

# Stability of C<sub>60</sub> chains: molecular dynamics simulations

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## Abstract

A linearly aligned structure of three C<sub>60</sub> fullerene, interconnected by two benzorods of same size, have been investigated under heat treatment. The overall structure resembles a section of a beaded string. Nine different lengths of benzorods have been considered, and the effect on the thermal stability have been investigated by means of molecular dynamics method. It has been found that the structure is thermally stable up to elevated temperatures, and the linear alignment of the structure is persistent, up to the temperature of decomposition.

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## 1. Introduction

Since the introduction of buckminster fullerene back in 1985 [1], many new applications have been suggested. In fact, C<sub>60</sub> and its derivatives are considered to be a new form of carbon, and they are studied extensively. The diversity of suggested applications is quite extraordinary. For example C<sub>60</sub> can be used in a photovoltaic device. After observation of photoinduced electron transfer from a conducting polymer to C<sub>60</sub>[2], many novel devices have been suggested regarding the matter [3]. However, C<sub>60</sub> tend to form molecular films with weak Van der Waals interactions, which is not very welcome neither in the processing nor in the actual use. Thus a variety of ways of forming stronger films have been suggested [4]. But these methods generally involve exposure to an active element that is intended to bond with C<sub>60</sub>, and thus they may have adverse effects on polymer and polymer–C<sub>60</sub> bond. Another interesting property of C<sub>60</sub> is its magnetic behaviour [5,6]. Magnetic effects can be observed either in a C<sub>60</sub> lattice [7] or by attaching various materials to an isolated buckyball [8]. It

has been observed in the former structure that this magnetic behaviour is localized in the hexagonal planes, and depend on the distance between C<sub>60</sub>[9]. Again creating aligned structures is of importance in this case, for proper functionalization.

In this work, various chain structures that are composed of C<sub>60</sub> and interconnecting benzorods have been studied. The benzorods are attached to selected hexagonal sites in C<sub>60</sub> nanoballs, in order to form a linearly aligned structure.

Benzorod is a recently proposed form for a carbon nanorod structure [10]. It is composed of horizontally aligned and dehydrogenated benzene rings stacked together, as shown in Fig. 1. The “*n*” in the notation *n* C6 for benzorods stand for the number of dehydrogenated benzene rings present. Since hexagonal orientation of carbon atoms is common in fullerene related structures and in graphene sheet, benzorod structure may prove to be an important building block in preparing aligned nanostructures. In the original work proposing this new form, electronic properties were calculated. Some interesting points have been reported, including that the benzorods may be conductors, and there is a length dependent orientation of HOMO and LUMO orbitals.

Benzorod is not experimentally synthesized yet, however calculations predict that it is stable up to elevated temperatures, thus it may be realizable. The ideal structure

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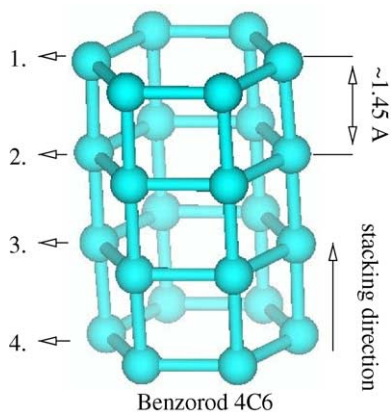


Fig. 1. The ideal structure of Benzorod 4C6.

of Benzorod contains four-membered rings in the six side faces. This kind of ring structure is both experimentally observed and theoretically studied in amorphous carbon [11]. Furthermore, there is experimental observation that four-membered ring structures are formed in between  $C_{60}$  under pressure [12], or other external influences [13]. It may be speculated that in the presence of loosely bonded or free carbon in the system of  $C_{60}$ , the proposed structure may be observed.

In the structures considered in the present work, chemically more active pentagons are left free which may prove to be more convenient in photovoltaic applications, especially when a bond with a polymer is required. Also, hexagonal planes are in alignment, thus it may have interesting magnetic behaviour. Structures with different  $C_{60}$  separation is possible, and devices that require rigid structure may be realized. Thermal stability of the structures considered are of importance. Structure with high thermal stability often means that the overall structure is stable and strong, thus may be realized in some experimental procedure. Also the geometry of the structure under ambient conditions may be different than the ideal geometry, and therefore, before any other electronic calculation, it is convenient to obtain relaxed geometry at different temperatures.

## 2. Method of calculation

One of the most suitable empirical many-body potential energy function (PEF) for this type of calculations is the Tersoff PEF for carbon [14]. This PEF describes the structural properties and energetics of carbon relatively accurate; including diamond crystal as well as the properties of the individual basal planes of graphite. Furthermore, fullerene related structures, such as carbon nanotube and buckyball, can also be simulated, and relatively accurate structural properties and energetics are obtained [15]. There is no explicit “bond” information in the Tersoff PEF and thus carbon atoms may rearrange under external influence without bond conservation restriction, unlike molecular

mechanics method [16]. Absence of long range interactions is of no significant importance in the structure considered.

In Tersoff PEF, the total interaction energy of a system of particles is taken to be the sum of total two-body and total three-body contributions

$$\Phi = \phi_2 + \phi_3 \quad (1)$$

Total two-body and three-body energies are expressed, respectively, as [17]

$$\phi_2 = A \sum_{i < j}^N U_{ij}^{(1)},$$

$$\phi_3 = -B \sum_{i < j}^N U_{ij}^{(2)} \left[ 1 + \beta^n \left( \sum_{k \neq i,j}^N W_{ijk} \right)^n \right]^{-1/2n} \quad (2)$$

here  $U_{ij}$  and  $W_{ijk}$  represent the two-body and three-body interactions, respectively.

$$U_{ij}^{(1)} = f_c(r_{ij}) \exp(-\lambda_1 r_{ij}), \quad (3)$$

$$U_{ij}^{(2)} = f_c(r_{ij}) \exp(-\lambda_2 r_{ij})$$

$$W_{ijk} = f_c(r_{ik}) g(\theta_{ijk}) \quad (4)$$

where

$$g(\theta_{ijk}) = 1 + \frac{c^2}{d^2} - \frac{c^2}{d^2 + (h - \cos \theta_{ijk})^2} \quad (5)$$

$$f_c(r) = \begin{cases} 1 & \text{for } r < R - D \\ \frac{1}{2} - \frac{1}{2} \sin \left[ \frac{\pi r - R}{2D} \right] & \text{for } R - D < r < R + D \\ 0 & \text{for } r > R + D \end{cases} \quad (6)$$

The parameters of the PEF for carbon are as follows [14]:  $A = 1393.6$  eV,  $B = 346.74$  eV,  $\lambda_1 = 3.4879 \text{ \AA}^{-1}$ ,  $\lambda_2 = 2.2119 \text{ \AA}^{-1}$ ,  $\beta = 1.5724 \times 10^{-7}$ ,  $n = 0.72751$ ,  $c = 38\,049$ ,  $d = 4.3484$ ,  $h = -0.57058$ ,  $R = 1.95 \text{ \AA}$ , and  $D = 0.15 \text{ \AA}$ .

The equations of motion of the particles are solved by considering the Verlet algorithm [18]. The system simulated has been considered to be isolated, which does not interact with its environment. Under these conditions the temperature of the system has been kept constant by considering the equality

$$\frac{1}{2} \sum_{i=1}^N \frac{v_i^2}{m_i} = \frac{3}{2} N k_B T \quad (7)$$

here  $T$  is the external temperature,  $k_B$  is the Boltzmann constant,  $m_i$  and  $v_i$  are the mass and speed of each atom. The speeds  $v_i$  are scaled at every MD step, so the temperature of the system is kept constant at a predetermined value. One MD time step is taken as  $10^{-16}$  s. The initial velocities of the particles are determined from the Maxwell distribution at the given temperature.

The simulations are carried out starting at low temperature (1 K) and the temperature of the system is

increased by a predetermined step (100 K) up to the system considered deformed. At every temperature rise the system is relaxed for about 40 000 time steps. This much steps were enough to reach equilibrium at every temperature rise. Stability of  $C_{60}$  chains against heat treatment show a dependence on the size (length) of the benzorod used.

### 3. Results and discussion

In each of the structures considered, there are three  $C_{60}$  nanoballs. These nanoballs are connected with two benzorods of same length, attached to a hexagon on the surface of  $C_{60}$ . The location of benzorod was chosen such that a linearly aligned geometry could be formed. Thus a hexagon with a symmetric counterpart on the opposite face of the  $C_{60}$  was used. By varying the length of these two benzorods, nine different structures were obtained. These structures are named as  $m C_{60}-n C_6$ , where  $m$  is the number of buckyballs present ( $m = 3$  in the present work) and  $n$  is the length of the benzorods connecting the buckyballs ( $n = 1-9$  in the present work).

Chain structures are shown in Figs. 2 and 3. Each segment, indicated by the name of the structure, in these figures show: relaxed configuration (leftmost), configuration at an intermediate temperature (middle), and the decomposed structure

(rightmost). The temperature of decomposition in the rightmost frames are just an estimate, because of the rather large value of the temperature increments (100 K).

Even at very low temperatures benzorods assume a length dependent form. This effect is also observable in the isolated benzorods. This is not completely surprising, since one should expect that the four-membered rings in the benzorod should prefer to be non-planar [19]. When an ideal benzorod (isolated and/or supported) is relaxed, its length shrinks and the general view of the benzorod looks like accordion pleats. The decrease in the length is due to geometric reorientation of rings in the benzorod system. In the new geometry, one of the rings disintegrate, such that former ring members are no longer within bonding distance of each other but the upper and lower rings. The upper and lower rings with respect to disintegrated ring tend to maintain its original form. Thus, an accordion pleat geometry is formed. The three benzenoid ring accordion pleat geometry is favored, such that the number of pleads are maximized through the benzorod. The pleads are stable up to elevated temperatures. The pleat geometry reduces the length of the chain compared to ideal geometry. There is about 0.8 Å shrinkage per pleat.

There is a slight elongation in  $C_{60}$  where the benzorods are connected. This is most possibly due to change in coordination number. At these sections, carbon atoms try to align into tetrahedral configuration seen in  $sp^3$  hybridization.

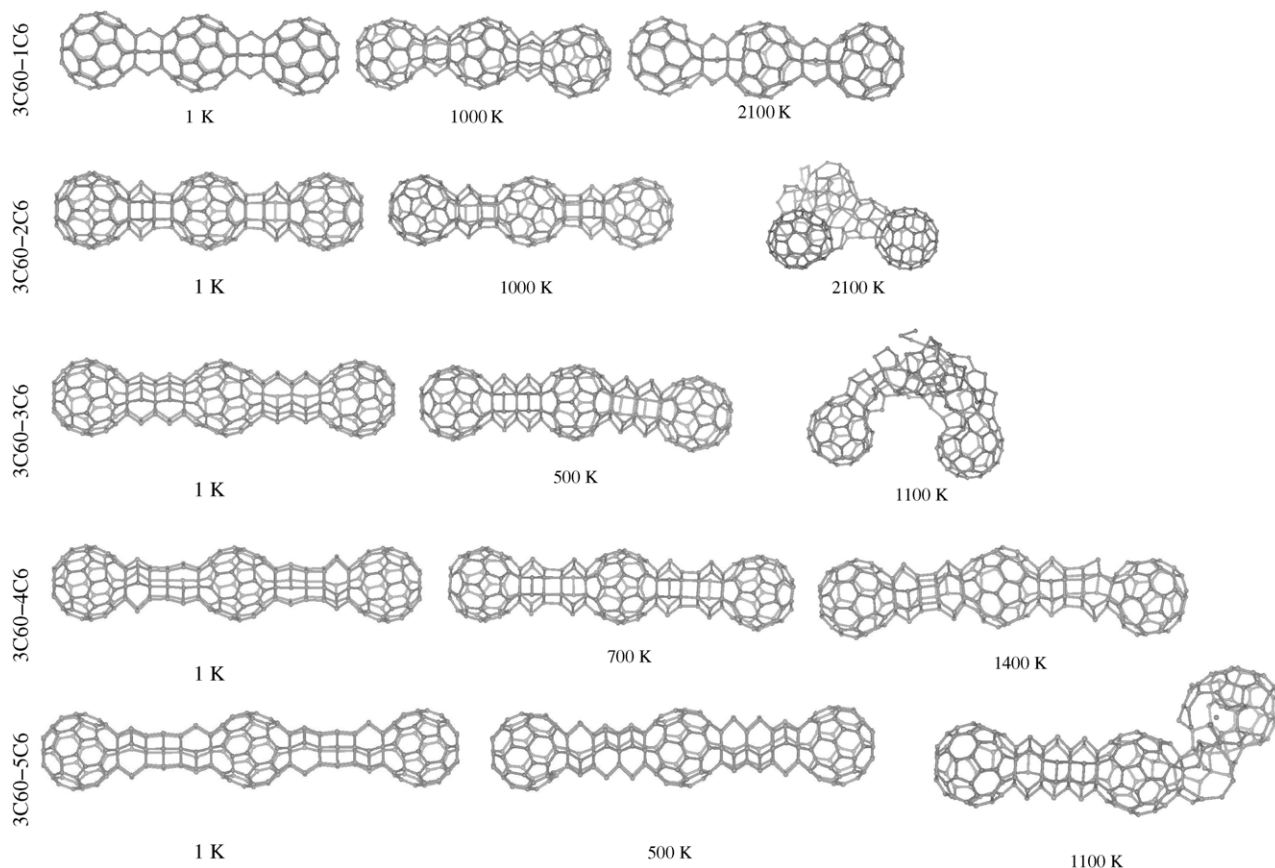


Fig. 2. Structures of 3C60-3C6-3C60-5C6 chains.

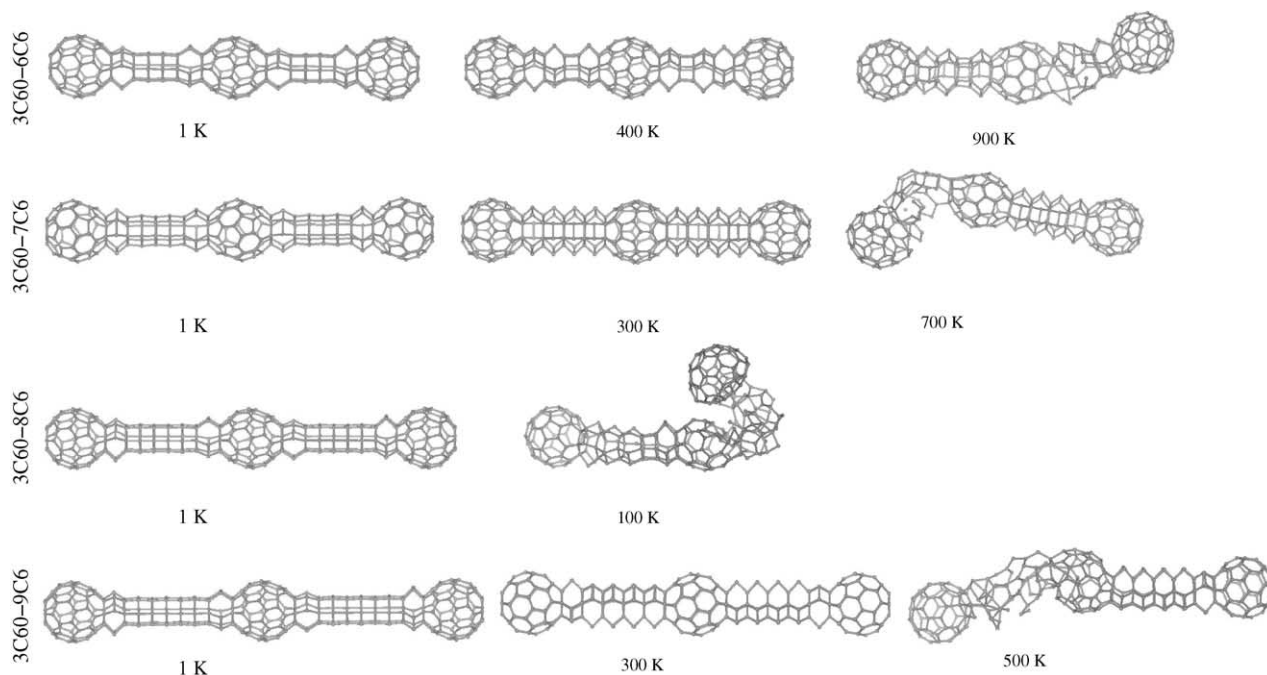


Fig. 3. Structures of 3C60-6C6-3C60-9C6 chains.

This seems to lower the thermal stability of that section. In chains with shorter benzorods, the decomposition is observed at around these locations. After 3C60-6C6, benzorods seem to be less stable, and thus decompose before the nanoballs. Starting from 3C60-7C6, length dependent nature of the thermal stability of benzorods can be observed. Compared to predicted thermal stability of standalone C<sub>60</sub> of 5000 K [20], the chains are considerably less stable, but in the crystalline configuration this temperature is observed at 1273 K [20], which is comparable with some of the chain structures considered in the present work.

The structures considered in this work are stable at the room temperature range, with one exception of 3C60-8C6. The stability degrades with increasing length of benzorods used, with a dependence on whether the number of dehydrogenated benzene rings added are even or odd. Since the structures are thermally stable at elevated temperatures, it may be possible to realize them experimentally. The structures considered are promising in creating aligned rigid nanomaterials. Chemically more active pentagons are left free for interaction with other material, and separation between C<sub>60</sub> may be controlled. Thus it may be used in magnetic, photovoltaic, and optical applications. The benzorod structure is different than even smaller carbon nanotubes due to presence of four-membered rings. Even at high temperatures, when the majority of the four-membered rings decompose, benzorods do not assume a nanotube like form (i.e. it does not show any of the cross-section geometries). However, it may be speculated that in the presence of catalyst material or under special conditions, the carbon atoms may rearrange to form carbon nanotubes with

similar sizes, since the difference is only in the geometry and four-membered rings are not so favored energy-wise.

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