Journal of Molecular Structure: THEOCHEM 861 (2008) 79–84

Contents lists available at ScienceDirect

Journal of Molecular Structure: THEOCHEM

journal homepage: www.elsevier.com/locate/theochem

Ab initio study on the structural, energetic and electronic features of the asymmetric armchair SWCNT junctions

Yuanfeng Ye [a], Milin Zhang [a], Jianwei Zhao [b,*], Hongmei Liu [b], Nan Wang [b]

[a] School of Materials Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, PR China
[b] School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, Jiangsu 210093, PR China

ARTICLE INFO

Article history:
Received 31 January 2008
Received in revised form 6 April 2008
Accepted 16 April 2008
Available online 29 April 2008

Keywords:
Carbon nanotubes
Ab initio calculations
Junctions
Molecular rectifier

ABSTRACT

The structural, energetic and electronic features of asymmetric armchair single-walled carbon nanotube (SWCNT) junctions have been studied by *ab initio* calculations at the B3LYP/6-31G*//HF/3-21G* levels. The junctions are composed of two SWCNTs with different radius, which are connected by a set of 5-membered and 7-membered carbon rings. The results show that the metallic–metallic junction is more energetically favorable if the junction is formed with a hexagon inserted between the pentagon–heptagon (5/7) pair defects in the armchair nanotube. The shift of the spatial distribution of HOMO and LUMO shows that the asymmetric electronic structure of the junction could be used as a molecular rectifier.

1. Introduction

Since the discovery by Iijima in 1991 [1], carbon nanotubes have attracted high attention regarding their unique electronic properties. The geometrical structure of a single-wall carbon nanotube (SWCNT) is determined by the circumference vector $C = na_1 + ma_2$, where a_1 and a_2 are translation vectors of the graphene sheet lattice. Both the armchair nanotube (n,n) and the zigzag nanotube $(n,0)$ have a non-chiral configuration. The (n,n) armchair nanotubes are metallic while the (n,m) tubes are semi-metallic if $n–m$ is a non-zero multiple of three, and semi-conducting otherwise [2]. At room temperature the individual semi-conducting nanotubes can function as field-effect transistors [3], while metallic nanotubes are used as single electron transistors at low temperature [4]. When two kinds of nanotubes (one semi-conductive and the other metallic) are connected, a unique junction is formed that may behave as a rectifying diode [5]. The electronic properties of the intra-molecular junctions, have currently received lots of research interest since SWCNTs are promising candidates for wiring of individual molecules as functional components into the nanocircuits.

Two nanotubes of different diameter can be connected by inserting pentagon–heptagon (5/7) pair defects into the perfect hexagonal lattice [6]. The junction varies according to the different number and location of the pentagon–heptagon pairs. In the zigzag $(n,0)$ SWCNT the pentagon and heptagon are close to each other (end to end). In contrast, in the armchair (n,n) SWCNT they adopt a head to head form and are linked by a carbon–carbon bond. In the case of connecting two SWCNTs which differ so greatly in diameter, it requires more 5/7 pairs in the junction. Furthermore those 5/7 pairs are distributed in the junction and may affect the electronic structure of the junction. In the previous studies, Frontera et al. have studied the distributions of two 5/7 pair defects in the zigzag SWCNT [7]. They compared the energies of several junctions and got a specified stable structure. However, the conclusion is questionable in the armchair SWCNT junction due to the structural particularity as shown in Fig. 1. Although in experiment the existence of junction can be proven by STM in the samples produced by laser ablation [8,9], the detailed topological defects and their distributions are hard to visualize.

In this paper we performed *ab initio* calculations to study the effect of introducing 5/7 pair defects into the network of armchair SWCNTs. We focused on the energetic, geometric and electronic features of the junctions with different distributions of 5/7 pair defects. Among the many possible joints [10], in particular four different types of joining one (6,6) and one (4,4) armchair nanotubes (Fig. 1) were studied and the energetic cost of each junction was analyzed by using homodesmotic equations [7]. Besides the chemical properties of the junction, the potential usage as molecular electronic device has been discussed as well.

2. Computational methods

The geometries of all SWCNTs included in this study were optimized initially at the restricted Hartree-Fock level with STO-3G

* Corresponding author. Tel./fax: +86 25 83596523.
E-mail addresses: zhaojw@nju.edu.cn, zhaojianweicn@yahoo.com.cn (J. Zhao).

0166-1280/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.theochem.2008.04.023

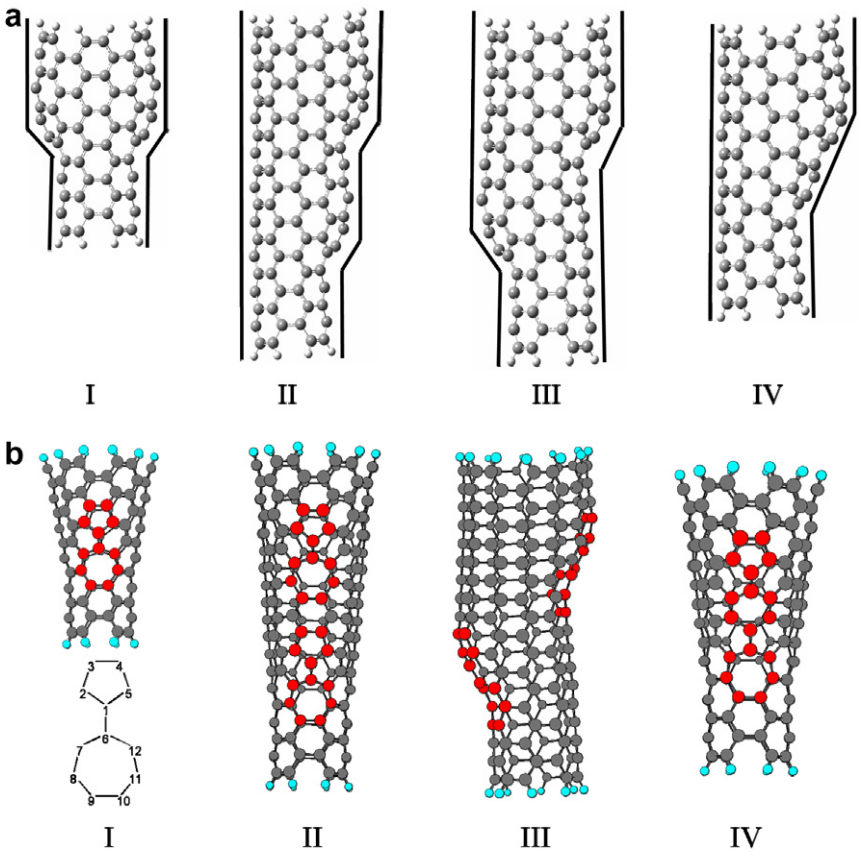

Fig. 1. (a) HF/3-21G* optimized structures of armchair nanotube junctions (I–IV) and (b) the defects in the four models which are shown in red color and the left-down is the codes of the 5/7 pair defect. (For interpretation of color mentioned in this figure the reader is referred to the web version of the article.)

basis set. These structural fragments have been used in the following connections to form junctions. The junctions were carefully connected by introducing 5/7 pair defects, and fully optimized at the HF/3-21G* level of theory using the Gaussian 03 program [11]. Previous studies have demonstrated that reliable quantitative results are obtained at this level of theory which is used to keep the size of the calculation approachable [12,13]. In order to include the electron-correlation effects and increase the accuracy in the energy prediction, single point calculations at B3LYP/6-31G* level of theory were carried out using the geometries optimized by HF/3-21G*.

3. Results and discussion

3.1. The geometric structure

Fig. 1 shows the relaxed structures at HF/3-21G* level (I–IV) of different joints connecting two armchair nanotubes, (6,6) and (4,4). Junction I contains two 5/7 pair defects distributed equidistantly around the circumference of the tube forming a cone-like junction. Junction II contains two 5/7 pair defects aligned along the cylindrical axis. In model III, the two 5/7 pair defects are distributed around the circumference of the tube as in nanotube I, but they are placed in different rows. In model IV, a hexagon is inserted between the pentagon and heptagon rings, giving rise to a reduction in the diameter of the nanotube equivalent to a double 5/7 pair defects. The difference of the distribution of the 5/7 pair defects will result in the difference of the ring-strain force and then affect the geometric structure. From the optimized structures, we can conclude that the pentagon ring is planar and the heptagon one is boat shaped which is similar to those in the zigzag SWCNT. Frontera's work shows that the difference of stability is mainly originated from the distortion of the defect pair [7]. So the bond angles play a more important role in the stability of SWCNT. The computed bond lengths and angles of the 5/7 and 5/6/7 defects are summarized in Table 1. To ensure the accuracy of these results the geometric discussions are built on the results of HF method. The average value of bond angles in four models is very similar while it is different in the zigzag SWCNT. Then what leads to the difference of the stability? In our previous work about the chemical properties of cyclic compounds, a new method to analyze the ring-strain energy has been proposed and it can be used effectively to evaluate the stability of system [14]. Analogy to that method in which three parameters named bond length, bond angle and dihedral-angle were defined, we can infer that the bond length and dihedral-angle will play a more important role in the current models. Finally the diversity of armchair and zigzag SWCNT can be explained by the different connection of pentagon ring and heptagon ring: the bond between the two rings increases the flexibility in the present models compared with that in the zigzag ones. The mean length of the particular bond in all the models is about 1.36 Å and shows the double bond character. The separation of the pentagon and heptagon rings changes conjugated situation of the defect part and then becomes the origin of the different stability for four junctions. In conclusion, both the distribution and the connection of the 5/7 defects affect the stability of the CNT junction both in the zigzag and armchair SWCNT.

3.2. The energetic features

By calculating cyclic conjugation energies, the homodesmotic reactions can be used to estimate aromaticity [10]. Here four