Theoretical study on effects of curvature of graphene in conjunction with simultaneous anion-π and π-π stacking interactions

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Abstract: A graphene sheet ($C_{102}H_{30}$) has been rolled up by computational quantum chemistry methods to construct single-walled carbon nanotube fragments (SWCNTFs). The anion-π interactions of F^- anion together with π-π stacking interactions of benzene on inner face and outer face of the central rings of SWCNTFs have been concurrently investigated. Structural parameters and energy data of the ternary benzene-SWCNTF-F^- complexes were considered. Also, effects of charge transfer and aromaticity were estimated to determine how curvature of graphene influences on simultaneous anion-π and π-π stacking interactions. Results indicate that curvature of graphene leads to structural changes in SWCNTFs which effects on simultaneous interactions of F^- anion and benzene with SWCNTFs. Also, results show that although π-π stacking is a weak interaction, but it can impact on order of binding energies in complexes involved both π-π stacking and anion-π interactions.

Keywords: graphene; anion-π; SWCNTFs; π-π stacking; aromaticity.

Introduction

Single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) are two familiar types of carbon nanotubes[1]. The p-orbital electrons of the graphene sheet bring together 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 alter which leads to partial σ- π hybridization[3].

Electronic properties of SWCNTs make them valuable biosensors[4,5]. CNTs have unique properties and contribute in drug delivery processes for treatment of various diseases[6]. For example, CNTs act as effective drug delivery carriers in cancer therapy[7]. CNTs deliver smaller doses of drugs in the body and lead to lower side effects and higher efficiency in the disease cell targeting processes[8].

Hui Li and coworkers have been performed molecular dynamic simulations to discover the configuration and quantity threshold of graphene nanoribbons (GNRs) inside a SWCNT. They showed that several GNRs twisted together when filling inside a SWCNT to form a curved structure in order to make best use of π-π stacking area. Also, they reported that the formation of multiple helical configurations of GNRs in SWCNT is influenced by effects of structure stability, initial arrangement and space of SWCNT[9].

Surface modification of SWCNTs through covalent or noncovalent 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 of these materials, noncovalent modifications increase solubility of SWCNTs and preserve geometric, electronic and mechanical properties of them.

SWCNTs with different diameters and changeable surface areas are good beds for interactions of ions[15]. Surface modifications of SWCNTs through noncovalent interactions improve structure of them. Anion-π interactions are noncovalent forces between anions and aromatic rings. The first X-ray crystal structure of anion-π interactions was reported by France Meyer and coworkers[16]. Also, there is data that suggest existence of these interactions in solution[17]. These interactions have roles in supramolecular chemistry[18], in anion channels[19,20], and in DNA or RNA[21]. Researcher showed that anion-π contacts exist in experimental protein structures between the standard aromatic residues (Trp, Phe, Tyr, and His) and anions (chloride and phosphate)[22]. Effects of anion-π interactions in chemical and biological systems involving anion and electron-deficient aromatic species have been studied by some authors[23]. A comprehensive study of the anion-

π interactions in supramolecular architectures have been recently performed between solvated first-row transition metal ions and the π-acidic ligands and results show that close anion-π contacts are critical for the stability of complexes[24].

Recently some authors reported the anion-π interactions on graphene flake which are unexpectedly strong compared to those on simple aromatic compounds and announced that these advantageous interactions may be valid to the design of a new class of neutral anion receptors and detectors[25].

Strength of the anion-π and π-π stacking interactions is controlled by several factors such as nature of anion and π systems. Thus, it is necessary to recognize effects of various factors which manage surface modification of SWCNTs through the anion-π and π-π stacking interactions.

In this work, a graphene sheet ($C_{102}H_{30}$) has been rolled up by computational quantum chemistry methods to construct single-walled carbon nanotube fragments (SWCNTFs). These SWCNTFs have the same number of atoms and represent parts of SWCNTs with different outer diameters. The anion-π interactions of F[-] anion together with π-π stacking interactions of benzene on inner face and outer face of the central rings of SWCNTFs have been simultaneously investigated. Structural parameters and energy data of all SWCNTFs, and ternary benzene-SWCNTF-F[-] complexes were studied. Also, effects of aromaticity were estimated to determine effects of curvature of graphene on simultaneous anion-π and π-π stacking interactions.

Computational methods

Structures of all monomers and complexes were optimized with Gaussian09 program package[26] at the M05-2X/6-31G(d) level of theory. Zhao and 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[27]. The diamagnetic and paramagnetic effects of ring currents related to aromaticity and anti-aromaticity can be evaluated by nucleus independent chemical shift (NICS) [28, 29] criterion. The NMR calculations have been performed at the M05-2X/6-31G(d) level of theory using GIAO (gauge independent atomic orbital) method[30].

Results and discussion

To investigate effects of curvature of graphene on mutual anion-π and π-π stacking interactions, a graphene sheet ($C_{102}H_{30}$) has been constructed using HyperChem 7.1 software[31]. To generate SWCNTFs, potential energy surface (PES) relaxed scans were performed and anion-π interactions of F[-] anion and π-π stacking interactions of benzene on inner face and outer face of central rings of these SWCNTFs were concurrently studied (See Scheme 1).
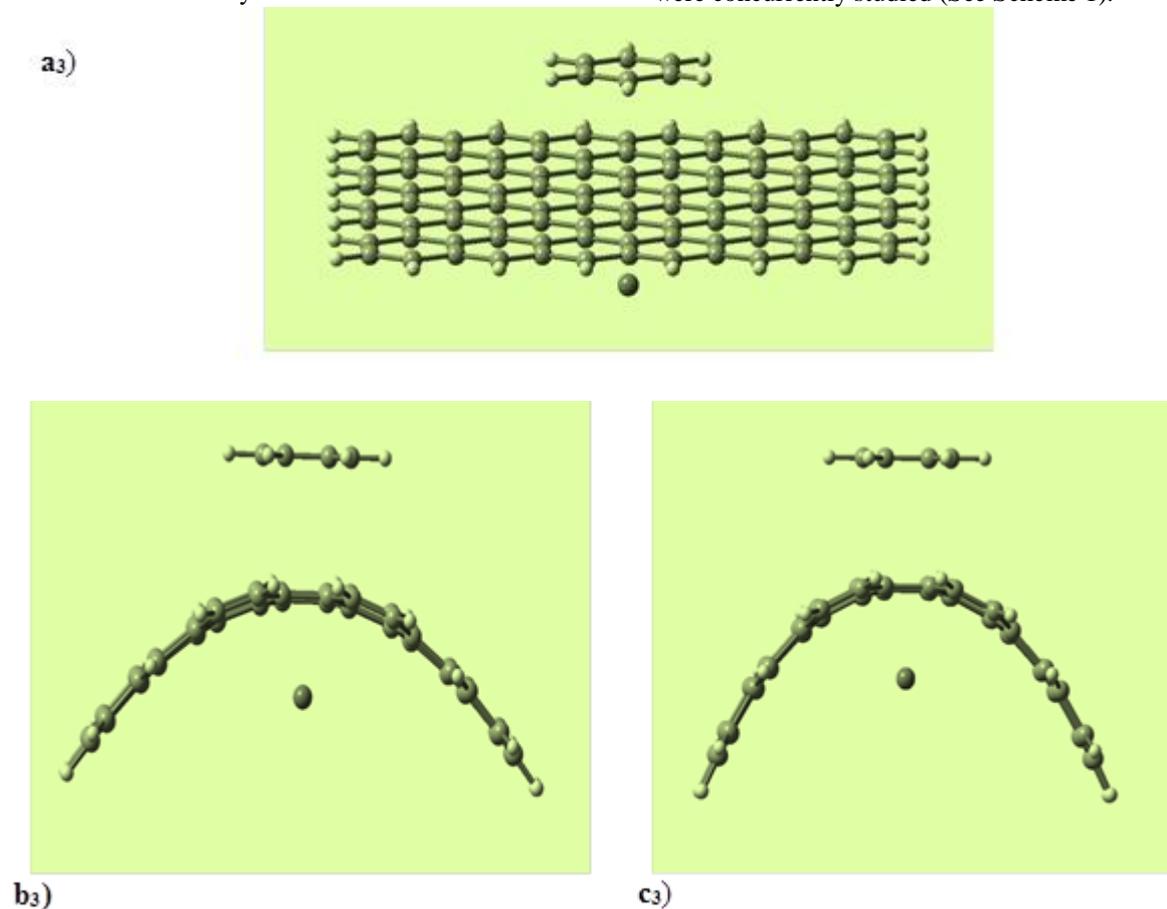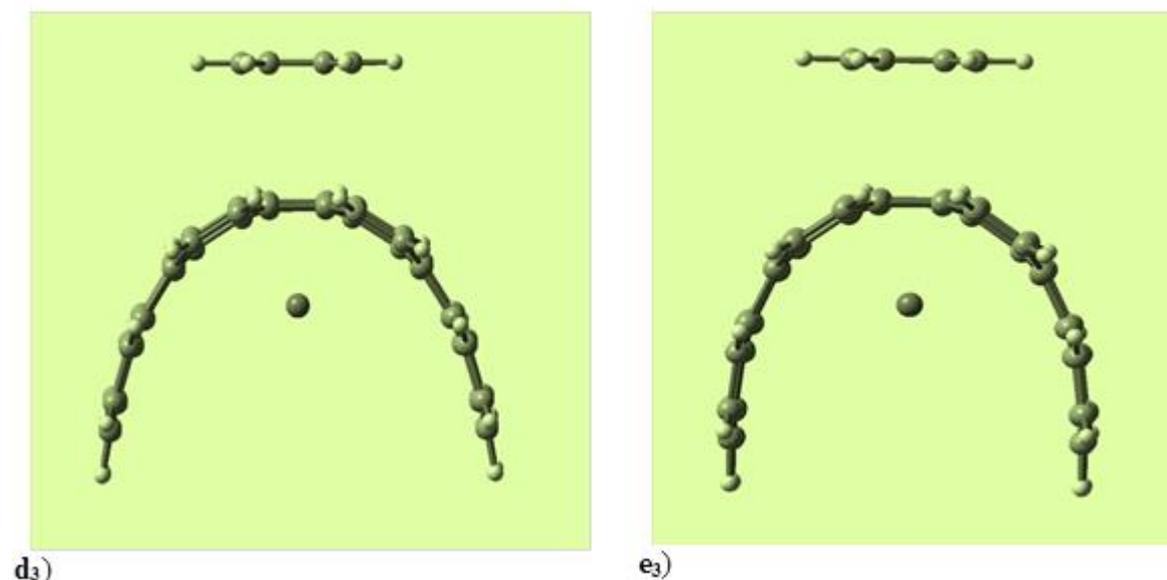
Scheme 1. Presentation of the simultaneous anion-π and π-π stacking interactions in complexes **a₃** to **e₃.**

Herein, a true strain parameter (R) is defined to give a better description of different curvature of complexes. Definition of this parameter is based on difference between distances of terminal hydrogens in graphene and SWCNTFs. Distances of these hydrogens are reduced during PES scans from graphene to SWCNTFs. In fact, each SWCNTF is compared with graphene and graphene is compared with itself. This parameter can estimate as below:

$$R = \mathrm{Ln}\,(r_0/r) \qquad \text{Eq.(1)}$$

In this equation, r_0 and r is the distances between terminal hydrogens of graphene and SWCNTFs, respectively. Thus, single layer graphene can be seen as a SWCNTF with R=0. In the present work, ternary benzene-SWCNTF-F⁻ complexes are named as **a₃** to **e₃**. Therefore, R for complex **a₃** is zero. On the other hand, R for complexes **b₃**, **c₃**, **d₃**, and **e₃** is 0.184, 0.320, 0.592, and 0.819, respectively. As can be seen, larger R values refer to complexes with more curvature. On the other hand, binary

SWCNTF-F⁻ complexes is named as **a₂** to **e₂**, and binary benzene-SWCNTF complexes is named as **a₂'** to **e₂'**.

Energy data

Binding energy of each ternary complex was computed as difference between energy of it and energies of monomers which build structure of it. Results indicate that binding energies of the benzene-SWCNTF-F⁻ complexes are in the range of 40.94 - 47.61 kcal mol⁻¹. Moreover, binding energies of binary SWCNTF-F⁻ complexes are in the range of 36.83 - 44.67 kcal mol⁻¹. On the other hand, binding energies of binary benzene-SWCNTF complexes are in the range of 3.47 - 5.19 kcal mol⁻¹. Thus, interactions between F⁻ anion and inner face of SWCNTFs have important role on size of binding energies in the benzene-SWCNTF-F⁻ complexes.

Results presented in Table 1 show that curvature of graphene firstly leads to decrement of binding energies of the benzene-SWCNTF-F⁻ complexes.

Table 1: Binding energy, (-ΔE), values (in kcal mol⁻¹) of the binary SWCNTF-F⁻ and benzene-SWCNTF complexes, and the ternary benzene-SWCNTF-F⁻ complexes.

complex	-ΔE	complex	-ΔE
a₂	36.83	**a₂'**	5.19
b₂	37.42	**b₂'**	3.77
c₂	39.29	**c₂'**	4.25
d₂	41.10	**d₂'**	3.48
e₂	44.67	**e₂'**	3.47

However, interactions of high curved SWCNTFs with F^- anion and benzene lead to larger binding energies for the benzene-SWCNTF-F^- complexes in comparison with complex a_3. The order of binding energies for the above mentioned ternary complexes is $b_3 < a_3 < c_3 < d_3 < e_3$ (where 3 refer to the ternary complexes). On the other hand, order of binding energies in the binary SWCNTF-F^- complexes is $a_2 < b_2 < c_2 < d_2 < e_2$ (where 2 refer to the binary complexes). Also, order of binding energies in the binary benzene-SWCNTF complexes is $e_2' < d_2' < b_2' < c_2' < a_2'$. As can be seen, unlike ternary benzene-SWCNTF-F^- complexes, π-π stacking interaction of benzene with more curved SWCNTFs leads to small binding energies for the benzene-SWCNTF complexes in comparison with the benzene-graphene (a_2') complex. Results of binding energies in the binary and ternary complexes demonstrate that order of binding energies in the ternary benzene-SWCNTF-F^- complexes is mostly in accord with order of binding energies in the binary SWCNTF-F^- complexes. The only difference between order of binding energies of the ternary complexes and binary SWCNTF-F^- complexes comes from π-π stacking interaction of benzene with graphene. As said, binding energy of complex a_2 is less than that for complex b_2. However, binding energy of the benzene-graphene complex (a_2') is more than that for complex b_2' and thus π-π stacking interaction of benzene with graphene in ternary complex a_3 leads to higher binding energy for it compared to complex b_3. This finding show that although π-π stacking is a weak interaction, but it can manipulate order of binding energies in complexes involved both π-π stacking and anion-π interactions.

Structural parameters

Central ring of graphene was considered as reaction center to study effects of curvature of graphene on structural parameters of SWCNTFs and ternary complexes. The equilibrium distance between F^- anion and central rings of SWCNTFs in the ternary complexes is denoted as $R_{anion...π}$. Also, the equilibrium distance between center of benzene and central rings of SWCNTFs is symbolized as $R_{π...π}$. All structural parameters are presented in Table 2. As can be seen, $R_{anion...π}$ values are smaller than $R_{π...π}$ ones. Results show that $R_{π...π}$ values in the ternary complexes increase in the following order: $a_3 < b_3 \cong c_3 < d_3 \cong e_3$. On the other hand, order of $R_{anion...π}$ values in these complexes is: $b_3 < c_3 < d_3 < e_3 < a_3$. Therefore, curvature of graphene leads to somewhat increase of distance of benzene from outer face of the central rings of SWCNTFs.

Table 2: Structural parameters (in Å) of the ternary benzene-SWCNTF-F^- complexes

Complex	C1-C2	C2-C3	$R_{anion...π}$	$R_{π...π}$
a_3	1.4150	1.4264	2.412	3.208
b_3	1.4113	1.4133	2.204	3.498
c_3	1.4127	1.4154	2.224	3.497
d_3	1.4140	1.4186	2.260	3.515
e_3	1.4144	1.4207	2.288	3.514

C atoms at central rings of SWCNTFs are numbered as C1, C2, C3, C4, C5, and C6. Therefore, six bonds (C1-C2, C2-C3, C3-C4, C4-C5, C5-C6, and C6-C1) are existed. Results indicate that some of above mentioned bonds at central rings of SWCNTFs have equivalent bond lengths. Thus, only magnitudes of bond lengths of two bonds (which named C1-C2 and C2-C3) are reported which are representative of all bonds at central rings of SWCNTFs. As can be seen in Table 2, both C1-C2 and C2-C3 bond lengths are firstly decreased from complex a_3 to b_3 and then these bond lengths are increased from complex b_3 to e_3. Moreover, these bond lengths in complex b_3 have smallest values. On the other hand, complex b_3 has smallest binding energy value in comparison with other complexes. In

fact, curvature of graphene leads to structural changes in SWCNTFs. These involved changes in C-C bond lengths at central rings of SWCNTFs. Therefore, above mentioned structural changes influence on magnitude of simultaneous interactions of F^- anion and benzene with SWCNTFs.

Charge transfer analysis

To connect energy data of the ternary benzene-SWCNTF-F^- complexes to the charge transfer effects, sum of atomic charges of the F^- anion, benzene, and SWCNTFs (in e) in the above mentioned complexes were calculated at the M05-2X/6-31g(d) level of theory. These results are presented in Table 3.

Table 3: Sum of atomic charges (in e) of the F⁻ anion, benzene (and its atoms), and SWCNTFs in the benzene-SWCNTF-F⁻ complexes.

Complex	F⁻	SWCNTFs	benzene	H atoms of benzene	C atoms of benzene
a_3	-0.7199	-0.2705	-0.0096	1.0031	-1.0128
b_3	-0.6930	-0.3007	-0.0067	1.0012	-1.0079
c_3	-0.6858	-0.1580	-0.0061	0.9993	-1.0054
d_3	-0.6812	-0.1535	-0.0051	0.9971	-1.0023
e_3	-0.6817	-0.3135	-0.0048	0.9961	-1.0009

As can be observed, negative atomic charge of F⁻ anion in the ternary complexes is decreased in comparison with free anion (before formation of complex). Instead, formation of the ternary complexes is accompanied by decrease of sum of atomic charges on benzene and SWCNTFs. Results of Table 3 reveal that sum of positive atomic charges on H atoms of benzene in the ternary complexes is increased (compared to 0.5897 e for free benzene).

Also, sum of negative atomic charges on C atoms of benzene in the ternary complexes is increased (compared to -0.5897 e for free benzene). Additionally, order of sum of atomic charges on benzene in the ternary complexes is: $a_3 < b_3 < c_3 < d_3 < e_3$. Correlations between sum of atomic charges on benzene and binding energies of the ternary complexes are depicted in Fig. 1.
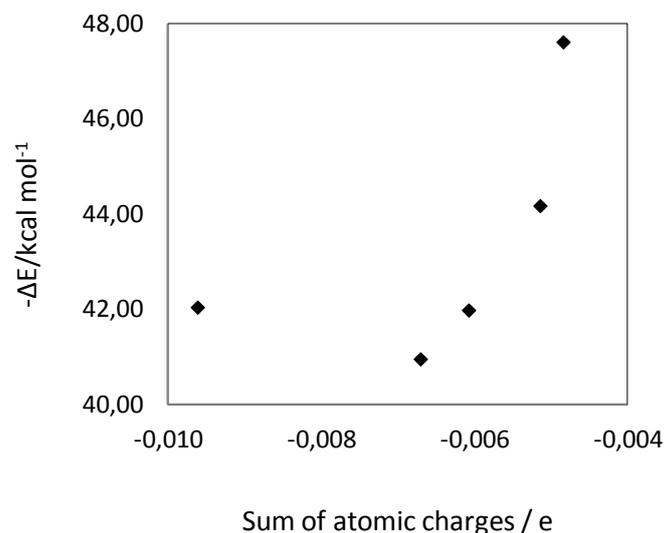
Figure 1: Correlations between sum of atomic charges on benzene and binding energies of the ternary benzene-SWCNTF-F⁻ complexes.

As can be seen, curvature of graphene and increase of the sum of atomic charges on benzene during formation of the ternary complexes leads to firstly decrease and then increase of the binding energies. In fact, although sum of atomic charges on benzene in complex b_3 is more than complex a_3, but binding energy of complex a_3 is larger than complex b_3. Therefore, in complexes formed from SWCNTFs which encompass weak interactions such as π-π stacking, effects of charge transfer and variations of charges on different atoms of a ring during formation of complexes may be important in magnitude of binding energies. However, as said structural changes of a curved SWCNTF in comparison with graphene (with R=0) has an essential role in this case.

NMR calculations

The NMR calculations have been performed at the M05-2X/6-31g(d) level of theory using GIAO method. The NICS(0) at center of, and NICS(1) at 1 Å above or below of central rings of 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 the made 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. Binding energies of the all binary and ternary complexes against NICS(1) values at central rings of SWCNTFs are shown in Fig. 2.
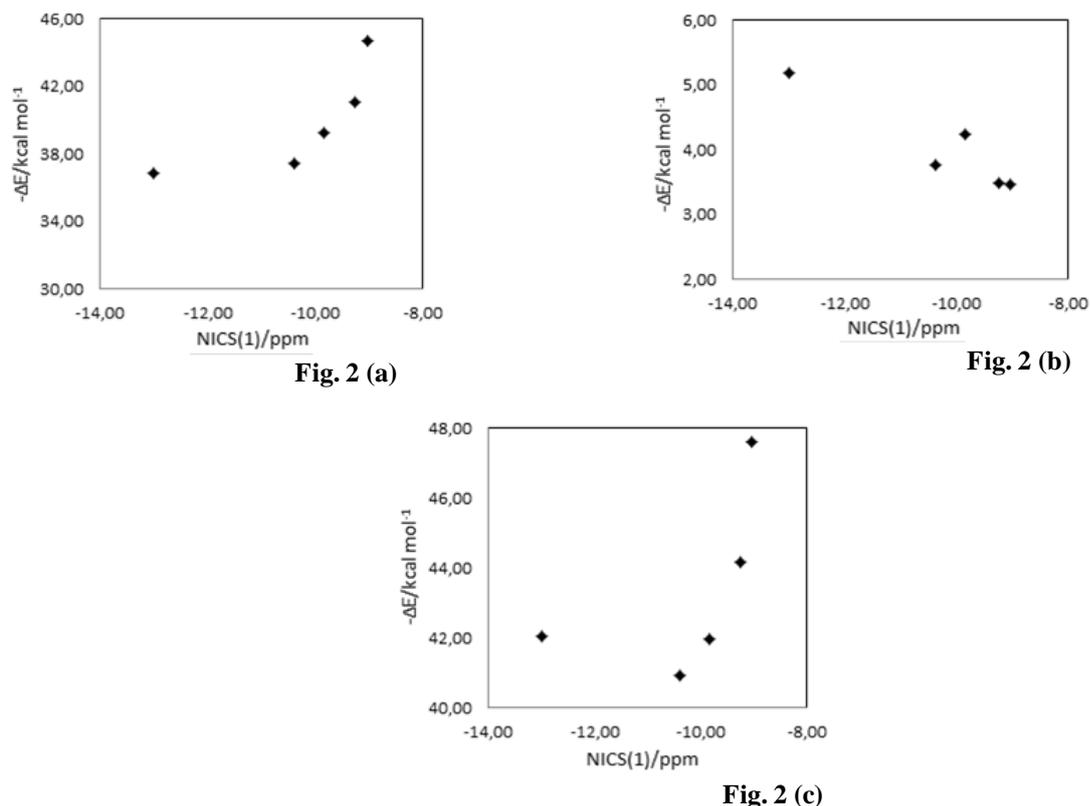
Fig. 2 (a)

Fig. 2 (b)

Fig. 2 (c)

Figure 2: Binding energies of the SWCNTF-F⁻ (a), benzene-SWCNTF (b), and benzene-SWCNTF-F⁻ (c) complexes against NICS(1) values above central rings of SWCNTFs.

As can be observed in Fig. 2 (a) and (b), decrease of aromaticity at central rings of SWCNTFs which caused by curvature of graphene is accompanied by increment/decrement of binding energies of the SWCNTF-F⁻/benzene-SWCNTF complexes. On the other hand, as can be seen in Fig. 2 (c), decrease of aromaticity at central rings of SWCNTFs goes firstly with decrement of binding energies of the ternary benzene-SWCNTF-F⁻ complexes, which is consistent with behavior of the binary benzene-SWCNTF complexes. Then, binding energies are increased by decrease of aromaticity at central rings of SWCNTFs. These results imply that although π-π stacking is a weak interaction, but it can influence on overall behavior of complexes, which encompass simultaneous anion-π and π-π stacking interactions, towards changes of aromaticity.

Conclusions

The order of binding energies for the ternary complexes is $b_3 < a_3 < c_3 < d_3 < e_3$. Also, order of binding energies in the SWCNTF-F⁻ complexes is $a_2 < b_2 < c_2 < d_2 < e_2$, and binding energies of the benzene-SWCNTF complexes is in the following order: $e_2' < d_2' < b_2' < c_2' < a_2'$.

The only difference between order of binding energies of the ternary complexes and binary SWCNTF-F⁻ complexes originates from π-π stacking interaction of benzene with graphene in complex a_3 which can manipulate order of binding energies in

complexes involved both π-π stacking and anion-π interactions.

The C1-C2 and C2-C3 bond lengths in complex b_3 have smallest values and complex b_3 has smallest binding energy value in comparison with other complexes.

Curvature of graphene leads to structural changes at central rings of SWCNTFs and these changes influence on magnitude of concurrent interactions of F⁻ anion and benzene with SWCNTFs.

Negative atomic charge of F⁻ anion in the ternary complexes is decreased in comparison with free anion and formation of the ternary complexes is accompanied by decrease of sum of atomic charges on benzene and SWCNTFs.

NMR studies show that weak π-π stacking interactions can influence on overall manners of complexes, which contain concurrent anion-π and π-π stacking interactions, towards changes of aromaticity.

Acknowledgment

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