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Reactivity Indexes and Structure of Fullerenes

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Additional information is available at the end of the chapter

Abstract

The discovery of fullerenes and their production in measurable quantities launched many studies about their reactivity and possible applications. Their peculiar structure opened possibilities for their study, initially replacing carbon atoms with alternative atoms. The surface also offers the possibility of attaching several species and the interior of their hollow structure represents a challenge because of the possibility of confining elements or molecules that may become less stable when attached to the exterior of the cage. These modifications may considerably affect both chemical and physical properties. In this chapter, we propose the encapsulation of 3–10 nitrogen atoms as aggregates inside the C_{70} cage. We also study the structures and reactivity indexes and the stabilization conferred as a result of being part of the fullerene. These aggregates are mainly of interest because of their possible application as energetic materials.

Keywords: polynitrogen, endohedral fullerenes, Density Functional Theory, reactivity indexes, C70, energetic materials

1. Introduction

Over the course of time, carbon materials have become important components not only everyday aspects of life, but also vanguard research. The enormous diversity concerning their uses and applications is constantly increasing, representing an area of constant development. Whether as part of a compound or in pure form, carbon has always attracted attention. At least in its purest forms, its structural diversity is extremely attractive (**Figure 1**).

Research on the formation and arrangement of carbon compounds that included long chains of this element in interstellar space lead to the discovery of fullerenes in 1985. Subsequently,
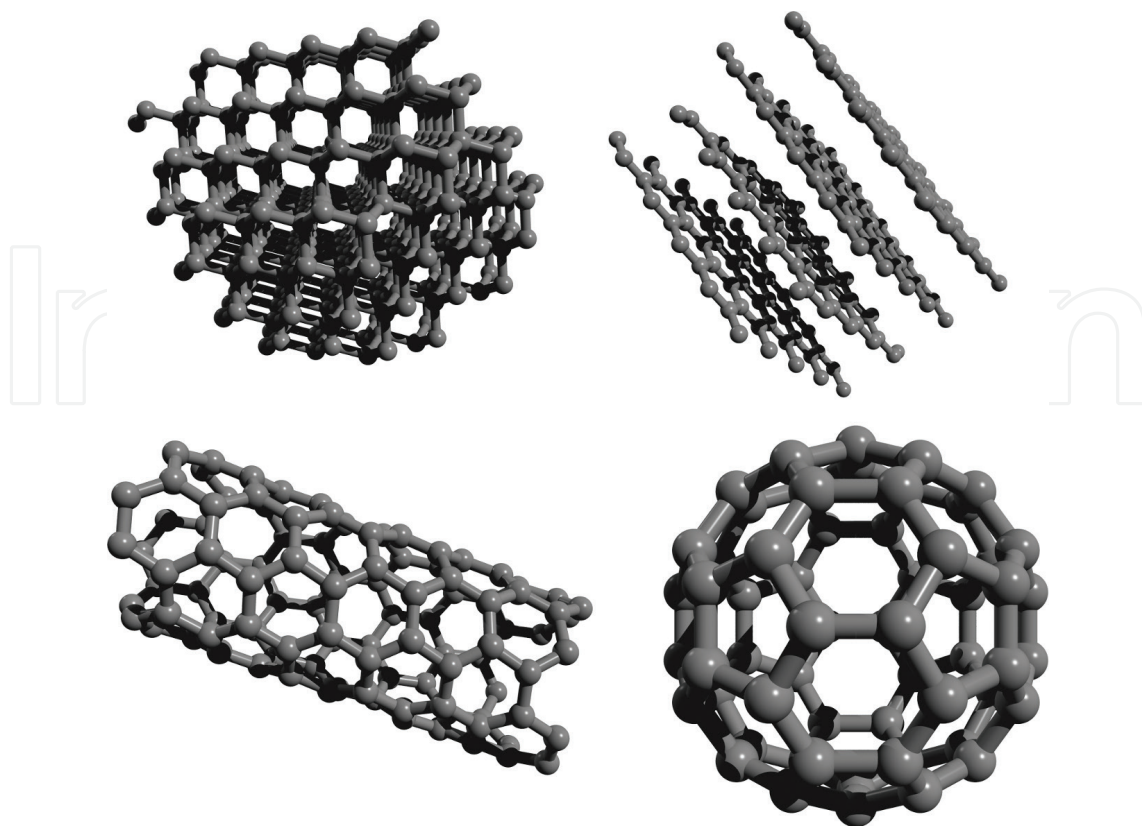
Figure 1. Allotropic forms of carbon. From left to right and up to down, diamond, graphite, nanotube and fullerene.

they were produced in measurable quantities for use in experiments [1–3]. Even though their study may have evolved accidentally, insufficient effort has been dedicated to understanding their structure, properties and applications. The best known examples of fullerenes are C_{60} and C_{70}, both of which consist of 12 pentagons, and only differ concerning the number of hexagons in their structure: 20 in the case of the first and 25 in the second. These differences result in the C_{60} structure, which is more like a soccer ball and C_{70}, which is more like a rugby ball (**Figure 2**). While C_{60} is more often known as a buckyball, the rest of the hollow structures are inscribed to the general fullerene group.

1.1. Types of fullerenes

Research into fullerenes has been extremely diverse, but can be categorized according to the structural aspect to be studied. Correspondingly, we have the following: exohedral fullerenes (with external ligands or molecules), endohedrals (with internal atoms or molecules) and heterofullerenes (with one or more carbon atoms in the cage replaced by heteroatoms).

Exohedral fullerenes have essentially resulted from efforts to "decorate" the surface of the fullerenes; mainly achieved by means of chemical functionalization. These types of fullerenes have proved to be extremely interesting, both for medical applications and for their possible applications in material sciences [4–8]. With respect to heterofullerenes, the substitution of carbon atoms by boron, nitrogen and silicon has been proposed; in the case of the first two, these have regularly

Figure 2. Comparison of C_{60} fullerene with a soccer ball and C_{70} with a rugby ball.

been as -BN- pairs, thus ensuring that isoelectronic species are obtained, although this has not necessarily been the only purpose; in the case of silicon, the main motive has been to search for useful applications in electronics [9–21]. Last but not least, endohedral fullerenes exist because of the fact that they are hollow; so they have the potential application of confining or protecting molecules, thus acting as carriers or stabilizers. Particularly, those with metallic atoms inside them—endohedral metallofullerenes—have been attractive for chemistry, physics and interdisciplinary areas, such as materials and biological sciences [22–25].

1.2. Polynitrogenated materials

Considerable interest in nitrogen compounds has emerged, especially those with a high content of this element, because of their particular properties and forms. Apart from the previously known molecular nitrogen (N_2), little was known of species with higher nitrogen content, until the synthesis of the azide anion (N_3^-) [26]. However, over time, new polynitrogenated species such as N_3, N_4, N_5^- and N_5^+ have been discovered or posited, whose synthesis has either represented a challenge or turned out to be surprisingly simple [27–30]. In spite of this, until now, the species with the highest content of nitrogen produced in measurable quantities has contained 5 nitrogen atoms, meaning that in particular the cyclopentazole anion could be considered as a motivator for theoretical studies on its formation, as well as representing a building block towards more complex structures [31–35]. As species with higher nitrogen content have proved to be very unstable with respect to decomposition to N_2, theoretical studies have outnumbered experimental ones. Of these, it has been determined that the preferred forms of N_4 and N_6 are acyclic, N_8 must be formed from an azide-pentazole (N_3–N_5) and that more complex

polynitrogens may exist such as N_7, N_{12}, N_{18}, N_{20} and a great etcetera [36–42]. Considering larger structures, there is no doubt that polyhedral or fullerene-type structures have provided inspiration, as they are considered as alternative polynitrogenous arrangements with a greater number of nitrogen atoms [18, 19, 21, 41, 43–47]. In this sense, a hollow structure could in principle be useful for storing internal molecules, which is why it is common to find hollow carbon structures as candidates for confining polynitrogenous species. Currently, the most notable examples have been studies of $N@C_{60}$, $N@C_{70}$ or even $N_2@C_{60}$ [48–52], which have extended the use of the C_{60} cage as a way of confining up to 16 nitrogen atoms [53, 54]. Also recently, the encapsulation of a polymer nitrogen chain in a carbon nanotube was conceived, as in principle this could be stable up to room temperature [55]. This contrasts with other proposed polynitrogenated phases of nitrogen that have been inspired by the analogy to phosphorus and arsenic, all superior in energy to the "cubic gauche" (CG). These have been proposed for extreme conditions and some experimental evidence has even been found for them [56–61]. Therefore, confinement represents an alternative for the stabilization of polynitrogenated species that are not necessarily related to high temperatures and pressure.

As our work group has studied fullerenes and their reactivity [7, 16, 62–65] and it has been proposed that C_{60} might be an ideal candidate for trapping nitrogen by a polymer [53, 54], the intention now is to show that C_{70} might also be an alternative way of storing polynitrogenous species, contributing to the development of new materials in the future.

2. Methodology

Initiating with considerable structural diversity, we calculated and modeled endohedral fullerenes; $N_n@C_{70}$ (n = 3–10). For this, we used the C_{70} structure that corresponds to the isomer from this composition and complies with the isolated pentagon rule, IPR. The Avogadro visualizer was used as an auxiliary [66]. Given the considerable number of possible isomers, we determined the minimum energy structures in two stages. Initially, we obtained the geometry optimizations for all molecules, using the PM6 method [67]. To ensure that the global minimum for each composition has been identified, the use of search algorithms, such as those inspired by genetic algorithms, is essential, but this is currently beyond the scope of this type of system. However, the diversity of proven structures inspires confidence in our determination of the most important and representative species. Subsequently, both the geometry and the electronic structure were refined for the lower energy isomers of each composition. Likewise, the calculation of vibrational frequencies was undertaken in order to corroborate that the stationary points located on the potential energy surface correspond to a minimum (NImag = 0). All this was undertaken using the hybrid functional B3LYP with the base set 6-311G [68, 69]. As the structures of the polynitrogen species in free state may differ according to charge, this factor was also evaluated, determining the structures for the isomers neutral, cation and anion. All calculations were performed using the Gaussian09 program [70].

We also calculated ionization energies (IE) and electron affinities (EA). These were therefore calculated to reveal the following energy differences: IE = E_{cation} − $E_{neutral}$, EA = $E_{neutral}$ − E_{anion}.

Chemical potential was computed by conceptual Density Functional Theory approximation. For an N electron system with an external potential v(r) and total energy E, electronegativity is defined as the partial energy derivative to the number of electrons at constant potential and then by the definition of Mulliken as the mean of IE and EA and the negative of electronegativity is the molecular chemical potential, μ:

$$\mu = -\chi = \left(\frac{\partial E}{\partial N}\right)_{v(r)} \approx -\frac{IE + EA}{2} \tag{1}$$

Chemical hardness was calculated as defined by Parr and Pearson [71], differentiating the chemical potential to the number of electrons, also at constant energy potential:

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_{v(r)} \approx \frac{IE - EA}{2} \tag{2}$$

Energies were also obtained for the stabilization reactions for polymer species within the C_{70} structure, applying the formula: $\Delta E = \Sigma E_{(products)} - \Sigma E_{(reagents)}$ for two possible schemes. In the first, the stabilization of isolated nitrogen atoms could be analyzed through the reaction $nN + C_{70} \rightarrow N_n@C_{70}$. In the second scheme, the reagents are substituted with nitrogen as found in standard state (N_2) or detected in experiments (N_3^-, N_5^-, etc.).

3. Results

It was previously reported that the methodology consisted of an optimization at the PM6 level. As the refinement and electronic structure were performed at the B3LYP/6-311G level, they are presented exclusively in the following.

For the majority of the structures obtained, neutral and charged species correspond to the same arrangement. In cases where it is not observed, it will be mentioned in due course.

3.1. Nn@C$_{70}$ structures and reaction energies

N_3. The minimum energy structure corresponds to a linear and centered N_3, which shows the same structure in charged and neutral systems, see **Figure 3**. There is also found a second stable structure that may closely resemble the association between the N_2 molecule and an "isolated" nitrogen atom. The difference in the relative energies exceeds 40 kcal/mol, leading us to assume that the linear isomer encapsulated in C_{70} would predominate, if it was ever produced. Distances between nitrogen atoms (1.20 Å) suggest a weaker bond than that observed for N_2 (1.11 Å).

Reaction energies were calculated based on various assumptions. First, it is considering only the stabilization due to the encapsulation of nitrogen atoms as reagents. Second, considering structures that can be found at room temperature as starting materials (**Table 1**).

The $3N + C_{70} \rightarrow N_3@C_{70}$ reaction was used to evaluate the role of the C_{70} box for the stabilization (or not) of 3 isolated nitrogen atoms, compared to placing them within the cage in polymer
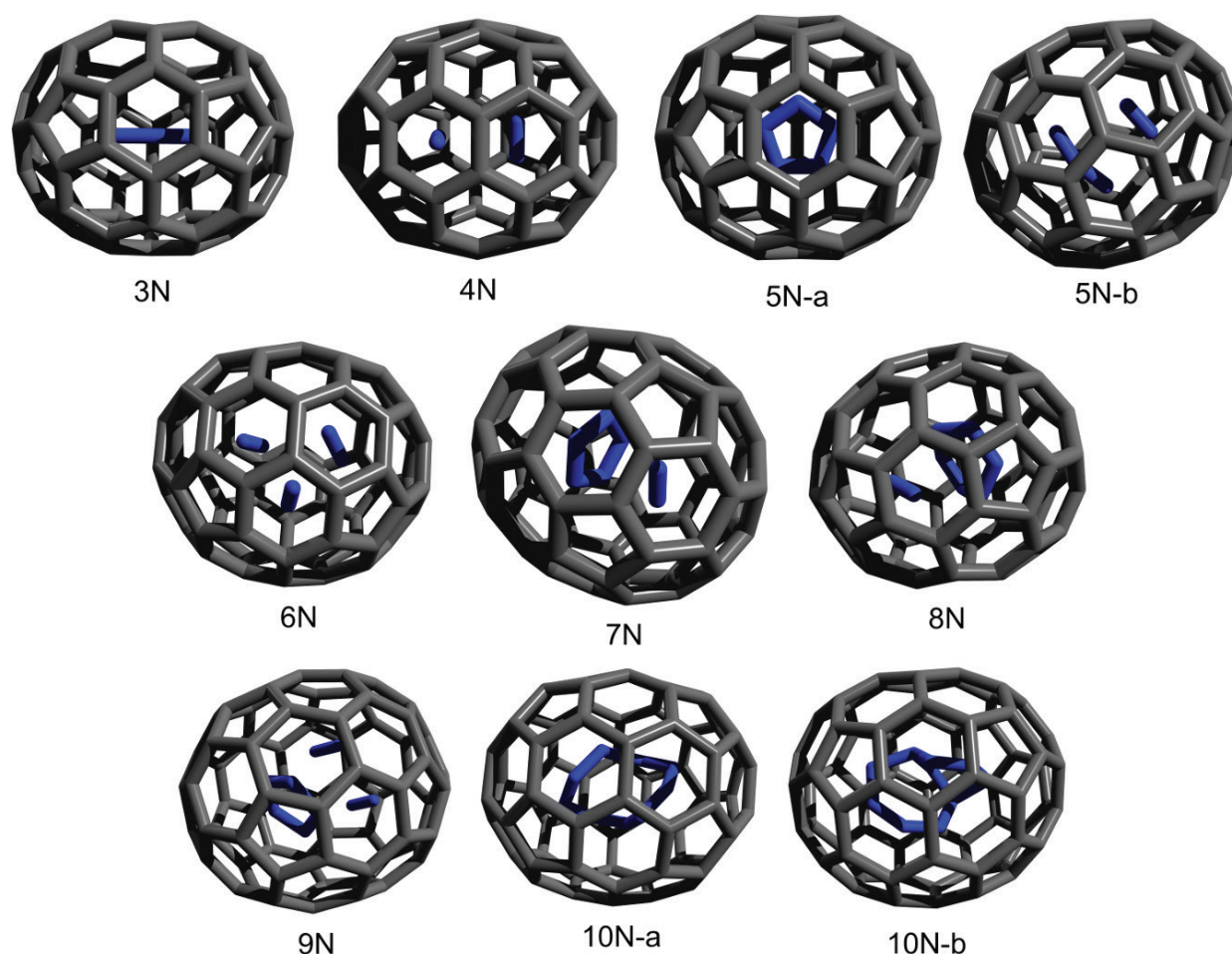
Figure 3. Structure of $N_n@C_{70}$, where n = 3–10, endohedral fullerenes, calculated using the B3LYP/6-311G method.

form as N_3. Apparently reactions are energetically favored. This energy difference is also highest for the cation, followed by the anion and finally the neutral (**Table 1**).

We evaluated energy differences for the reactions presented, while attempting to evaluate the role of the box, when initial material consisted of existing structures (such as N_3^- and N_2, rather than isolated nitrogen atoms). Evidently, as is stated in **Table 1**, the cation has lower ΔE energy. This molecule would be the most viable option at the time of the reaction, as the carbon cage would effectively stabilize the nitrogen polymer. Similarly, fullerene C_{70} is able to stabilize and cage the anion polynitrogen, as it also has a negative ΔE value. Contrastingly, in the case of the neutral structure, this is not predicted as a favorable reaction. In spite of this, stabilization of $N_2 + N$ in the C_{70} cage is favorable (ΔE = −60.44 kcal/mol).

N_4. We analyzed structures consisting of two pairs of N_2 molecules, **Figure 3**, in almost parallel positions (with an approximate distance of 2.67 Å between the two N_2 pairs). An arrangement very similar to the neutral one was observed for the charged systems. Unstable structures for charged systems were also found, as in essence they could almost be considered as 4 atoms with no obvious interacting link.

The stabilization of arrangements of 4 nitrogen atoms in the cage was evaluated in terms of reaction energy, results for which are shown in **Table 1**. Evidently, the encapsulation would be

Nn@C$_{70}$	Anion	Neutral	Cation
For n = 3	$2N + N^- + C_{70} \rightarrow N_3@C_{70}^-$	$3N + C_{70} \rightarrow N_3@C_{70}$	$2N + N^+ + C_{70} \rightarrow N_3@C_{70}^+$
	−495.82	−383.89	−544.51
	$N_3^- + C_{70} \rightarrow N_3@C_{70}^-$	$1.5N_2 + C_{70} \rightarrow N_3@C_{70}$	$N_3^+ + C_{70} \rightarrow N_3@C_{70}^+$
	−39.13	101.29	−106.97
For n = 4	$3N + N^- + C_{70} \rightarrow N_4@C_{70}^-$	$4N + C_{70} \rightarrow N_4@C_{70}$	$3N + N^+ + C_{70} \rightarrow N_4@C_{70}^+$
	−678.69	−606.42	−764.55
	$N_2 + N_2^- + C_{70} \rightarrow N_4@C_{70}^-$	$2N_2 + C_{70} \rightarrow N_4@C_{70}$	$N_2 + N_2^+ + C_{70} \rightarrow N_4@C_{70}^+$
	−69.85	40.49	−145.73
For n = 5	$4N + N^- + C_{70} \rightarrow N_5@C_{70}^-$	$5N + C_{70} \rightarrow N_5@C_{70}$	$4N + N^+ + C_{70} \rightarrow N_5@C_{70}^+$
5 N-a	−764.51	−652.59	−814.12
5 N-b	−745.26	−646.04	−804.31
5 N-a	$N_5^- + C_{70} \rightarrow N_5@C_{70}^-$	$2.5N_2 + C_{70} \rightarrow N_5@C_{70}$	$2N_2 + N^+ + C_{70} \rightarrow N_5@C_{70}^+$
	−0.13	156.04	−167.21
5 N-b	$N_2 + N_3^- + C_{70} \rightarrow N_5@C_{70}^-$	$N_2 + N_3 + C_{70} \rightarrow N_5@C_{70}$	$N_2 + N_3^+ + C_{70} \rightarrow N_5@C_{70}^+$
	34.89	73.75	−43.31
For n = 6	$5N + N^- + C_{70} \rightarrow N_6@C_{70}^-$	$6N + C_{70} \rightarrow N_6@C_{70}$	$5N + N^+ + C_{70} \rightarrow N_6@C_{70}^+$
	−881.66	−807.24	−965.47
	$2N_2 + N_2^- + C_{70} \rightarrow N_6@C_{70}^-$	$3N_2 + C_{70} \rightarrow N_6@C_{70}$	$2N_2 + N_2^+ + C_{70} \rightarrow N_6@C_{70}^+$
	50.62	163.12	−23.19
	$N_5^- + N + C_{70} \rightarrow N_6@C_{70}^-$	$N_5^- + N^+ + C_{70} \rightarrow N_6@C_{70}$	$N_3 + N_3^+ + C_{70} \rightarrow N_6@C_{70}^+$
	−117.29	−385.00	−131.54
		$N_3^- + N_3^+ + C_{70} \rightarrow N_6@C_{70}$	
		−255.14	

Table 1. Reaction energies due to the encapsulation of nitrogen structures for Nn@C$_{70}$, where n = 3–6, obtained at B3LYP/6-311G level of theory.

energetically favored. Similar to that observed in the previous isomer, it is predicted that the interaction with the cationic system would be greater than with the anionic or with the neutral one.

Analyzing encapsulation reactions initiating with different materials (such as N$_2$, neutral and charged), evidently the neutral one is not predicted to be energetically favorable. This would lead to a structure which could be very interesting for possible high energy density material (HEDM) applications, a field where metastable compounds and single nitrogen-nitrogen bonds are encouraged. However, the distance between nitrogen atoms (1.11 Å) is characteristic for a triple bond, which discards (at least in principle) this structure as a candidate. For charged systems, the reaction energy is favorable. This gives an idea of the role played by the C$_{70}$ cage in general, as it stabilizes systems with higher charge density.

N$_5$. The geometries for N$_5$@C$_{70}$ nitrogen polymers are shown in **Figure 3**. Captions 5 N-a and 5 N-b symbolize the optimized structures, noting that 5 N-a represents a cycle of 5 nitrogen atoms that is quite similar to cyclopentazole; a system found only as an anion [29, 31]. Distances between nitrogen atoms (~1.34 Å) for the cycle suggest a double-like bond. Contrastingly, 5 N-b isomers essentially consist of two systems; N$_2$ and N$_3$, separated by approximately 2.4 Å. We attempted to optimize a structure similar to N$_5^+$ that was predicted theoretically; however, our efforts were in vain, as all the structures presented fragmentation. Distances between nitrogen atoms are, for bended N$_3$ fragment, 1.19 Å, whereas for N$_2$ dimer 1.11 Å.

Geometry acquired by 5 N-a molecule represents the most stable. The energy of neutral 5 N-b is 6.5 kcal/mol greater than 5 N-a, which may be considerable, but would not be as difficult to achieve under experimental conditions. Likewise, the energy difference between the anion and cation systems exceeds 10 kcal/mol, with the cyclic isomers proving the most stable.

The formation energies of the different N$_5$@C$_{70}$ isomers were calculated by assuming that nitrogen atoms were the material at initiation, indicating at all times that this reaction would be favored. The highest value corresponded to cationic species, followed by anionic species and finally neutral species. Changing the reagents for other species reveals interesting dilemmas. Assuming formation with the pentazolate anion would imply a slightly favored reaction, but when substitute for N$_2$ + N$_3^-$, these systems become energetically unfavorable. Although this approach might discourage synthesis, it could also act as a motivator, as it would be considered as metastable and a candidate for high energy material, HEDMs.

N$_6$. For N$_6$@C$_{70}$, the most favored structure corresponds to the arrangement of three N$_2$ molecules, separated 2.4 Å each of the other (**Figure 3**). For previous reports of N$_6$@C$_{60}$ [53, 54], the lower energy structure corresponds to the pot-shaped hexagon, in contrast to that presented here. We suggest that this difference is due to the larger volume of C$_{70}$ as compared to C$_{60}$, which allows a bigger dispersion within the cage. Cyclic structure with boat-shaped conformation is found 100 kcal/mol greater in energy than reported here and, therefore, is not considered as a possible candidate.

When the reactants are represented by isolated nitrogen atoms, formation energy shows an energetically favorable reaction. However, by changing the reactants for N$_2$, the prediction becomes highly unfavorable. We undertook analysis by changing the reagents, finding that when we proposed charged species as reactants, negative formation energies appeared. We attribute this mainly to the stabilization of charges by the cage.

N$_7$. Of isomers identified in this system, lowest energy consisted of an N$_5$–N$_2$ partnership, similar to that found previously for C$_{60}$ [53, 54]. Other systems involving N$_3$ with 2N$_2$ or even rings of N$_7$ proved to be stable but considerably higher in energy (**Figure 3**). Bond distances for nitrogen-nitrogen in the pentagon are 1.31–1.33 Å long, which indicate a double bond. The second energy isomer in order (with N$_3$ and 2N$_2$ fragments) is 28 kcal/mol higher in energy, whereas a distorted heptagon N$_7$ cycle is about 90 kcal/mol higher. This is an indication that the pentagon-N$_2$ association would be the only isomer found in a hypothetical experiment.

Reaction energies show that the stabilization of individual nitrogen atoms is favored, whereas if the reagents are exchanged for others found experimentally such as N$_5^-$ + N$_2$, this would not

be the case. Again this presents a possible other use (as HEDM) for this type of molecule. We also present alternative reactions with energetically favored schemes, which we essentially attribute to the stabilization of charges in the fullerene cage (**Table 2**).

N_8. The most stable isomer for this composition consists of the assembly between a hexagon and a dimer as two separate units. Bond distances for N—N are around 1.33–1.34 Å, more related to a double bond. Likewise, isomers that involve the formation of a distorted—but unstable—octagon are found with considerably higher energies, making it possible to ensure

Nn@C$_{70}$	Anion (−)	Neutral (0)	Cation (+)
For n = 7	$6N + N^- + C_{70} \rightarrow N_7@C_{70}^-$	$7N + C_{70} \rightarrow N_7@C_{70}$	$6N + N^+ + C_{70} \rightarrow N_7@C_{70}^+$
	−979.94	−866.37	−1026.35
	$N_2 + N_5^- + C_{70} \rightarrow N_7@C_{70}^-$	$3.5N_2 + C_{70} \rightarrow N_7@C_{70}$	$3N_2 + N^+ + C_{70} \rightarrow N_7@C_{70}^+$
	107.89	265.72	−55.99
	$2N_2 + N_3^- + C_{70} \rightarrow N_7@C_{70}^-$	$N_5^- + N_2^+ + C_{70} \rightarrow N_7@C_{70}$	
	123.67	−148.76	
For n = 8	$7N + N^- + C_{70} \rightarrow N_8@C_{70}^-$	$8N + C_{70} \rightarrow N_8@C_{70}$	$7N + N^+ + C_{70} \rightarrow N_8@C_{70}^+$
	−1615.18	−1528.77	−1688.71
	$N_3 + N_3^- + N_2 \rightarrow N_8@C_{70}^-$	$4N_2 + C_{70} \rightarrow N_8@C_{70}$	$3.5N_2 + N^+ + C_{70} \rightarrow N_8@C_{70}^+$
	187.33	392.54	70.88
	$N_3 + N_5^- \rightarrow N_8@C_{70}^-$	$N_5^- + N_3^+ + C_{70} \rightarrow N_8@C_{70}$	
	171.55	−41.48	
For n = 9	$8N + N^- + C_{70} \rightarrow N_9@C_{70}^-$	$9N + C_{70} \rightarrow N_9@C_{70}$	$8N + N^+ + C_{70} \rightarrow N_9@C_{70}^+$
	−1046.85	−995.79	−1149.58
	$N_5^- + 2N_2 + C_{70} \rightarrow N_9@C_{70}^-$	$4.5N_2 + C_{70} \rightarrow N_9@C_{70}$	$4N_2 + N^+ + C_{70} \rightarrow N_9@C_{70}^+$
	364.43	459.75	144.23
	$3N_2 + N_3^- + C_{70} \rightarrow N_9@C_{70}^-$	$N_3^- + N_3^+ + N_3 + C_{70} \rightarrow N_9@C_{70}$	
	380.20	−47.35	
For n = 10	$9N + N^- + C_{70} \rightarrow N_{10}@C_{70}^-$	$10N + C_{70} \rightarrow N_{10}@C_{70}$	$9N + N^+ + C_{70} \rightarrow N_{10}@C_{70}^+$
b	−1143.41	−981.87	−1192.45
a	−1150.42	−996.12	−1184.66
	$N_3^- + 3.5N_2 + C_{70} \rightarrow N_{10}@C_{70}^-$	$5N_2 + C_{70} \rightarrow N_{10}@C_{70}$	$4N_2 + N_2^+ + C_{70} \rightarrow N_{10}@C_{70}^+$
a	438.36	621.14	396.74
	$N_5^- + 2.5N_2 \rightarrow N_{10}@C_{70}^-$		
	422.59		

Table 2. Reaction energies due to the encapsulation of nitrogen structures for Nn@C$_{70}$, where n = 7–10, obtained at B3LYP/6-311G level of theory.

that this isomer would predominate in an experiment. The nitrogen hexagon shows distances that suggest double bonds, ranging from 1.31 to 1.35 Å, whereas for the unstable octagon they range from 1.26 to 1.39 Å.

Similarly, the reaction energy from the stabilization of nitrogen atoms shows that this would be a favored case, starting with the cation, followed by the anion and finally the neutral. Changing the reactants it is found that metastable species would be formed with molecules present at laboratory conditions, such as N_2 and N_5^-. This alternate reaction scheme opens up the possibility to produce HEDM candidates.

N_9. The most favored structure for this encapsulation consists of the assembly formed from an N_5 ring and two dimers parallel to this. Nitrogen-nitrogen bonds for the cycle are very similar to the corresponding for similar cycles (1.3–1.33 Å) and the distance to N_2 is about 2.29 Å. Qualitatively, it is similar to that found for C_{60}, although with considerably greater distances [53, 54]. Stable structures involving ensembles formed with N_3 and $3N_2$ species are 18.78 kcal/mol higher in energy. The fact that it is preferred a more complex structure instead simple ones, indicates us to suggest a more determinant role of the C_{70} cage in the stabilization of the structure. The negative values of the reaction energy reflect the stabilization of the polynitrogenated species and evidently the reaction is more favored when the system is positively charged, after which follows the negative system and finally the neutral system. The energy difference revealing a positive energy reflects an unfavorable and endergonic reaction, although probably with metastable products. Moreover, by exploring other reaction paths to obtain the isomers of 9 nitrogen atoms, favorable reactions are obtained.

N_{10}. As the amount of nitrogen atoms in the fullerene cage increases, a greater variety of nitrogen polymer structures can be perceived. For this system, the neutral minimum corresponds to a distorted cycle of 10 atoms, which contrasts with that reported previously for C_{60} [53, 54]. However, the second energy structure for charged systems (with an energy difference not exceeding 8 kcal/mol compared to the most stable) corresponds to that reported for C_{60}. Bonding distances between nitrogen atoms are 1.23–1.43 Å for the lowest energy isomer and 1.24–1.48 Å for the second. The formation energy starting from isolated nitrogen atoms shows negative values, suggesting stabilization on the part of the box for N_{10}, which is highest for the cation, followed by the anion and finally the neutral. The formation reaction that initiates from a variety of reagents, such as N_3^-, N_5^- and N_2, shows positive values, which suggest metastable structures.

3.2. Global reactivity indexes

We obtained the following chemical reactivity indexes: ionization potential, electron affinity, as well as electronic hardness and chemical potential and the results are summarized in **Table 3**. For ionization potentials, apparently fullerenes encapsulating 3–8 nitrogen atoms fall within a range of 7.4–7.6 eV. Notably, when the fullerenes contain 4 and 6 nitrogen atoms, the force with which the nitrogen endohedral fullerenes retain the electrons is slightly greater than when encapsulating between 3 and 5 nitrogen atoms. When encapsulating between 7 and 8 nitrogen atoms, this force tends to be the same, but with 9 nitrogen atoms within the

	I	A	μ	η
$N_3@C_{70}$	7.51	4.49	−6	1.51
$N_4@C_{70}$	7.61	2.77	−5.19	2.42
$N_5@C_{70}$	7.47	4.49	−5.98	1.49
$N_6@C_{70}$	7.61	2.87	−5.24	2.37
$N_7@C_{70}$	7.54	4.56	−6.05	1.49
$N_8@C_{70}$	7.54	3.39	−5.46	2.08
$N_9@C_{70}$	7.81	1.85	−4.83	2.98
$N_{10}@C_{70}$	6.3	6.33	−6.31	−0.02

Table 3. Global reactivity indexes for Nn@C$_{70}$, where n = 7–10, obtained at B3LYP/6-311G level of theory.

fullerene, this energy increases to 7.81 eV, implying that more energy is required in order to remove an electron. Contrastingly, when there are 10 nitrogen atoms within the fullerene network, it is easier to remove an electron because the ionization potential decreases. The even/odd effect observed in the first clusters may be explained by the resistance of systems with closed shell (even number of nitrogens) to be ionized, in contrast to those with an open shell (odd number of nitrogens) that contrarily would present a greater tendency to lose an electron, resulting in a closed shell.

The odd/even behavior of endohedral fullerenes, on gaining an electron and forming a negative ion, is also reflected in electron affinity; as apparently when C$_{70}$ fullerenes encapsulate 3, 5 and 7 nitrogen atoms, the energy released is greater than when 4, 6 and 8 nitrogen atoms are caged. Notably, the energy of 8 nitrogen atoms increases to a lesser degree than 4 and 6 atoms of nitrogen. When encapsulating 9 and 10 nitrogen atoms, the sequence tends to change, because higher energy release corresponds to the 10 nitrogen structure and the lower energy release corresponds to the 9 nitrogen structure.

In terms of electronic chemical potential, endohedral fullerenes: of 4, 6 and 8 N atoms present the highest values for chemical potential, so they tend to accept electrons. Fullerenes of 3, 5 and 7 atoms have the lowest value, so they can donate electrons more easily. However, on reaching 9 and 10 atoms, the sequence changes because the isomer with 9 nitrogen atoms is the one that has the highest value of chemical potential than all other values, whereas the one with 10 nitrogen atoms has the lowest value of all.

With respect to overall hardness, there is a sequence ranging from 3 to 7 nitrogen atoms where the highest hardness values are the even numbers. These, therefore, have the greatest resistance for modifying their electronic density. The lowest hardness values correspond to the odd numbers of nitrogen atoms. At 8 nitrogen atoms, the sequence changes direction: now the odd number of nitrogen atoms is the one that presents the greatest value for global hardness, besides being the molecule that is least reactive in terms of hardness. Considering the case of N$_{10}$, this structure has the lowest hardness value. Consequently, it can modify
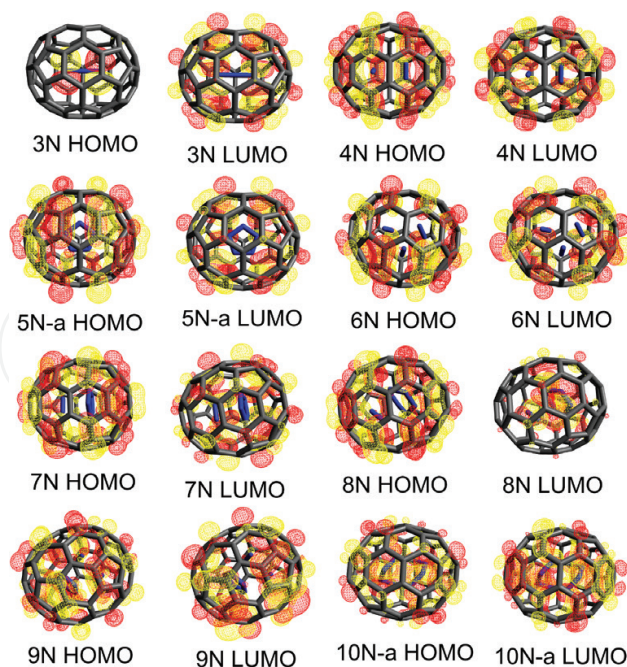
Figure 4. Frontier orbitals for $N_n@C_{70}$, where $n = 3-10$, endohedral fullerenes, calculated using the B3LYP/6-311G method.

its electronic density more easily, so that it represents the most reactive molecule. Previous results for C_{60} encapsulation [53] showed a reduced HOMO-LUMO gap, as the number of nitrogens increased: 2, 4, 6, 8, 10. This is somewhat similar to the results for hardness, as one of the approximations to this parameter is precisely the HOMO-LUMO gap (**Figure 4**).

3.3. Analysis of frontier orbitals

Previous studies have mentioned that from 2 to 10 nitrogen atoms, there would be a charge transfer from the C_{60} cage to the nitrogen polymer, explained as resulting from the greater ionization and electronegativity potential of N compared to C. For more than 10 nitrogen atoms, there would be a reverse transfer from the nitrogen to the carbon atoms. This was attributed to reduced space availability and overlapping of orbitals [53]. In this work, the frontier orbitals of the most stable structures were analyzed, showing that there is an appreciable contribution from frontier orbitals to the nitrogen atoms. This implies that there must be areas susceptible to receiving charge density. It is especially interesting that when the number of N atoms within the fullerene increases, the contribution of Nitrogen-centered orbitals for LUMO is even greater. Particularly, in the case of N_8 and higher systems, a very considerable contribution of HOMO is observed, and a sure indication that possible interactions with the cage are initiating. This may also relate to the suggestion that greater interaction between the cage and the N_n takes place, as the amount of nitrogen atoms increases. The reaction energy may also result from this, particularly as it is apparent that from N_3 to N_7 there is a more or less constant increase of 150 kcal/mol in stabilization energy. This reaction energy changes with N_8 and higher, suggesting greater participation on the part of the cage and its interaction with N_n.

4. Conclusions

The C_{70} fullerene is viable for storage and stabilization of nitrogen aggregates of at least 3–10 atoms, without presenting any concurrent structural deformation in the carbon network or obvious interaction (bond-like) between the nitrogen atoms and the carbon of the fullerene.

Evidently, the formation energy from the isolated nitrogen atoms is favored in all cases and from N_3 to N_8 there is a progressive increase, indicating the role of the cage as an encapsulator and stabilizer of polynitrogenous structures. When we propose the formation of endohedral fullerenes, initiating with materials that can be found under laboratory conditions, we predict that metastable structures will form, a fact that may be of interest in the potential use of these materials as HEDMs. The stabilizing contribution of the cage becomes more evident, as the number of nitrogen atoms within it increases, manifested in a considerable contribution on the part of frontier orbitals as potential charge stabilizers.

As C_{70} fullerene is a large molecule of approximately 1 nm diameter, nitrogen, polymers of 3–7 nitrogen atoms prefer to remain as nitrogen molecules or as azides. However, from 8 atoms onwards, the fullerene cage begins to have greater interaction with the nitrogen polymers, reflected in the fact that these begin to compact and create more complex nitrogen polymers (in the form of rings).

According to indexes of global chemical reactivity, endohedral fullerenes present an odd/even behavior that corresponds to that expected for open layer species (odd number of electrons: lower ionization potential and hardness, greater electronic affinity and chemical potential) and closed layer (even number of electrons: greater ionization potential and hardness, lower electronic affinity and chemical potential). However, for 8, 9 and 10 encapsulated nitrogen atoms, there is a change in behavior. This coincides with the change in formation energies and the analysis of frontier orbitals, reflecting greater participation of the cage in fullerene behavior. The fact that smaller fullerenes have been able to encapsulate more atoms is an indication that the point of saturation in this structure has not yet been reached, providing an incentive to find new structures with greater complexity, as the degree of encapsulation progresses. These would thus constitute candidates for energetic materials and studies are ongoing.

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