

π -stacking interaction between carbon nanotubes and organic moleculesF. Tournus,^{1,*} S. Latil,^{1,2} M. I. Heggie,² and J.-C. Charlier^{1,3}¹*Unité de Physico-Chimie et de Physique des Matériaux (PCPM), Université catholique de Louvain (UCL), Place Croix du Sud, 1 (Bâtiment Boltzmann), B-1348 Louvain-la-Neuve, Belgium*²*Department of Chemistry, University of Sussex, Falmer, Brighton BN1 9QJ, United Kingdom*³*Research Center in Micro and Nanoscopic Materials and Electronic Devices (CERMIN), Université catholique de Louvain (UCL), B-1348 Louvain-la-Neuve, Belgium*

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The π -stacking interaction between various planar organic molecules is investigated within the framework of *ab initio* calculations. The adsorption of these molecules on the sidewall of the cylindrical carbon structure induces a small binding energy compared to conventional covalent functionalization. Such a weak interaction is found to be only physisorption and leads to minor and predictable modifications of the electronic structure. These changes in the electronic behavior of the host carbon nanotube are ruled by the relative positions of the molecular levels of the isolated molecule and both the valence and conduction bands of the perfect tube.

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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, whose properties can be tailored by chemical functionalization of the tubes.²

Aromatic compounds are known to interact with graphite, and consequently with the graphitic sidewalls of CNTs.³ This kind of physisorption and 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.⁴

The weak intermolecular forces in a system composed of a closed-shell molecule immobilized on a CNT surface are often referred to as π -stacking interaction. These interactions manifest themselves for example in the solubilization of CNTs in aromatic solvents⁵ or between CNTs and conjugated organic polymers.⁶ Strictly speaking, the concept of the π electron is only valid for planar systems, where the electronic states are either symmetric (σ states) or antisymmetric (π states) upon reflection, as in a graphene sheet. However, in the CNT case, the tricoordinated carbon atoms are distributed on a cylinder, leading to a nonplanar system. The concept of the π electron can be extended,⁷ by constructing on each carbon atom a monoelectronic π orbital orthogonal to the three σ orbitals (directed along the C-C bonds). Consequently, a CNT and a planar organic molecule interact via their so-called π electrons,⁸ allowing π -stacking functionalization, as opposed to covalent functionalization which leads to bond formation or bond breaking. Within this π -stacking scheme, the two subsystems keep their individuality. The intermolecular forces originate from interacting π electrons and include the van der Waals interaction.

In this work, we report on the π -stacking interaction between CNTs and organic molecules, with a particular focus on benzene, using density functional theory (DFT). Our re-

sults illustrate that the π -stacking interaction between simple planar organic molecules and CNTs is weak and only induces minor changes in the electronic structure of the host tube.

Density functional theory,⁹ with the widely used approximations for the exchange-correlation term, namely, the local density approximation (LDA) or the class of generalized-gradient approximations (GGAs), is known not to give a perfect description of weakly bound systems. However, DFT gives a better description of these systems than empirical methods and is able to capture the underlying physics. In addition, DFT calculations are found to be reliable for interacting graphitic systems.^{10–12}

Within the DFT technique, the Kohn-Sham orbitals can be expanded into various basis sets. While plane waves present the advantage to form a complete basis set (easy control of the convergence), localized basis sets are more appropriate for the present study, as they allow supercells containing over hundred atoms. As preliminary tests, the adsorption of benzene on a graphene sheet has been investigated, using different codes and approximations.

A first calculation has been performed with the ABINIT code,¹³ using norm-conserving Troullier-Martins pseudopotentials¹⁴ and a plane-wave basis with a 30 Ha cutoff energy. A $5 \times 5 \times 1$ graphene supercell was used with a corresponding $3 \times 3 \times 1$ Monkhorst-Pack grid for the Brillouin zone k -point sampling. In parallel, simulations with the same model have been performed using a localized basis set with the AIMPRO (Ref. 15) and SIESTA (Ref. 16) codes. In the former case, Bachelet-Haman-Schlüter pseudopotentials¹⁷ have been used, together with a basis of two p -like plus three d -like (*pddd*) Gaussian functions centered on each C atom and four p -like (*pppp*) orbitals on each H atom. In the latter case, Troullier-Martins pseudopotentials¹⁴ have been used with localized pseudo-atomic-orbitals¹⁸ (double- ζ plus polarization and extended $3s$ orbitals for C and double- ζ for H) to describe the valence electrons.

The results obtained using the three different codes agree when the basis set superposition error¹⁹ (BSSE) is corrected for the *ab initio* calculations performed using a localized

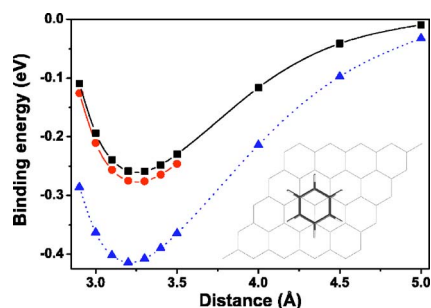


FIG. 1. (Color online) Atomic structure (inset) and binding energy curve for the adsorption of a benzene molecule on a graphene sheet. The results obtained using the AIMPRO code with (squares) and without (triangles) BSSE correction are compared to those obtained with the ABINIT code (circles) within the LDA.

basis set. In this case, the energy difference $E(\text{graphene} + \text{benzene}) - [E(\text{graphene}) + E(\text{benzene})]$ is not the correct adsorption energy. The first term of this expression corresponds to the energy of the complete system (the graphene sheet plus the benzene molecule), while the two last terms are related to the energy of the isolated graphene sheet and the one of the benzene molecule, respectively. Indeed, the basis set is not the same for the three calculations: the basis set dimension is larger for the complete system, resulting in a lower total energy and an artificial energy gain. Consequently, the correct binding energy, which really comes from the interaction between the two subsystems, can be computed by the so-called counterpoise method,¹⁹ using “ghost” atoms: $E_{\text{adsorption}} = E(\text{graphene} + \text{benzene}) - [E(\text{graphene} + \text{benzene}_{\text{ghost}}) + E(\text{graphene}_{\text{ghost}} + \text{benzene})]$.

During the simulation, the benzene molecule is kept parallel to the graphene surface. The most stable geometry is found when its center is positioned over a carbon atom of the sheet (see Fig. 1). For each graphene-benzene distance the system is kept frozen, i.e., no structural optimization is performed. Equilibrium distances of 3.25, 3.25, and 3.27 Å, and binding energies of 0.28, 0.26, and 0.24 eV have been calculated using ABINIT, AIMPRO, and SIESTA respectively.²⁰ These adsorption energies are smaller than the one (0.35 eV) predicted by Fisher and Blöchl,²¹ using a projector augmented plane-wave method and performing an atomic relaxation, which could explain such a deviation.

The choice of the LDA is not fortuitous²² and has been dictated by some test calculations within the Perdew-Burke-Ernzerhof GGA,²³ using SIESTA. While the LDA is known to overestimate binding energies, the GGA on the contrary underestimates them. This behavior is particularly problematic when considering weakly interacting systems,²⁴ such as for example π -stacking interaction between two molecules. Indeed, according to the GGA, two graphene layers are almost repulsing themselves, resulting in a quasinull interlayer binding energy and an interlayer distance far too large, whereas the LDA value is very close to the experimental one.^{10,12} In the same way, when the BSSE is carefully taken into account, almost no binding energy is observed between two parallel benzene molecules or between a benzene and a graphene sheet within the GGA. The GGA has therefore been dismissed to study the adsorption of organic molecules on CNTs.

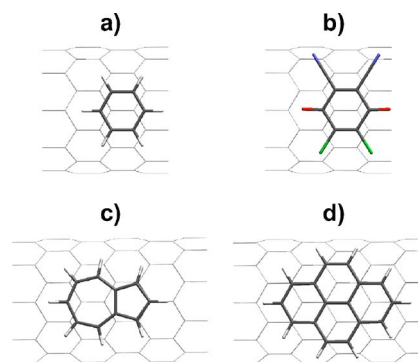


FIG. 2. (Color online) Atomic structures of the different molecules adsorbed on the sidewall of a (10,0) CNT: (a) benzene (C_6H_6), (b) DDQ ($\text{C}_8\text{N}_2\text{O}_2\text{Cl}_2$), (c) azulene (C_{10}H_8), and (d) pyrene ($\text{C}_{16}\text{H}_{10}$).

Following the preceding considerations, a robust numerical procedure based on the LDA plus BSSE correction is constructed,²⁵ using the SIESTA code to investigate the adsorption of planar organic molecules on a single-wall CNT.²⁶ The various molecules that have been considered are benzene (C_6H_6), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, $\text{C}_8\text{N}_2\text{O}_2\text{Cl}_2$), azulene (C_{10}H_8), and pyrene ($\text{C}_{16}\text{H}_{10}$), as illustrated in Fig. 2. While the adsorption of benzene has been studied more extensively²⁷ (on different CNTs, with various diameters and chiralities), the three other molecules have only been investigated when adsorbed on a (10,0) zig-zag CNT. The molecules are tangentially oriented to the surface of the tube, at a distance of 3.2 Å apart from the tube sidewall, in the configurations illustrated in Fig. 2. The supercells are chosen to be large enough to avoid any interaction between the CNTs [hexagonal cell with a 40 Å lattice parameter in the (x,y) plane] and between the molecules adsorbed on a given tube (two or three CNT cells in the z direction). A eight k -point or four k -point sampling has been used depending on the size of the cell, and the real-space integration has been performed on a grid corresponding to an 80 Ry cutoff energy.

The calculated binding energies are 0.20 eV for benzene, 0.61 eV for DDQ,²⁸ 0.26 eV for azulene, and 0.42 eV for pyrene. Neither atomic relaxation nor the check of the most favorable position of the molecule on the CNT surface has been performed, in order to reduce the computational effort.²⁹ Nevertheless, these values give a reliable order of magnitude for the adsorption energy, which is much smaller than what is observed for covalent functionalization of CNTs ($\sim 1-3$ eV). However, our binding energies for benzene and DDQ deviate highly from those of Zhao *et al.*³ who reported 0.10 and 0.32 eV, respectively. These deviations could be attributed to the fact that Zhao *et al.* have used the GGA without any BSSE correction. As already mentioned, this correction is crucial, otherwise a positive binding energy can be inferred for systems that are in fact repulsive: this is indeed the case for a benzene molecule 3.2 Å apart from a (10,0) CNT surface, within the GGA.

Moreover, the apparently good agreement between the calculated adsorption energy of benzene calculated by Zhao *et al.*³ and the measured heat of adsorption on graphitic car-

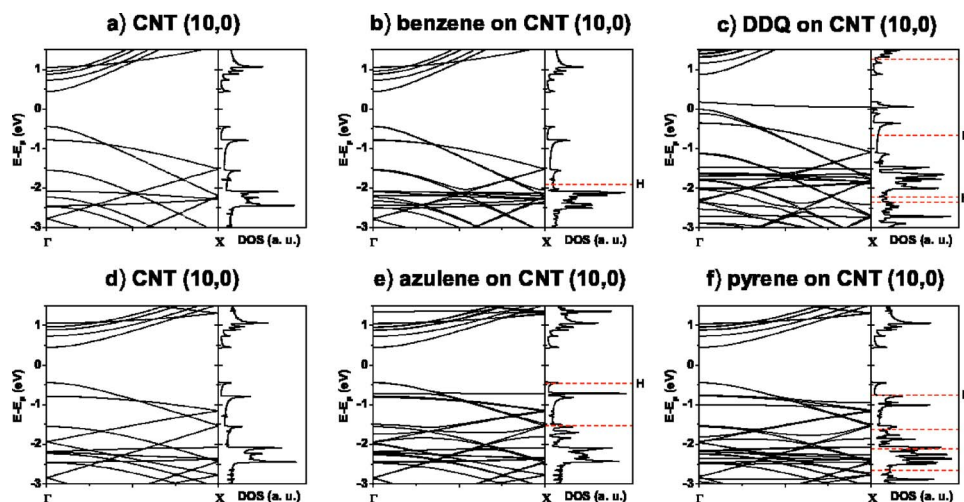


FIG. 3. (Color online) Band structures and electronic densities of states (DOS) of an isolated (10,0) CNT with two (a) or three (d) unit cells and of a benzene (b), DDQ (c), azulene (e), or pyrene (f) molecule adsorbed on a (10,0) CNT. In the DOS panel, the energies of the electronic states of the isolated molecule are indicated by dotted (red) lines, H and L corresponding, respectively, to the HOMO and LUMO levels.

bon is in fact erroneous.³⁰ The true experimental adsorption energy is 0.41 eV, which is closer to our calculated value for benzene adsorption on graphene or on a (10,0) CNT, thus giving confidence on these results. Interestingly, the DDQ adsorption corresponds to the highest binding energy, which is three times larger than for benzene. This result will be discussed later, together with the modifications induced by the DDQ molecule on the electronic structure of the host tube.

Considering the adsorption of benzene on CNT, the most favorable configuration consists in positioning the benzene molecule over the middle of a C-C bond (position called “bridge”) when the diameter of the nanotube is not too large [this has been verified for (4,4), (7,0), (8,0), (5,5), (9,0), (8,2), (10,0), and (6,6) tubes].²⁷ For these systems the equilibrium distance runs between 3.20 and 3.27 Å. On the contrary, the adsorption of benzene on graphene, which corresponds to an infinite-radius CNT, is found to be more stable when the molecule lays over a carbon atom (position called “stack”). Such a situation implies that the most favorable adsorption geometry must evolve from bridge to stack when increasing the nanotube diameter,³¹ with a crossover at a given size that is found to depend on the CNT chirality. In fact, our calculations show that for a 9.63 Å diameter (7,7) CNT the stack configuration is slightly preferred to the bridge one, whereas for a 13.50 Å diameter (17,0) CNT the bridge position is still a little bit lower in energy. These results disagree again with the work of Zhao *et al.*³ which states that the benzene adsorption is insensitive to the tube size and chirality. Other important details related to the adsorption of benzene on CNT are discussed in a separate paper.²⁷

The influence of the benzene adsorption on the electronic structure of the host nanotube is also investigated *ab initio*. Only a slight modification of the band structure and the electronic density of states (DOS) is observed in Fig. 3(b) when compared to the isolated (10,0) CNT [Fig. 3(a)]. This result is consistent with the fact that the π -stacking interaction cor-

responds to a very small binding energy between the benzene molecule and the CNT. In fact, the DOS of the entire system (CNT+molecule) is nearly the superposition of the individual DOS of the isolated benzene and CNT, which is obvious since both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of benzene fall in the valence and the conduction band of the CNT, respectively. As observed in Fig. 3(b), the HOMO of benzene just leads to flatbands slightly downshifted, around 2 eV under the Fermi level. In this range of energy, the bands originating from the CNT are also modified to some extent, revealing a change in the electronic distribution. Actually, these bands correspond to mixed benzene-CNT states, as illustrated in Fig. 4. Such a mixed character of a band does not imply any overlap between the CNT and the molecule orbitals, as it would be the case in a hybridization process. In the present case, the states on the benzene and on the CNT simply are in the same energy range.³² Consequently, it seems more relevant to qualify the adsorption of benzene on a CNT as a physisorption. Indeed, although the adsorption does not only involve van der Waals

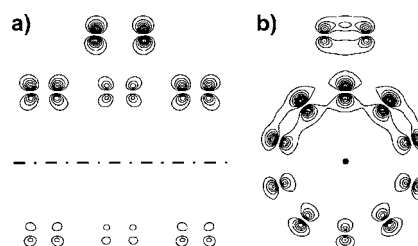


FIG. 4. Isodensity contours for a benzene molecule adsorbed on a (10,0) CNT, corresponding to the wave function at the Γ point situated 2.5 eV under the Fermi energy. The system is viewed in a plane containing the tube axis (dash-dotted line) (a) or perpendicular to the axis (b). This mixed state does not display any significant overlap between the benzene and the CNT. Each isoline corresponds to a 0.005 e/bohr^3 (a) and a 0.002 e/bohr^3 (b) increase in the electronic density.

forces, its characteristics (energetics, geometry, electronic structure, etc.) are not those of a chemisorption.

Note that the influence of the adsorbed benzene on the electronic structure is equivalent whatever the position of the molecule on the tube. Moreover, this statement is valid for all the CNTs considered. As the total DOS is determined by the two separate subsystems and only weakly affected by the π -stacking interaction, the semiconducting or metallic character of the CNT will not be affected by the benzene adsorption, due to the energetic position of its molecular levels with respect to the valence and conduction bands of the tube.

The situation is different for the adsorption of DDQ, where a flatband localized on the molecule is observed just on top of the valence band of the CNT [see Fig. 3(c), which corresponds to a 3.2 Å distance]. This band is in fact the former LUMO level of the DDQ [dotted line in the right panel of Fig. 3(c)] which has been pulled up, together with the deeper molecular levels (in particular the HOMO). The system is almost metallic, although a very small gap is present whose value varies with the energy width of the smearing function used in the calculation. Once more, although some bands correspond to an electron localization on both the DDQ and the CNT, there is no real hybridization.

Among the molecules considered in this work, the DDQ appears as a special case as it is a well-known π -electron acceptor with a very high electron affinity, corresponding to a LUMO very deep in energy. Consequently when a DDQ molecule is adsorbed on a CNT sidewall, the LUMO of the isolated molecule is positioned in the valence band of the CNT. An electron transfer from the tube to the DDQ occurs, resulting in an upward shift of the molecular levels until an equilibrium is reached (with a certain amount of electron transferred). In the limit of a vanishing smearing energy width, the system would then be a metal. Interestingly, when the DDQ and the nanotube are closer to each other, they interact more strongly and we find that when the distance is decreased: the splitting of the initially doubly degenerate highest state of the valence band of the tube increases; the small gap (partly due to a finite energy smearing) increases; and the electron transfer also increases.

The interaction between the DDQ and the CNT is stronger than for the benzene because it involves a significant charge transfer (around 0.2 electron, from a Mulliken population analysis³³) from the tube toward the molecule. Though no sharp distinction can be made between a chemisorption and a physisorption, the adsorption of DDQ, like that of benzene, displays characteristics that are closer to the case of a physisorption. Once more, the π -stacking interactions are not only van der Waals forces and, in particular, they involve a weak charge-transfer interaction.

The analysis performed for benzene and DDQ suggests that knowing the energetic position of the electronic levels of the isolated molecule allows to infer how the electronic structure of the CNT will be modified upon adsorption. In this way, two other planar molecules, azulene and pyrene, are investigated. The positions of their HOMO levels [topmost dotted line in the right panel of Figs. 3(e) and 3(f)] lie in the CNT valence band (pyrene) or just on top of it (azulene). It is thus not surprising that these systems behave like benzene on a CNT: the gap is unchanged. Flatbands are still distinguish-

able as reminiscent of the former molecular states, and the total DOS corresponds to the sum of the individual ones [see Figs. 3(e) and 3(f)]. A small downshift of the molecular states is also observed, indicating a slight charge transfer from the molecule toward the CNT. This charge transfer occurs because the Fermi energy (middle of the HOMO-LUMO gap) is slightly higher for the isolated molecule than for the isolated CNT. Then, the CNT work function is the key quantity that must be considered to predict the modifications of the electronic structure and the direction of the charge transfer upon adsorption of a planar organic molecule on a nanotube. According to the recent calculations of Shan and Cho,³⁴ our results, established for a (10,0) tube, must be valid for almost every CNT. Moreover, our conclusions are very similar to those of Simeoni *et al.*⁶ on the interaction between CNTs and conjugated organic polymers, which indicates that they may be valid for an entire class of systems where the CNT functionalization involves π -stacking interactions.

In conclusion, *ab initio* calculations on simple planar molecules have illustrated that the π -stacking interaction between organic molecules and CNTs is weak and induces minor and predictable changes in the CNT electronic structure. A special care has been taken in the choice of the exchange-correlation functional and in the use of a BSSE correction to perform a reliable theoretical study of such a weak interaction. No real hybridization between the molecule and the CNT states have been observed, although a mixing of the states can occur, suggesting that the adsorption is only a physisorption. Even though the accurate geometry and energy of adsorption may depend on the tube size and chirality, the same trends are met for all CNTs: the evolution of the electronic properties upon adsorption is ruled by the relative position of the molecular states and the CNT valence and conduction bands. With its efficient electron acceptor behavior, the DDQ molecule is a special case where adsorption implies an electron transfer from the tube towards the molecule, leading to a metallic character of the global system. In general, for the functionalization of a semiconducting CNT, the HOMO and LUMO of a molecule have then to be adapted to the situation, depending if a metallic or semiconducting behavior is desired. On the other hand, a metallic CNT remains metallic upon π -stacking functionalization. However, even if in both cases the electronic properties of the host nanotube are only weakly affected, further investigations are needed to determine the repercussions of adsorption on the transport properties, which could be modified.³⁵

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