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Augmentation of the lifetime of cyclo[18]carbon accustomed to carbon nanotube and zeolite

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Abstract

Recently synthesized cyclo[18]carbon which is characterized as polyynes D_{9h} has a very short lifetime even at 5K temperature. Its automerization is proposed through a transition state which is reported as a D_{18h} symmetric cumulene. In the present article, an experimentally viable method for the enhancement of the lifetime of this compound is reported. The carbon nanotube is employed for this purpose. We also report that adopting numerous molecules of cyclo[18]carbon in the womb of a zeolite cage, wire-like countenance construction is feasible.

Keywords: Cyclo[18]carbon; Carbon nanotube; Zeolite-Y; Hartree-Fock; Coupled Cluster

1. Introduction

Cyclo[18]carbon[1-5] is the 1st sp-hybridized carbon allotrope which is synthesized by Kaiser et. al.[2] and then characterized by several research groups [3-5]. Though, at present, its application in material science or in any other field of research is not translucent. Of course, there is monstrous prospect of its impersonation, in assorted areas of material science, synthetic chemistry and energy materials [5-8]. It is lamentable that presently synthesized cyclo[18]carbon which is formulated on bilayer NaCl on Cu(111) at 5K temperature by using atom manipulation technique, has a very short lifetime. But, for its fecund embodiment in versed technology, we have to synthesize it in such a fashion that it should subsist for usable finite time. To reach this destination, we embed it with carbon nanotube (CNT) and zeolite.

Cyclo[18]carbon was first predicted by Hoffmann in 1966 [9] which was pursued by appreciable theoretical and experimental studies [2,10-21]. The density functional theory (DFT) [18] and Møller-Plesset perturbation theory (MP) [19] computation reported that the lowest energy state of cyclo[18]carbon is of cumulenic D_{18h} symmetry where all carbon atoms are sp² hybridized and all carbon-carbon bonds are the double bonds. Contrary to this, the ground state optimized geometry of cyclo[18]carbon at the Hartree-Fock [12] and Coupled Cluster (CC) [13] level of theory prognosticate the presence of all sp hybridized carbon which are attired in an alternative single and triple carbon-carbon bonds. A high-level Monte Carlo computation [20] endorses the upshot of the Hartree-Fock and CC results i.e. a polyynes D_{9h} symmetric structure of cyclo[18]carbon which is equiponderate with the experiment [2].

Subsequent theoretical exploration by Nandi et. al. [5] after the experimental synthesis of cyclo[18]carbon, point out that though the ground state symmetry is D_{9h} , it should experience an automerization between two respective geometries through a cumulenic D_{18h} state. Nandi et. al. denominated this state as a "Transition State". A similar conclusion is made by Glib et. al.[4] also. But, we expostulate this presumption because a true transition state should

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have only one imaginary mode of vibration along with the bond breaking or bond making. Thus, there would not be cumulenenic D_{18h} symmetry. Contrariwise, DFT and MP computation substantiated that the cumulenenic D_{18h} symmetric state of cyclo[18]carbon is an optimized state on the potential energy surface with all positive modes of vibration [18,19]. Henceforth, we may conclude that the cumulenenic D_{18h} symmetric state is the geometric excited state of cyclo[18]carbon. According to Nandi et. al., this excitation energy is 9.6 kcal/mol. This energy barrier is quite high enough as the experiment is performed at 5K. Thus, automerization would be practically possible through quantum tunneling only which is smeared in the reported article by Nandi et. al.

1.1. Computational details

In the present work all these calculations are done using Gaussian 09 package [22]. Since Hartree-Fock calculation able to reproduce the correct geometry of cyclo[18]carbon [12], i.e. alternate single and triple carbon-carbon bond as reported by Kaiser et. al. [2]. We perform all our calculation at Hartree-Fock level of theory. Due to the computation limitation we used 6-31G basis for our calculation. The calculations regarding Zeolite-Y alpha cage, the structure of the zeolite frame was set to freeze using oniom. Optimized geometries are verified with frequency check. Optimization criteria are not changed from the default values. Single-layer of CNT (truncation is done with hydrogen atom) with different core sizes (carbon numbers are 32, 36 and 40 respectively) are chosen for our study.

2. Results and discussions

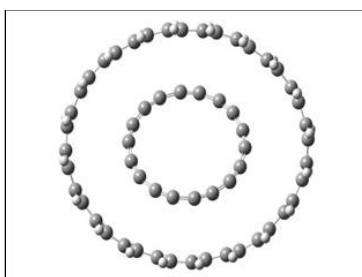


Figure 1 Optimized geometry of cyclo[18]carbons inside CNT.

It is observed that the CNT of 40 carbon atom is capable of appropriate stabilization. Both CNT and cyclo[18]carbon rings are co-centric, though, there is an angle between their molecular planes. The optimized geometry of this system is presented in **Figure-1**. For smaller cavity CNT, cyclo[18]carbon ring moves outside of CNT. The single carbon-carbon bond is shorter than normal C – C bond while carbon-carbon triple bond is nearly the same as an ideal triple bond.

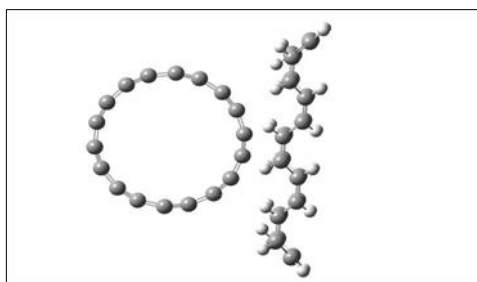


Figure 2 Optimized geometry of cyclo[18]carbons inside of 32 carbon mono-layer CNT

When 32 carbon mono-layer CNT is used as the host container it is observed that cyclo[18]carbon ring moves out of the CNT cavity (**Figure-2**). Similar is true for 36 carbon mono-layer CNT (**Figure-3**). The only difference between them is the orientation of the molecular plane of cyclo[18]carbon and CNT. For 32 carbon CNT, cyclo[18]carbon ring plane is perpendicular to the CNT cavity plane. But, in case of 36 carbon CNT, the angle between these planes are very small. Thus, we have chosen 40 carbon CNT and found that both the planes are parallel. In computational chemistry, stabilization energy of a system is calculated as a measure of the difference of energy between the composite system and the components. But, here we are not interested to compute the overall stability of the system i.e. the composite system of cyclo[18]carbon within the cavity of CNT or zeolite. Of course, the composite system is stabilized. We want to calculate how much the cyclo[18]carbon ring get extra stabilization which is important because this stabilization energy is related to its real existence. The more it will stabilize, the more the chance of its real existence and technological implementation. For this purpose, we optimized cyclo[18]carbon without any host (let energy of this is E_{c18}^{bare}) and

then inside the host at the same level of theory and basis. After the optimization of cyclo[18]carbon inside a host we just remove the host without disturbing the ring. Now we calculate the energy of the ring at the same level of theory without any optimization (let energy of this cyclo[18]carbon ring is $E_{c18}^{encased}$). Thus, according to our consideration, the stability of the cyclo[18]carbon due to the encapsulation is given as

$$E_{c18}^{stabilization} = E_{c18}^{encased} - E_{c18}^{bare} \quad (1)$$

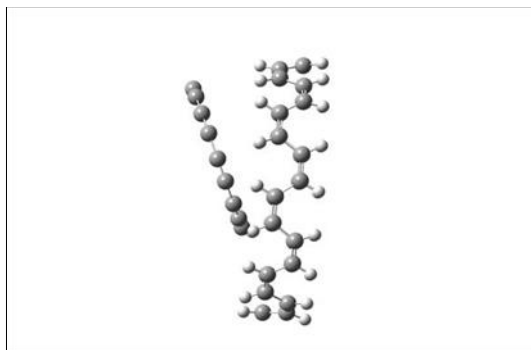


Figure 3 Optimized geometry of cyclo[18]carbons inside of 36 carbon mono-layer CNT

Here we want to emphasize again that $E_{c18}^{stabilization}$ is stability of the ring only which is different from the total stabilization of the system due to encapsulation. This is illustrated in **Figure-4**. We found that in both the C_{18} rings, all single bonds and triple bonds are equivalent. But, the encapsulated ring has the shorter single bonds as well as the shorter triple bonds. The values for the bare ring are 1.37Å (single bond) and 1.21Å (triple bond) while the encapsulated ring has 1.36Å (single bond) and 1.12Å (triple bond) respectively.

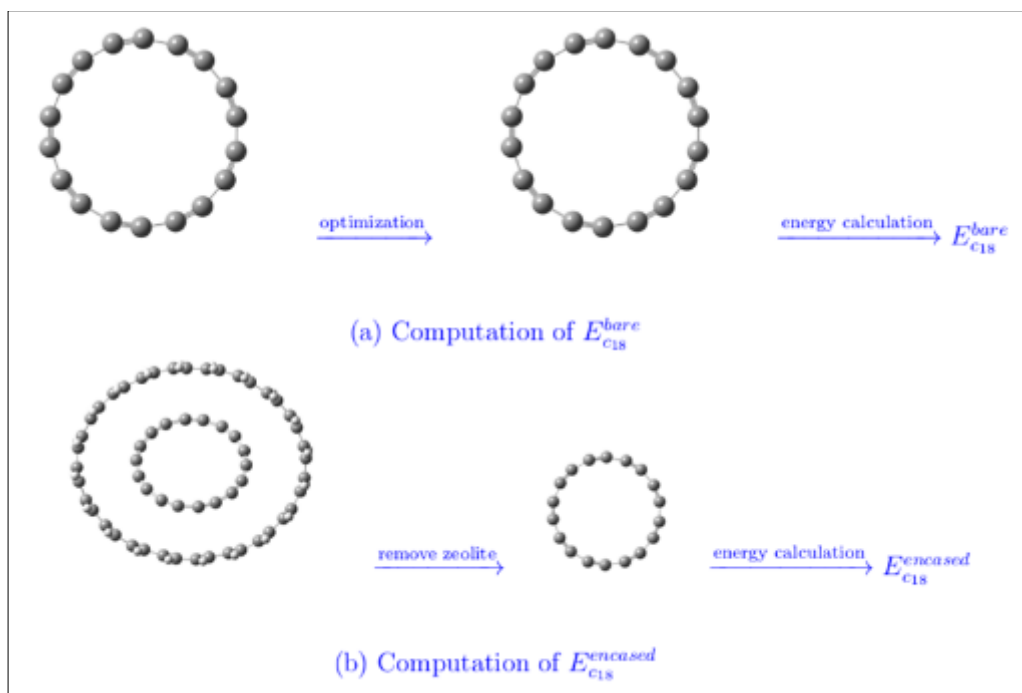


Figure 4 Calculation of molecular stabilization of cyclo[18]carbon due to encapsulation

The extra stabilization energy of strung cyclo[18]carbon inside the chosen CNT is -1.05 kcal/mol. Thus, if the synthesis is steered in an apposite CNT, it is prospective that the lifetime of cyclo[18]carbon would be prolonged. Now the question is, why encapsulation gives rise extra stabilization? Is there any orbital overlap between CNT and cyclo[18]carbon? We have also investigated this. So far we observed that there is no orbital overlap between CNT and cyclo[18]carbon ring. All occupied orbitals are located over either on the CNT ring or on the C_{18} ring. Two such orbitals are presented in **Figure-5**. We found that HOMO of the composite system is completely located over the CNT back-bone.

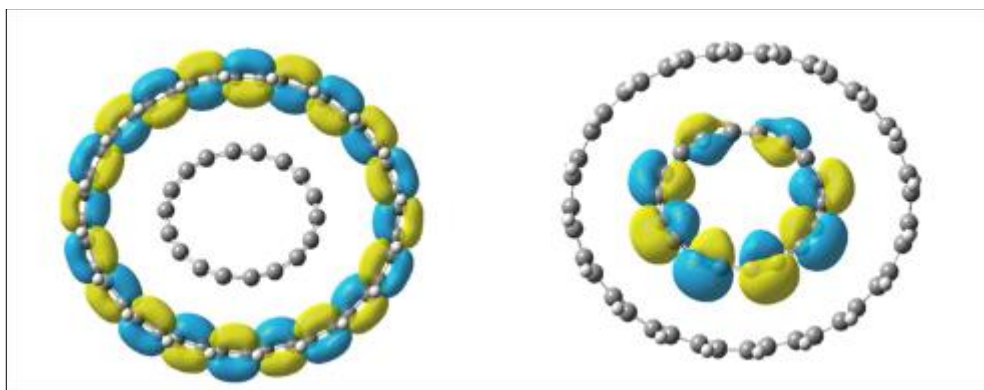


Figure 5 Orbital picture of (a) highest occupied orbital located over CNT and (b) highest occupied orbital over cyclo[18]carbon ring.

Unfortunately, the imposition of cyclo[18]carbon in the womb of an alpha cage of zeolite-Y destabilizes it. Though, the destabilization energy is minimal, 0.14 kcal/mol. But, it is possible to make a wire-like countenance with two untrammelled cyclo[18]carbons at the interior of the excavation of zeolite cage recherche in this perusal. The optimized geometry is presented in **Figure-7** (a). Conversely, analogous wire-like gestalt is not possible for CNT (see **Figure-7** (b)). It may be due to the lack of a strong confinement effect.

The stability computation of cyclo[18]carbon within the alpha cage of zeolite-Y is per-formed with 6-31G basis employing Gaussian 09 at the Hartree-Fock level. Here, the crystal structure of zeolite-Y is taken from the crystallographic database which is kept unchanged during the optimization process. As mentioned before, wire formation with cyclo[18]carbons is possible when it is placed amidst the zeolite core.

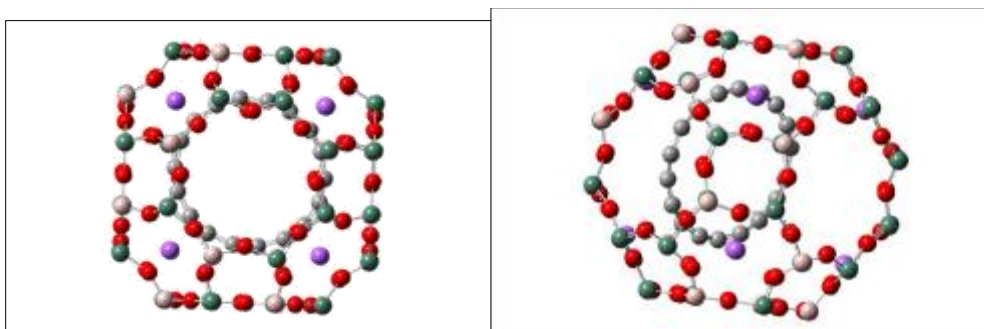


Figure 6 Optimized geometry of cyclo[18]carbon inside the alpha cage of zeolite-Y from two different view point.

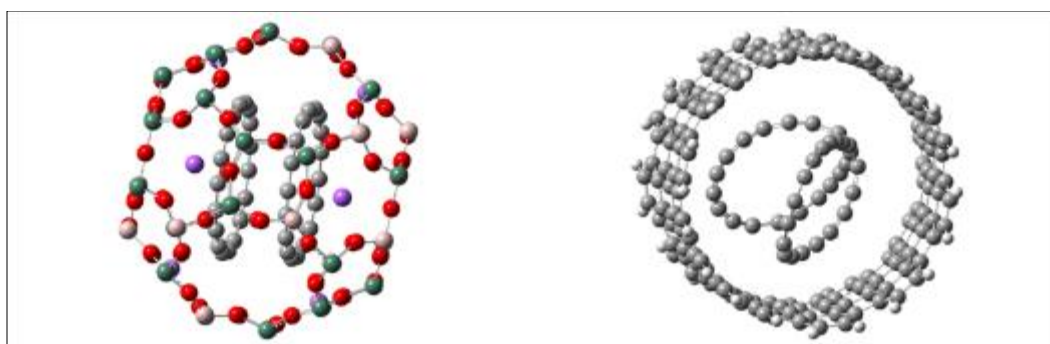


Figure 7 Optimized geometry of two untrammelled cyclo[18]carbons (a) inside the alpha cage of zeolite-Y (b) inside CNT.

3. Conclusion

In this work, we have tried to propose a proper way to synthesize cyclo[18]carbon such that its existence in room would be possible, through DFT calculation. We have also prescribed how wire formation may be possible. Thus, this annotation should enlighten the infliction of cyclo[18]carbon in future technology. Present work of molecular engineering of cyclo[18]carbon with CNT and zeolite as the host is lucrative and prudential. This contrivance for augmentation of the lifetime of cyclo[18]carbon may foster diversified researchers in various fields of theory and experiment.

Compliance with ethical standards

Disclosure of conflict of interest

No conflict of interest to be disclosed.

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