Effects of Structure and Partially Localization of the π Electron Clouds of Single-Walled Carbon Nanotubes on the Cation-π Interactions

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ABSTRACT: *A $C_{102}H_{30}$ graphene sheet has been rolled up to construct Single-Walled Carbon NanoTube Fragments (SWCNTFs) as parts of armchair carbon nanotubes by computational quantum chemistry methods. Non-covalent cation-π interactions of the Na^+ cation on the central rings of SWCNTFs have investigated. The binding energies of the Na^+-SWCNTF complexes versus true strain parameter (R) change in three brands. Structural parameters, electron charge density values, and also effects of aromaticity on the binding energies were gauged. Results show that partially localization of the π electron clouds of SWCNTFs enhances strength of the cation-π interactions in some cases. Thus, changing the π electron clouds of SWCNTs may help to improve surface modification of these materials through the cation-π interactions, which has important applications such as storage of electric energy by transportation of cations through the walls of SWCNTs and enhancement of the hydrogen adsorption compared to pure SWCNTs.*

KEYWORDS: *Cation-π; Graphene sheet; Electron charge density; Aromaticity; π Electron cloud.*

INTRODUCTION

Carbon NanoTubes (CNTs) are allotropes of carbon. Single-Walled Carbon NanoTubes (SWCNTs) and Multi-Walled Carbon Nanotubes (MWCNTs) are two well-known types of these materials [1].

The p-orbital electrons of the graphene sheet organize in band valence (π) and conduction (π*) bands [2]. When graphene sheet is rolled up to the cylindrical form of SWCNT, its π and π* electron clouds change which causes partial σ- π hybridization [3]. *Naseri et al.* have investigated adsorption of some organic dyes from aqueous solution onto graphene nanosheets [4]. Results o indicated that graphene has exceptional capacity to remove organic dyes from solution and can be considered as an excellent adsorbent.

Electronic properties of SWCNTs make them valuable biosensors [5,6]. CNTs have unique properties and contribute in drug delivery processes for treatment of various diseases [7]. For example, CNTs act as effective drug delivery carriers in cancer therapy [8]. CNTs deliver smaller doses of drugs in the body and lead to lower side effects and higher efficiency in the disease cell targeting processes [9].

Surface modification of SWCNTs through covalent or non-covalent interactions is an effort to increase solubility of these materials in various solvents [10-14]. Unlike covalent functionalization of SWCNTs, which somewhat distorts the electronic and structural properties

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of these materials, non-covalent modifications increase solubility of SWCNTs and preserve geometric, electronic and mechanical properties of them.

Cation-π interactions are non-covalent forces between a monopole (cation) and a quadrupole (π system). These interactions have basically different nature than bonding between transition metals and π systems which has covalent characteristics [15,16]. The amino acid side chains of phenylalanine, tryptophan, tyrosine and histidine can bind to the cations and charged amino acid side chains. Moreover, macromolecular binding sites consist of anionic groups which have an affinity for the cations. Thus, cation-π interactions emerge in these situations and contribute to the structure and function of proteins [17]. Also, DNA bases participate in cation-π interactions [18,19].

Cation-π interactions are essential for binding and activating nicotinic acetylcholine receptors through making structural changes to a tryptophan residue [20]. Indeed, these interactions have fundamental roles in selective activating of brain receptors by nicotine [21,22]. Furthermore, cation-π interactions stabilize buildup of positive charge in transition states and catalyze chemical reactions [16].

Some authors showed that SWCNTs can self-assemble during growth into moderately ordered two dimensional ropes [23]. These SWCNT ropes can be doped to form metallic conductors which have positive applications [24,25]. Alkali-doped SWCNTs absorb higher amounts of hydrogen than pure SWCNTs [26,27]. Also, alkali-doped SWCNTs have utilized in chargeable lithium batteries [28,29]. In fact, these devices act on the basis of cation-π interactions and facilitate storage of electric energy by transportation of cations through the walls of SWCNTs [30].

George Froudakis et al. have studied cation-π interactions on outer sidewalls of different SWCNTs by ab anitio and Molecular Mechanic calculations. They showed that cation is located on top of a phenyl group of the nanotubes and concluded that cation-π interaction is not affected by the type of cation or the diameter of the nanotubes [31].

Effect of the curvature of SWCNTs on lithium storage has been investigated by ab anitio and Molecular Dynamic simulations. Results revealed that cations remain attached to the SWCNTs even at room temperature [32].

Surfactants with small cations (H⁺, Li⁺ and Na⁺) can modify electronic properties of SWCNTs. Therefore, cation-π interactions play significant roles in selective modification of SWCNTs [33]. The influence of electronic factors and aromaticity of the π system on the cation-π interactions have been explored in polycyclic systems by *Narahary Sastry et al.* [34]. They showed that Li⁺ and Na⁺ cations bind to both the convex and concave faces of bulky bowls, but there is more preference for binding to the convex faces. Also, they revealed that binding of the cations is controlled by electronic factors and is independent of the bowl depth.

SWCNs with different diameters and changeable surface areas are good beds for interactions of ions [35]. Surface modifications of SWCNTs through non-covalent interactions improve electronic structure of them. Because alkali-doped SWCNTs are able to absorb higher amounts of hydrogen than pure SWCNTs and cation-π interactions facilitate storage of electric energy by transportation of cations thorough the walls of SWCNTs, it is necessary to recognize effects of various factors which manage surface modification of SWCNTs through the cation-π interactions.

Strength of the cation-π interactions is controlled by several factors such as nature of the cation and π systems. It seems that, delocalization and localization of the π electron clouds of SWCNTs to be important in non-covalent functionalization of these materials through the cation-π interactions.

In this work, a $C_{102}H_{30}$ graphene sheet has rolled up by computational quantum chemistry methods to construct single-walled carbon nanotube fragments (SWCNTFs) as parts of armchair carbon nanotubes. These SWCNTFs have the same number of atoms and represent parts of SWCNTs with different outer diameters. The cation-π interactions of the Na⁺ cation on the central rings of SWCNTFs have investigated. Interactions of cations with SWCNTs modify surfaces of these materials and cation-SWCNT complexes have important applications such as in storage of electric energy and can also adsorb higher amounts of hydrogen compared to pure SWCNTs. Therefore, better interactions of cations with SWCNTs make them more usable in storage of electric energy and adsorption of hydrogen. Thus, effects of various factors on cation-π interactions of Na⁺ cation on SWCNTFs (which represent behavior of
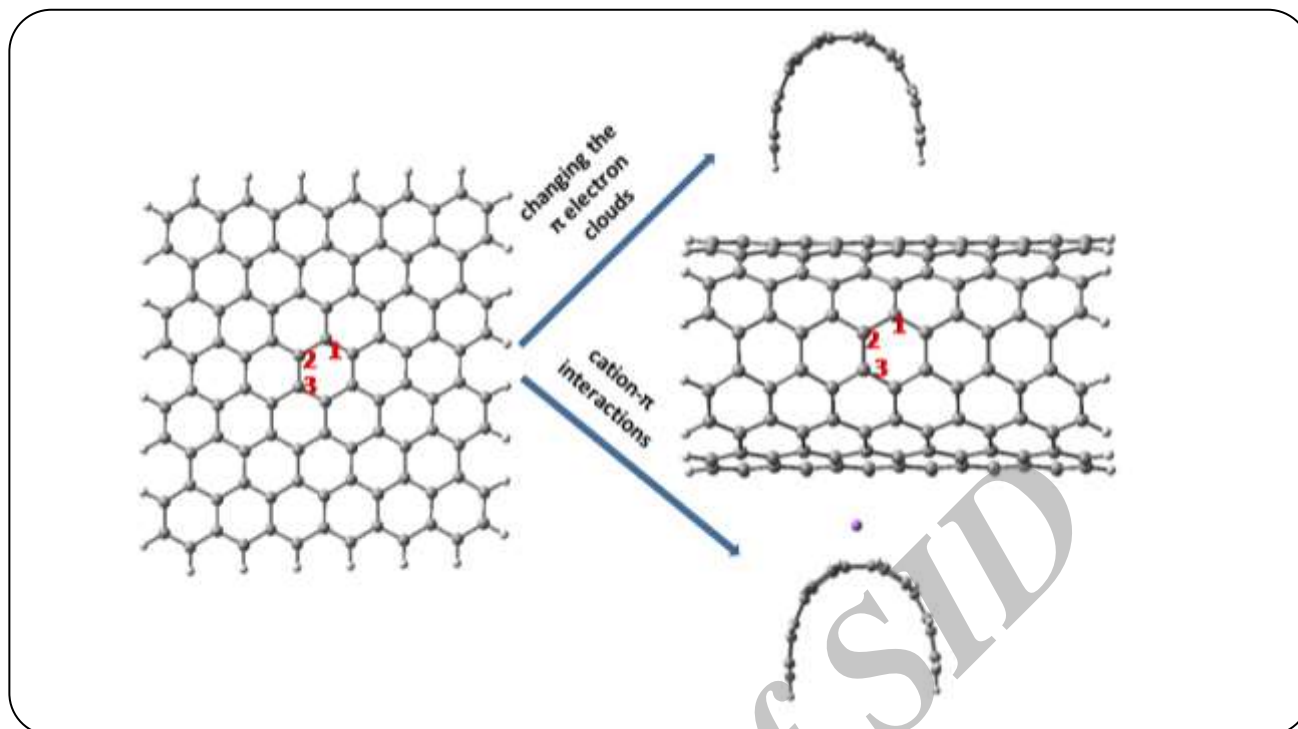
Scheme 1: Rolling up the $C_{102}H_{30}$ graphene sheet and making armchair SWCNTFs for investigation of effects of structure and changing the π electron clouds of SWCNTFs on the cation-π interactions.

SWCNTs) were examined to find how can make cation-SWCNTF complexes with large binding energies.

COMPUTATIONAL METHODS

Structures of all monomers and complexes were optimized with Gaussian09 program package [36] at the M05-2X/6-31G (d) level of theory.

Zhao & Truhlar proposed that the M05-2X functional compensates the deficiencies of other hybrid functionals by incorporating an improved treatment of spin kinetic energy density in both the exchange and correlation functionals. The M05-2X functional has been utilized for evaluation of the cation-π binding energies [37].

The topological properties of electron charge density have been calculated by the AIM method on the wave functions obtained at the M05-2X/6-31G(d) level of theory using AIM2000 program [38]. The diamagnetic and paramagnetic effects of ring currents related to aromaticity and anti-aromaticity can be evaluated by Nucleus Independent Chemical Shift (NICS) [39,40] criterion. The NMR calculations have been performed at the M05-2X/6-31G(d) level of theory using GIAO (gauge independent atomic orbital) method [41].

RESULTS AND DISCUSSION
Structural parameters and energy data

A $C_{102}H_{30}$ graphene sheet was constructed with HyperChem 7.1 software [42]. This graphene sheet has the C_{2v} symmetry (see scheme 1). To make SWCNTFs, Potential Energy Surface (PES) relaxed scans have performed. In fact, distances of terminal hydrogens of the graphene sheet were fixed as redundant coordinates. These distances were reduced by 10 Å during 100 step-by-step full optimizations. Thus, each SWCNTF has a true strain parameter (R) which can be estimated as below:

$$R = Ln (r_0/r) \tag{1}$$

In this equation r_0 and r are the distances between terminal hydrogens of the graphene sheet and SWCNTFs, respectively. The binary Na^+-graphene and Na^+-SWCNTF complexes are made from 1:1 ratio of Na^+:graphene and Na^+:SWCNTF, respectively. Thus, interaction energy of each binary complex is obtained from difference between energy of it and energies of the constituting monomers:

$$\Delta E_{Na+-graphene}=E_{Na+-graphene}- (E_{Na+} + E_{graphene}) \tag{2}$$

$$\Delta E_{Na+-SWCNTF}=E_{Na+-SWCNTF}-(E_{Na+}+ E_{SWCNTF}) \tag{3}$$

Non-covalent cation-π interactions of the Na^+ cation on the central rings of graphene and SWCNTFs have investigated. Binding energies of all Na^+-SWCNTF complexes versus R values have depicted in Fig. 1. As can be seen, ΔE values change in three brands. To explain this binding energy changes, the most important structural parameters of all complexes have studied. Results show that the cation-π interactions of the Na^+ cation on the central rings of SWCNTFs lead to increment of bond lengths of these rings (C1-C2 or C2-C3 bonds in scheme 1). However, unlike covalent functionalization, these interactions don't deform surfaces of SWCNTFs. In Fig. 2, ΔE values against the C1-C2 bond lengths of all binary complexes have demonstrated. As can be seen, binding energies against the C1-C2 bond lengths change in three brands. In the first brand (■), ΔE values nearly are the same, but C1-C2 bond lengths are not the same. In the second brand (▲), decrement of ΔE values is followed by increment of the C1-C2 bond lengths. On the other hand, increment of ΔE values in the third brand (×) is accompanied by increment of the C1-C2 bond lengths. Results show that rolling up the graphene sheet firstly lead to decrement of the C1-C2 bond lengths. However, this decrement in the C1-C2 bond lengths continues to a minimum and then increment of the C1-C2 bond lengths occurs. Thus, structural features of SWCNTFs influence the cation-π interactions. In fact, rolling up the graphene sheet leads to changes in the π electron clouds of SWCNTFs and results in different cation-π binding energies.

The equilibrium distance between the Na^+ cation and graphene or each SWCNTF is denoted as $R_{cation...π}$. Correlations between $R_{cation...π}$ values and binding energies may help to answer the observed changes in the ΔE values. These correlations have shown in Fig. 3 for all binary complexes. As can be observed, in the first (■) and second (▲) brands, increment of binding energies is accompanied by increment of $R_{cation...π}$ values. In the third brand (×), complexes with the lower $R_{cation...π}$ values have the higher binding energies. In this brand, increment of ΔE values goes with increment of the C1-C2 bond lengths. These increases in the C1-C2 bond lengths mean that hyper conjugation effects diminish in these bonds which arise from lower overlapping between the p orbitals. In fact, the π electrons are somewhat localized in this case. Therefore, cation-π interactions on SWCNTFs
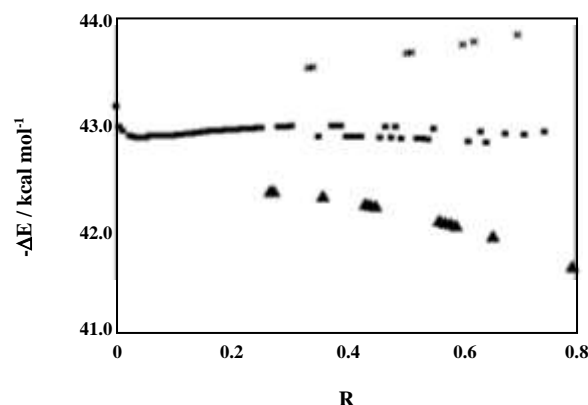

Fig. 1: The binding energies of the Na^+-graphene and Na^+-SWCNTF complexes versus true strain parameter for the first (■), second (▲), and third (×) brands.
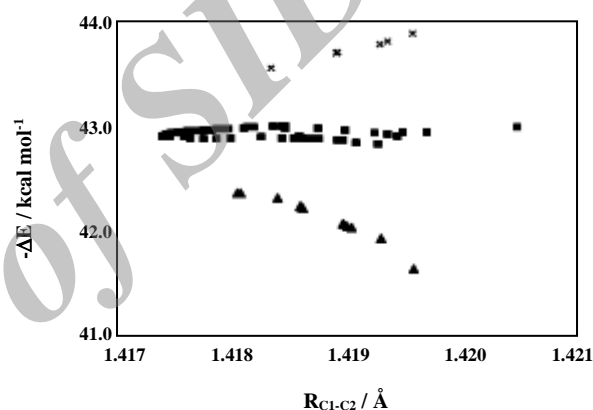

Fig. 2: The binding energies of the Na^+-graphene and Na^+-SWCNTF complexes against the C1-C2 bond lengths for the first (■), second (▲), and third (×) brands.
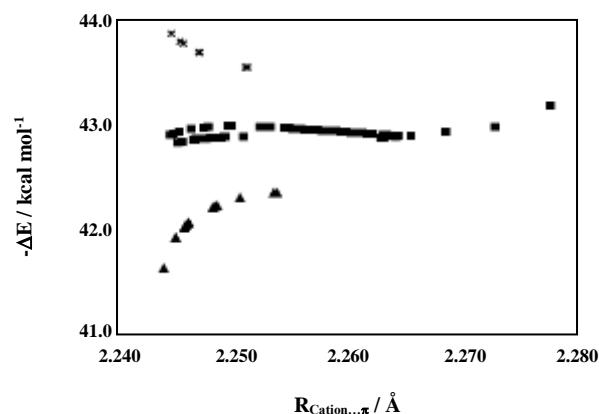

Fig. 3: The binding energies of the Na^+-graphene and Na^+-SWCNTF complexes against vertical distance between the Na^+ cation and SWCNTFs for the first (■), second (▲), and third (×) brands.
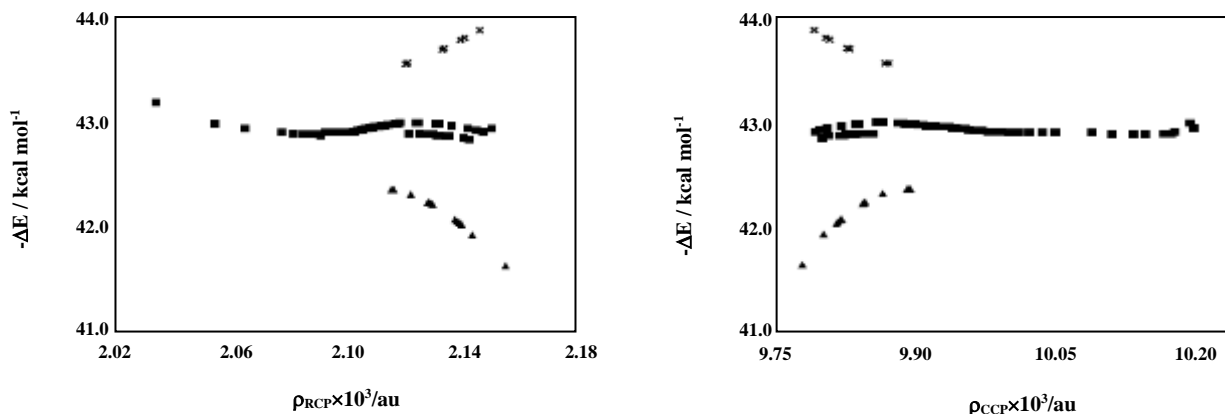
Fig. 4: The binding energies of the Na⁺-graphene and Na⁺-SWCNTF complexes versus ρ_{RCPs} at the central rings of the graphene sheet and SWCNTFs (a) and versus ρ_{CCPs} (b) for the first (■), second (▲), and third (×) brands.

reveal that partially localization of the π electron clouds of SWCNTFs lead to enhancement of the binding energies to some extent.

Results show that interactions of the Na⁺ cation with the partially localized π electron clouds of SWCNTFs lead to decrement of $R_{cation...π}$ values. On the other hand, interactions of the Na⁺ cation with the delocalized π electron clouds of SWCNTFs lead to increment of $R_{cation...π}$ values. Thus, delocalization and localization of the π electron clouds of SWCNTFs can become important in the cation-π interactions and alter the $R_{cation...π}$ values.

In accord with the Koopmans theorem [43] ionization energy (I) and electron affinity (A) can be considered as -E_H and -E_L (E_H and E_L are HOMO and LUMO energies), respectively. On the basis of the Mulliken theory [44], tendency of a species to liberate electron at its ground state is considered as electron chemical potential which can be evaluated as below:

$$μ = - (I + A)/2 \qquad (4)$$

Results revealed that increment of R is accompanied by decrement of E_H and E_L values of SWCNTFs. Indeed, E_H and E_L values of the Na⁺-SWCNTF complexes are lower than the graphene sheet and SWCNTFs. Thus, non-covalent cation-π interactions on SWCNTs increase tendency of these materials to release electrons.

Surface modification of SWCNTs by imidazolium-based ionic liquids has been reported [32]. However, further studies revealed that only surfactants with small cations (H⁺, Li⁺ and Na⁺) can modify electronic properties of SWCNTs. Also, DNA and proteins can change electronic

structure of SWCNTs [35]. Results of this study also indicate that electronic properties of SWCNTs change upon non-covalent cation-π interactions.

AIM analysis

To interpret the observed changes in the binding energy values of the Na⁺-graphene and Na⁺-SWCNTF complexes, AIM calculations have performed on the wave functions obtained at the M05/2X 6-31G(d) level of theory. Electron charge density values at the bond critical points (ρ_{BCP}) of all monomers and complexes confirm the structural parameters. Formation of the Na⁺-graphene and Na⁺-SWCNTF complexes leads to enhancement of the electron charge density values at the ring critical points (ρ_{RCP}) of the central rings of the graphene sheet and SWCNTFs. Results show that increment of R goes with increment of ρ_{RCP} values at the central rings of the Na⁺-graphene and Na⁺-SWCNTF complexes. Therefore, rolling up the graphene sheet leads to enhancement of the electron charge density values at the central rings of SWCNTFs. In Fig. 4a, the binding energies versus ρ_{RCP} values at the central rings of the Na⁺-SWCNTF complexes have presented. As can be seen, in the first (■) and second (▲) brands, decrement of ρ_{RCP} values is followed by increment of binding energies. In contrast, increment of ρ_{RCP} values in the third brand (×) is accompanied by increment of the binding energies. In fact, in the first (■) and second (▲) brands, interactions of the Na⁺ cation with the delocalized π electron clouds of SWCNTFs lead to increment of $R_{cation...π}$ values.
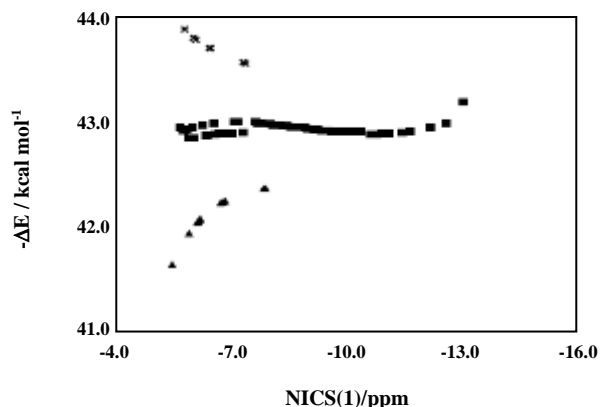
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Fig. 5: The binding energies of the Na$^+$-graphene and Na$^+$-SWCNTF complexes against NICS(1) values at the central rings of the graphene sheet and SWCNTFs for the first (■), second (▲), and third (×) brands.

On the other hand, in the third brand (×), interactions of the Na$^+$ cation with the partially localized π electron clouds of SWCNTFs lead to decrement of $R_{cation...\pi}$ values. Therefore, electron charge densities at rings of SWCNTs manipulate $R_{cation...\pi}$ values. These results show that properties of the π electron clouds of SWCNTs influence the surface modifications of these materials through the cation-π interactions. In Fig. 4b, the binding energies versus ρ_{CCP} values of the Na$^+$-SWCNTF complexes have shown. Comparison of Fig. 5a and Fig. 5b indicate that in the first (■) and second (▲) brands, decrement of ρ_{RCP} values at the central rings of the graphene sheet and SWCNTFs is equivalent to increment of ρ_{CCP} values. As was said, delocalization of the π electron clouds of SWCNTFs is important for enhancement of ΔE values in these cases. However, increment of ρ_{RCP} values in the third brand (×) is comparable to decrement of ρ_{CCP} values. In this case, partially localization of the π electron clouds of SWCNTFs plays imperative role in favor of enhancement of ΔE values. Consequently, ρ_{RCP} and ρ_{CCP} values explain effects of delocalization and partially localization of the π electron clouds of SWCNTs on surface adaptation of these materials through cation-π interactions.

NMR calculations

The NMR calculations have been performed at the M05-2X/6-31G(d) level of theory using GIAO method.

The NICS(0) and NICS(1) values at the central rings of the graphene sheet and SWCNTFs were calculated. Results prove that rolling up the graphene sheet leads to decrement of these values. In fact, rolling up the planar graphene sheet leads to changes in the π electron clouds of SWCNTFs. The NICS(0) values reveal effects of σ-bonds at rings, while NICS(1) ones reflect π-bond effects at rings. Therefore, NICS(1) is a better criterion than NICS(0) and stands for the π-aromaticity at rings.

The binding energies of the Na$^+$-graphene and Na$^+$-SWCNTF complexes versus NICS(1) values at the central rings of the graphene sheet and SWCNTFs have shown in Fig. 5. As can be seen, in the first (■) and second (▲) brands, decrement of NICS(1) values is followed by decrement of the binding energies. As was said, in these cases delocalization of the π electron clouds of SWCNTFs (which is related to the π-aromaticity) has major role on enhancement of ΔE values. In contrast, in the third brand (×) different behavior is observed. In this case, decrement of NICS(1) values leads to increment of the binding energies. Thus, partially localization of the π electron clouds of SWCNTFs (which is related to the less π-aromaticity) is an essential factor which enhances the cation-π binding energies. This consequence is in good consistent with the results of AIM analysis and emphasizes the role of partially localization of the π electrons in augmentation of the cation-π binding energies. It should be noted that rolling up the graphene sheet ($C_{102}H_{30}$) leads to decrease of aromaticity at rings of each obtained SWCNTF compared to the previous one and graphene sheet. The 100 step-by-step PES relaxed scans make SWCNTFs which have rings with low aromaticity and therefore partially localized π-electron clouds in comparison with graphene. Further rolling up leads to more localized rings at walls of the made carbon nanotubes. However, further rolling up weren't performed to make carbon nanotubes because 100 step-by-step PES relaxed scans make necessary partially localization at rings of SWCNTFs.

CONCLUSIONS

A $C_{102}H_{30}$ graphene sheet has been rolled up through 100 step-by-step optimizations by computational quantum chemistry methods to build Single-Walled Carbon Nanotube Fragments (SWCNTFs) as parts of armchair carbon nanotubes with different outer diameters.

Non-covalent cation-π interactions of the Na$^+$ cation on the central rings of SWCNTFs have been investigated. The binding energies of all Na$^+$-SWCNTF complexes versus true strain parameter change in three brands. Structural characteristics of SWCNTFs influence the cation-π interactions. Surface modifications through the cation-π interactions increase tendency of SWCNTs to liberate electrons. In some Na$^+$-SWCNTF complexes delocalization of the π electron clouds of SWCNTFs (which is related to the π-aromaticity) is significant and leads to increment of the cation-π binding energies. In contrast, partially localization of the π electron clouds of SWCNTFs (which is related to the less π-aromaticity) is an important factor which enhances the cation-π binding energies in some cases. Changing the π electron clouds of SWCNTs may help to improve surface modification of these materials through the cation-π interactions, which has important applications such as in storage of electric energy by transportation of cations through the walls of SWCNTs and enhancement of the hydrogen absorption compared to pure SWCNTs.

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