Modification of the structural and electronic properties of graphene by the benzene molecule adsorption

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A B S T R A C T

A survey of the literature data on the adsorption of benzene on graphene or carbon nanotubes indicates that the distance between the graphene sheet and benzene molecule is determined from weak van der Waals forces (≈ 3.40 Å). In our theoretical study, it was found that the benzene/graphene structure (in a specific configuration with carbon atoms located at the atop positions, stacked directly on the top of each other) forms strong covalent bonds, if the distance between the graphene and benzene is about 1.60 Å. Such a short distance corresponds to about a half of the usual separation between the graphite layers. It was also shown that at such a short distance the carbon atoms of the benzene molecule move towards the graphene sheet, whereas the hydrogen atoms move in a different direction, thus breaking the benzene planar structure.

In addition to the structural optimization, the calculated electronic and optical properties (significantly modified by the adsorbed benzene molecule) are presented as well.

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1. Introduction

Carbon is an interesting and important element not only because it forms millions of organic compounds with other elements but also due to its capability to form a variety of allotropes. It is known that there are many allotropic modifications of carbon with very diverse physical properties. Two well-studied allotropes of carbon, the diamond and graphite, were known since antiquity. Another allotrope of carbon, graphene, is a two-dimensional structure. Although it was theoretically proved that a free ideal two-dimensional film cannot be obtained due to instability with respect to folding or twisting [1–3], recently graphene has been obtained experimentally [4]. Moreover graphene is often called the "mother of all graphitic materials" [5] since the graphite or nanotube is just derivatives of graphene with other dimensionality. Like other nano materials, graphene has been a subject of numerous experimental and theoretical studies. The nature of graphene itself suggests that due to its specific single-layered structure interactions of other atoms and/or molecules with a single graphene sheet can significantly modify the structural and electronic properties of such a combined system [6–9].

In most of the previous studies, which have been focused on the adsorption of benzene on graphene [10–12], graphite [13] or carbon nanotubes [14–16], the distance between the graphene sheet and benzene molecule is based on the weak van der Waals forces (≈ 3.35 Å). In a resent theoretical study [17], it was found that two graphene layers with the carbon atoms located at the atop positions (stacked directly on the top of each other) tend to form strong covalent bonds when the distance between their planes is 1.56 Å. Such a distance is about of the half of the usual separation between the graphite layers. Although such a configuration of two graphene layers was found to be metastable when comparing to that one bound by weak van der Waals forces, the activation energy required for the destruction of this phase is large enough to make its existence possible at room temperature. In addition, the calculated by Nakada and Ishii [18] equilibrium distance between the single carbon adatom and graphene is also less than 1.65 Å.

Since the distance between atoms is one of the crucial parameters, which determines the electronic properties of nanostructures and their interaction with environment, in the present work we focused our attention on a thorough analysis (in the density functional density – DFT – framework) of new possible structural configurations of the benzene/graphene with a small separation between them. The main goal of this work was to understand the implications of the adsorbed molecules on the structural properties of a single graphene layer. The benzene molecule was chosen for an analysis of its adsorption on the graphene sheet due to the following reasons: (i) the size and overall appearance of the aromatic ring of benzene resembles the graphene's aromatic ring and (ii) resemblance of their main
structural units may result in efficient interaction between both of them.

As a result of our analysis, it was shown that closely located graphene layer and benzene molecule strongly affect the geometry of each other because of strong covalent interaction between the carbon atoms from graphene and benzene. In addition to the analysis of the structure of the considered systems, calculations of the band structure, Mulliken effective charges and electron density difference in the space between atoms were also calculated to support the conclusions about modified shape of both benzene molecule and graphene layer.

2. Computational methods

All presented calculations were performed using the CASTEP module [19] of Materials Studio. The exchange-correlation functional was represented by the LDA (local density approximation) based on the Ceperley and Adler data as parameterized by Perdew and Zunger [20,21]. The cutoff energy of the plane waves, which determines the size of the basis set, was taken as 500 eV; the ultrasoft potentials were used for all elements (carbon and hydrogen), which form the considered structures. The Monkhorst-Pack \( k \)-point grid was set as \( 3 \times 3 \times 1 \) for the Brillouin zone integration; all performed calculations were not spin-polarized.

For graphene modeling we were used the super-cell technique considering a \( 6 \times 6 \times 1 \) unit cell containing 72 carbon atoms. The pristine graphene sheet or molecule and each molecule/graphene system were placed into the \( 14.65 \times 14.65 \times 10.00 \) Å super-cell. A single benzene molecule was adsorbed in the central region of the graphene sheet with considering a hollow adsorption site (Fig. 1). The horizontal distance between benzene molecules (after repeating the super-cell) is about 10.5 Å. As the starting geometry for optimization we took 1.6 Å for initial distance between the graphene and the benzene molecule. The convergence parameters for the geometry optimization were as follows: for the energy \( 2.0 \times 10^{-5} \) eV/atom, for the maximum force 0.05 eV/Å, and for the maximum displacement 0.002 Å.

For the test calculations we have also used the LDA and GGA (generalized gradient approximation) of Perdew, Burke, and Ernzerhof (PBE) functionals [22,23] without and with dispersion corrections (for van der Waals interactions). Such corrections were: OBS (Ortmann, Bechstedt, and Schmidt) [24] and TS (Tkatchenko and Scheffler) [25] dispersion correction for the LDA and GGA functionals, respectively. A use of different calculating settings allows to check out the overall consistency of the performed calculations. Also an additional system – namely, a complex consisting of two molecules: benzene and coronene – was calculated as well using the GAUSSIAN 09 program [26] with the second-order Muller-Plesset (MP2) method and 6-31G basis set to check out the variations of the structural properties of complexes with prevailing either covalent or van der Waals bonds between different molecules.

Application of the DFT-based techniques of calculations to our systems is justified by well-established fact [17] that while van der Waals interaction is weak and not always is described accurately enough by a local DFT, it works much better for the systems, exhibiting well-pronounced covalent interaction between constituting atoms.

3. Results and discussion

3.1. Structural properties

As shown previously [10–16], the adsorption of benzene on graphene, graphite or carbon nanotubes is governed by weak van der Waals forces, with the separation of about 3.40 Å. Our calculations show that in case of hollow configuration the outcome of the geometry optimization process depends on starting position of the benzene molecule and graphene layer. If the initial distance is greater than 1.6 Å the optimized structure of benzene molecule is planar (with bonds lengths and angles as for the isolated molecule). The optimization procedure converged when the benzene–graphene separation was 3.30 Å; the whole complex is held together by the van der Waals forces (Fig. 2).

We note here in passing that the calculated by DFT (without dispersion corrections) adsorption energy of benzene/graphene system (van der Waals) is found to be \(-0.2\) eV, which is in good agreement with the calculated values reported by Zhang et al. \((-0.16\) eV, [12]), by A.Z. AlZahrani \((-0.25\) eV, [11]), and by Tournus et al. \((-0.2\) eV, benzene adsorption on carbon nanotube [16]).

If, however, initial benzene–graphene distance is less or equal to 1.6 Å (close to the local minimum, according to Ref. [17]), the optimization result is quite different. The planar structures of both benzene molecule and graphene layer are no longer preserved (Fig. 3). The six carbon atoms from the benzene molecule adopt the planar geometry at 1.563 Å above the plane formed by the six carbon atoms from the graphene sheet (located immediately under the benzene ring) in the hallow configuration. This value is in excellent agreement with the estimated similar distance of 1.56 Å obtained by Andres et al. [17] (where they found the metastable configuration of two graphene layers stacked directly on the top of each other and bonded by strong chemical bonds). At the same time, the six carbon atoms from the graphene sheet are moving slightly towards the benzene molecule, reaching the height of 0.93 Å above the rest of the graphene layer. The six hydrogen atoms from the benzene molecule are moving away from the graphene sheet. The optimized structure looks like out-of-plane and shows strong interaction between benzene molecule and graphene layer (Fig. 3). All geometrical parameters of these benzene–graphene and benzene–coronene configurations are listed in Table 1. We have calculated the main geometrical characteristics (like bond lengths, angles between bonds, separation between the graphene sheet and absorbed molecules) using different functionals with/without corrections, as described in Section 2.

The results of the population analysis and bond order estimations show that there occurs a considerable change of properties of the C–C bond in both graphene and benzene. If the C–C bond
order in the isolated benzene molecule is 1.5 [17] (the same value is taken for graphene), our calculations show that these values are considerably reduced to 0.64 for benzene and 0.68 for those carbon atoms in graphene lying immediately under the aromatic ring of benzene.

The bond order of the C–C bonds located beneath the hydrogen atoms of benzene is 0.88. Such a decrease of the bond order indicates enhancement of the ionic coupling between the carbon atoms within the aromatic rings of the benzene and graphene, which is also confirmed by re-distribution of the electron density caused by the strong covalent interaction between the benzene molecule and graphene.

At the same time, the bond order of the C–C bond formed by one carbon atom from benzene and one carbon atom from graphene is 1.0, which indicates strongly covalent interaction between these two aromatic rings located at the distance of 1.56 Å. We also note here that our value of the C–C bond is very close to that one (0.92) obtained in Ref. [17] for two parallel graphene layers.

Our calculated C–C–C and C–C–H angles of benzene on the top of graphene are measured to be 120° and 115.7°, respectively. Our calculations give an energy difference between two considered configurations (with the covalent and van der Waals interactions) of about 1.245 eV per one C–C bond.

Similar calculations, when performed for the benzene/coronene system, lead to practically the same results: at the initial distance less than 1.6 Å both molecules no longer keep their planar structure (Fig. 4) due to strong covalent interaction between them. We also note here that the GAUSSIAN-calculated benzene–coronene distance for van der Waals interaction (3.47 Å) is close to the value of 3.54 Å reported by the authors of Ref. [27].

3.2. Electronic properties

The calculated electronic band structures of the benzene/graphene complexes in two different considered cases are depicted in Fig. 5. Fig. 5a shows the calculated band structure in the case, when the distance between graphene and benzene is 3.30 Å (van der Waals interaction).

As seen from the figure, the band structure is an intermediate case between a metal and a gapless semiconductor, since there is no distinct band gap. However, it should be stressed out that although the overall appearance of the band structure diagram is gapless, there are band gaps of about 3 eV at the F and Q special points of the Brillouin zone. The total density of states (DOS) at the Fermi level is very small in this case (~2.4 electrons/(eV cell)), and such a complex can be described as a semimetal. The maximum DOS value in the valence band is 36.81 electrons/(eV cell) (at $E = -6.32$ eV), whereas the DOS maximum for the conduction band is 15.87 electrons/(eV cell) (at $E = 2.12$ eV).

On the contrary, Fig. 5b shows the band structure of the system with strong covalent bonds between benzene molecule and graphene layer (characterized by a small separation between both of them). The system becomes a semiconductor with the calculated band gap at the G point (center of the Brillouin's zone) of about 0.80 eV. This result is in a very good agreement with the estimated value of 0.91 eV (Andres et al. [17]), obtained for two parallel graphene layers.

Formation of the chemical bond between particular atoms can be assessed by considering the electron density difference (Fig. 6), which shows various cross-sections in the space between the benzene molecule and graphene layer at the distance of 1.56 Å. The electron density is shifted toward the hydrogen atoms (Fig. 7). This clearly indicates the formation of covalent bonds between benzene molecule and graphene sheet. The effective Mulliken charges [28] of covalently bonded benzene/graphene system are shown in Fig. 8. Due to the sp3 hybridization and covalent bond formation between carbon atoms from benzene and graphene the benzene molecule gets slightly positively charged and the carbon atoms of graphene (around atoms of benzene ring) have a small negative charge. In the case of configuration bonded with van der Waals forces the benzene molecule is uncharged, whereas the ring of graphene under benzene molecule is slightly positively charged.
In the present paper we have identified significant changes of the electronic and structural properties of a single graphene layer with a benzene molecule absorbed at its top. We have found that – depending on the separation between the graphene layer and benzene molecule – two opposite situations can be realized. The first one is characterized by the strong covalent bonding between graphene and benzene, which is formed at a short separating distance of 1.60 Å. In addition to this covalent bonding (confirmed by the calculated electron density difference distributions), the geometrical shapes of both graphene and benzene are changed. The aromatic ring of benzene and the aromatic ring of graphene located directly under it move towards each other. In addition to this noticeable change of geometrical configuration, the electronic properties are also modified: the gapless graphene (in the absence of benzene) is transformed into the semiconducting material with the calculated band gap of 0.8 eV. Besides, the re-distribution of the electron density leads to the appearance of slightly negative charges on the carbon atoms.

**Table 1**

Structural data (interatomic distances and angles between chemical bonds) for the graphene–benzene and benzene–coronene complexes.

<table>
<thead>
<tr>
<th>Structural unit</th>
<th>Benzene–graphene (CASTEP)</th>
<th>Benzene–coronene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Van der Waals interaction</td>
<td>Strong covalent bonding</td>
</tr>
<tr>
<td></td>
<td>LDA</td>
<td>LDA (OBS)</td>
</tr>
<tr>
<td>Ring of graphene sheet located directly under benzene</td>
<td>( a_{C-C} = 1.41 \text{ Å} )</td>
<td>( a_{C-C} = 1.42 \text{ Å} )</td>
</tr>
<tr>
<td>Benzene</td>
<td>( \angle C-C-C = 120^\circ )</td>
<td>( \angle C-C-C = 120^\circ )</td>
</tr>
<tr>
<td>( a_{C-H} = 1.09 \text{ Å} )</td>
<td>( a_{C-H} = 1.09 \text{ Å} )</td>
<td>( a_{C-H} = 1.09 \text{ Å} )</td>
</tr>
<tr>
<td>( \angle C-C-C = 120^\circ )</td>
<td>( \angle C-C-C = 120^\circ )</td>
<td>( \angle C-C-C = 120^\circ )</td>
</tr>
<tr>
<td>( \angle C-C-C = 120^\circ )</td>
<td>( \angle C-C-C = 119.9^\circ )</td>
<td>( \angle C-C-C = 119.9^\circ )</td>
</tr>
<tr>
<td>Benzene–graphene (distance between layers)</td>
<td>( d = 3.30 \text{ Å} )</td>
<td>( d = 3.085 \text{ Å} )</td>
</tr>
<tr>
<td>Benzene</td>
<td>( \ randomNumber \text{ Å} )</td>
<td>( \ randomNumber \text{ Å} )</td>
</tr>
<tr>
<td>Benzene–coronene (distance between layers)</td>
<td>( \ randomNumber \text{ Å} )</td>
<td>( \ randomNumber \text{ Å} )</td>
</tr>
</tbody>
</table>

**Fig. 4.** Optimized structure of benzene (top) and coronene (bottom) system at covalent bonding distance of 1.60 Å.

**Fig. 5.** Electronic band structure: (a) Van der Waals-like distance and (b) chemical bonding between molecule of benzene and graphene sheet.
The second situation is that one of a weak van der Waals interaction between the graphene and benzene at a greater distance of about 3.3 Å. In this case, both graphene and benzene keep their planar structure. The calculated band gap disappears, which leads to enhanced metallic behavior.

Formation of such controlled defects on the top of a single graphene layer can be important for application of such complexes in 2D electronics. It can be also important to modify and stabilize the defect-induced changes by the external pressure and/or doping with other molecules and/or single atoms which may enhance desirable electronic properties by providing additional electrons to the conduction band and/or additional holes to the valence band.

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References


Fig. 6. A side view of the cross-section of electron density difference between benzene and graphene.

Fig. 7. Isosurface of cross-section density difference (three atoms: hydrogen of benzene, carbon of benzene, and carbon of graphene).

Fig. 8. Effective Mulliken charges (the atoms without labels are not charged). A top view (from the benzene molecule's side). The carbon atoms from graphene located right under the benzene aromatic ring are neutral. The carbon atoms of benzene are shown as the black spheres for better visibility.