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Electronic properties of carbon nanotoroidal structures

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Abstract

Electronic properties of five carbon nanotori (C_{170}, C_{250}, C_{360}, C_{520}, and C_{750}) have been investigated by performing Extended-Hückel type calculations. Carbon nanotori considered is of Fonseca type having five-fold symmetry. It has been found that highest occupied molecular orbital–lowest occupied molecular orbital gaps of nanotori considered are very small, thus they may contain mobile electrons; pentagons and heptagons in the knee-regions act as an electron trap; and all the nanotori have a DOS distribution with common features.

Keywords: Carbon nanotorus; Hückel method; Electronic structure

1. Introduction

After the discovery of fullerenes [1] and nanotubes [2], other forms of carbon nanostructures have attracted much attention. The experimental observation of nanohoops [3–6] led theorists to propose the existence of nanotoroidal structures which are much smaller in radius [7–14].

Carbon nanotori structure have rather interesting features for possible utilization in nanotechnology. Some nanotori have rather significant magnetic properties [15,16] which may further be supported by doping magnetic material. This property alone makes this structure an important part of future electronic and optical research. Furthermore, a carbon nanotoroidal structure might be utilized as a containment vessel. If the resulting structure can be opened and re-sealed like fullerene (which may just be the case due to presence of heptagons and pentagons), it will be quite useful in nanobionic and nanobiometric applications such as controlled medicine delivery.

To bend a nanotube into a torus requires much energy. However, inclusion of pentagon and heptagons into nanotubes provides the required positive and negative curvature and thus reduce the energy of the structure. Mathematically, there are different ways to cover the surface of a torus with hexagons, pentagons and heptagons [17–19]. In general, five- or six-fold symmetric structural geometry in tori are possible.

In this work, we use five-fold symmetric nanotori models generated with a recently developed algorithm [20] utilizing the method of Fonseca et al. [19]. Fonseca-type nanotori consist of nanotubes, joined by 'knee-regions'. Curvature of the knee-regions is given by pentagon–heptagon pairs. We investigate the electronic properties of the carbon nanotori C_{170}, C_{250}, C_{360}, C_{520} and C_{750} by utilizing the Extended-Hückel method [21]. In a recent study [22] these tori were found to be thermally stable up to very high temperatures (up to approximately 2900–4400 K) using empirical potential energy function via molecular-dynamics simulation method.

2. Method of calculation

The structures of the five different carbon nanotoroids considered in this work have been generated by using a recently developed algorithm [20]. All the nanotoroidal structures considered possess five-fold symmetry with respect to the toroid-axis. The geometry optimization of the generated nanotoroids have been carried out by performing molecular-mechanics method [23] considering the MM+ force field [24]. The Polak–Ribiere conjugate gradient search algorithm [25] was employed in order to find the minimum energy configuration.

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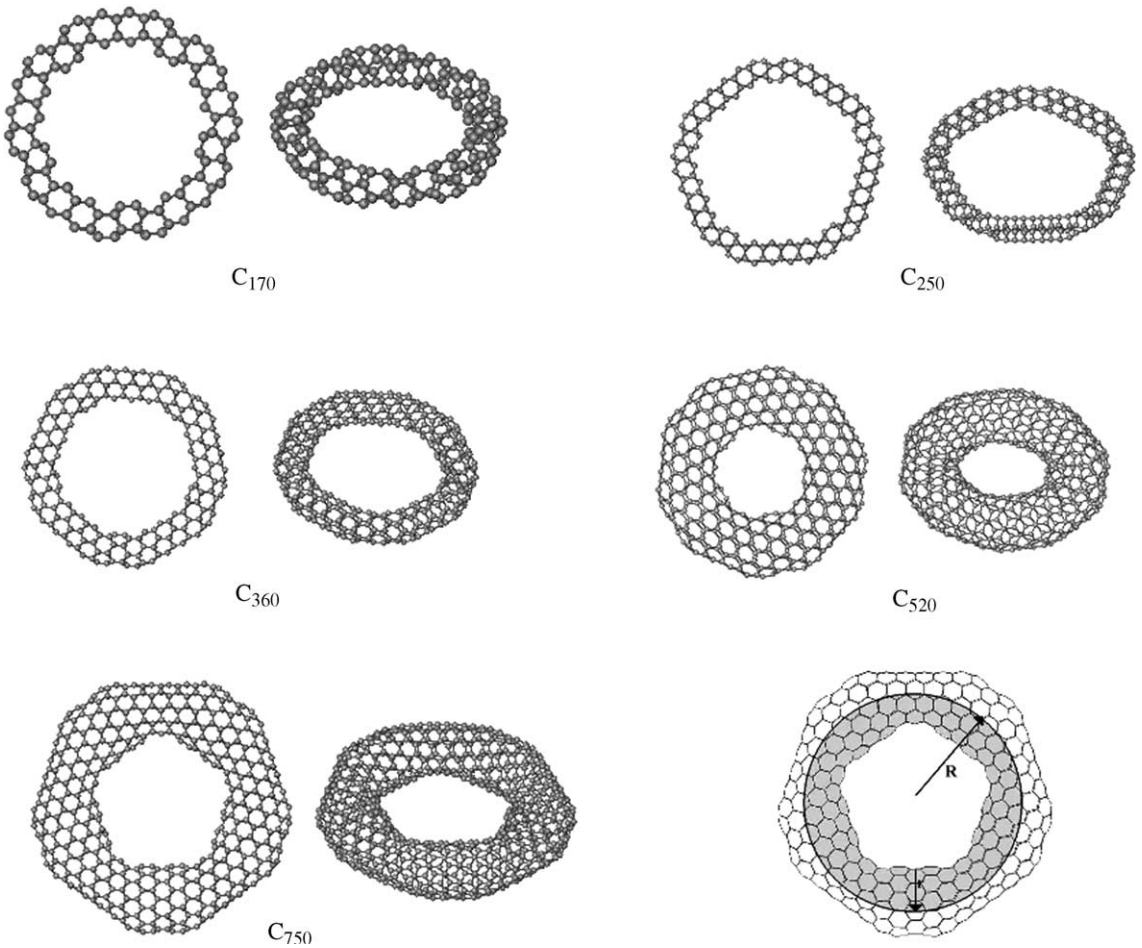

Fig. 1. Geometries of the nanotoroids considered.

After the molecular-mechanics geometry optimization, the electronic properties of the nanotoroids have been obtained by performing single-point energy calculations through the Extended-Hückel method [21] with unweighted Hückel constant 1.75. As it is well known the Extended-Hückel method calculates the energy eigenvalues for independent delocalized π electrons using an incidence matrix in which the diagonal elements are the binding energies of electrons and the off-diagonal elements are the interaction energies between two atomic orbitals. The particular method we have employed uses empirical values for the incidence matrix, thus the overall calculation is semi-empirical. Using the Hückel method, the electron distribution along the structure can also be determined. For all the calculations in this work, HyperChem-7 package program [26] was used.

3. Results and discussion

In this work, various carbon nanotoroidal cage structures have been investigated theoretically by performing the Extended-Hückel calculations. The geometry of the carbon nanotoroids considered are shown in Fig. 1 with the corresponding definitions of the geometrical parameters R and r. The numerical values of the geometrical parameters R and r of the tori as well as the calculated total energy and the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) eigenvalues are given in Table 1. Naturally the absolute value of the total energy increases with increasing number of atoms. From the table, it can be seen that there is no apparent relation between the number of atoms in the tori and the difference between HOMO and LUMO energies.

Table 1
Geometrical parameters (R, r) and calculated energies of carbon nanotoroidal structures

Toroid	r (Å)	R (Å)	E (kcal/mol)	HOMO (eV)	LUMO (eV)	ΔE (eV)
C_{170}	1.2	9.3	-269,794.6	-9.726	-9.592	0.134
C_{250}	1.5	12.6	-396,941.4	-9.550	-9.485	0.065
C_{360}	2.0	13.1	-577,420.1	-9.786	-9.553	0.233
C_{520}	3.0	12.0	-837,992.8	-10.076	-10.038	0.038
C_{750}	3.1	14.6	-1,209,117.0	-10.085	-9.769	0.316

E, total energy; HOMO, highest occupied molecular orbital eigenvalue; LUMO, lowest unoccupied molecular orbital eigenvalue; ΔE, difference between HOMO and LUMO energies.

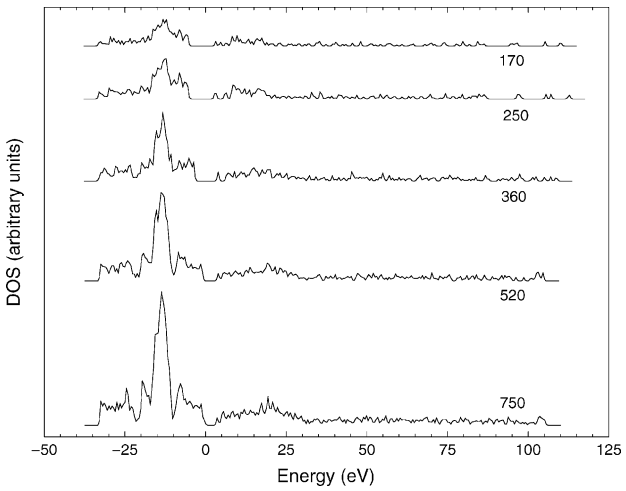

Fig. 2. DOS distribution of the nanotoroids considered.

Fig. 2 displays the density of states (DOS) of the five different carbon nanotoroids considered. The DOS plots have been obtained from the histograms of the Hückel molecular orbital eigenvalues of the nanotoroids by applying Gaussian broadening method. The maximum distribution of the Hückel eigenvalues of the nanotoroids considered takes place at about -15 eV almost for all the nanotoroid models considered. As it is seen in the DOS plots, in all the models considered, there is a gap located at around 0 eV. C_{170} has the largest ($\sim$7 eV) and C_{750} has the smallest ($\sim$2.5 eV) gap in this region. This gap is also apparent in the work of Bai et al. [27] where partial eigenvalue sums for C_{240}, C_{480} and C_{960} are computed. This gap separates only the positive and negative eigenvalues into two groups. Both HOMO and LUMO eigenvalues take place in the same region (in the negative part) of the DOS distribution and located at the bottom of the main peak (at about -10 eV). The frontier molecular orbital eigenvalue gap, namely the HOMO–LUMO gap, ΔE, are also given in Table 1.

The magnitude of the peak of the DOS increases as the number of atoms increase, as expected, which is an indication of the increasing number of 'mobile' electrons. Since the system has closed geometry, the behavior of mobile electrons is a point of debate. One point of interest may be the contribution of these mobile electrons to the magnetic behavior [15].

HOMO–LUMO gaps found in the present calculation range in 0.04–0.32 eV. Hückel calculations on different isomers of C_{240} showed that the HOMO–LUMO gaps range in 0–0.5 eV [15] which is in good correspondence of the values we encounter.

The 2D and 3D excess charge density distributions are displayed in Fig. 3. Charge distribution in the interior region of the larger toroids, C_{520} and C_{750}, is relatively less with respect to the rest of the toroids considered. From geometrical point of view this is observed in the case $r > 2$ Å. Furthermore, negative excess charge is localized mainly at the knee-regions.

As an overall conclusion we may state that the nanotori considered exhibit some promising electronic structure.

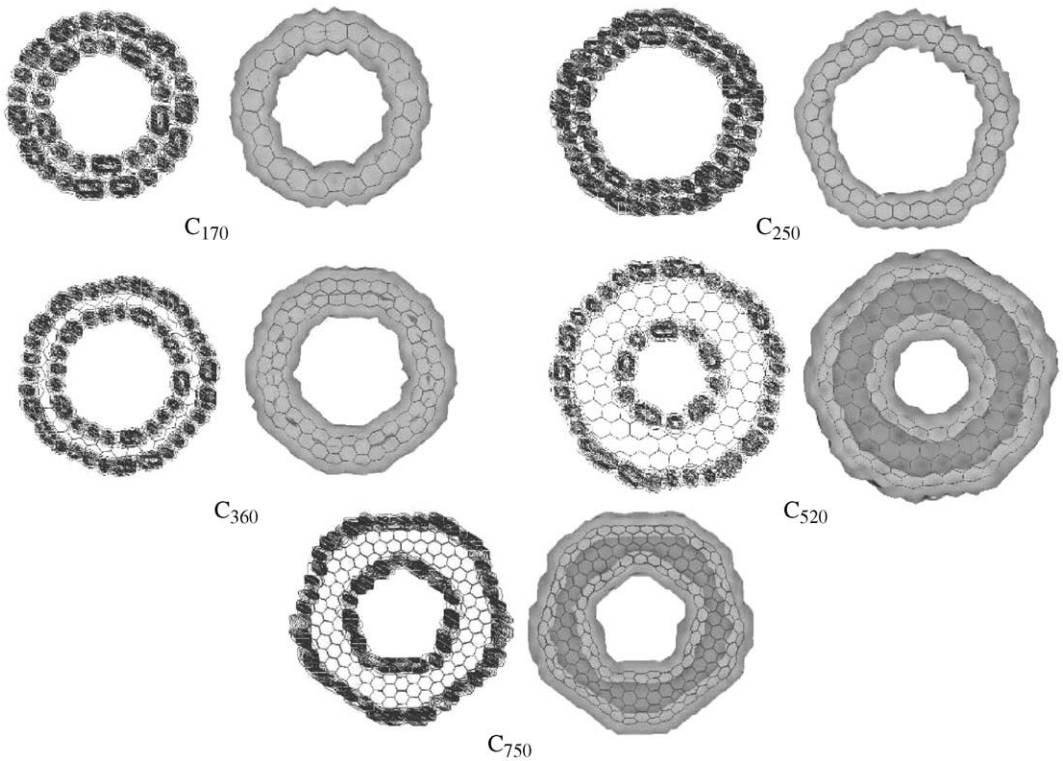

Fig. 3. 2D and 3D charge distribution of the nanotoroids considered.

Presence of the mobile electrons may be utilized in magnetic applications. Knee-regions in the structure are negatively charged. This may be utilized as attachment points for positively charged materials such as some proteins. Furthermore if the nanotori were to be utilized as nanogears, this negative charge accumulation may prove to increase longevity, since the contact range would be increased. The larger nanotori have an interior region that is mostly charge free, and thus they may be utilized for many applications intended for cage structures. More accurate ab initio calculations may show more interesting features of these structures.

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