

Thermal stability of benzorods: Molecular-dynamics simulations

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Abstract

Thermal stability of benzorods 2C₆–20C₆, which are obtained by stacking n ($n = 2$ –20) dehydrogenated benzene, have been investigated by molecular-dynamics simulations. It has been found that these structures assume a geometrical form depending on the number of dehydrogenated benzene layers, and they are stable under heat treatment up to elevated temperatures with a dependence on length.

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1. Introduction

Carbon based materials became of importance early in the century [1,2]. Since then, there is an ever-growing number of proposed forms and commercial applications. Later, this trend hit the size of nanometer [3–6], and gained a whole new aspect with the introduction of the famous fullerene molecule [7]. There are many fullerene related carbon nanostructures, such as carbon nanotubes [8], nanorods [9–11], nanotori [12,13], etc. These structures exhibit intriguing electronic properties, along with unusual structural stability, and this makes them highly popular in future commercial applications. One interesting point is that the non-planar carbon macromolecules were not unknown to society before the introduction of fullerene itself. In fact, the basic building block of C₆₀, namely corannulene, was encountered and extensively studied in the 1970s [14,15]. Even a structure in the shape of a football was proposed [16,17], which will be called the buckminsterfullerene after 1990. The common point in many carbon nanostructures is that they contain unusual aromaticity due to hybridization of carbon atoms. This makes benzene a plausible choice as a building block for carbon nanostructures.

Various nanowires gained importance as the field improved. They are proposed to be integral part of electronic devices in the future [18]. Using nanowires, instead of nanotubes, has some advantages in the current technology. Since placing the nanotubes in the correct place is a problem due to their size, growing nanowires using lithographically prepared sources is preferable [19]. Furthermore, nanowires may act as functional part in a quantum computer [20]. Diamond nanorods are an increasingly popular example [21–23]. Molecular wires involving benzene are often modelled in a planar geometry such as polyacene and polyphenanthrene [24,25]. Although benzene is planar, nanorod structure may be obtained by stacking layers of dehydrogenated benzene together. This structure, named as benzorod by the author, was proposed and studied electronically for the first time in a recent work [26]. In that work, it was found that the benzorods may be conductors, and have an interesting distribution of HOMO–LUMO orbitals which make them a promising candidate for STM tips and molecular wires. Furthermore, they were found to be structurally stable according to semiempirical calculations. However, the benzorods studied were relatively small, and the effect of ambient temperature remained unknown. Since electron–phonon coupling is an important issue in this kind of nanostructure [27], the geometrical realignment due to ambient temperature is of importance.

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In this work, structural stability of benzorods containing 2–20 layers of dehydrogenated benzene (which will be named as n C6 ($n = 2$ –20) from now on) under heat treatment have been investigated by performing molecular-dynamics (MD) simulations. In the simulations, an empirical many-body potential energy function (PEF) developed for carbon has been used.

2. The PEF and the MD simulation

The empirical many-body potential energy function developed for carbon [28] is used in the calculations. 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 [29]. There is no explicit “bond” information in the Tersoff PEF and thus carbon atoms may rearrange under external influence without bond conservation restriction. Absence of long range interactions is of no significant importance in the structure considered.

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

$$\begin{aligned} \phi_2 &= A \sum_{i < j}^N U_{ij}^{(1)}, \\ \phi_3 &= -B \sum_{i < j}^N U_{ij}^{(2)} \left[1 + \beta^n \left(\sum_{k \neq i, j}^N W_{ijk} \right)^n \right]^{-1/2n} \end{aligned} \quad (2)$$

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

$$U_{ij}^{(1)} = f_c(r_{ij}) \exp(-\lambda_1 r_{ij}), \quad U_{ij}^{(2)} = f_c(r_{ij}) \exp(-\lambda_2 r_{ij}) \quad (3)$$

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

where

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

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

The parameters of the PEF for carbon are as follows [28]: $A = 1393.6$ eV, $B = 346.74$ eV, $\lambda_1 = 3.4879 \text{ \AA}^{-1}$, $\lambda_2 = 2.2119 \text{ \AA}^{-1}$, $\beta = 1.5724 \times 10^{-7}$, $n = 0.72751$, $c = 38049$, $d = 4.3484$, $h = -0.57058$, $R = 1.95 \text{ \AA}$, and $D = 0.15 \text{ \AA}$.

The equations of motion of the particles are solved by considering the Verlet algorithm [30]. The canonical ensemble molecular-dynamics NVT [30] is proceeded. The periodic box was taken to be very large, thus effectively the PBC was not applied. 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

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

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 temperature step, so the temperature of the system is kept constant at a predetermined value. One 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 distorts. The “distortion condition” is defined as, either a large geometrical aberration, or a few atoms breaking loose. Each system distorted at a different temperature. At every temperature rise the system is relaxed for about 50 000 time steps. This much steps were enough to reach equilibrium at every temperature rise.

3. Results and discussion

Benzorods at various temperatures are shown in Figs. 1 and 2. The highest temperature for each benzorod is the point where the structure considered to be distorted (see Fig. 3).

As mentioned above, benzorods are generated by stacking dehydrogenated benzene rings together (shown in Fig. 4). Each ring, or layer, is initially in alignment with the others and the interlayer separation is about 1.4 \AA . Thus in an ideal structure of infinite length created in this manner, the average coordination number would be 4. However the resulting geometry of the four-bonded carbon atoms is not tetragonal, and thus somewhat strained. This strain effect has some interesting consequences. When there are a group of three rings, the middle ring distorts, i.e. it moves outside the bonding radius of the other ring members, and each member becomes a “joint” connecting the other two layers. These “joint” atoms align themselves in a planar geometry such that there is an angle of approximately 108° between the “bonds” connecting the two layers. This geometry is clearly

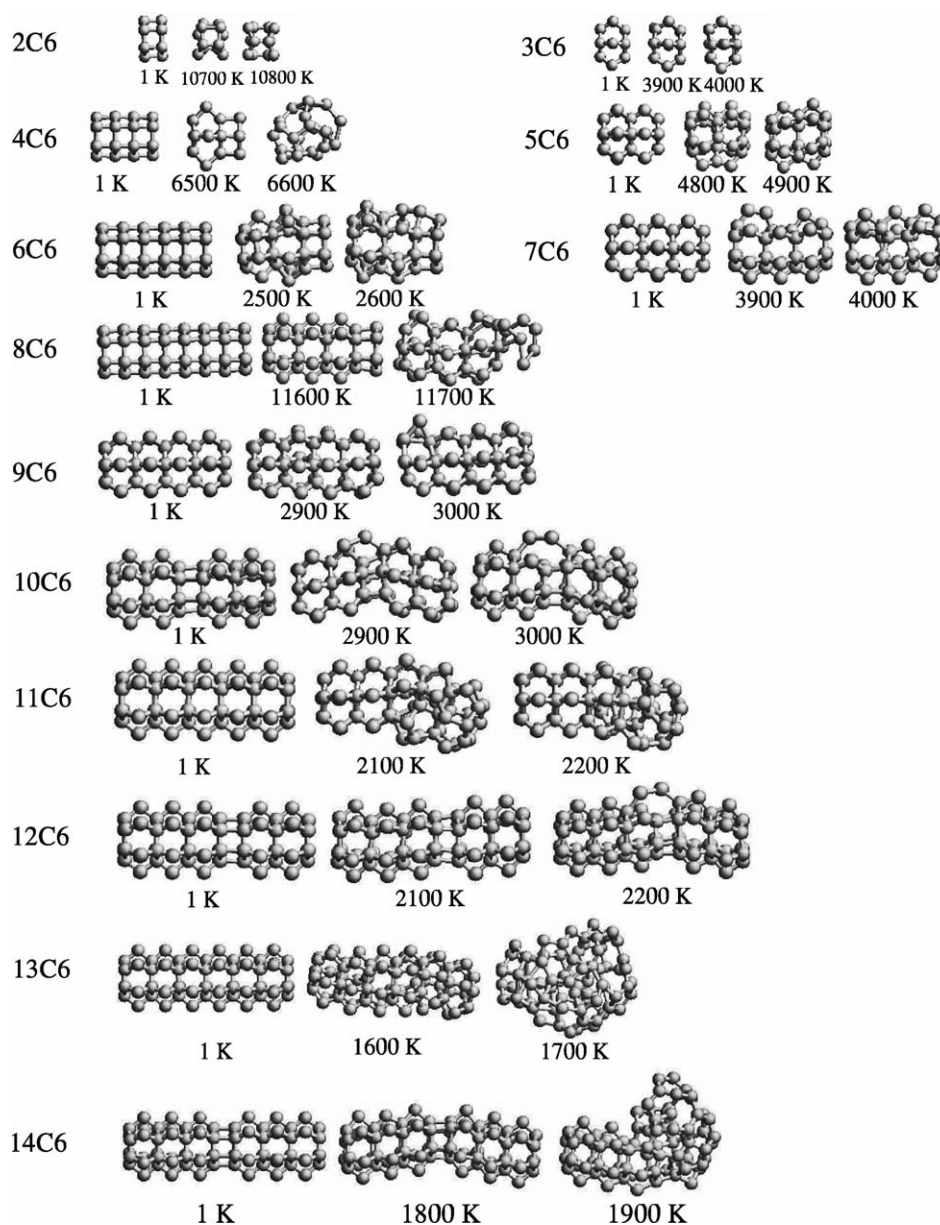


Fig. 1. Benzorods 2–14C6 at various temperatures.

observed in benzorod 3C6. When there are more than three rings, the 3C6 geometry is favored, and the structure aligns itself such that 3C6-like geometry is maximized through the length. When there is an even number of rings however, one of the layers is left-out. This left-out layer maintains the original geometry (2C6-like geometry) with its neighboring layer. The smallest benzorod with a left-out layer is 4C6. Left-out layer geometry has a preferred location. In most of the cases studied the left-out layer geometry was encountered in the middle of the structure or as close as possible. The exceptions are the 6C6 and 8C6 benzorods. The left-out layer in these two benzorods appear in the ends most probably due to their smaller length. Lastly, the ideal benzorod geometry seems to be stable up to room temperature for lower (and even) number of benzorod

rings. When temperature is increased above room temperature, geometry assumes the above described form. This form is again symmetrical along its axis, which we define along the stacking direction. The structural detail of this geometry is shown in Fig. 5. Please notice that, due to oscillations, this geometry is not the potential minimum, but an instantaneous picture during the course of MD simulations, namely a snapshot at the last MD step.

At this point, it may be asked whether this structural form is due to inadequacies of Tersoff potential. Tersoff potential, in its second parametrized form as of 1988, is capable of simulating energetics and structure of both surfaces and bulk materials. A later derived potential of similar form for hydrocarbons revise the parameters considering these inadequacies [31]. In order to verify that the predicted

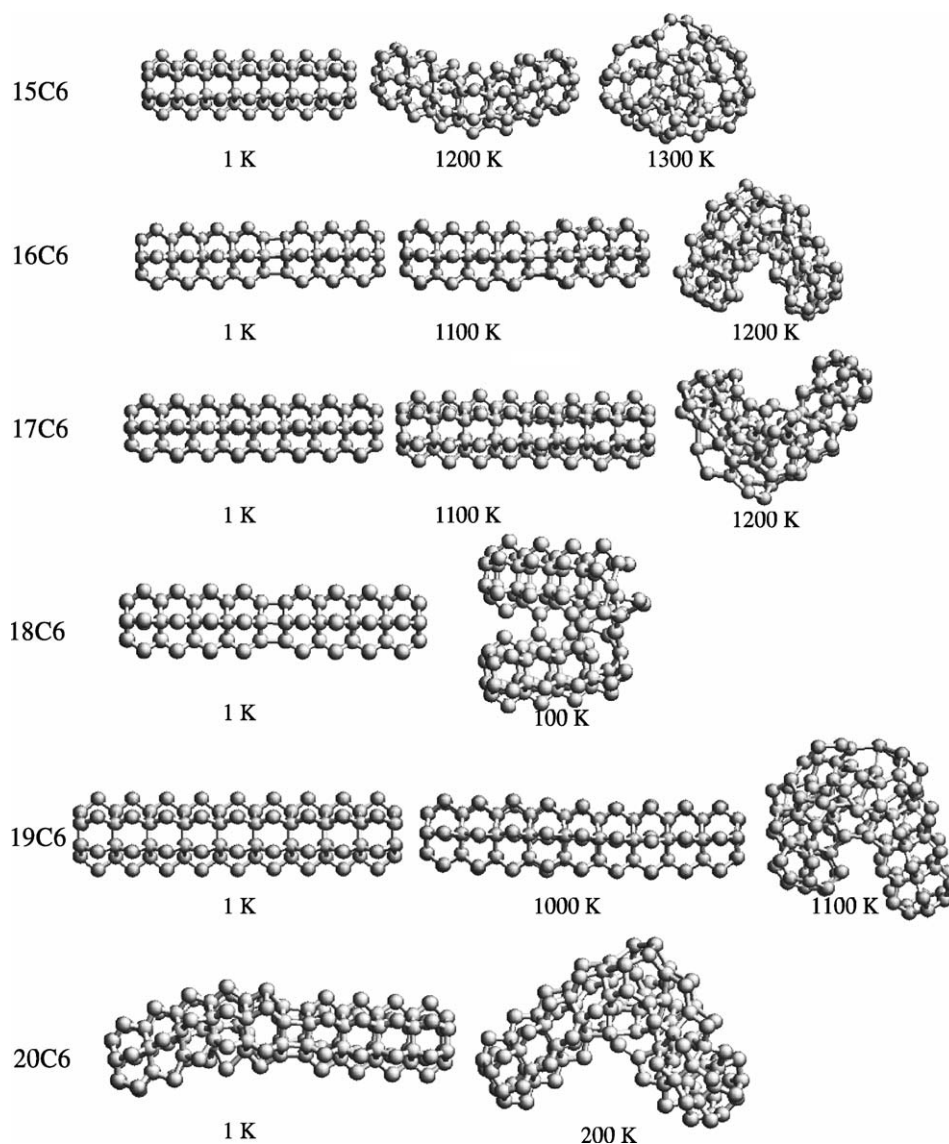


Fig. 2. Benzorods 15–20C6 at various temperatures.

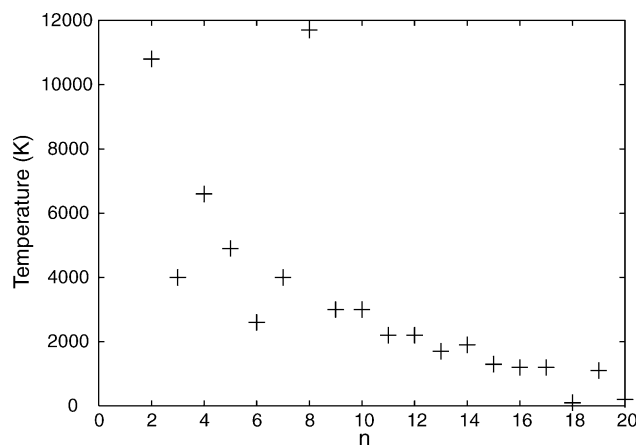
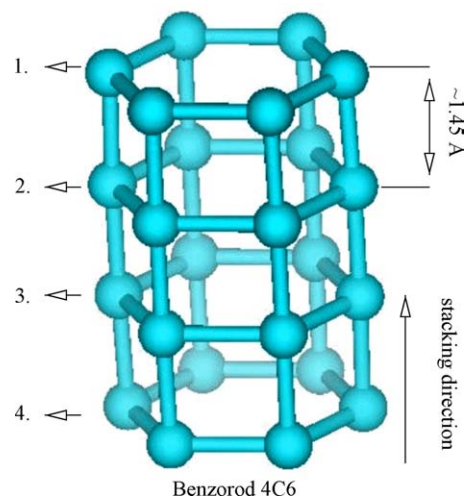
Fig. 3. Dependence of distortion temperature on the number of dehydrogenated benzene rings n .

Fig. 4. Ideal benzorod detail.

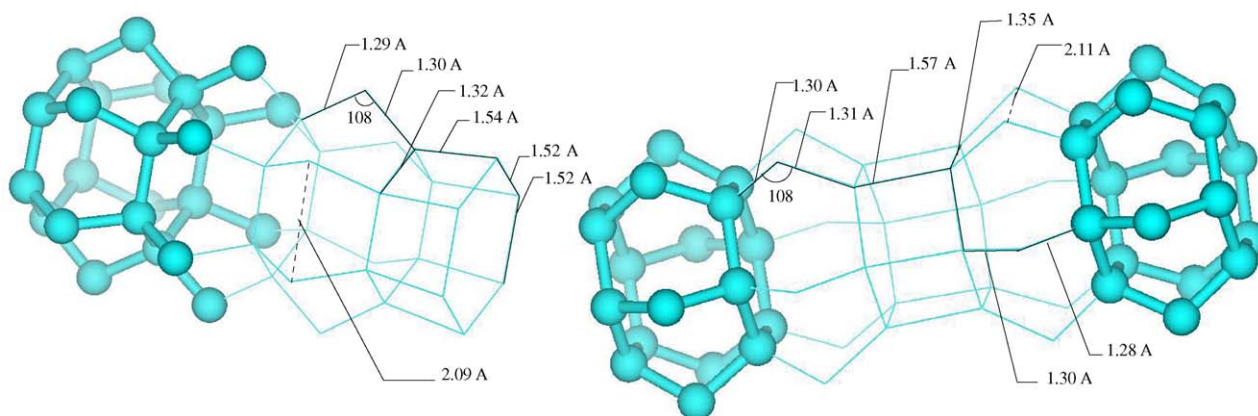


Fig. 5. Structural detail of 8C6 and 10C6 at room temperature (instantaneous situation, all values are not given, since molecule is completely symmetric along its axis).

structural geometries do not suffer from these inadequacies, selected ideal benzorod geometries were geometry-optimized using a derivative of MM force field [32] (from Hyperchem 7.51 package [33]) and Tersoff–Brener potential [34] (using corresponding functions from Numerical Recipes [35] and Tbttools [36]) separately. Both potentials yielded nearly identical geometries. Since geometry optimization method does not use temperature or velocity information, obtained geometries are the absolute minimum energy configurations, which in turn explain why the structure aligns itself into this form in the long run. Furthermore, using MM+ and Hyperchem, a similar MD algorithm was created, and using this algorithm selected geometries were tested. The results were quite similar geometrically. In addition to this, using the second algorithm, the effect of random velocity generation step was observed. Using different seeds in this step only effects when the system reaches equilibrium. Since this happens generally in only a few thousand MD steps at most, contribution of this effect is negligible in the present calculation (Fig. 5).

In order to verify that empirical potential results are comparable to semiempirical calculation results we have performed further calculations on 3C6, 4C6, and 5C6 ideal benzorod structures. First these structures were optimized by applying MM calculations with MM+ force field, then the

structures reoptimized by performing semiempirical self-consistent-field molecular-orbital calculation at PM3 [37] level. The results of these test calculations are shown in Fig. 6. As can be seen from Figs. 1 and 6, empirical potential results (in Fig. 1, at 1 K) generate similar results with that of PM3 results (in Fig. 6).

The overall thermal stability of the benzorods is length dependent. In general when the number of rings increases thermal stability decreases. Distortion temperature versus number of dehydrogenated benzene rings plot is shown in Fig. 1. The biggest fluctuation in this general trend is 8C6 with distortion temperature of about 11 700 K. The peculiar location of the left-out layer seems to increase the stability. The 8C6 is found to be the most stable structure against heat treatment among the models considered. This structure is exceptionally strong and keeps its form up to 11 600 K. When the number of rings pass 12, the major structural deformation under heat treatment is bending. The bending occurs at the middle, and at the location of left-out layer if present.

As an overall conclusion it may be stated that these structures are thermally stable, depending on the length. The geometry assumes a form depending on the number of dehydrogenated benzene rings present. The possibility of stiffness in some of the benzorods may be utilized in structural applications, such as a scaffold where the “joint-

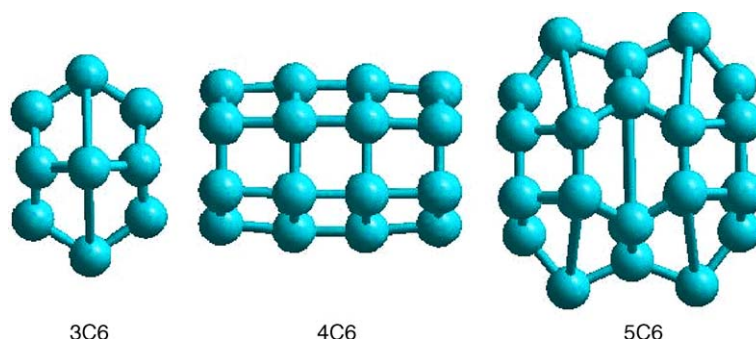


Fig. 6. PM3 optimized structures of 3C6, 4C6, and 5C6.

region” atoms act as connecting points to other structures; particularly in nanomachines as joining elements and/or connection elements.

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