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Confinement of the Pentanitrogen Cation Inside Carbon Nanotubes

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Abstract. In recent years, the field of polynitrogen chemistry has seen a sparking activity, with new outstanding theoretical and experimental results. Polynitrogen clusters are excellent candidates for high-energy density materials, but their intrinsic instability poses great challenges for the synthesis and the subsequent storage. In this work, we explore by means of quantum chemical calculations the confinement of the pentanitrogen cation, N_5^+ , inside carbon nanotubes of different diameters. The interaction of the two fragments is such that a charge transfer from the nanotube to the nitrogen cation occurs and leads to the subsequent decomposition of N_5^+ , thus resulting in an overall unstable system. Nonetheless, preliminary results on the confinement of the neutral N_8 chain (as the product of an $N_5^+ + N_3^-$ addition) are presented, where it is shown that the encapsulation decreases the overall energy of the complex system. Two stable N_8 isomers are discussed and a first investigation on possible decomposition pathways is carried out.

Keywords: Carbon Nanotubes, HEDM, Molecular Confinement, Polynitrogen, Pentanitrogen Cation

1 Introduction

Probably the most peculiar property of nitrogen is the incredible energy difference between single, double and triple bond[1]. Three times the energy of a single bond corresponds to less than half of the energy of a triple bond; thus it should not come as a surprise that nitrogen exists naturally only in its molecular form. Single- and double-bonded polynitrogen (PN) clusters contain a huge amount of energy and have been proposed as possible high-energy density materials (HEDM)[1, 2]. Additionally to their potential to store energy, they have an innocuous effect on the environment, since decomposition of pure nitrogen

clusters usually leads to the release of N_2 only.

The N_3^- azide anion was the first pure nitrogen molecule experimentally synthesized in a lab[3] and after this achievement in 1890, it took more than a century before the pentanitrogen cation N_5^+ was successfully isolated in 1999 by Christe and coworkers[4]. Since then, an incredible amount of work has been done trying to predict new stable species entirely composed by nitrogen as HEDM candidates.

Many theoretical and partly experimental investigations focused on possible pure nitrogen salts composed by the ions N_3^- , N_5^+ and N_5^- [5–10]. Other groups focused more on the possibility to either synthesize new PN molecular crystals or identify novel molecular nitrogen phases[11, 12], both of which are often attainable only under extreme conditions. Most notably, the cubic gauche polymeric nitrogen form was successfully synthesized a few years ago under very high temperature and pressure[13].

In recent years, different PN clusters and molecular crystals were theoretically predicted and some were experimentally obtained [14–20]. In 2017, two main achievements renovated once again the interest in the field, namely the isolation and characterization of *cyclo*- N_5^- pentazolate[21] and the synthesis of the cubic gauche form of nitrogen under near-ambient conditions[22].

Despite the recent successes, other ways to stabilize (and hopefully store) single- and double-bonded PN clusters were proposed too, in particular molecular confinement. For the latter approach, carbon nanomaterials such as fullerenes, carbon nanotubes (CNTs) and graphene layers appear as ideal candidates. By spatially confining PN clusters inside the cavity of such materials, thanks to less geometrical freedom as well as non-bonded interactions with the hosting system, the guest fragments may be favorably stabilized and stored. First investigations in this direction have proposed the encapsulation of nitrogen chains inside carbon nanotubes and have theoretically predicted, as well as later experimentally observed, the feasibility of this approach[22–27]. Besides carbon nanotubes, other types of carbon nanostructures as well as other nanomaterials have been proposed as valid alternatives[28–32].

In this work, we extend our previous contribution[33] in which we studied the confinement inside carbon nanotubes of the simplest PN cluster, the azide anion, by investigating the second-longest experimentally accessible PN compound, the pentanitrogen cation. Furthermore, we discuss preliminary results on a more challenging system: an encapsulated molecular N_8 chain confined inside a (5, 5) CNT.

The article is organized as follows: the next Section lists the computational details of the calculations carried out in this study. In the Results Section, we firstly present and discuss the main findings regarding the pentanitrogen cation, and secondly, we include some preliminary results regarding the encapsulation of N_8 . Finally, in the Conclusions Section, we highlight the main achievements of this work and briefly outline the aim of this research.

2 Computational Details

Carbon nanotubes used in this work were treated as finite-size systems, with addition of hydrogen atoms at the two ends in order to saturate the dangling carbon atoms. Two classes were considered, namely zigzag nanotubes with helical indices $(n, 0)$ and armchair nanotubes with helical indices (m, m) . In the case of $(n, 0)$ CNTs, n was chosen equal to 8, 10 or 12, while for armchair nanotubes, the values of m considered were 4, 5 or 6. This choice of indices provided CNTs with a diameter in the range comprised between 6.26 Å and 9.40 Å. The length of the nanotubes was ≈ 13.57 Å for zigzag and ≈ 15.43 Å for armchair CNTs, respectively.

The fragment geometries used in the unrelaxed interaction energies calculations were optimized using density functional theory (DFT), employing the Becke exchange energy functional[34, 35] and the Lee-Yang-Parr correlation energy functional[36] (B3LYP). The CNTs were optimized for the lowest electronic state at this level of theory, namely the triplet and singlet state for zigzag and armchair nanotubes, respectively. The polynitrogen molecules were minimized for the closed-shell singlet state.

On the other hand, calculations involving N_8 as well as the relaxation of any complex systems, were carried out using the APFD density functional[37], which will be discussed directly in the Results section.

In all calculations, the double- ζ 6-31G basis set[38] was used for hydrogen and carbon, while diffuse and polarization functions were added for nitrogen (6-31+G*). Interaction energies presented in this work were corrected for the basis set superposition error using the counterpoise correction scheme introduced by Boys and Bernardi[39]. The single point energies involving the pentanitrogen cation were calculated either by second-order Møller-Plesset perturbation theory (MP2) or second-order n -electron valence perturbation theory (NEVPT2)[40–42], while the preliminary study on N_8 was carried out entirely using DFT. The need for multireference perturbation theory (NEVPT2) resulted necessary for zigzag nanotubes, which similarly to other low-dimensional zigzag hydrocarbons have a ground state of open-shell character. Reference wavefunctions for calculating NEVPT2 energies were obtained using the complete active space self-consistent field (CASSCF) method[43]. The active space used was that of 10 electrons in 10 molecular orbitals, all belonging to the carbon nanotube.

All calculations in this contribution were carried out using either the 2015.1 version of the MOLPRO program package[44, 45] or the Gaussian09 software, version D01[46]. Natural population analyses (NPA)[47] were performed using the NBO program version 3.1[48] bundled in the Gaussian09 software, while all figures including molecular structures were generated using the Avogadro program[49].

3 Results

The first approach of this study consisted in the calculation of unrelaxed interaction energies between the N_5^+ cation confined inside different carbon nanotubes,

where the N_5^+ was placed in the middle of the nanotubes, from both the edges and the wall. The computed values are plotted in Figure 1 as a function of the CNTs diameter. For all nanotubes except the smallest (4,4) one, the energy is

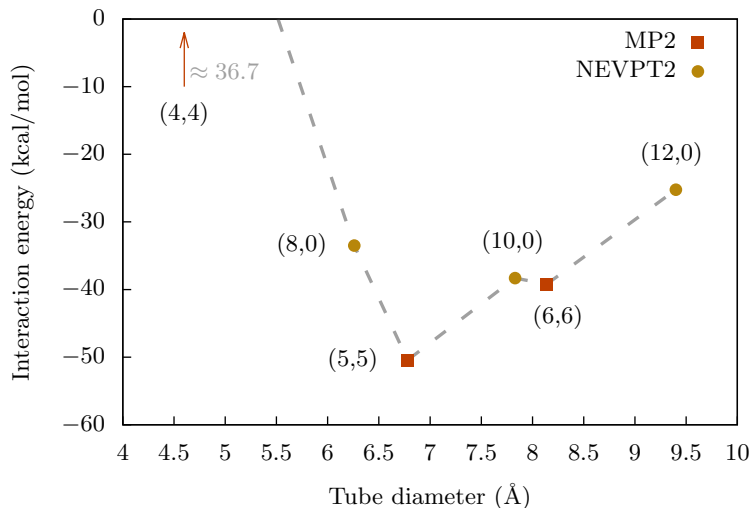


Fig. 1. Unrelaxed interaction energies as a function of the CNT diameter

negative, thus suggesting a favorable interaction between the two fragments. The magnitude of the interaction appears to be independent from the helicity of the CNT and to relate only to the diameter of the latter. This is due to the distance of the confined species from the nanotube wall. The small bump observed for nanotubes (10,0) and (6,6) is most likely due to the different methodologies applied to obtain the energies.

In the case of armchair nanotubes, the ground state of the complex system is a closed-shell singlet state, thus allowing the account of relaxation effects by performing a geometry optimization using restricted DFT. This is not the case for zigzag nanotubes, where a multireference approach is strictly required, since broken-symmetry DFT fails to accurately describe the electronic structure of the ground state. Luckily, the most favorable interaction is observed for the (5,5) CNT, with a value of -50.44 kcal/mol. Thus, we have relaxed the $N_5^+@CNT(5,5)$ system using DFT in combination with the APFD exchange and correlation functional[37]. One of the shortcomings of DFT is the inability of accurately describing long-range dispersion effects by means of standard GGA or hybrid density functionals. In recent years, different schemes to solve these problems have been devised and the APFD functional was designed with this goal in mind. In particular, dispersion effects are accounted for from an empirical dispersion scheme based on spherical atom dispersion terms. In our previous

study, we have observed a good performance of the APFD functional, especially the ability to accurately reproduce MP2 interaction energies[33]. Surprisingly, the relaxation process led to the breaking of the N_5^+ compound confined in the nanotube. The decomposition process happens barrierless, as can be seen from Figure 2, where the relative energies and a few intermediate geometries of the PN species are depicted. In order to ensure the bond breaking was not an

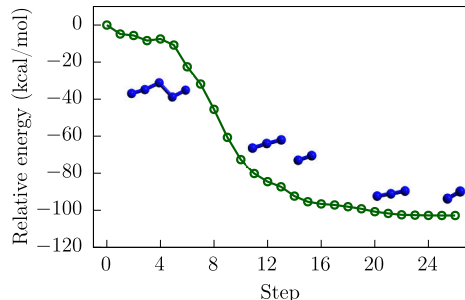


Fig. 2. Relative energies w.r.t. step zero during the relaxation process. Geometries at steps 7, 11 and 26 are depicted along the curve without the surrounding nanotube for better representation.

artifact due to the choice of functional, the optimization was repeated with the B3LYP density functional with inclusion of the D3 dispersion scheme[50]. Also in this case however, the result was the same with the breaking of the confined guest system happening barrierless.

Additional to the system $N_5^+@CNT(5, 5)$, the relaxation using the APFD functional was performed on the smaller (4, 4) and larger (6, 6) CNTs, respectively. In both cases, the confined cation breaks again after a few optimization cycles, leading to final conformations exemplified by Figure 3 for one of the two nanotubes.

In order to investigate the nature of the bond breaking, we performed a series

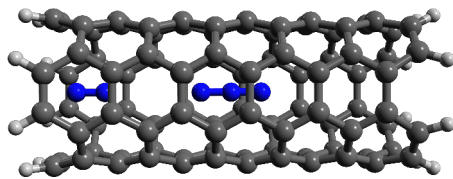


Fig. 3. Final structure of $N_5^+@CNT(4, 4)$

of natural population analyses of the APFD electron density. The analysis of the N_5^+ cation in gas phase assigned the partial atomic charges according to

Figure 4. The molecule is symmetric and belongs to the C_{2v} molecular point

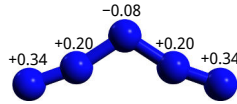


Fig. 4. Partial atomic charges of the N_5^+ cation in gas phase

group and thus its charge distribution is symmetric with respect to the central nitrogen atom. By repeating the NPA on the nitrogen cation confined inside the (5,5) CNT before the geometry relaxation, a significantly different charge distribution appears, as can be seen in Figure 5. Note how only the partial

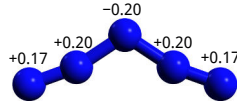


Fig. 5. Partial atomic charges of the N_5^+ cation confined inside the cavity of a (5,5) CNT

charges of the two external atoms as well as the central one are affected, because of their vicinity to the nanotube wall. The total sum of the partial charges on the N_5^+ is 0.57, implying a (partial) charge transfer from the nanotube to the cation.

A third and last NPA on the fully relaxed geometry revealed that after bond breaking, an even larger charge transfer occurred and a total of two electrons were given by the nanotube to the nitrogen species. Figure 6 shows the partial charge distribution of the two (nitrogen) fragments, where the total charge on the N_3 fragment is virtually minus one, while that of N_2 is approximately zero. The double electron transfer is most likely the trigger of the dissociation hap-

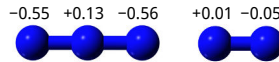


Fig. 6. Partial atomic charges of the decomposed fragments after relaxation inside the cavity of a (5,5) CNT

pening inside the cavity.

It was shown in a previous work[10] that the N_5^\bullet radical species dissociates barrierless into the products N_3^\bullet radical and neutral N_2 . In order to be sure that this decomposition is described correctly by our methodological approach, we

successfully reproduced the dissociation using the APFD functional.

For the first electron transfer from the CNT to the N_5^+ to occur, the electron affinity (EA) of the pentanitrogen cation has to be larger than the ionization potential (IP) of the carbon nanotube. The IP of a hydrogen-terminated (5,5) CNT was studied by Buonocore *et al.* [51] and estimated to be between 4.2 and 5.2 eV depending on the approach used to compute it. The (vertical) electron affinity of N_5^+ on the other hand, is obtained in this work according to the formula $EA = E(N) - E(N + 1)$, where N stands for the number of electrons and $E(N)$ and $E(N + 1)$ are total electronic energies computed at the geometry of the system with N electrons. The value calculated for N_5^+ using the APFD functional is 6.37 eV, thus resulting in an estimated difference between the EA of N_5^+ and the IP of CNT(5,5) in the range ≈ 2.17 – 3.17 eV. Although this is just a qualitative result, it proves how it is energetically favorable for the nanotube to transfer an electron to the cation, triggering the decomposition reaction. Therefore, we argue that there would not even be the necessity for the second electron transfer in order for the bond breaking to occur. Note that the charge transfer could be in principle influenced by the finite-size model of the CNT used in this work, since the IP depends on the length of the system. However, in Ref. [51] it is shown that the CNT IP decreases as a function of the length of the tube, thus in the limit of an infinite nanotube, the transfer would be even more favored by the smaller IP. Consequently, we argue that by modeling the CNT using periodic boundary conditions, the first electron transfer would be observed as well, initiating the decomposition of N_5^+ . Finally, to understand the second charge transfer process, an argument based on EA and IP is certainly harder to make as it is not known a priori at which moment of the reaction the transfer occurs and it would require a more detailed study which goes beyond the scope of this investigation.

A possible way to avoid the electron transfer process and the subsequent decomposition, is the encapsulation into the cavity of a counterion together with N_5^+ , such that the interaction between the two confined species is stronger than that of the cation with the CNT. A possible candidate is the azide anion, which is proven to be favorably confined inside carbon nanotubes[33]. Moreover, the reaction $N_5^+ + N_3^- \rightarrow N_8$ was extensively studied by Fau and Bartlett showing all possible reaction pathways in gas phase[7].

In that work, the authors have come to the conclusion that linear isomers of molecular N_8 are not stable at ambient conditions due to low activation barriers leading to dissociation. In particular they suggested that the lattice energy of a crystal made by N_5^+ and N_3^- ion pairs could increase sufficiently the barriers and make N_8 stable. In 2014, a crystal structure for the N_8 molecule was theoretically predicted by DFT calculations to be stable at ambient conditions, although not composed by the ion pair, but instead by a combination of the linear isomers[14]. Here, we present some preliminary results on the confinement of two N_8 linear isomers inside the cavity of a (5,5) carbon nanotube. From the different stable isomers identified in Ref. [7], we consider in the following only the EEE and

EZE conformers (adopting the same nomenclature of Ref. [7]) represented in Figure 7, as they appear particularly suited for confinement inside CNTs due to their linear structure. For both isomers, there are two possible decomposi-

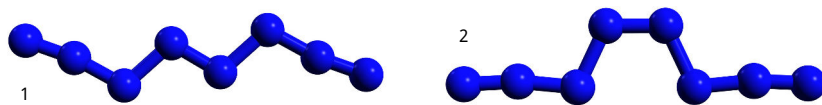


Fig. 7. Two stable N_8 isomers, (1) the EEE conformation and (2) the EZE conformation

tion pathways: in one case a terminal N_2 molecule detaches from the chain and produces $N_6 + N_2$, while in the second case, both external N_3 fragments simultaneously break away from the central nitrogen atoms, resulting in $2N_3 + N_2$. The scheme in Figure 8 graphically depicts the relative electronic energies of the various conformers calculated in gas phase using the APFD functional. The structures depicted correspond to the EZE isomer only, but are representative for the EEE conformer too. The electronic energy difference between the two

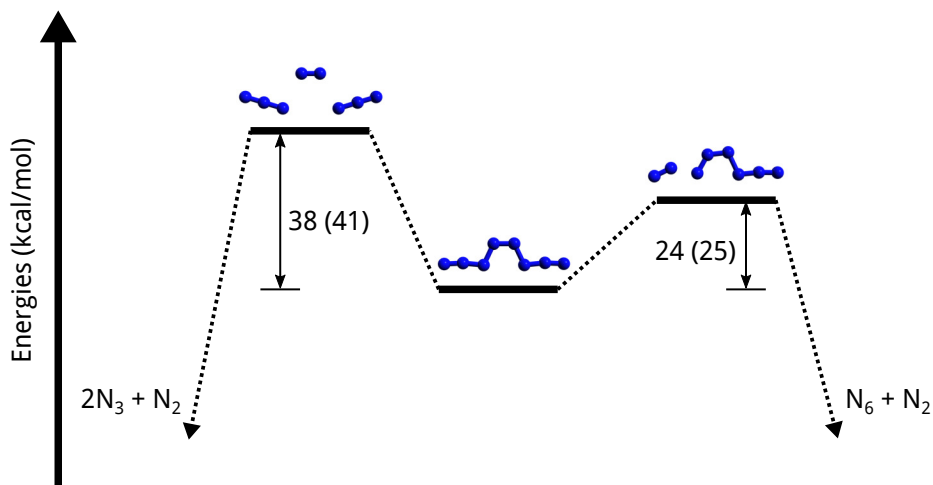


Fig. 8. Potential energy surface of the N_8 decomposition pathways in gas phase. Molecules and numbers depicted correspond to the EZE conformer, while the values in parenthesis refer to the EEE conformer.

stable isomers is within 1 kcal/mol and, as can be seen from Figure 8, the activation energies for the decomposition reactions are similar for both the EZE and the EEE conformations (numbers in parenthesis).

Proceeding as in the first part of this contribution, we computed the interaction energies of both isomers confined inside a (5,5) CNT, after a geometry relaxation of the entire system. The computed energies for the EEE and the EZE isomers are -42.48 kcal/mol and -37.34 kcal/mol, respectively, both showing a clear favorable interaction. Subsequent frequency calculations ensured that both structures are true minima of the potential energy surface and thus stable states. A notable effect of the nanotube on N_8 can be appreciated by the energy difference of the two isomers when confined in the cavity. From a difference of less than 1 kcal/mol, the EEE conformation is now more stable than the EZE conformation by 5.27 kcal/mol.

For both stable conformations, the transition state structures (Figure 9) of the two known decomposition pathways in gas phase (as illustrated for EZE in Figure 8) were confined inside the carbon nanotube with the aim to investigate if the gas phase transition states remain such when confined in the CNT. If that is the case, we are interested in the activation energies to undergo decomposition. Preliminary results suggest that not all the transition states depicted in Fig-

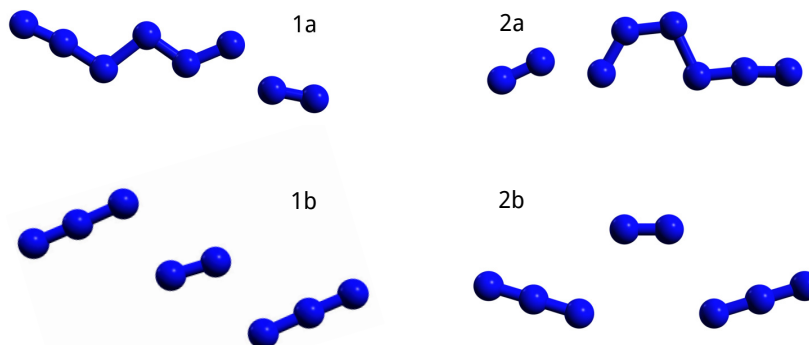


Fig. 9. Transition state structures of the decomposition reactions in gas phase for (1) the EEE conformer and (2) the EZE conformer

ure 9 are still valid inside a (5,5) CNT. Of the four structures shown in Figure 9, only (1a) appears to be a transition state. This is probably due to the more linear conformation (with respect to the other three geometries) which might “fit” better in the cavity, such that the molecule does not undergo a large distortion. Such an interpretation is valid also for the stable isomers, as the EEE conformer, being slightly more “linear” than the EZE one, is favored by approximately 5 kcal/mol over the EZE structure. We argue that steric effects are likely to play a crucial role in favoring certain isomers over others, selectively closing certain reaction pathways and possibly giving rise to new stable and metastable structures otherwise not existing in gas phase.

Nonetheless, on the base of these preliminary results only, it is yet not possible to make definitive conclusions, and a full exploration of the potential energy

surface for the different reactions inside carbon nanotubes still has to be carried out.

4 Conclusions

In the present contribution we studied the confinement of the pentanitrogen cation inside carbon nanotubes by means of high level quantum chemical calculations. A combination of wave function methods and density functional theory was used to obtain interaction energies, relaxation effects and allowed for a charge distribution analysis, based on natural bond orbitals. It is shown that, despite favorable unrelaxed interaction energies between N_5^+ and carbon nanotubes, a charge transfer from the host system to the guest cation is responsible for triggering the decomposition of the latter into the azide anion and molecular nitrogen. As previously shown in the literature[10] and confirmed here, a single electron is enough to initiate the barrierless decomposition of the pentanitrogen cation. Such a transfer initially occurs because the electron affinity of N_5^+ is larger than the ionization potential of the carbon nanotube. This process eventually leads to a second charge transfer, in which the intermediate N_3 radical gains a second electron from the nanotube, resulting in $N_3^- + N_2$.

A possible way to circumvent the decomposition, is the addition of a counterion in the cavity, which might stabilize N_5^+ . To this end, we presented preliminary results of the encapsulation of N_8 inside a (5, 5) CNT, as a possible result of the reaction $N_3^- + N_5^+ \rightarrow N_8$. We have not yet explicitly considered the reaction, but instead have investigated if the possible N_8 product is favorably hosted in the cavity of the carbon nanotube.

Preliminary results show that two linear isomers of N_8 stable in gas phase are stable inside the nanotube too, with favorable interaction energy. Moreover, the relative energy difference between the two isomers is slightly increased by few kcal/mol. The transition states of two decomposition pathways existing in gas phase were considered, suggesting that not all of them remain valid when confined. The results so far obtained for N_8 appear to be explicable in terms of geometric effects, where the “more” linear EEE isomer is more stable than the EZE isomer. A similar argument is valid for the transition states too.

Despite being still an ongoing research, these findings suggest that steric effects due to the restricted space available in the cavity can close certain reaction pathways and favor certain isomers over others. The diameter of the nanotube could be used as a tunable parameter providing fine control on the encapsulated molecule. In particular, the aim is to either increase the activation energy or even close the reaction pathways leading to decomposition of N_8 , thus favoring selected isomers inside the cavity. The final goal of this research is to propose alternative ways to store polynitrogen molecules without recurring to extreme conditions. Still, one has to face the problem of producing the stable PN system in the first place, but also in this case, CNTs can serve the purpose and perform as a nanoreactor.

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