Augmentation of the life time of cyclo[18]carbon accustomed with carbon nanotube and zeolite

Wahida Rahaman, † and Arijit Bag*, ‡

Department of Chemical Sciences, Indian Institute of Science Education and Research Kolkata, 741246, West Bengal, India, and Department of Applied Sciences, Maulana Abul Kalam Azad University of Technology, Simhat, Haringhata, 741249, West Bengal, India

E-mail: bagarijit@gmail.com

Recently synthesized cyclo[18]carbon which is characterized as polyyne $D_{9h}$ has a very short lifetime even at 5 K 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.

*To whom correspondence should be addressed
†Department of Chemical Sciences, Indian Institute of Science Education and Research Kolkata, 741246, West Bengal, India.
‡Department of Applied Sciences, Maulana Abul Kalam Azad University of Technology, Simhat, Haringhata, 741249, West Bengal, India
Cyclo[18]carbon is the 1st sp-hybridized carbon allotrope which is synthesized by Kaiser et al.\textsuperscript{1} and then characterized by several research groups.\textsuperscript{2–4} Though, pro tempore, 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.\textsuperscript{4–7} It is lamentable that presently synthesized cyclo[18]carbon which is formulated on bilayer NaCl on Cu(111) at 5 K 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\textsuperscript{8} which was pursued by appreciable theoretical and experimental studies.\textsuperscript{1,9–20} The density functional theory (DFT),\textsuperscript{17} Møller-Plesset perturbation theory (MP)\textsuperscript{18} computation reported that the lowest energy state of cyclo[18]carbon is of cumulenic $D_{18h}$ symmetry where all carbon atoms are $sp^2$ 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\textsuperscript{11} and Coupled Cluster (CC)\textsuperscript{12} 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\textsuperscript{19} endorses the upshot of the Hartree-Fock and CC results \textit{i.e.} a ployyne $D_{9h}$ symmetric structure of cyclo[18]carbon which is equiponderant with the experiment.\textsuperscript{1}

Subsequent theoretical exploration by Nandi \textit{et. al.}\textsuperscript{4} 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 \textit{et. al.}\textsuperscript{4} denominated this state as a "Transition State". A similar conclusion is made by Glib \textit{et. al.}\textsuperscript{3} also. But, we expostulate this presumption because a true transition state should have only one imaginary mode of vibration along with the bond breaking or bond making. Thus, there would not be cumulenic $D_{18h}$ symmetry. Contrariwise, DFT and MP computation substantiated that the cumulenic $D_{18h}$ symmetric state of cyclo[18]carbon is an optimized state on the potential energy surface with all positive modes of vibration.\textsuperscript{17,18} Henceforth, we may conclude that the cumulenic $D_{18h}$
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 5 K. Thus, automerization would be practically possible through quantum tunneling only which is smeared in the reported article by Nandi et. al.

In the present research, it is observed that the single carbon-carbon bond is shorter than normal C–C bond while carbon-carbon triple bond is nearly the same as an ideal C≡C. 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. 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 untrammeled cyclo[18]carbons at the interior of the excavation of zeolite cage recherche in this perusal. The optimized geometry is presented in Figure 1 (a). Conversely, analogous wire-like gestalt is not possible for CNT (see Figure 1 (b)). It may be due to the lack of a strong confinement effect.

![Figure 1: Optimized geometry of two untrammeled cyclo[18]carbons (a) inside the alpha cage of zeolite-Y (b) inside CNT.](image)

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. Hartree-Fock level calculations are accomplished with Gaussian 09\textsuperscript{21} program package. It is observed that the CNT of 40 carbon atom is capable of appropriate stabilization. Both CNT and cyclo[18]carbon ring are co-centric,
though, there is an angle between their molecular planes. The optimized geometry of this system is presented in Figure 2. For smaller cavity CNT, cyclo[18]carbon ring moves to the outside of CNT.

![Figure 2: Optimized geometry of cyclo[18]carbons inside CNT.](image)

The stability computation of cyclo[18]carbon within the alpha cage of zeolite-Y is performed 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. 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.

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**References**


