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Ab initio study of benzene adsorption on carbon nanotubes

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The adsorption of a benzene molecule on carbon nanotubes (CNTs) with various diameters and chiral angles is investigated within the *ab initio* framework. The physisorption of such an organic molecule is an example of noncovalent functionalization involving π-stacking interactions and corresponding to a weak binding energy. Our calculations show that for small diameter tubes, the most favorable adsorption site is one type of C—C bond. The disparities between the inequivalent bonds of a CNT are discussed in terms of the π orbital axis vector misalignment. Moreover, the curvature and the chirality effect on benzene adsorption are analyzed, showing that large diameter nanotubes are the most reactive ones.

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I. INTRODUCTION

The nanometrical dimensions of carbon nanotubes (CNTs), together with the unique electronic structure of a graphene sheet, make the electronic properties of these one-dimensional structures highly unusual.[1] CNTs have thus been quickly incorporated into electronic devices, which properties can be tailored by chemical functionalization of the tubes.[2]

Aromatic compounds are known to interact weakly (physisorption) with graphite, and consequently also with the graphitic sidewalls of CNTs.[3,4] This kind of noncovalent functionalization of CNTs with organic molecules does not significantly perturb the atomic structure of the CNT in contrast to its covalent counterpart. On the other hand, the presence of organic molecules on the sidewall of a CNT could modify its electronic and transport properties.[5,6] Besides, a good knowledge of the CNTs reactivity and of the repercussion of adsorption are thus needed for their potential application as sensors.[6,7]

The weak intermolecular forces between two sp^2-like systems, including the van der Waals interactions, are often called π-stacking interactions as they originate from interacting π electrons of the two systems. These interactions are for example responsible for the interlayer bonding in graphite and are also present in the solubilization of CNTs in aromatic solvents.[8,9] Though the concept of π electron is only valid for molecular systems presenting a planar symmetry, it can be extended, following the idea of Haddon[10] and its π orbital axis vector (POAV), to nonplanar systems with tricoordinated carbon atoms.

In the present work, the adsorption of a benzene molecule on various CNTs is investigated using *ab initio* calculations. Our results show that for small achiral tubes, the most favorable adsorption site is one type of bond. The disparities between the inequivalent bonds of a CNT are interpreted in terms of the POAV misalignment angle. Moreover, both the curvature and the chirality effect on benzene adsorption are analyzed.

II. COMPUTATIONAL PROCEDURE

Density functional theory,[11,12] which in principle gives the true ground state energy and electronic density of any system, is known to give an imperfect description of the long range van der Waals (vdW) interactions within the widely used local density approximation (LDA) or generalized-gradient approximations (GGA) for the exchange-correlation energy. Nevertheless, DFT has proven to be quite successful and in good quantitative agreement with experimental data for sp^2-like materials, especially graphite.[13,14] In addition, DFT gives a better description of these systems than empirical methods and is able to capture the underlying physics. Consequently, the DFT technique seems to be reliable to study adsorption of benzene on CNTs.

DFT-LDA has thus been chosen to study the benzene adsorption on various CNTs. The choice of the LDA is not fortuitous and is more suitable than the GGA to study weakly interacting systems like the π-stacking interaction on sp^2-like materials. Indeed, the GGA is known to usually underestimate binding energies. This is problematic for example in the case of graphite where, within the GGA, two graphene layers are almost unbound, leading to a far too small interlayer binding energy and a far too large interlayer distance; whereas the LDA value is very close to the experimental one.[15] In a same way, two parallel benzene molecules are found to be unbound using the GGA, whereas our LDA results are in quite good agreement with high level quantum chemistry calculations.[16]

DFT calculations can be performed with different basis sets used to expand the Kohn-Sham orbitals. While plane waves form a complete basis set (with an infinite cutoff energy), allowing an easy control of the convergence with the cutoff energy, localized basis sets are more appropriate for the present study which involves supercells containing over hundred atoms. In the latter framework, the weak interaction energy between two subsystems (the benzene molecule and the CNT) must be computed with particular care. In fact, the correct interaction energy E_{int} cannot be calculated using the energy of the complete system $[E(\text{CNT}+\text{C}_6\text{H}_6)]$ and those of

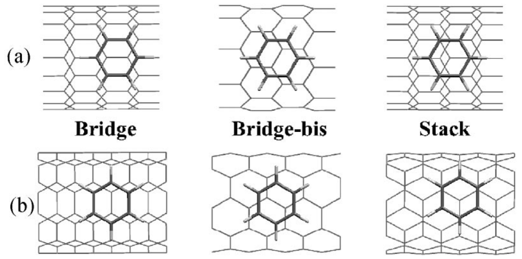

FIG. 1. Different configurations considered for the adsorption of a benzene molecule on a (9,0) zig-zag CNT (a) and on a (5,5) armchair CNT (b).

the isolated molecule and CNT [respectively $E(C_6H_6)$ and $E(\mathrm{CNT})$] by the relation:

$$E_{\mathrm{int}} = E(\mathrm{CNT} + C_6H_6) - [E(\mathrm{CNT}) + E(C_6H_6)].$$

Indeed, the basis is not the same for the different calculations: the basis set dimension is larger for the complete system, implying more degrees of freedom in the variational determination of the energy and leading to an unphysical energy lowering. This basis set superposition error (BSSE) must be corrected and the true interaction energy, can be determined by the counterpoise method[20] using "ghost" atoms,

$$E_{\mathrm{int}} = E(\mathrm{CNT} + C_6H_6) - [E(\mathrm{CNT}_{\mathrm{ghost}} + C_6H_6) + E(\mathrm{CNT} + C_6H_{6\mathrm{ghost}})].$$

The "ghost" molecule corresponds to additional basis wave functions centered at the atomic position of the benzene molecule or the CNT, but without any atomic potential. The determination of adsorption energies using this BSSE correction is found to be in good agreement with the direct calculation performed using plane waves.[4]

Our calculations are performed with the SIESTA code, which has proven to be very efficient for large atomic systems.[21] This code is based on a pseudopotential approach[22,23] and on a basis of localized pseudoatomic orbitals for the valence electron wave functions[24] (split-valence[25] double-ζ basis plus polarization and extended 3*s* orbitals for C and double-ζ for H). The calculations are performed with a diagonalization method (as opposed to the order N method implemented in the code[26]) using the LDA as parameterized by Perdew and Zunger.[27]

Large supercells are used to avoid interaction between the CNTs and between neighboring benzene molecules adsorbed on a tube: a hexagonal cell with a 40 Å lattice parameter in the (x,y) plane and two or four CNT cells in the z direction. For zig-zag tubes, the cell parameter is 8.64 Å and corresponds to two CNT unit cells, whereas for armchair tubes, its value is 9.98 Å, corresponding to four CNT unit cells (see Fig. 1). The real space grid is equivalent to a plane wave cutoff energy of 80 Ry. In each case, a $1\times1\times8$ Monkhorst-Pack k-grid is used for the Brillouin zone sampling. The CNTs are perfect cylinders obtained by rolling up a graphene sheet with a 1.44 Å nearest neighbor distance. The isolated benzene molecule is relaxed (residual forces lower than 15 meV/Å) and then kept frozen upon adsorption on the CNT. Moreover, only some particular geometries, with the molecule approaching radially the CNT, are considered in the present study. The relative numerical accuracy on the interaction energy (computed with a BSSE correction) is estimated to be of the order of around 1 meV.

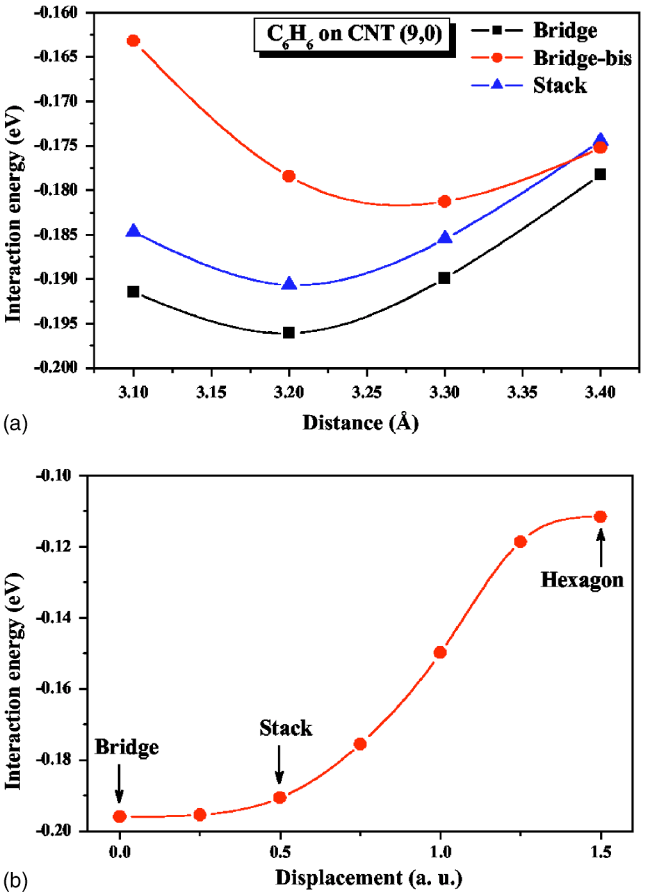

FIG. 2. (Color online) Calculated interaction energy between a benzene molecule and a (9,0) zig-zag CNT. (a) Adsorption curves corresponding to the "bridge" (squares), "bridge-*bis*" (circles), and "stack" (triangles) configurations. (b) Energy curve for a benzene molecule sliding along the tube axis, at a 3.2 Å distance. The "hexagon" configuration corresponds to the molecule over a hexagon of the tube.

III. RESULTS

A. Adsorption of benzene on a (9,0) CNT

Figure 2(a) displays the adsorption energy curves computed for a benzene molecule over a (9,0) CNT in the configurations depicted in Fig. 1(a). The two kinds of inequivalent C—C bonds of the CNT lead to the two configurations named, respectively, "bridge" and "bridge-*bis*" depending if the center of the benzene lies over the center of a bond parallel or not to the tube axis. In the "stack" configuration, the center of the molecule is just over an atom of the CNT.

First, Fig. 2(a) shows that the benzene adsorption energy on a (9,0) CNT is quite small, around 0.2 eV, which implies that with such a weak interaction the BSSE is crucial, for calculations using a localized basis set. There is a noticeable difference between the inequivalent adsorption sites and the adsorption energy runs from 182 meV to 196 meV, while the equilibrium distance[28] runs from 3.20 Å to 3.27 Å. As a comparison, the most stable configuration for benzene adsorption on a graphene sheet (the benzene molecule over a carbon atom) leads to a distance of 3.27 Å and to an energy gain of 235 meV. Oppositely to graphene, the most favorable structure is the "bridge" one, with the benzene molecule over a C—C bond. Surprisingly, as far as the adsorption energy is concerned, there is a bigger difference between the two types of bonds than between a bond and a carbon atom.

Our calculations show that benzene adsorption has a very little effect on the electronic structure.[4] There is only a small hybridization between the CNT states and those of the benzene molecule, and the adsorption is a physisorption. The total electronic density of states (DOS) corresponds to the simple superposition of that of the two separate systems (with a slight energy shift indicating a charge transfer from the molecule to the tube). For an isolated benzene molecule, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) lie, respectively, in the valence and the conduction band of the (9,0) CNT which possesses a tiny gap due to curvature. The position of adsorption of the benzene molecule has almost no influence on the electronic structure of the system. Only the states situated around 2 eV under the Fermi level, that correspond to the former HOMO of benzene, are slightly perturbed by a displacement of the molecule on the CNT surface.

Secondly, the rotation and the translation of benzene on the CNT surface have been investigated. As illustrated in Fig. 2(b), the benzene molecule can easily slide on a C—C bond (the "stack" configuration being just 5 meV higher in energy than the "bridge" one), whereas it is far more difficult to pass over a hexagonal face of the CNT: the configuration labelled "hexagon" is 85 meV higher in energy and is then highly improbable for the adsorption of benzene. The molecule can also slide along a C—C bond that is not parallel to the tube axis and, considering the adsorption energy value of the "bridge-*bis*" and the "stack" positions, the energy barrier for the diffusion of benzene on the CNT surface can be estimated around 15 meV.

Moreover, the rotational barrier, for a rotation of the molecule around the axis passing through its center and normal to the CNT surface, is also found to be of about 4–5 meV with the molecule either over a C—C bond or a carbon atom. This implies that a very low temperature would be necessary to observe benzene molecules immobile on a CNT. For all these calculations, the system was kept frozen, with a perfect unrelaxed cylindrical CNT and a benzene molecule identical to an isolated one. This approximation does not seem too crude, since the interaction between the CNT and the benzene molecule is very weak. In addition, the conclusions concerning the adsorption of benzene are found to be the same with a relaxed CNT (with residual forces lower than 2 meV/Å). It has also been noticed that the adsorbed benzene molecule, when free to relax, does marginally deform itself and stays planar to a very good approximation.

This first study of benzene adsorption on a (9,0) CNT raises several questions: How about other CNTs? What is the influence of the chiral angle, of the electronic properties, of the curvature? In the limit of an infinite radius CNT, it ends up in a planar graphene sheet with only one kind of C—C bond and where the most favorable adsorption of the benzene molecule is on top of a carbon atom. Then, there must be a change in the most stable position with increasing diameter of the tubes. What is this diameter and does it depend on the CNT chirality? In order to try to answer these questions, the adsorption of a benzene molecule on other tubes has been investigated.

B. Adsorption of benzene on zig-zag and armchair CNTs

Within the same numerical framework as in the preceding paragraph, the energy curves for the adsorption of a benzene molecule have been computed for various zig-zag [(7,0), (8,0), (10,0), (13,0), and (17,0)] and armchair [(4,4), (5,5), (6,6), and (7,7)] CNTs. The three positions of adsorption represented in Fig. 1 have still been considered, where for the armchair tubes, the "bridge" configuration corresponds to the benzene molecule being over a C—C bond perpendicular to the tube axis. For each tube, the binding energy and the equilibrium distance of the different configurations are reported in Table I. For an easy comparison, the adsorption energies are also reported on a curve for zig-zag [see Fig. 3(a)] and armchair [see Fig. 3(b)] CNTs.

The fact that the electronic properties of the CNT are preserved upon benzene adsorption, is found to be a general feature. In particular the gap is conserved and thus a CNT keeps its semiconducting or metallic behavior. This noncovalent functionalization by π-stacking is then completely different from covalent functionalization, which strongly modifies the properties of the CNT.[29]

Figure 3(a) suggests that for the zig-zag tubes considered, the binding energy is increasing with decreasing curvature (i.e., increasing CNT radius). This trend is the same for the three different configurations. In addition, while the energy difference between the "bridge" and the "stack" position is getting smaller and smaller with increasing tube diameter, the disparity between the two inequivalent bonds remains roughly the same. For the 13.5 Å diameter (17,0) tube, the "bridge" position is still the most stable. On the other hand, for armchair tubes, whereas the binding energy is also increasing with the CNT size both in the "stack" and "bridge-*bis*" configuration, it is decreasing for the "bridge" one from the (4,4) to the (7,7) tube. The "bridge"-"bridge-*bis*" gap is then quickly decreasing with the tube diameter. Moreover, the "stack" position becomes the most favorable (slightly lower in energy than the "bridge" position) for the 9.6 Å diameter (7,7) tube, as in the case of graphene.

Besides, considering a given configuration for both the zig-zag and the armchair tubes, the binding energy does not show a monotonous variation with respect to the CNT radius (see Table I). For example, in the "stack" position, it appears that a benzene molecule is less bound to an armchair tube than to a zig-zag tube of almost the same curvature. This nonmonotonous evolution is also met for the equilibrium distances, though in case of the "stack" configuration they are found to increase with the CNT diameter. This result suggests that benzene adsorption on a CNT depends on its cur-

TABLE I. Binding energy (E_b) and equilibrium distance (d_{eq}) for the different positions of benzene adsorption on various CNTs. For each tube, the value of its radius (R) and of the POAV misalignment angle (ϕ, see Sec. IV) are given. The binding energy of the most stable position is in bold.

Tube			Bridge		Bridge-*bis*		Stack	
(n,m)	R (Å)	ϕ (°)	E_b (meV)	d_{eq} (Å)	E_b (meV)	d_{eq} (Å)	E_b (meV)	d_{eq} (Å)
(4,4)	2.75	26.7	**195**	3.25	173	3.23	176	3.20
(7,0)	2.78	27.0	**189**	3.19	178	3.26	183	3.20
(8,0)	3.18	23.4	**193**	3.19	178	3.27	185	3.20
(5,5)	3.44	21.2	**193**	3.26	178	3.24	184	3.21
(9,0)	3.57	20.6	**196**	3.20	182	3.27	191	3.21
(10,0)	3.97	18.4	**196**	3.21	181	3.27	192	3.21
(6,6)	4.13	17.5	**190**	3.27	181	3.25	188	3.22
(7,7)	4.81	15.0	190	3.27	185	3.25	**191**	3.23
(13,0)	5.16	14.0	**199**	3.22	185	3.27	196	3.23
(17,0)	6.75	10.7	**204**	3.22	188	3.28	202	3.24
graphene	∞	0	229	3.27			**235**	3.27

vature and its chiral angle and that the evolution with these parameters is not trivial.

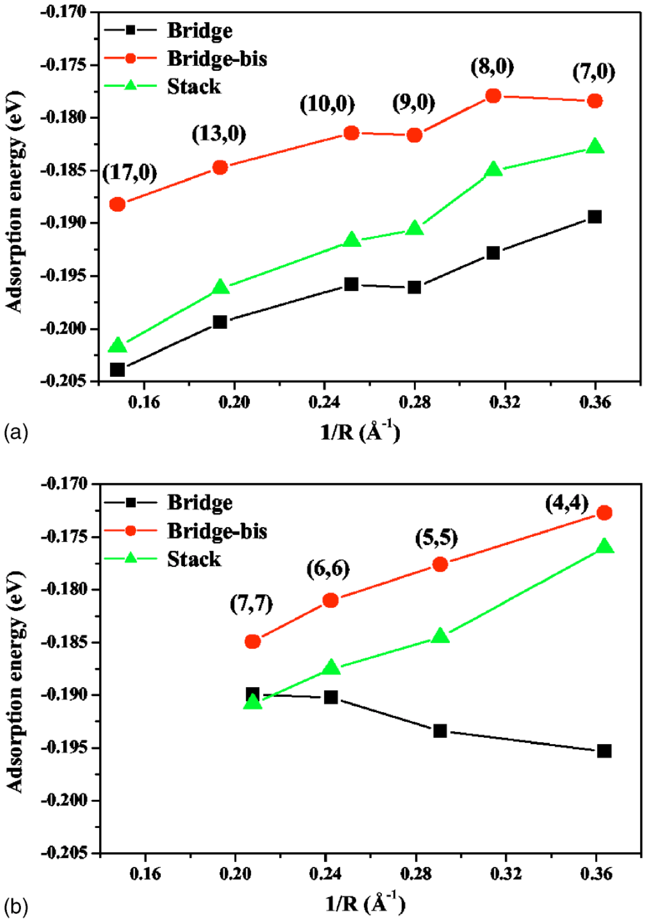

FIG. 3. (Color online) Calculated adsorption energies for the different configurations of a benzene molecule adsorbed on a zig-zag (a) or on an armchair (b) CNT of radius R. The squares correspond to the "bridge" position, the circles to the "bridge-*bis*" one, and the triangles to the "stack" one, respectively.

IV. DISCUSSION

Our calculations show that the inequivalent C—C bonds of a CNT react differently with benzene, leading to different values of the adsorption energy. In order to understand what characteristic of a type of bond makes it more favorable for benzene adsorption, one have first to look in detail what differentiates the bonds of a CNT. For the following considerations, the CNTs are assumed to be perfect cylindrical rolled up graphene sheets. For a general chiral tube, while all the carbon atoms are equivalent as they have the same environment, three types of inequivalent bonds exist. These bonds differ from each other by their length and their orientation with respect to the tube axis. For zig-zag and armchair CNTs, only two different C—C bonds are present, one of which is either parallel or perpendicular to the axis of the tube. Due to curvature, the more the bond is aligned with the axis, the longer the bond is.

As a first idea, one may think that the length of the bond plays a key role in the binding with benzene. However, this is not the case since the "bridge" configuration (the most favorable for both zig-zag and armchair small tubes) corresponds to the shortest bond of armchair CNTs, whereas it corresponds to the longest one of zig-zag tubes. Consequently, the behavior observed in our *ab initio* calculations should come from a more subtle difference between the bonds. The geometrical difference has indeed a repercussion on the local electronic density around the bond. A relevant parameter to differentiate the bonds can be extracted from the analysis of the orientation of the POAV on neighboring carbon atoms. The POAV has indeed already been used to discuss the reactivity of some systems.[30,31]

As mentioned in the Introduction, the concept of π electron can be applied in the case of a non-planar system with tricoordinated carbon atoms, like a CNT.[10,31] In such a case, a hybrid monoelectronic wave function is constructed on each carbon atom, by mixing s and p atomic orbitals, resulting in a π orbital orthogonal to the three σ orbitals (directed towards the three neighbors of the carbon atom). Within this

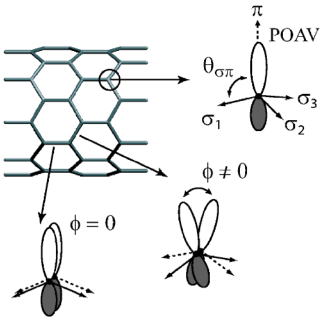

FIG. 4. Schematic representation of a π orbital on a carbon atom, directed along the POAV and orthogonal to the three σ orbitals. A schematic view illustrates the different misalignment angles ϕ for the two inequivalent bonds of a (9,0) CNT.

model, the direction of the p_π orbital used to construct the hybrid π orbital, together with the degree of s-mixing, can be obtained by solving a quite simple system of equations determined by the local geometry.[32,33] The direction of the π orbital is then called the π orbital axis vector (POAV). The angle $\theta_{\sigma\pi}$ (see Fig. 4) between the POAV and a σ direction (i.e., a bond) indicates the degree of "pyramidalization" and the hybridization. For $\theta_{\sigma\pi}=90°$ (planar system), the σ orbitals are in a sp^2 hybridization and the π orbital is a pure p_z orbital. For $\theta_{\sigma\pi}=109°28'$ (tetrahedral system), the σ orbitals are in an sp^3 hybridization and the π orbital can be conversely written $s^{1/3}p$. In the case of CNTs, $\theta_{\sigma\pi}$ has an intermediate value, that decreases as the inverse of the CNT radius R and reaches 90° at the limit $R\rightarrow\infty$ [see Fig. 5(a)].

As far as the C—C bonds of a CNT are concerned, the curvature leads to a misalignment of the POAV of neighboring carbon atoms, and consequently to a dihedral angle ϕ which is different for each type of inequivalent bond. For zig-zag and armchair tubes, the bond related to the "bridge" configuration corresponds to $\phi=0$, whereas $\phi\neq 0$ for the other type of bond (the "bridge-*bis*" configuration), as illustrated in Fig. 4. In the case of chiral tubes, there are three nonzero values of ϕ.

In addition to the pyramidalization angle and the *s*-*p* mixing [Fig. 5(a)], the value of the angle ϕ has been computed for each type of bond of every CNT with a radius up to 15 Å, by determining the POAV (Ref. 34) [see Fig. 5(b)]. The nonzero values of ϕ for both the zig-zag and armchair tubes lie on a curve that simply varies as $1/R$. On the other hand, there is a strong dispersion of the values of ϕ for the chiral tubes. Nevertheless, they are all under an $1/R$ envelope, which implies that the ϕ values and the difference between inequivalent bonds are significant only for small diameter CNTs. Interestingly, for a given curvature, chiral tubes may display a ϕ value higher than that of zig-zag or armchair tubes. The misalignment angle between the POAVs of a bond can reach values as high as 30° or 40° for the smallest synthesized CNTs.[35] Note that the situation is very different for C_{60} where there is no misalignment, although a pyramidalization of the carbon atoms exists.[36]

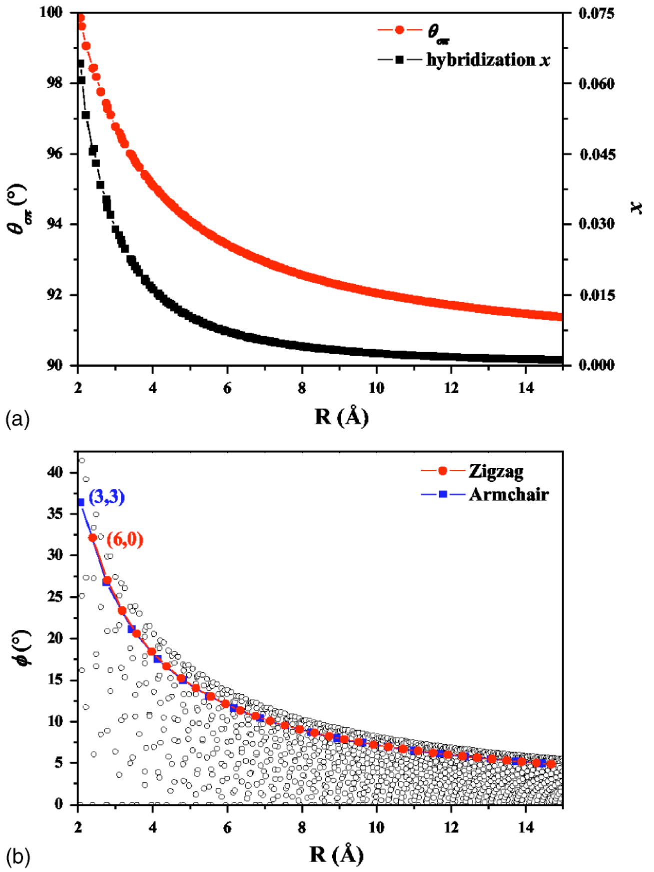

FIG. 5. (Color online) (a) Evolution of the pyramidalization angle $\theta_{\sigma\pi}$ (circles) and of the amount of *s*-*p* mixing (squares) in the π orbital (s^xp hybridization), with the radius R of a CNT. (b) Evolution of the misalignment angle ϕ between the POAVs, for each type of inequivalent bonds of a CNT with radius R. For zig-zag and armchair tubes, the value corresponding to the bond with $\phi\neq 0$ is reported on a curve (respectively, circles and squares). Both tubes are in fact on the same curve presenting a $1/R$ variation. The remaining open circles correspond to chiral tubes for which there are three different values of ϕ.

Coming back to the adsorption of benzene, the preceding considerations suggest that for a given CNT the most favorable bond for benzene adsorption is the one with the smallest value of ϕ. This is true for both the zig-zag and armchair tubes. The adsorption energy difference between the inequivalent bonds of a CNT can thus be expected to be related to this misalignment angle, and should thus vanish at the limit $R\rightarrow\infty$ (a graphene sheet, where there is only one type of C—C bond). This simple rule, observed for zig-zag and armchair tubes, is particularly satisfied for armchair CNTs where the energy difference between the "bridge" and "bridge-*bis*" configurations is decreasing with the size of the tube. On the other hand, in the case of zig-zag tubes, this energy difference remains almost unchanged when the CNT radius is increased. However, in the limit $R\rightarrow\infty$, the difference must vanish since the bonds become equivalent. This shows that benzene adsorption on zig-zag tubes is more sensitive to the POAV misalignment than on armchair tubes.

In order to check the assumption that the most stable position for benzene adsorption on a bond is driven by the misalignment angle, the adsorption of a benzene molecule on a chiral (8,2) CNT has been investigated within the same *ab initio* approach. This tube has a radius of 3.64 Å, leading to

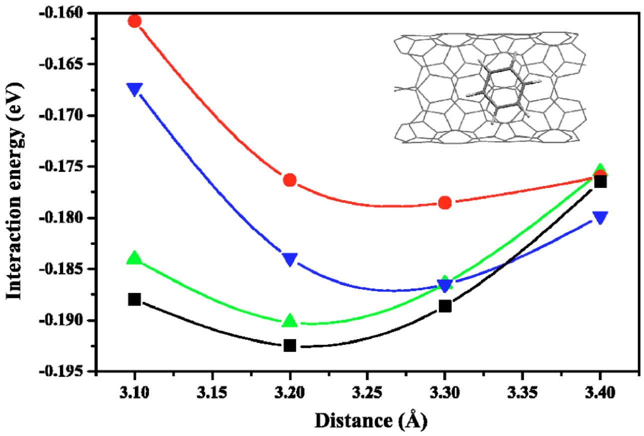

FIG. 6. (Color online) Calculated adsorption curves of a benzene molecule on a (8,2) CNT (see inset). The configurations with the molecule over different types of C—C bonds with a different value of ϕ are considered: $\phi=8.5°$ (squares), $\phi=14.5°$ (down triangles), and $\phi=23.0°$ (circles). The adsorption curve over a carbon atom ("stack" configuration) is also represented (up triangles).

a curvature very close to the (9,0) one. The tube also displays three different kinds of bonds characterized by the following misalignment angles: $\phi=8.5°$, 14.5°, and 23.0°, respectively. The calculated adsorption curves are reported in Fig. 6. The three binding energies (179 meV, 187 meV, and 192 meV) are found to increase with decreasing values of ϕ. Moreover, the "stack" configuration corresponds to a binding energy of 190 meV, very close to the one calculated for the (9,0) CNT. The results obtained for the (8,2) tube can be further compared to those obtained for the (9,0) tube. For a CNT of such a diameter, the binding energies predicted for the adsorption of benzene over a C—C bond follow the order of the misalignment angles: $E_b=196$, 192, 187, 182, and 179 meV for $\phi=0$, 8.5°, 14.5°, 20.6°, and 23.0°, respectively. This comparison suggests that the benzene adsorption on a CNT bond is indeed closely related to the POAV misalignment. The fact that the reactivity of inequivalent bonds is different could induce a selective adsorption of benzene on a tube, and could even lead to a self-organization of the molecules at the nanotube surface.

Nevertheless, the considerations on the POAV misalignment cannot completely explain the disparity between adsorption on zig-zag and armchair tubes, i.e., effect of the chiral angle. They give clues to explain the differences between the inequivalent bonds of a given CNT, but only provide a qualitative understanding. For example it is not possible to predict, just from the ϕ values, the "bridge"-"bridge-*bis*" binding energy difference, or its evolution with the CNT radius. The π-stacking interactions, and consequently the adsorption energy of a benzene molecule on a tube, are mainly determined by the overlap between the π orbitals of the two subsystems. This overlap varies with the subtle changes in the electronic density induced by the geometry of a CNT (curvature and chirality effect) and by a locally different environment (adsorption position effect). The adsorption curves display some unintuitive features and the effect of the chiral angle, in particular the different "stack"-"bridge" crossover size for zig-zag and armchair tubes, is hardly explainable with such simple arguments.

The curvature effect manifests itself with the general trend of a higher reactivity for large diameter tubes. This can be qualitatively understood since the overlap between the CNT and the benzene orbitals increases when the curvature decreases, leading to an enhancement of the "adherence." However, the picture is not as simple, as illustrated by the binding energy increase with curvature for the "bridge" configuration predicted for small armchair tubes. This suggest that there is a competitive curvature effect, that could be the hybridization change for the π orbital on the carbon atoms of the CNT. Indeed, the *s-p* mixing of the π electron increases with curvature [see Fig. 5(a)], so that the π orbital directionality is enhanced, potentially resulting in a higher overlap with the electronic wave functions of the benzene molecule. However, this evolution of the π orbital hybridization corresponds to a different behavior of the adsorption energies for zig-zag tubes. Anyway, one may take the advantage of the curvature dependence of both the adsorption energy and geometry for tube differentiation and diameter-selective reactions. The unusual fact that the tubes with the lowest curvature are the most reactive for the benzene adsorption, and possibly for the physisorption of other planar organic molecules, is an interesting point. It is indeed opposed to what is observed for covalent functionalization where the reactivity increases with the curvature.[31,37–40]

V. CONCLUSION

In conclusion, the adsorption of a benzene molecule on various CNTs has been studied with *ab initio* calculations, within the density functional theory. This reaction involves weak π-stacking interactions and is an example of noncovalent functionalization of CNTs. The calculated binding energy is around 0.2 eV per benzene molecule and the molecule-tube surface distance (around 3.2 Å) is of the same order as the usual separation between two sp^2-like systems (i.e., interplanar distance in graphite). For each tube and position investigated, the electronic properties of the CNT are unchanged upon benzene adsorption, the total DOS being just the superposition of the individual DOS of the two separate systems. For tubes with small radii, the most favorable position is the "bridge" one with the benzene molecule situated over a C—C bond. The inequivalent bonds of a given CNT lead to different adsorption energies, which are related to the POAV misalignment with the following general rule: the smaller the POAV misalignment angle is, the more favorable the benzene adsorption is. This rule has been checked in the specific case of a chiral (8,2) CNT which possesses three different kinds of bonds. The adsorption energies vary with the curvature and the chiral angle of the tube, and of course with the position of the molecular adsorption. There is a crossover, at different sizes for zig-zag and armchair nanotubes, when the position of the benzene over a carbon atom becomes more stable than the one over a bond. Except for small armchair tubes, the tubes investigated display the general trend of a reactivity that decreases with the curvature. These predicted effects could lead to a selective adsorption of benzene on CNTs. The disparities between the inequivalent bonds of a tube should also induce different behaviors for other reactions, even in the case of a covalent functionalization where the kinetics could depend on the type of bond.

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