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Transition from Carbon Nanoballs to Nanocapsules With Reference To Structural and Molecular Electronic Properties

Mudassir M. Husain
Physics Section, Department of Applied Sciences and Humanities, Faculty of Engineering and Technology,
Jamia Millia Islamia, New Delhi-110025, India.

Abstract: We have investigated theoretically the variation in energetics and electronic properties during the gradual transition from spherical or nearly spherical form (as in case of armchair) to capsule formation. The zigzag and armchair configurations of carbon nanostructures with different length to diameter (l/d) ratio have been studied. Zigzag C_{80} and (9,0) single wall nanocapsules, armchair C_{70} and (5,5) carbon nanocapsules (Cncs) system have been theoretically investigated. We have used semi-empirical molecular orbital method, at the level of PM3 type quantum mechanical model. The geometry of these molecular systems has been suitably optimized. The parameters studied are various molecular properties, energy values, frontier orbital (HOMO and LUMO) energies, heats of formation, interfrontier energy gap (ΔE_g), density of states (DOS), electron difference density (EDD) and electrostatic difference potential (EDP) of the capsules. The structures studied were found to be stable with a minimum energy band gap respectively of 3.73 and 4.66 eV, in case of zigzag and armchair configuration and exhibit insulating properties.

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***Keywords*:** Carbon nanocapsule, frontier orbitals, density of states (DOS), electron difference density (EDD), electrostatic difference potential (EDP).

I. Introduction

Since 1990, fullerene research has blossomed in a number of different directions and has attracted a great deal of attention to the area of Carbon Science. Carbon based nano materials like fullerenes [1], nanotubes [2], nanocones [3, 4] have enormous potential of application due to their unique physical, chemical, mechanical, electrical and electronic properties. The term "nanocapsules" (and nanoencapsulation") emerged in literature for carbon encapsulating materials at the beginning of 1990s [5-9]. The study of structure and physical properties of the nanocapsules has become important due to the increasing relevance of the field of nanoscience and nanotechnology [10]. During the last few years, there has been intense activity in the field of nanocapsules, both theoretical and experimental. Şakir et al. [11] applied semi-empirical method (PM3) in order to explore the structure and electronic properties of lithium endohedral doped carbon nanocapsules. Structural and electronic properties of *n*Li and *n*Li^+ (*n* =1-3) doped mono-vacancy defected carbon nanocapsules systems were investigated theoretically by semi-empirical and DFT methods [12]. Multifunctional metal-doped carbon nanocapsules (which have applications in molecular electronics, catalysis, light harvesting and nanomechanics) have been investitigated theoretically [13]. Suytein et al. [14] suggested that nanocapsules have an edge over other nanostructures, for adsorption of hydrogen gas in adsorption conditions and its storage in normal conditions. The analysis of the process responsible for nanocapsule charging with methane (storage and desorption) has also been reported [15]. On the basis of first-principles simulation of encapsulation of molecular hydrogen in C_{120} nanocapsules, Ganji [16] predicted that the hydrogen adsorptive capacity of C_{120} nanocapsules was higher than that of $C_{60.}$ Ganji et al. [17] theoretically studied the hydrogen storage capacity of C_{120} nanocapsules using density functional theory (DFT), On the basis of their findings they suggested that the C_{120} nanocapsules were a novel material for energy storage. It is obvious from these events that it is crucial to explore the structure and electronic properties of different nanosized capsules. They may used for storing different gases (hydrogen, methane and noble gases) and have other potential applications.

II. Computational technique

Initially zigzag C_{80}, armchair C_{70} carbon nanoballs and zigzag (9,0), armchair (5,5) carbon nanocapsules are constructed. Fig. 1 shows the shortest and the longest structures while Fig. 2 shows the intermediate zigzag systems. In a related context, Fig. 3 shows the shortest and the longest structures, while Fig. 4 shows the intermediate armchair carbon nanostructures, under investigation. These structures has been optimized by parametric model 3 (PM3) which is a semiempirical method [18]. It may be noted that PM3 is a very reliable method to predict the molecular geometries and estimate the heat of formation of carbon system. As far as speed is concerned, it is a fast computational method as compared to *ab initio* and DFT techniques

[19]. This method applied to ground state conformations of nitrogen and boron substituted fullerenes shows good agreement with *ab initio* results [20]. The dimensions of the systems studied have been indicated in the relevant figures. Initially, the geometry of all the systems was optimized classically, using molecular mechanics (MM) method [21] taking into consideration mm+ force field [22]. This initial steps makes it easier to perform full optimization by quantum mechanical methods. The next step is to subject these classically optimized systems to geometry optimization using self-consistent field molecular orbital at Parametic Method (PM3) level, in restricted Harte-Fock (RHF) formalism [23]. The Polak-Ribiere optimizer was used in geometry optimization. The convergence criterion employed was that the gradient magnitude should become less than 1.0×10^{-3} kcal/Å mol . The entire calculation was performed in ground state of the system in its singlet state configuration. The calculations were done using HyperChem 7.51 [24] package program. Quantumwise Atomistics program [25] is used for calculating the density of states (DOS), Electron difference density (EDD) and electrostatic difference potential (EDP).

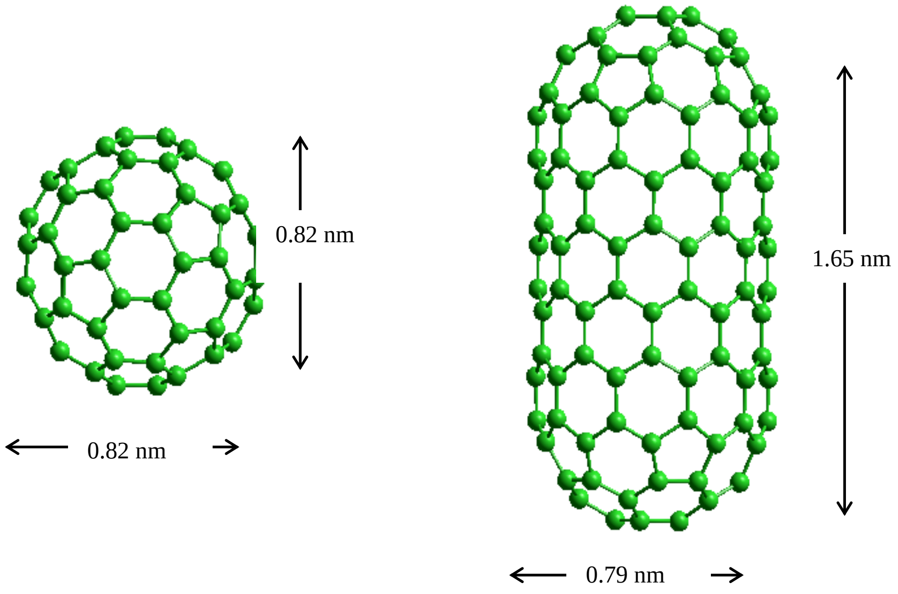
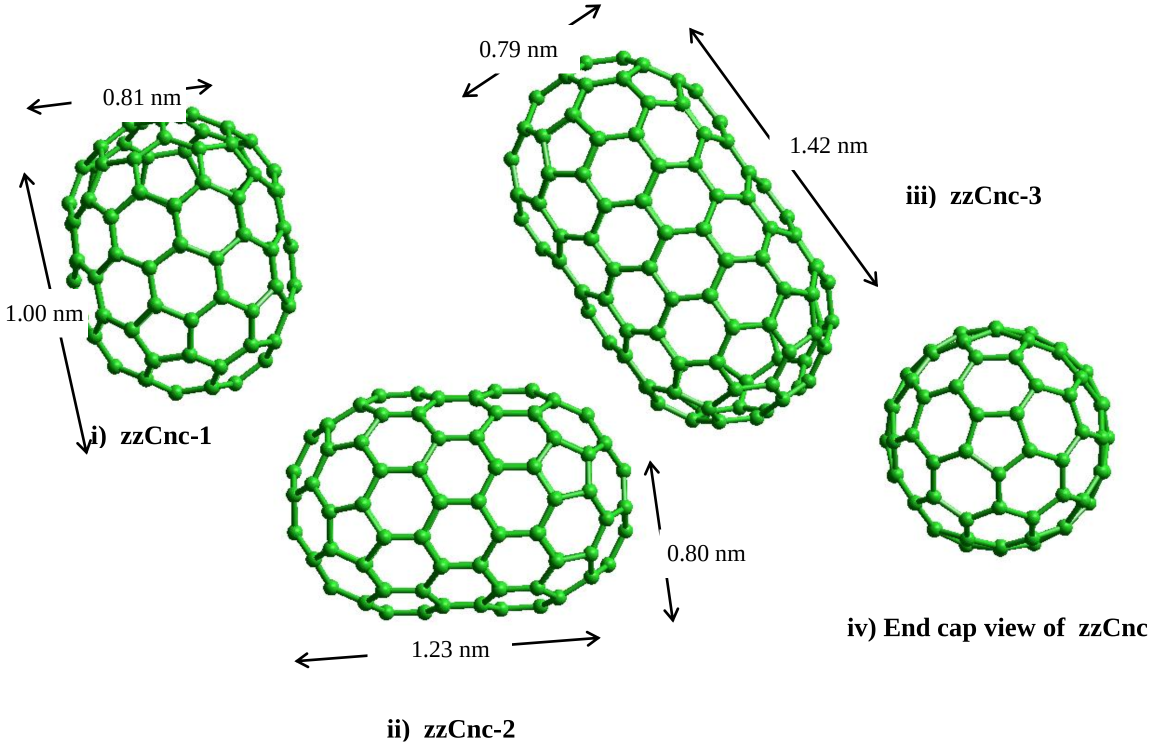


Fig. 1. Optimized structure of zzC$_{80}$ and zzCnc4.



i) zzCnc-1

ii) zzCnc-2

iii) zzCnc-3

iv) End cap view of zzCnc

Fig. 2. Optimized structures of zigzag carbon nanocapsules.

Table 1. Calculated Energy (in kcal/mol unless otherwise stated) of zzC_{80} and(9,0) zigzag carbon nanocapsules .

Quantity	**zzC_{80}**	**zzCnc-1**	**zzCnc-2**	**zzCnc-3**	**zzCnc-4**
Total no. of atoms	80	100	120	140	160
l/d	1.00	1.23	1.53	1.79	2.10
Total energy	-217943.00	-272479.34	-327063.03	-381678.22	-436442.85
Binding energy	-1237.00	-15971.83	-19254.03	-22567.71	-26030.84
Isolated atomic energy	-205206.00	-256507.50	-307809.00	-359110.50	-410412.00
Electronic energy	-3617915.00	-5147180.22	-6845360.50	-8695216.00	-10646513.81
Core-core interaction	3399972.03	4874700.88	6518297.35	8313541.53	10210070.96
Heat of formation	934.200	1117.165	1252.772	1356.89	1311.55
HOMO (eV)	-9.098	-8.385	-8.311	-8.2136	-8.957
LUMO (eV)	-3.36	-4.516	-4.525	-4.482	-3.060
ΔE_g(eV)	5.73	3.87	3.79	3.73	5.89

l/d: length to diameter ratio

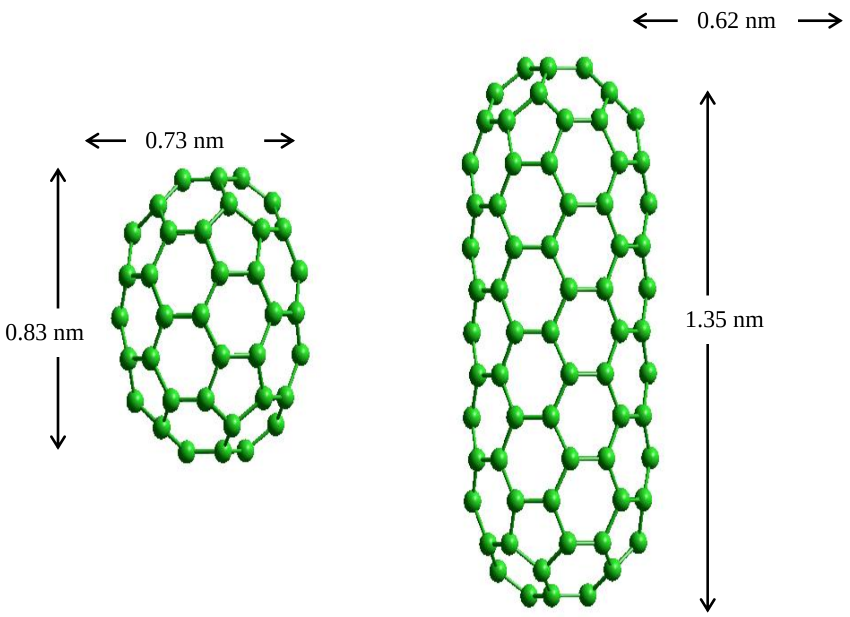
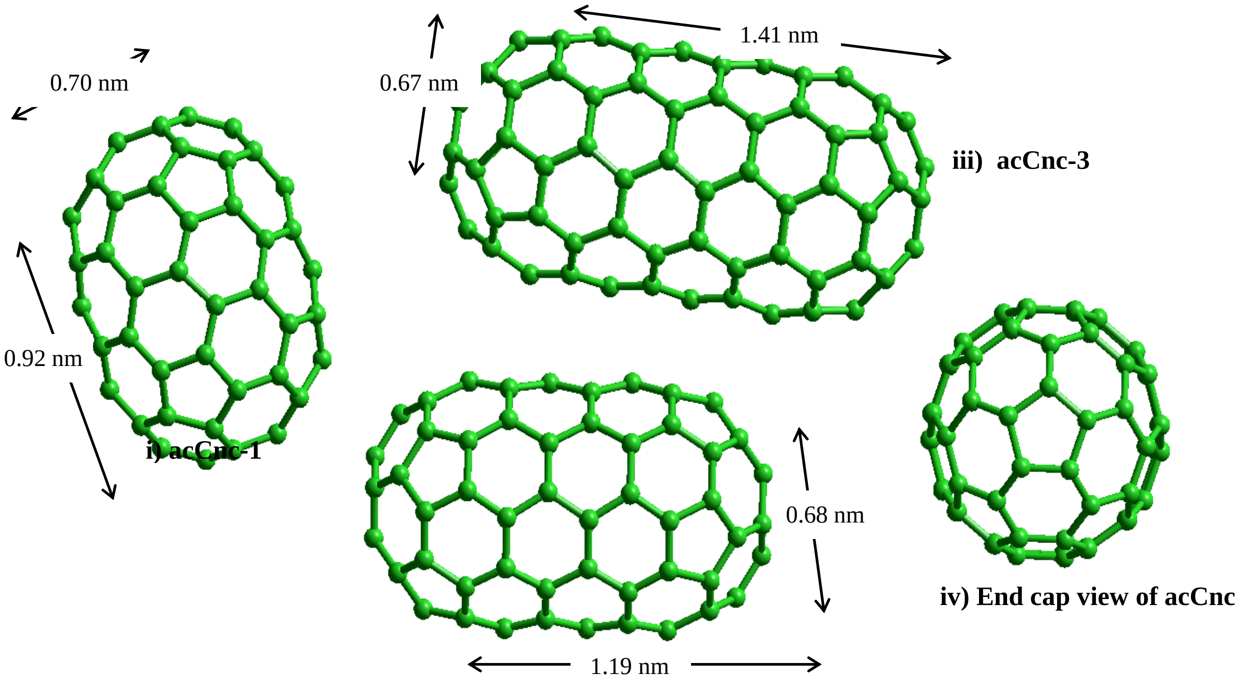


Fig. 3. Optimized structure of acC_{70} and acCnc-4.



i) acCnc-1

iii) acCnc-3

iv) End cap view of acCnc

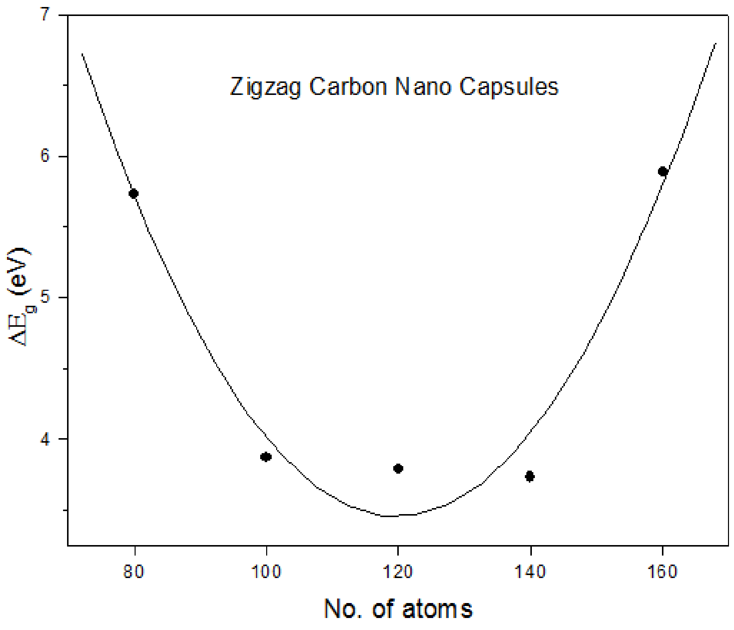
ii) acCnc-2

Fig. 4. Optimized structures of armchair carbon nanocapsules (PM3 results).

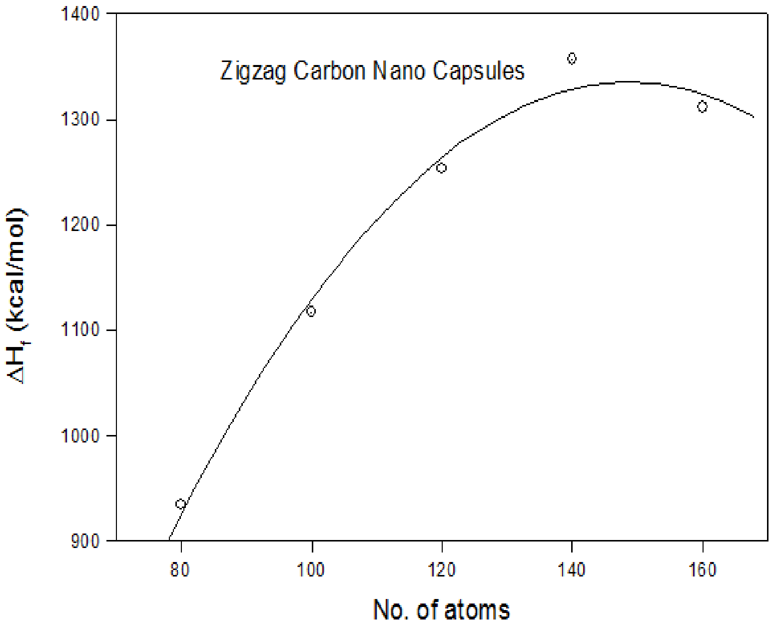
Table 2. Calculated Energy (in kcal/mol unless otherwise stated) of acC$_{70}$ and (5,5) armchair carbon nanocapsules .

Quantity	**acC$_{70}$**	**acCnc-1**	**acCnc-2**	**acCnc-3**	**acCnc-4**
Total no. of atoms	70	80	100	120	130
l/d	1.11	1.30	1.75	2.10	2.19
Total energy	-190667.31	-217920.38	-272508.91	-327097.13	-354483.09
Binding energy	-11112.07	-12714.38	-16001.41	-19255.11	-21023.34
Isolated atomic energy	-179555.25	-205206.00	-256507.50	-307809.00	-333459.75
Electronic energy	-2938431.88	-3632786.25	-5151395.50	-6628044.50	-7697149.38
Core-core interaction	2747764.57	3414865.83	4878886.88	6500947.21	7342666.29
Heat of formation	850.23	956.819	1087.587	1218.69	1192.35
HOMO (eV)	-9.74	-8.37	-8.44	-8.24	-9.41
LUMO (eV)	-2.72	-3.7098	-3.395	-3.065	-2.52
ΔE_g(eV)	7.02	4.66	5.05	5.18	6.89

l/d: length to diameter ratio

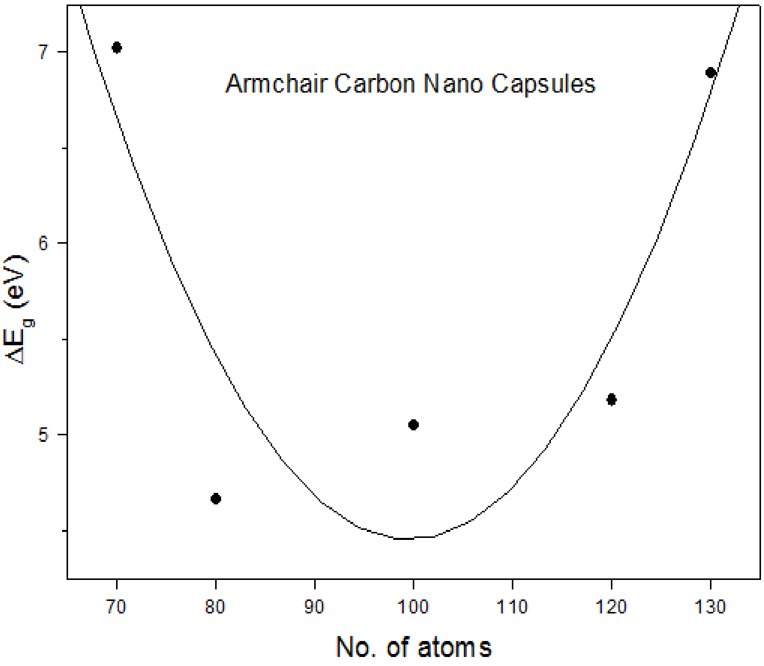


(i)

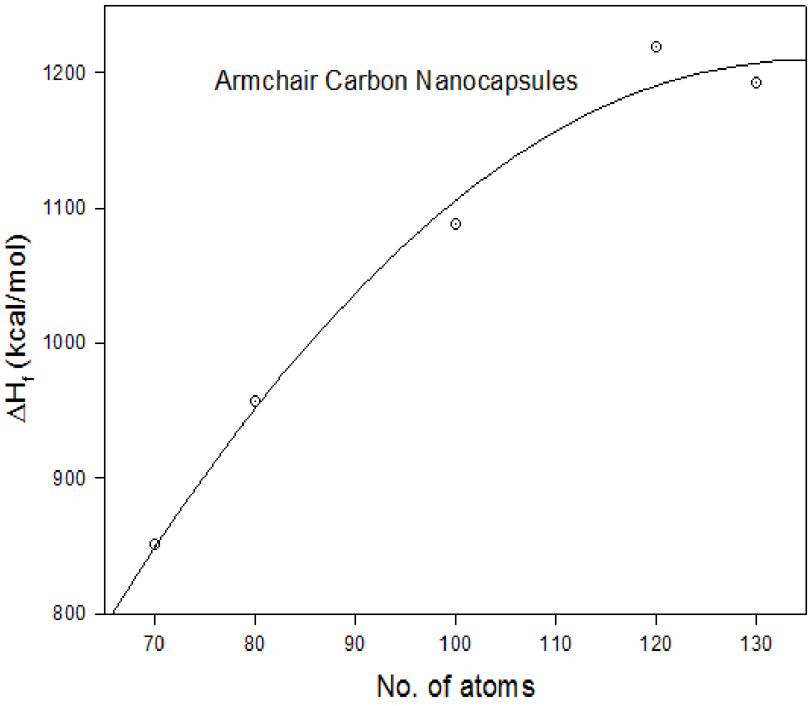


(ii)

Fig. 5. Variation of the energy band gap (i) and heat of formation (ii) on moving from spherical to capsule formation.



(i)



(ii)

Fig. 6. Variation of the energy band gap (i) and heat of formation (ii) on moving from spherical to capsule formation in armchair configuration

III. Results and discussion

To investigate the structural and electronic properties of single wall carbon nanocapsules (SWCncs), both zigzag and armchair configurations were constructed. These structures were then optimized using PM3 method; the advantages of choosing this method and the details of calculation have already been discussed above. The length to diameter (l/d) ratio for these zigzag and armchair systems lies in the range 1.00 - 2.10, and 1.11 - 2.19 respectively. These ranges are chosen because they exhibit the variation of structural and electronic parameters when the carbon nanostructures undergo shape (spherical to capsule) and size transformation.

3.1. Zigzag naostructures

We have considered zzC_{80} as the smallest zigzag nanostructure, then gradually increase its length, by adding successively one unit of single wall carbon nanotube (9,0), so as to form a nanocapsule. The various carbon nanocapsule systems in zigzag configuration are denoted by zzCnc-1(100), zzCnc-2 (120), zzCnc-3 (140) and zzCnc-4 (160); the value inside the brackets denotes the number of atoms in that particular system. The PM3 optimized geometry of the shortest (zzC_{80}) and the longest (zzCnc-4) zigzag nanostuctrues; and the intermediate structures between these two extremes of this class are illustrated in figures (Fig. 1-2). The dimensions of the systems are also mentioned in these figures. The length to diameter (l/d) ratio for these nanostructure systems lies in the range 1.00-2.10. A ratio of 1.00 characterises zzC_{80} which is spherical in shape. The different molecular properties calculated for these five zigzag nanostructures, alongwith some thermodynamical properties of the systems such as total energy, binding energy, isolated atomic energy, electronic energy, core-core interaction and heat of formation are presented, in Table 1. Fig. 5 (i) shows the variation of energy band gap with the size of the systems. The smallest system zzC80 has a band gap of 5.73 eV. The gap decreases rapidly as the system undergoes structural change and forms a capsule. For zzCnc-3 the energy band gap has the lowest value of 3.73 eV. This value is the minimum as compared other members and shows that this system is most reactive. The energy band gap then again rises for zzCnc-4 and exceeds that of zzC_{80}. The heat of formation (ΔH_f) for these systems is positive, indicating that the process of formation is endothermic. Fig. 5(ii) shows the plot of heat of formation for various zigzag structures, the heat of formation is least for zzC80 i.e. 934.20 kcal/mol. It then increases and reaches its maximum value for zzCnc-3 and further shows a decreasing trend. The carbon nanocapsule zzCnc-3 (which has smallest ΔE_g energy band gap) has the maximum value of ΔH_f . Fig. 7 shows a comparison of the density of states for spherical and capsule form. The 2-D plot of electron density difference and electrostatic difference potential are shown in Fig. 8 (a,b) and (c,d) respectively. These plots shows some interesting features, the negative charge is developed along the walls and the a positive charge on the ends of the capsules.

3.2. Armchair nanostuctures

The members of this group are denoted by acC_{70} , acCnc-1(80), acCnc-2(100), acCnc-3(120) and acCnc-4(130). Table 2 displays the PM3 calculated values of structural, electronic and thermodynamic properties of armchair carbon nanostructures. The smallest member of this group is acC_{70} , for which l/d ratio is 1.11; and it is not completely spherical. Fig 6(i) shows the plot of ΔE_g of these structures. It is observed that the energy band gap for acC_{70} is the maximum (7.02 eV). As the system undergoes shape transformation and forms a capsule, the energy band immediately becomes a minimum (4.66 eV) for acCnc-1. Then it again increases as the length of the capsules increases and for the longest capsule (acCnc-4), the energy band gap becomes 6.89eV. In this configuration, as the capsule is formed from nearly spherical structure; there is a sharp dip in energy band gap which is different from the zigzag case. In zigzag, the energy attains a minimum value for zzCnc-3 and not for zzCnc-1. The more reactive member in this case is acCnc-1. The process of armchair structure formation here is again endothermic, as the heat of formation is positive; although the values are lower as compared to zigzag structures. The trend of heat of formation for armchair Fig. 6(ii) is similar to that of zigzag structures, it first increases, reaches a maximum and then decreases. Fig. 8 shows a comparison of the density of states for spherical and capsule form in case of armchair configuration. The 2-D plot of electron density difference and electrostatic difference potential are shown in Fig. 10 (a,b) and (c,d) respectively.

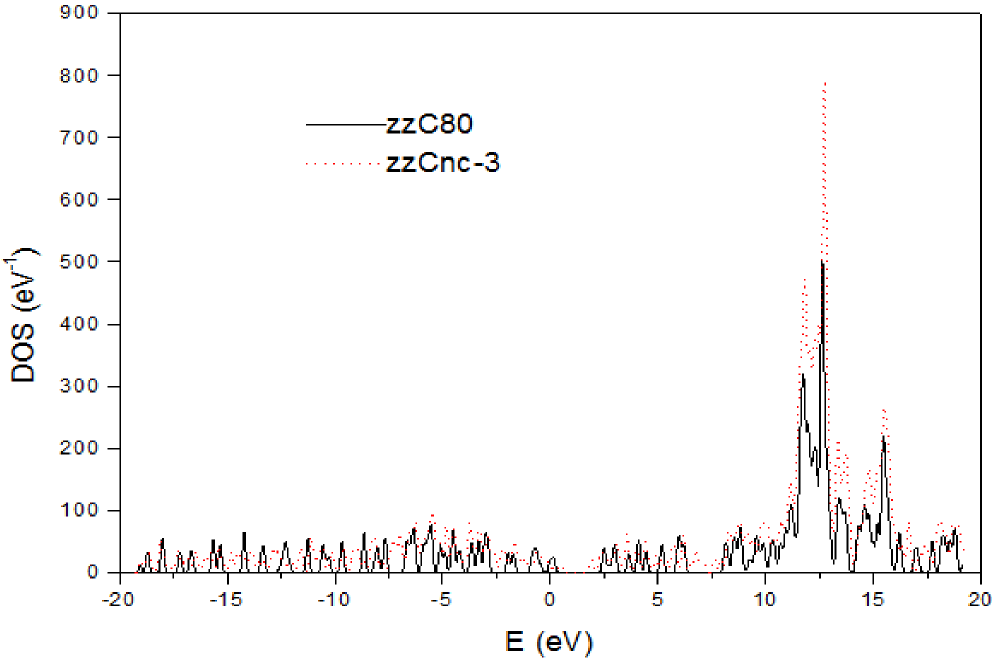


Fig. 7. Density of states (DOS) of zizzag spherical and capsule structures.

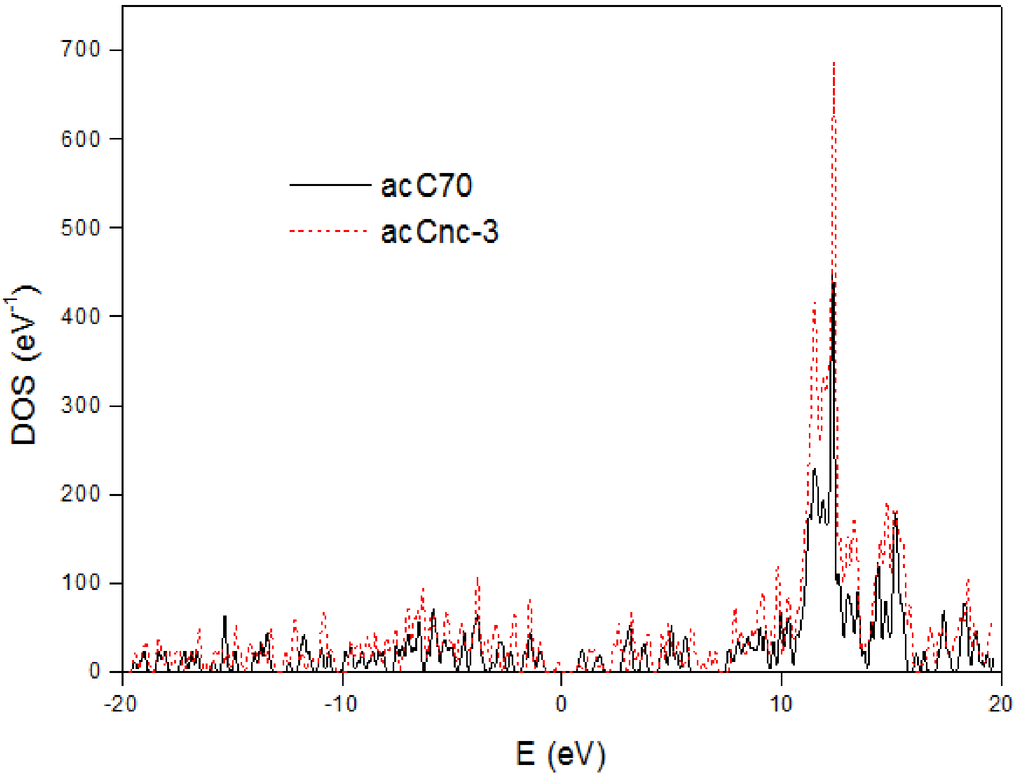
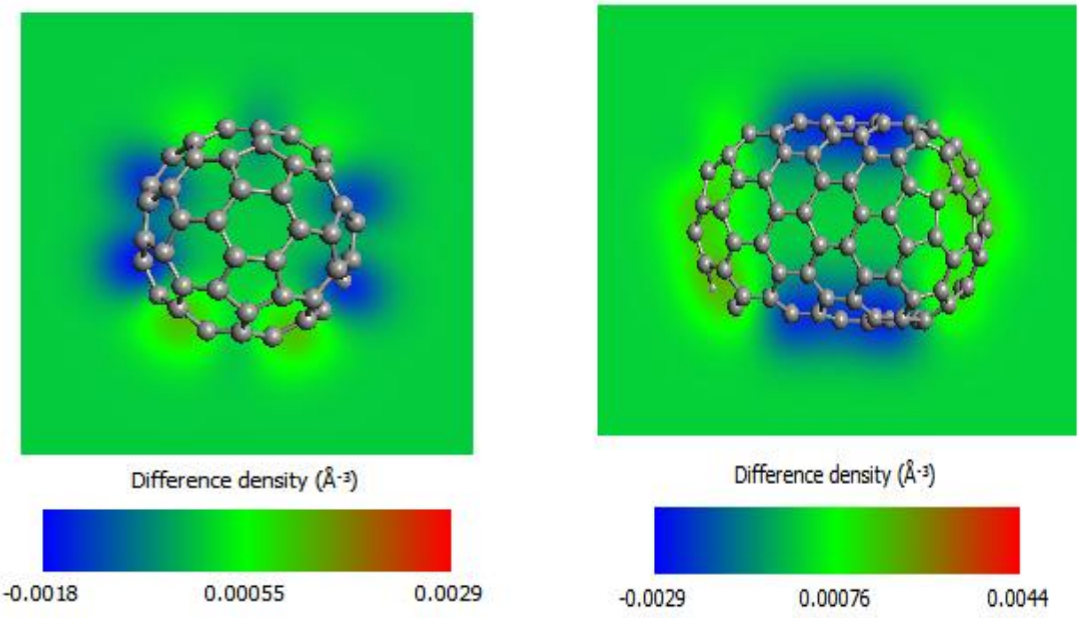
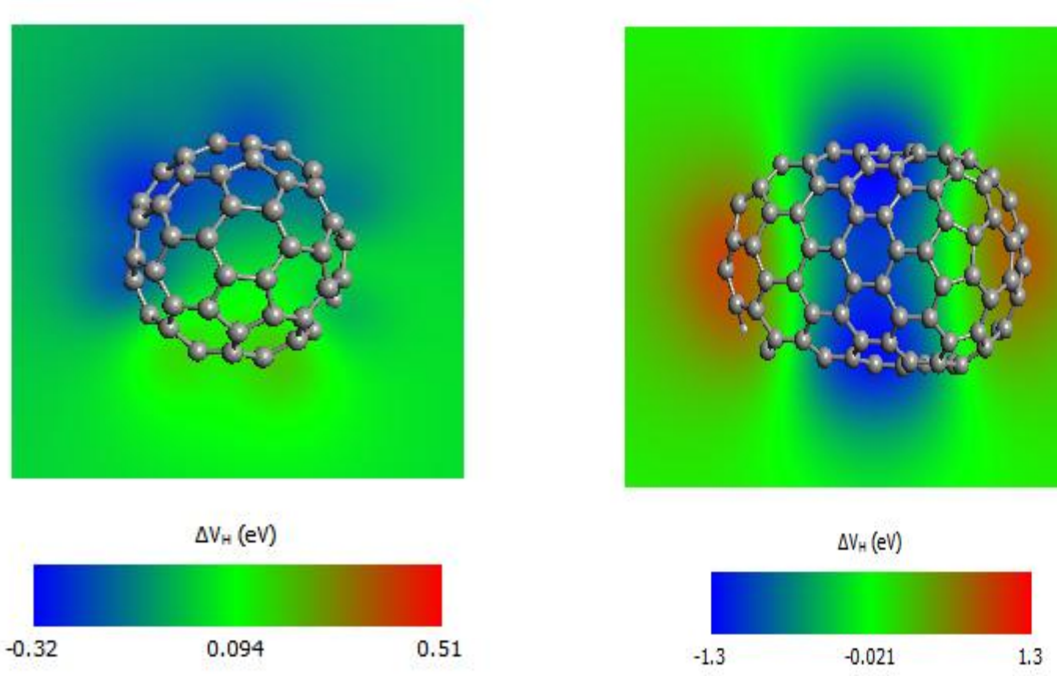


Fig. 9. Density of states (DOS) of armchair spherical and capsule structures.

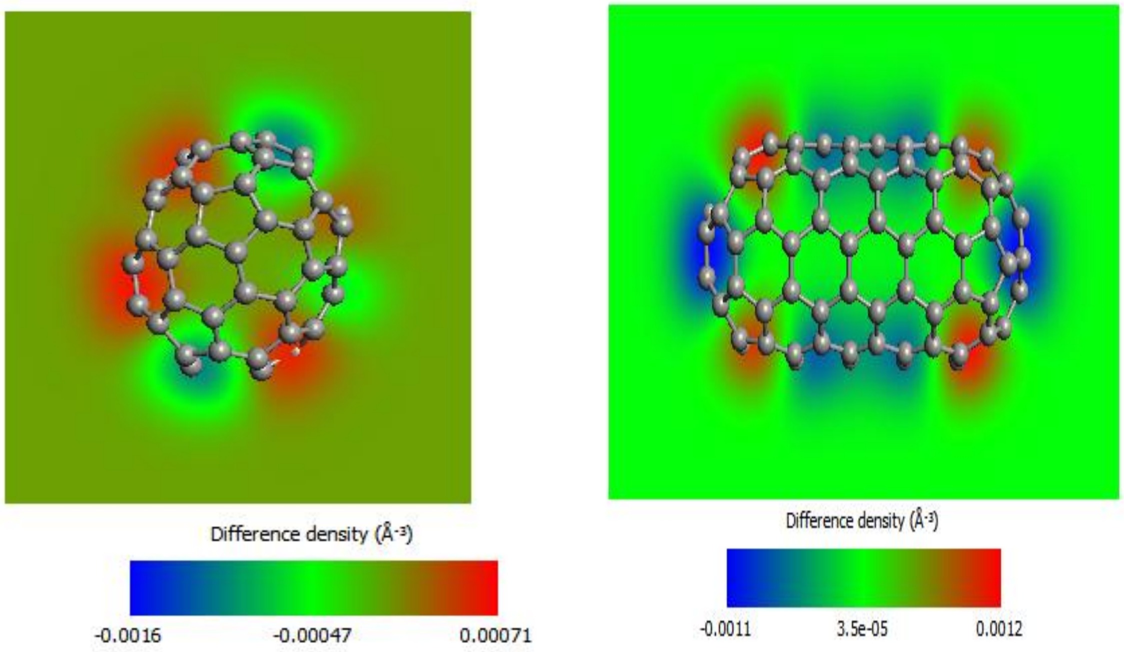


(a) (b)

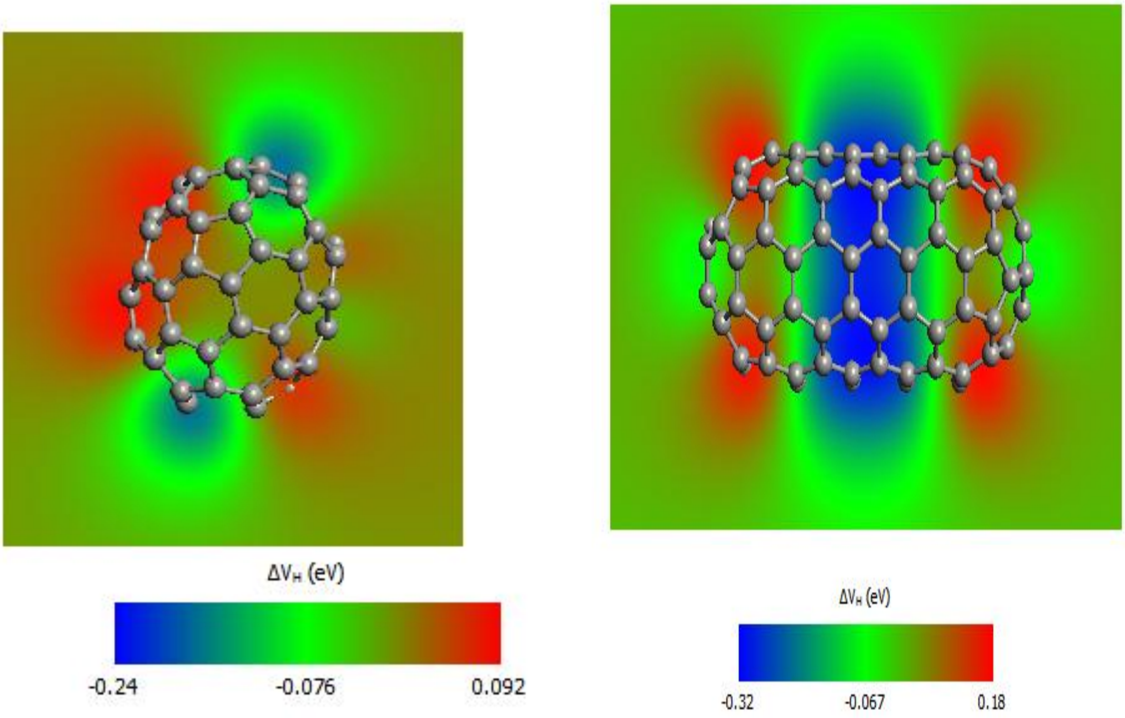


(c) (d)

Fig. 8. Electron difference density (a,b) and electrostatic difference potential (c,d) of zigzag structures



(a) (b)



(b) (d)

Fig. 10. Electron difference density (a,b) and electrostatic difference potential (c,d) of armchair structures

IV. Conclusions

To summarize, we have carried out theoretical investigations by performing PM3 semi-empirical molecular orbital calculations, in the context of RHF type quantum chemical treatment. The purpose has been to explore the variation in structural, electronic and thermodynamical properties; when these systems undergo shape and size transformation. We have observed that the energy band gap and heat of formation follow definite trends; as size is varied; both in zigzag and armchair configurations. The band gap in case of armchair carbon nanocapsules is greater than that in zigzag form; establishing that zigzag form of fullerenes or capsules are more reactive.

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