results of the IRC calculations for isomers N<sub>8</sub>( $C_{2v}$ )-A, N<sub>8</sub>( $C_s$ ), N<sub>8</sub>( $C_{2v}$ )-B and N<sub>8</sub>( $O_h$ ), respectively. To the best of our knowledge, this is the first work regarding the dissociation barriers of N<sub>8</sub>( $C_{2v}$ )-A and N<sub>8</sub>( $C_s$ ). Table 2 presents the values of their AEs and DEs. It should be noted that azidopentazole has been found to be the lowest energy isomer of N<sub>8</sub>, but ref. 49 and 50 already ruled out the possibility that this could be a good candidate for a HEDM.

Regarding the  $N_8(C_{2v})$ -A isomer, we found a decomposition path that leads to  $N_6(C_{2v})$ -A +  $N_2$  (Fig. 6). It passes through an intermediate resulting from the opening of a triangular ring of the initial structure. The isomerization barrier that is determinant to the decomposition process was found to be 23.72 kcal mol<sup>-1</sup> (AE). Although not as high as that of prismane, this isomer might be an interesting candidate for production.



Fig. 9 Isomerization path of  $N_8(O_h)$  into  $N_8(C_{2v})$ -B. Following the scheme of Fig. 2.

Table 2 Activation energy barriers (AE), dissociation energies (DE) and dissociation energies per nitrogen atoms (DE/n) in kcal mol<sup>-1</sup> for the  $N_8$  isomers

Structure	Method	AE	DE	DE/n
N <sub>8</sub> (C <sub>2v</sub> )-A	M06-2X	22.26	375.47	46.93
	SOGGA11-X	23.72	363.13	45.39
	CCSD(T)-F12		367.69	45.96
	M06-2X	31.65	352.27	44.03
$N_8(C_{2v})$ -B	SOGGA11-X	29.34	341.44	42.68
	CCSD(T)-F12		344.10	43.01
	M06-2X	3.33	350.60	43.83
$N_8(C_s)$	SOGGA11-X	4.53	339.09	42.39
	CCSD(T)-F12		341.98	42.75
	M06-2X	24.11	450.31	56.29
$N_8(O_h)$	SOGGA11-X	24.06	436.51	54.56
	CCSD(T)-F12		435.88	54.49



Fig. 10 Decomposition path of  $N_{10}(C_s)$  isomer obtained from IRC calculation following the scheme of Fig. 2.

On the other hand, the N<sub>8</sub>( $C_s$ ) isomer did not present promising results, as its predicted barrier for decomposition into N<sub>6</sub>( $C_{2v}$ )-A + N<sub>2</sub> is only 4.53 kcal mol<sup>-1</sup> (see Fig. 7).

More interesting results were achieved for the  $N_8(C_{2y})$ -B isomer within our calculations. At the preliminary exploration using the def2-SVP basis set, only one barrier was found to be relevant. However, when we reoptimized the minima and TSs using the def2-TZVPP basis set, another barrier presented a similar and promising result, and we report both. First, a mechanism that leads to a  $D_{2d}$  structure followed by decomposition to  $N_6(C_{2h}) + N_2$  with an activation energy of 30.84 kcal  $mol^{-1}$  (upper panel in Fig. 8). Second, a direct decomposition route through a structure opening transition state yielded an activation energy of 29.34 kcal  $mol^{-1}$ , leading to an open chain  $N_8(C_1)$  isomer (lower panel in Fig. 8). Both barriers are high and show similar values, and thus  $N_8(C_{2\nu})$ -B may be another relevant candidate. Fau and Bartlett<sup>62</sup> reported that isolated open chains of N8 possess a relatively low decomposition barrier. In their work, this C1 structure is easily decomposed to N<sub>6</sub> + N<sub>2</sub>.<sup>62</sup>



Fig. 11 Decomposition path of  $N_{10}(D_{5h})$  isomer obtained from IRC calculation following the scheme of Fig. 2.

Still regarding  $N_8(C_{2v})$ -B, it should be noted that a TS directly connecting it to full dissociation, was obtained by Schmidt *et al.*<sup>68</sup> at the MP2/6-31G(d) level, with an AE of 20 kcal mol<sup>-1</sup>, but could not be reproduced within our calculation method. Gagliardi *et al.*<sup>66</sup> found (employing B3LYP/cc-pVTZ calculations) two pathways for this structure: one similar to that shown in the upper panel of Fig. 8, with a barrier of 43.3 kcal mol<sup>-1</sup>, and another for isomerization of  $N_8(C_{2v})$ -B into another structure of 28.2 kcal mol<sup>-1</sup>. In summary, the final AE value reported in ref. 66 is similar to the one reported here.

Extensive research has been performed on the octaazacubane allotrope,<sup>6,44,47,66,68,69</sup> N<sub>8</sub>( $O_h$ ). Engelke and Stine<sup>44</sup> studied the concerted symmetry forbidden  $D_{4h}$  dissociation path N<sub>8</sub>( $O_h$ )  $\rightarrow$  4N<sub>2</sub> and found a 162 kcal mol<sup>-1</sup> energy barrier at RHF/4-31G\* level, in good agreement with the work of Evangelisti and Gagliardi<sup>47</sup> (159 kcal mol<sup>-1</sup> at CASSCF/VDZP level) considering the same constrained  $D_{4h}$  path. However, both studies agree that octaazacubane dissociation should occur in a less symmetric path. On the other hand, an almost barrierless pathway to the total decomposition of the isolated N<sub>8</sub>( $O_h$ ) into 4N<sub>2</sub> (2.5 kcal mol<sup>-1</sup>) was obtained by Gimaldinova *et al.* within the frame of the non-orthogonal tight-binding model for describing interatomic interactions.<sup>6</sup>

The lowest energy TS linked to  $N_8(O_h)$  that we managed to find in the present study lies 24.06 kcal mol<sup>-1</sup> above it. According to our IRC calculations, this TS actually connects  $N_8(O_h)$  to the  $N_8(C_{2v})$ -B isomer. Our proposed isomerization pathway agrees with the results of ref. 66, 68 and 89. After isomerization,  $N_8(O_h)$  may readily follow the  $N_8(C_{2v})$ -B decomposition path already discussed and presented in Fig. 8. Therefore, analogously to the  $N_8(C_{2v})$ -B isomer, octaazacubane may also be of experimental relevance, but with the advantage of generating 28% more energy upon full dissociation.

Octaazacubane,  $N_8(O_h)$ , presents the highest DE/*n* ratio among all polyN studied here, which can be attributed to its strained prismatic structure where each N atom makes 3 single bonds. On the other hand, our calculations show that  $N_8(C_{2\nu})$ -B (which does not show a caged structure) shows the highest activation energy for the 8 atoms polyN. As will be summarized



Fig. 12 Decomposition path of  $N_{10}(C_1)$  isomer obtained from IRC calculation following the scheme of Fig. 2.

#### Paper



Fig. 13 Decomposition path of  $N_{10}(C_{3v})$  isomer obtained from IRC calculation following the scheme of Fig. 2.

later, although it is possible to draw correlations between the geometric shape and DE values, a similar analysis often fails to explain the calculated AEs. Finally, the relatively small difference between the dissociation barriers of  $N_8(C_{2v})$ -B and  $N_8(O_h)$  (5.3 kcal mol<sup>-1</sup>) compared to the significant difference between their DEs (95 kcal mol<sup>-1</sup>) should be taken into consideration.

#### 3.3 N<sub>10</sub>

Four allotropes of  $N_{10}$  have been considered in the present work. Fig. 10–13 present the results of the IRC calculations for isomers  $N_{10}(C_s)$ ,  $N_{10}(D_{5h})$ ,  $N_{10}(C_1)$  and  $N_{10}(C_{3v})$ , respectively. To the best of our knowledge, this is the first work to provide fully relaxed dissociation mechanisms for these structures. The numerical results are gathered in Table 3. The difference between the two exchange correlation functionals employed in the case of the  $N_{10}$  structures follows the same trend observed for the previous structures: both functionals predict very similar AE barriers, but M06-2X predicts larger DEs.

The branched chain isomer  $N_{10}(C_s)$  possesses a small decomposition barrier 7.73 kcal mol<sup>-1</sup> and may not be a good candidate for HEDM. Together with the other chain isomer

Table 3 Activation energy barriers (AE), dissociation energies (DE) and dissociation energies per nitrogen atoms (DE/n) in kcal mol<sup>-1</sup> for the N<sub>10</sub> isomers

Structure	Method	AE	DE	DE/n
$N_{10}(C_{s})$	M06-2X	7.14	305.30	30.53
	SOGGA11-X	7.73	299.23	29.92
	CCSD(T)-F12		312.74	31.27
	M06-2X	23.97	513.39	51.34
$N_{10}(D_{5h})$	SOGGA11-X	25.81	498.12	49.81
	CCSD(T)-F12		499.31	49.93
	M06-2X	9.02	463.42	46.34
$N_{10}(C_1)$	SOGGA11-X	9.55	449.47	44.95
	CCSD(T)-F12		454.18	45.42
	M06-2X	7.24	471.95	47.19
$N_{10}(C_{3v})$	SOGGA11-X	8.22	457.24	45.72
	CCSD(T)-F12		459.62	45.96

explored in this work ( $N_6(C_{2h})$ ), they represent the lowest DE/*n* ratio. Interestingly,  $N_6(C_{2h})$  has a decomposition barrier 2.5 times larger than  $N_{10}(C_s)$ , despite the analogous structures, which again indicates the difficulty in correlating the AE value with molecular shape.

The prismatic  $N_{10}(D_{5h})$  isomer decomposes in a stepwise fashion, passing through two different intermediates, to reach a chain isomer (Fig. 11). As reported by Strout,<sup>55</sup> such acyclic forms of N<sub>10</sub> tend to present low activation barriers towards dissociation, and thus the system will easily dissociate from there. Therefore, if there is available energy for  $N_{10}(D_{5h})$  to surpass the first isomerization barrier (25.81 kcal  $mol^{-1}$ ), it will promptly undergo dissociation. This barrier is comparable to those presented by  $N_8(C_{2v})$ -B and  $N_8(O_h)$  isomers which, together with a large energy released upon full dissociation (DE), makes  $N_{10}(D_{5h})$  the most attractive polyN within the  $N_{10}$ structures according to our calculations. The just published study employing reaction dynamics<sup>89</sup> obtained a similar transition state, but the B3LYP reported energy barrier is substantially lower (13 kcal  $mol^{-1}$ ). Since the B3LYP functional is well known to underestimate barrier heights,90,91 with a MUE about four times higher than the functionals employed here,<sup>76</sup> our AE value should be more realistic.

Even though  $N_{10}(C_1)$  and  $N_{10}(C_{3v})$  present cage-like structures and high energy content (as given by DE/*n*), their rather small decomposition energy barriers (AE) make them not suitable for HEDM application. This is also the case for smaller polyN such as  $N_8(C_s)$  and  $N_6(C_{2v})$ -B, although all of them present significant DEs. Therefore, despite caged structures are consistently related to higher DEs, this is not the main factor governing their decomposition barriers. Symmetry seems to play an important role, as specific prismatic structures with peripheral  $N_4(D_{2h})$  rings tended to yield higher kinetic stability, as well as DEs. Like the other prismatic structures of smaller nuclearities approached here,  $N_{10}(D_{5h})$  is the isomer that releases the greatest amount of energy towards full decomposition into  $N_2$  molecules.

#### 4 Discussion

For summarizing the results we first present a graph based on the Evans-Polanyi principle,92 relating activation energy with reaction energy, which is shown in Fig. 14. Although no clear correlation between AE and DE is observed, this graph is helpful for a general overview. First of all, the two graphs show that both functionals (one hybrid-GGA and one of meta-GGA type), are in very good agreement and the exact same conclusions can be drawn from both. In fact, analysing all structures calculated in this work, the difference between the two functionals in predicting DE is on average 3.1%, with a SEM of 0.1%. The SOGGA11-X functional is in better agreement with the benchmark calculations, in average deviating from the CCSD(T)-F12 ones by only 1.5% with a SEM of 0.4%. As for the AE values, the two funcionals always agree qualitatively in predicting the order of increasing AE. The difference between their calculated AEs is on average 1.19 kcal mol<sup>-1</sup> which is indeed their expected accuracy.



Fig. 14 Evans–Polanyi plot. The results of the M06-2X functional are given in the upper panel, while SOGGA11-X ones are in the lower panel.

We have also classified the structures into chains, rings, cages and caged prisms, which is presented in Fig. 14 in different colors. It is clearly seen that prismatic structures always show large activation energies towards unimolecular decomposition, and that of prismane  $N_6(D_{3h})$  is specially high. This plot is helpful for an easy visualization of polyN molecules that display high values for both AE and DE, and thus could be good candidates for HEDMs. Besides the prismatic structures,  $N_8(C_{2v})$ -B shows a surprisingly high activation energy, and could be one of the best candidates explored here. The chain structure of  $N_6(C_{2h})$  shows a significant decomposition barrier, even though it is the structure that releases the least amount of energy upon dissociation into nitrogen molecules. It is worth recalling that Greschner *et al.*<sup>41</sup> proposed a stable molecular

Although we have shown that all prismatic structures show high activation energies, it is seen that having a caged structure is not a sufficient condition. All caged structures present a high energy content (DE) but for some reason it is relatively easy to break some of them (small AE). Ring structures often have low activation energy, and are easier to break but, as seen before,  $N_8(C_{2v})$ -B is an exception.

For a global analysis of all results given in the previous section, and also aiming to find correlations between the

energetic properties with electronic and structural ones, we have calculated several molecular parameters such as HOMO–LUMO gap, average bond order, average bond length and asphericity for all polyN structures reported here. After the calculations we plotted these properties against AE, DE and DE/*n*, which are all given in the ESI† for both DFT functionals.

None of the molecular parameters explored here were found to correlate with AE. If such correlation existed, it would be very useful for predicting the dissociation barriers of new polyN structures obtained in the future, since exploring their high dimensional PES in the search for the lowest TS is a very difficult task.

The average bond lengths and average bond orders were found to be correlated with DE and DE/*n*. The latter is shown in Fig. 15, where it is seen that lower bond orders (and higher bond lengths, as given in the ESI†) generally mean higher dissociation energy. It is interesting to see that DE/*n*, which is more related to the energy content of a structure than DE, can be clearly stratified among the four geometrical categories (chain, ring, cage and caged prism), which was not observed in the case of DE (see Fig. 14). Although caged prisms have higher DE/*n* than caged structures, their average bond orders are similar, lying below 0.9. Ring structures have average bond



**Fig. 15** Dissociation energies per nitrogen atoms in function of the average bond orders. Results at the def2-TZVPP level of theory. M06-2X (upper panel) and SOGGA11-X (lower panel).

orders from 0.95 to 1.14, while chained structures show the largest values, as more double bonds are possible.

### 5 Conclusions

In this work, the unimolecular decomposition routes for several polynitrogen allotropes were predicted at the SOGGA11-X/def2-TZVPP and M06-2X/def2-TZVPP levels of theory. These two methods were shown to yield similar results, compare well with highly accurate CCSD(T)-F12 ones, and the same conclusions can be drawn from both.

Though the potential barriers for some polyN have been previously explored in the literature, this work provides new accounts on the unconstrained decomposition of six structures:  $N_8(C_{2v})$ -A,  $N_8(C_s)$ , and all four  $N_{10}$  isomers, including the prismatic one. Furthermore, new mechanisms involving prismane and  $N_8(C_{2v})$ -B were obtained.

By using the same computational methods for three different sizes, and several geometrical shapes for each, we were able to extract interesting information about this class of chemical systems. First, it is shown that the energy content (DE/n, which may be released if these substances are used as energy sources) can be clearly stratified between chain, ring, cage and prismatic cage structures. This variable shows a linear correlation with average bond size and average bond order.

The energy barriers towards unimolecular decomposition (AE) could not be correlated to any electronic or geometrical property of the molecule. If such correlation existed, it would be very useful for screening newly proposed polyN structures, as the search for the dissociation transition states is a very time consuming task.

Comparing between individual structures, it is found that prismane  $(N_6(D_{3h}))$  shows a very high dissociation barrier and, if it could be synthesized, would be very stable, perhaps allowing its storage at ambient conditions. Upon triggering its dissociation reaction, it would deliver a very large amount of energy, without producing any pollutant products.

All prismatic cage structures are shown to have considerably high activation energies as well. Although  $N_8(O_h)$  and  $N_{10}(D_{5h})$ do not display an AE as high as that of prismane, they also have a very large energy content. An unexpected promising case was  $N_8(C_{2v})$ , a boat-like structure that displays an activation energy even higher than those of the  $N_8(O_h)$  and  $N_{10}(D_{5h})$  prismatic structures.

The present overall survey of possible polyN structures may serve as a guide for future computational work, to direct efforts in finding crystal structures and other properties only for the most promising and kinetically stable polyN structures.

# Conflicts of interest

There are no conflicts of interest to declare.

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