Adsorption of Monocyclic Carbon Rings on Graphene: Energetics Revealed via Continuum Modeling

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Supporting Information

ABSTRACT: Gas-phase spectroscopic detection of tiny carbon clusters is a recent success story in the area of carbon cluster research. However, experimental production and isolation of these clusters are extremely difficult because of their high reactivity. One possibility to isolate the generated clusters would be to deposit them on graphene and to desorb them for subsequent use. One of the pertinent questions toward realizing this would be the energetics of the adsorption process. Therefore, in this work, the energetics for the adsorption of the monocyclic carbon rings (C_n with n = 10, 12, 14, 16, 18, 20, and 22) on a graphene sheet are investigated using the analytical approaches, developed earlier by Hill and co-workers. The adsorption process here is driven by the noncovalent interactions between the carbon rings and the graphene sheet. The analyses of the interaction energies as a function of both the vertical distance Z and the rotational angle \( \phi \) are performed in order to determine the preferred orientations, equilibrium positions, and binding energies for the adsorption of various carbon rings on graphene. We find that the preferred orientation of the rings with respect to the graphene sheet is the parallel orientation. The results from continuum, discrete—continuum, and discrete models are in good agreement. Further, computations using density functional theory and quantum mechanics/molecular mechanics approaches are performed, and comparisons of the computed energetics with the data from the models are reported. Finally, we highlight the scope and the limitations of the analytical models.

INTRODUCTION

Graphene, a two-dimensional nanomaterial reported for the first time in 2004, possesses excellent electronic, mechanical, thermal, chemical, optical, and transport properties. Since its discovery, it has been widely used in nanoelectronic devices, transparent conductors, nanocomposite materials, and more recently in biomedical applications, such as drug loading and delivery. Owing to its large surface area and porous structure, graphene is found to be an excellent adsorbent for atomic and molecular systems. The adsorption properties of various atoms and molecules on graphene have been examined theoretically and experimentally for potential applications such as gas sensing and separation, filters for removing toxic compounds, and chemical sensors for detecting molecules at small concentrations. Hydrogen storage using graphene as a substrate has also drawn a lot of attention in recent times.

Carbon forms clusters more readily than any other element because of its strong and directional covalent bonding character. Among the carbon clusters, small clusters have attracted much attention from both experimental and theoretical communities in recent years because of their important role in various fields. There are astrophysical evidences for the presence of these clusters in the chemistry of carbon stars and comets and in interstellar molecular clouds as stable species or reactive intermediates. In particular, they have been proposed as possible carriers of the diffuse interstellar bands. Small carbon clusters are thought to be the building units of fullerenes, and various studies suggest that carbon growth continues sequentially from linear chains to monocyclic, bicyclic rings and eventually to fullerenes as a function of cluster size. Tiny carbon clusters are known to be present in hydrocarbon flames and other soot-forming systems. They are also thought to be intermediates in the gas-phase chemistry taking place in chemical vapor deposition systems for the production of thin diamond films. There are theoretical studies, indicating that some solids synthesized from small carbon clusters are potential candidates for carbon-based superconductors. It has been found that the carbon clusters smaller than C_10 possess low-energy linear structures. When the cluster size increases from C_10, the ring stability increases because of the reduction in angle strain and the added stability arising from an additional C=C bond. Theoretical studies have revealed that the most stable structures for carbon clusters with 10, 12, 14, 16, 18, 20, and

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22 atoms are monocyclic rings.\textsuperscript{31–38} It has been found in recent years that even for some small clusters such as C\textsubscript{4}, C\textsubscript{8}, and C\textsubscript{6}, ring isomers are isoenergetic with or are lower in energy than their linear counterparts.\textsuperscript{39–43} Among carbon rings, the C\textsubscript{6n+2} rings (C\textsubscript{10}, C\textsubscript{14}, C\textsubscript{18}, and C\textsubscript{22}) attract special attention. The C\textsubscript{4n+2} rings are suitable model systems for studying many-body quantum effects because they exhibit a competition between Hückel aromaticity, second-order Jahn–Teller effect, and Peierls instability at large sizes, each of which favors different structures and the real structure is a balance between these effects, which tends to vary with the size of the ring.\textsuperscript{44–50} Monocyclic carbon rings are highly reactive, transient species and are extremely difficult to produce and study in the laboratory. Even though great progress has been made recently in observing and identifying carbon rings unlike in the past where only linear chains were observed in the vast majority of experimental studies.\textsuperscript{51–62} Questions concerning the structure and chemistry of carbon rings have been difficult to address because of their highly reactive nature and the difficulty of isolating them experimentally.

In view of the above, one might ask the following questions: (i) can adsorption on graphene serve as a useful strategy for isolating monocyclic carbon rings? (ii) What are the energetics for the adsorption of various carbon rings on graphene? Therefore, in this article, the adsorption of monocyclic carbon rings, C\textsubscript{n} with n = 10, 12, 14, 16, 18, 20, and 22, on a graphene sheet is investigated using an analytical approach, developed earlier by Hill and co-workers.\textsuperscript{63–66} Continuum models for describing the interactions involving various carbon-based systems have earlier been successfully employed in the literature.\textsuperscript{67–72} The adsorption of a carbon ring on graphene is driven by the noncovalent interactions between the ring and the graphene sheet, and consequently, the interaction potential between two tiny elements on the ring and the sheet can be described using the Lennard-Jones 12-6 potential function.\textsuperscript{73}

The total interaction energy between the ring and the sheet can be subsequently evaluated by adding up the contributions from all of the tiny elements of the rings and the sheet. The analytical study comprises the continuum, discrete—continuum, and discrete models. The graphene sheet is modeled as a continuum structure in the continuum and discrete—continuum models, whereas the carbon rings are treated as continuum structures in continuum model and as discrete structures in the discrete—continuum and discrete models. In the continuum representation, carbon rings are denoted as circular rings of radii r with uniform linear density of carbon atoms and the graphene sheet is represented as an infinite sheet lying in the xy plane with uniform density of carbon atoms. In the discrete—continuum and the discrete models, carbon rings are treated as tiny atomic clusters with well-defined geometries that are obtained by performing electronic structure calculations on each of the rings. In the discrete model, graphene is represented by a model system, circumcircumcoronene (C\textsubscript{96}H\textsubscript{24}), the geometry of which is also obtained from the electronic structure calculations.

**Continuum Model.** In the continuum model, a carbon ring is modeled as a circular ring of continuous distribution of carbon atoms and a graphene sheet is represented by an infinite plane with uniformly distributed carbon atoms. The relative position of a carbon ring with respect to the graphene sheet is described by two parameters, namely, the vertical distance Z from the plane to the center of the ring and the rotational angle \(\phi\) describing the orientation of the ring with respect to the plane of the sheet, wherein \(Z \in (0, \infty)\) and \(\phi \in [0, \pi/2]\). A schematic illustrating the key parameters in the continuum model for the interaction between a carbon ring and a graphene sheet is illustrated in Figure 1. The total interaction energy between the ring and the graphene sheet is given by \(E_{\text{cont}}\) can be rewritten as:

\[
E_{\text{cont}} = bn_{s}(-A_{\text{cont}}L_{b} + B_{\text{cont}}L_{b})
\]

where the atom and surface densities of the carbon ring and the graphene sheet, respectively. \(b\) refers to the radius of the ring. The above equation for \(E_{\text{cont}}\) can be rewritten as:

\[
E_{\text{cont}} = bn_{s}(-A_{\text{cont}}L_{b} + B_{\text{cont}}L_{b})
\]

where \(J\) is defined by

\[
J = \frac{32}{\pi^{2}}\beta^{2}a^{2}n_{s}
\]
The interaction energies for various orientations of the rings and for various positions of the centers of the rings with respect to the graphene sheet can thus be evaluated if the corresponding vertical offsets positions of the carbon atoms in the rings are known.

**Discrete Model.** In the discrete model, carbon rings and graphene are represented as discrete atomistic structures. Graphene is modeled by considering circumcyclohexarenone (C96H24), which has earlier been employed as a model system for graphene in numerous theoretical studies. The geometry of the 3D rings and C96H24 are obtained from electronic structure calculations. The interaction energies are evaluated as a sum total of the contributions from individual atom–atom pairs and can be written as

\[
E_{\text{dis}} = \sum_{i} \sum_{j} \left( -\frac{A}{\rho_{ij}^6} + \frac{B}{\rho_{ij}^{12}} \right)
\]

where \( \rho_{ij} = [x_i^2 + y_i^2 + z_i^2]^{1/2} \) is the distance between an atom on the ring and an atom on the graphene sheet.

**COMPUTATIONAL METHODS**

Computations are performed using DFT and QM/MM approaches. In the DFT study, the calculations are performed at the B97D level of theory. B97D is a dispersion-corrected density functional which is being widely used to describe long-range dispersion interactions in noncovalently interacting systems and is therefore appropriate for the study of the interactions reported in this study. The geometry optimizations of the carbon rings (Cn), model system of graphene (C96H24), and the carbon ring–graphene model complexes are carried out at the B97D level of theory using the 6-31G(d,p) basis set in the Materials Science Suite implemented in Schrödinger software. The single-point energy calculations are then carried out at the 6-311G(d,p) level using the same functional (B97D/6-311G(d,p))/B97D/6-31G(d,p)) in Gaussian 09 software. The binding energies for the adsorption of the carbon rings on graphene are computed using

\[
E_{\text{binding}} = E_{\text{carbon ring}} + E_{\text{C96H24}} - E_{\text{complex}}
\]

where \( E_{\text{carbon ring}} \) and \( E_{\text{C96H24}} \) are the energies of the isolated carbon ring and isolated C96H24, respectively. \( E_{\text{complex}} \) is the energy of the carbon ring–C96H24 complex. All of the reported binding energies are corrected for the basis set superposition errors using the counterpoise correction scheme. In the DFT

\[
J_n = \int_0^{2\pi} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{1}{\rho^{2n}} \, dx \, dy \, d\theta
\]

The procedure for evaluating \( J_n \) has earlier been described in detail by Hill and co-workers. The final analytical expression for \( J_n \) can be written as

\[
J_n = \frac{2\pi}{n-1} (b \sin \phi + Z)^{2-2n} \int_{2n-2}^{1/2} \Gamma \left( \frac{1}{2} \right) \sin \phi + Z \right)
\]

where \( \Gamma(x,y,z) \) is the ordinary hypergeometric function. The interaction energies for various orientations of the rings and for various positions of the centers of the rings with respect to the graphene sheet can thus be evaluated if the corresponding vertical offset positions of the carbon atoms in the rings are known.

**Discrete–Continuum Model.** In the discrete–continuum model, a carbon ring is modeled as a discrete cluster of carbon atoms and the graphene sheet is modeled as an infinite plane of uniformly distributed carbon atoms. The relative positions of various carbon atoms in the ring with respect to the graphene sheet are described by the vertical offset distances \( \epsilon \) of the atoms from the plane of the sheet, as illustrated in Figure 2. The total interaction energy between a graphene sheet and a carbon ring is given by the sum of the interaction energies of each of the carbon atoms in the ring with the graphene sheet and is given by

\[
E_{\text{dis–con}} = \sum_{i} n_i \int \left( -\frac{A}{\rho_{i}^{6}} + \frac{B}{\rho_{i}^{12}} \right) \, d\sigma
\]

where \( \rho_{i} = [x_i^2 + y_i^2 + z_i^2]^{1/2} \) is the distance between a carbon atom on the ring and a surface element \( d\sigma \) on the graphene sheet. The above equation for \( E_{\text{dis–con}} \) can be rewritten as

\[
E_{\text{dis–con}} = \sum_{i} n_i \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left( -\frac{A}{\rho_{i}^{6}} + \frac{B}{\rho_{i}^{12}} \right) \, dx \, dy
\]

\[
E_{\text{dis–con}} = \sum_{i} \sum_{j} \left( -\frac{A}{\rho_{ij}^{6}} + \frac{B}{\rho_{ij}^{12}} \right)
\]

where \( \rho_{ij} = [x_i^2 + y_i^2 + z_i^2]^{1/2} \) is the distance between an atom on the ring and an atom on the graphene sheet.

Figure 1. Schematic illustrating the key parameters in the continuum model for the interaction between a carbon atom on a carbon ring and a graphene sheet.

Figure 2. Schematic illustrating the key parameters in the discrete–continuum model for the interaction between a carbon atom on a carbon ring and a graphene sheet.
study for the adsorption of single carbon rings on graphene, many sites on the graphene model are probed for adsorption and the geometries which exhibited maximum binding energies corresponding to a single carbon ring–graphene model pair are reported in this article.

In the QM/MM study, the carbon rings form various QM components and various polycyclic aromatic hydrocarbon models representing graphene form the MM components. Graphene is represented by the model systems, C_{60}H_{180}, C_{88}H_{244}, C_{150}H_{60} and C_{216}H_{56}. The QM components are treated at the B97D level of theory, and the MM component is described using the universal force fields (UFFs). The geometry optimizations of the carbon rings (C_{n}) are carried out at the B97D level of theory using the 6-31G(d,p) basis set, and the geometry optimizations of the graphene models are carried out using the UFF scheme. The electrostatic interactions between the QM and MM regions in the carbon ring–graphene model complexes are accounted for using the electrostatic embedding scheme. The geometry optimizations of the carbon ring–graphene model complexes are carried out using the two-layered ONIOM (our own n-layered integrated molecular orbital and molecular mechanics) scheme implemented in the Gaussian 09 software at the same level at which separate components are optimized. The single-point energies of the complexes are further calculated at the ONIOM (B97D/6-311G(d,p):UFF//B97D/6-31G(d,p):UFF) level. The binding energies of the carbon rings on the graphene models are given by

\[ E_{\text{binding energy}} = E_{\text{QM carbon ring}} + E_{\text{MM graphene model}} - E_{\text{ONIOM complex}} \]

\( E_{\text{QM carbon ring}} \) is the energy of the carbon ring calculated employing the DFT model, \( E_{\text{MM graphene model}} \) is the energy of the graphene model calculated employing the MM model, and \( E_{\text{ONIOM complex}} \) is the ONIOM energy of the carbon ring–graphene model complex. In the hybrid QM/MM study, similar to the DFT study, many sites on the graphene models are probed for the adsorption of the carbon rings. Binding energies calculated using various models for graphene are compared, and conclusions are drawn based on them (see the Supporting Information for further details). In addition to the calculations above, the energetics of adsorption of dimers of some carbon rings on C_{216}H_{12} are also studied using the hybrid QM/MM method. The computational methodology for this study is given in the Supporting Information.

**RESULTS AND DISCUSSION**

The energetics for the adsorption of the C_{10}, C_{12}, C_{14}, C_{16}, C_{18}, C_{20}, and C_{22} monocyclic carbon rings on graphene are analyzed by numerically evaluating the interaction energies based on the continuum, discrete–continuum, and discrete models using Mathematica. We first describe the results of the continuum model. Initially, electronic structure calculations are performed at the B3LYP/6-311++G(d,p) level on each of the monocyclic carbon rings using the Gaussian 09 suite of programs. The radii of various carbon rings are then computed from the optimized geometries of each of the rings (see Figure 3 and Table 1). The numerical values of the atomic line densities (\( n_{l} \)) of the carbon rings are then obtained as the ratio of the total number of atoms to the circumference of the rings (Table 1). The atomic surface density for the graphene sheet is taken to be 0.3812 atoms/Å². The numerical values of the Lennard-Jones parameters, C–C attractive constant, \( A \), and C–C repulsive constant, \( B \), used in our calculations are 17.4 eV·Å⁶ and 2.9 × 10⁴ eV·Å¹², respectively. We first discuss the results of the numerical evaluation of the interaction energies as a function of the vertical distance \( Z \) at various rotational angles, \( \phi \) for the binding of C_{10}, C_{12}, C_{14}, C_{16}, C_{18}, C_{20} and C_{22} on graphene. We analyze the adsorption of various rings at \( \phi = 0\degree, 30\degree, 45\degree, 60\degree, \) and 90° on graphene. The plots of the interaction energy as a function of the vertical distance for the interaction of various carbon rings with the graphene sheet at different rotational angles, evaluated using eq 3, are shown in Figure 4. When a carbon ring is at very large distance from the graphene sheet (\( Z \geq 12.0 \) Å), the interaction energy is zero. As it approaches the sheet, the interaction energy decreases. When the ring is sufficiently close to the graphene sheet, it experiences strong repulsive interactions which then raise the interaction energy. It is clear from Figure 4 and Table 2 that the binding energies (negatives of the interaction energies) for each of the rings decrease and the equilibrium distances between the ring and the graphene sheet increase as \( \phi \) varies from 0° to 90°. From Table 2, we also note that the binding energies for the interaction between the rings and the graphene sheet increase as the number of carbon atoms in the rings increases for all of the orientations. This is to be expected because the total interaction energy is the sum total of the contributions from all of the individual atom pairs formed between the atoms of the carbon ring and the graphene sheet, and the number of such pairs increases with the increase in the ring size. The binding energies per carbon atom (\( E_{\text{ba}} \)) for the adsorption of various carbon rings at various orientations with respect to the graphene sheet are given in the Supporting Information (see Table S1 and Figure S1).

We now discuss the results of the numerical evaluation of the interaction energies as a function of the rotational angle \( \phi \) for the adsorption of C_{10}, C_{12}, C_{14}, C_{16}, C_{18}, C_{20}, and C_{22} on graphene at various vertical positions of the rings with respect to the sheet. The plots of the interaction energy as a function

\[
\begin{array}{ccc}
\text{carbon ring} & \text{radius (Å)} & \text{atomic line density, } n_{l} \text{ (Å}^{-1}) \\
C_{10} & 2.0640 & 0.7708 \\
C_{12} & 2.4772 & 0.7707 \\
C_{14} & 2.8749 & 0.7747 \\
C_{16} & 3.3037 & 0.7705 \\
C_{18} & 3.6823 & 0.7777 \\
C_{20} & 4.1105 & 0.7741 \\
C_{22} & 4.4931 & 0.7790 \\
\end{array}
\]

Figure 3. Optimized geometries of various monocyclic carbon rings.

Table 1. Radii and Atomic Line Densities of Various Monocyclic Carbon Rings
of $\phi$ for various values of $Z$ evaluated using eq 3 are shown in Figures 5–7. It can be observed from Figures 5–7 that there are three different domains of interaction energy profiles corresponding to various values of $Z$ and the range of these domains is different for each ring. The first energy profile domain corresponds to the case where the ring is near the graphene surface. In this domain, the minimum energy is always obtained at $\phi = 0^\circ$. In other words, in this domain, the orientation at which the interaction energy is minimum is the parallel orientation. The second domain corresponds to the situation where the ring is at an intermediate distance from the graphene sheet, and the parallel orientation is no longer the minimum energy configuration. Rather, a tilted orientation is preferred. The third domain corresponds to values of $Z$ for which the ring is far from the graphene sheet, and the minimum energy is obtained at $\phi = 90^\circ$, indicating that the perpendicular orientation is the most preferred orientation in this domain. It can be observed from Figure 5 that the preferred orientation is the parallel orientation for all of the rings at $Z = 3.5$ Å. For $Z \geq 4.0$ Å, the parallel orientation is no longer preferred. Rather, a tilted/perpendicular orientation is preferred. At $Z = 4.5$ and 5.0 Å, all of the rings prefer tilted
It can be seen from Figure 6 that all of the rings except the $C_{10}$ ring prefer tilted orientation at $Z = 5.5$ Å. The $C_{10}$ ring prefers perpendicular orientation at $Z = 5.5$ Å. On similar lines, we find that the $C_{12}$, $C_{14}$, $C_{16}$, $C_{18}$, $C_{20}$, and $C_{22}$ rings turn to perpendicular orientation at $Z = 5.8$, $6.2$, $6.6$, $7.0$, $7.4$, and $7.8$ Å, respectively. At $Z = 9.0$ Å, all of the rings prefer perpendicular orientation for adsorption on graphene (see Table 3). The domains of $Z$ values for the binding of each of the rings on the graphene sheet are summarized in Table 4. All of the rings prefer parallel orientation at short distances, to attain favorable $\pi-\pi$ interactions, maximizing interactions between various atom–atom pairs. At larger distances, the rings prefer tilted orientation, eventually going to perpendicular orientation as this enables some atoms to get closer to the sheet. In other words, it is not possible to maximize atom–atom interactions at large distances for parallel orientations. However, larger rings experience more repulsions than smaller rings upon tilting as some of the ring atoms are too close to the graphene sheet and repulsive terms become dominant. Therefore, the
distance at which larger rings switch to perpendicular configuration increase with the increase in the ring size.

We now present the results obtained using the discrete–continuum model. The interaction energies in the discrete–continuum model are evaluated using eq 8, provided that the vertical offset distances of various carbon atoms of the rings with respect to the graphene sheet are known. We illustrate the results here for the adsorption of the C_{14} and C_{20} rings on graphene. The vertical offset distances of the carbon atoms of the C_{14} ring and the C_{20} ring (carbon atoms of the rings labeled in Figure S2 of the Supporting Information) from the graphene sheet at various vertical positions of the ring centers and at various rotational angles are given in the Supporting Information (Tables S2 and S3). The vertical positions of the ring centers chosen for each orientation correspond to the positions in the lowest energy configurations obtained using the continuum model (see Table 2). The vertical offset distances for various atoms in the rings at various orientations are computed from their optimized geometries obtained from electronic structure calculations using Chemcraft. A comparison of the computed binding energies from the continuum model and the discrete–continuum model for the adsorption of the C_{14} and C_{20} rings on graphene at various values of \( \phi \) and \( Z \) is shown in Tables 5 and 6, respectively. The binding energies obtained using the two approaches are in very good agreement. Out of the two models described here, the

Figure 7. Comparison of the orientation dependence of the interaction energies obtained using the continuum model for the interaction of various carbon rings with the graphene sheet at \( Z = 7.5, 8.0, 8.5, 9.0, 9.5, \) and 10.0 Å.

Table 3. Binding Energies, \( E_b \), for the Adsorption of Carbon Rings at Various Vertical Positions with Respect to the Graphene Sheet

| ring/position | \( Z = 4.0 \) Å | \( Z = 5.0 \) Å | \( Z = 6.0 \) Å | \( Z = 9.0 \) Å |
|---------------|----------------|----------------|----------------|----------------|
| \( C_{10} \)   | 0.3415 9.74    | 0.2148 55.01   | 0.1325 89.95   | 0.0206 89.95   |
| \( C_{12} \)   | 0.4098 8.02    | 0.2578 42.97   | 0.1875 89.95   | 0.0278 89.95   |
| \( C_{14} \)   | 0.4778 6.30    | 0.3008 36.09   | 0.2302 72.19   | 0.1971 89.95   |
| \( C_{16} \)   | 0.5464 6.30    | 0.3437 30.93   | 0.2632 56.15   | 0.0501 89.95   |
| \( C_{18} \)   | 0.6147 5.72    | 0.3867 27.50   | 0.2961 48.13   | 0.0667 89.95   |
| \( C_{20} \)   | 0.6829 5.15    | 0.4297 24.06   | 0.3290 41.82   | 0.0919 89.95   |
| \( C_{22} \)   | 0.7513 4.58    | 0.4725 22.34   | 0.3618 37.81   | 0.1292 89.95   |
respectively. A comparison of the computed binding energies for various ring orientations shows that the preferred orientation of the rings is the parallel orientation. Therefore, the discrete model calculations are performed on the continuum models with those selected distances of each of the atoms in the framework of the continuum and discrete models.

Although the continuum model is the easiest to implement, it is difficult to obtain using quantum chemical calculations because they demand extensive computational time. However, the adopted models possess some limitations. Although the continuum model is the easiest to implement, it suffers from the loss of details of the atomistic picture because the rings and the sheet are represented by uniform densities of carbon atoms. On the other hand, the discrete model suffers from the not-so-accurate representation of the graphene sheet by the C96H24 model system. Interestingly, within the framework of the continuum and discrete—continuum models employed here, we see that the equilibrium distance for the rings when they are parallel to the graphene sheet turns out to be Z = 3.44 Å irrespective of the size of the ring (Table 2). When the rings are oriented parallel to the graphene surface, ϕ = 0° and the Jn term in the continuum approach (eq 5) reduces to

\[ J_n = \frac{2\pi^2}{n-1} Z^{2-2n} F(2n-2, 1/2; 1; 0) \] (12)

Therefore, the Z-dependence of the interaction energy reduces to

\[ E_{\text{cont}} = \frac{\beta}{2\pi^2} \left(\frac{A}{Z^6} + \frac{2B}{SZ^2}\right) \] (13)

Now, the minimum in the interaction energy would correspond to \( \frac{dE_{\text{cont}}}{dZ} = 0 \), solving which we obtain Z = 3.44 Å. Indeed, an analysis of the interaction energy term in the discrete—continuum model as given in eq 8 also yields the same result. When ϕ = 0°, for a given Z, all of the atoms in a given ring have the same vertical offset distance e. Therefore, the minimum in \( E_{\text{dis-con}} \) corresponds to \( \frac{dE_{\text{dis-con}}}{de} = 0 \), implying e = 3.44 Å. Thus, we see that within the framework of the continuum model is relatively easier to handle because the number of parameters needed in the continuum model is less compared to that of the discrete—continuum model where one needs the vertical offset distances of each of the atoms in the ring at various positions of the ring centers and at various orientations.

We now compare the results obtained so far from the continuum and discrete—continuum models with those obtained from the discrete model. In the discrete model, graphene is represented by circumcicromorone, C96H24. From the results of the continuum model, it is clear that the preferred orientation of the rings is the parallel orientation. Therefore, the discrete model calculations are performed on various ring–C96H24 complexes for the ϕ = 0° case. The interaction energies are evaluated from the position coordinates of the optimized geometries of the rings and C96H24 obtained from electronic structure calculations by using eq 9. The numerical values of the Lennard-Jones parameters, C–H attractive constant, A, and C–H repulsive constant, B, used in our calculations are 5.62 eV Å^6 and 9.2 × 10^16 eV Å^12, respectively.5,6,4 A comparison of the computed binding energies from the continuum model and the discrete model for the adsorption of various carbon rings on graphene is shown in Table 7. The binding energies obtained using the two approaches are in good agreement.

Table 4. Domains of Z Values for the Adsorption of Carbon Rings at Various Orientations with Respect to the Graphene Sheet

| carbon ring | range of Z (Å) | parallel (ϕ = 0°) | tilted (0° < ϕ < 90°) | perpendicular (ϕ = 90°) |
|-------------|---------------|------------------|----------------------|-------------------------|
| C10         | Z < 4.0       | 4.0 ≤ Z < 5.4    | Z ≥ 5.4              |
| C12         | Z < 4.0       | 4.0 ≤ Z < 5.8    | Z ≥ 5.8              |
| C14         | Z < 4.0       | 4.0 ≤ Z < 6.2    | Z ≥ 6.2              |
| C16         | Z < 4.0       | 4.0 ≤ Z < 6.6    | Z ≥ 6.6              |
| C18         | Z < 4.0       | 4.0 ≤ Z < 7.0    | Z ≥ 7.0              |
| C20         | Z < 4.0       | 4.0 ≤ Z < 7.4    | Z ≥ 7.4              |
| C22         | Z < 4.0       | 4.0 ≤ Z < 7.8    | Z ≥ 7.8              |

Table 5. Comparison of the Binding Energies Obtained Using the Continuum and Discrete—Continuum Models for the Interaction of Various Carbon Rings with the Graphene Sheet at Various Values of ϕ and Z

| ϕ (°) | Z (Å) | binding energy (eV) |
|-------|-------|---------------------|
|       |       | continuum model     | discrete—continuum model |
| 0°    | 3.44  | 0.6223              | 0.6226                  |
| 30°   | 4.60  | 0.3383              | 0.3380                  |
| 45°   | 5.21  | 0.2772              | 0.2760                  |
| 60°   | 5.67  | 0.2459              | 0.2441                  |
| 90°   | 6.06  | 0.2239              | 0.2233                  |

Table 6. Comparison of the Binding Energies Obtained Using the Continuum and Discrete—Continuum Models for the Interaction of the C20 Ring with the Graphene Sheet at Various Values of ϕ and Z

| ϕ (°) | Z (Å) | binding energy (eV) |
|-------|-------|---------------------|
|       |       | continuum model     | discrete—continuum model |
| 0°    | 3.44  | 0.8891              | 0.8893                  |
| 30°   | 5.23  | 0.3934              | 0.3901                  |
| 45°   | 6.09  | 0.3206              | 0.3228                  |
| 60°   | 6.75  | 0.2848              | 0.2801                  |
| 90°   | 7.30  | 0.2621              | 0.2620                  |
models that we employ, minimum energy configurations for
the binding of all of the monocyclic rings on graphene for
parallel orientation correspond to a vertical distance of 3.44 Å
from the sheet. This is however not what one would expect
and could be seen as a limitation of the models that are
employed for the analysis. The formalisms of continuum and
discrete−continuum models that we have employed do not
also take into account the structural distortions in the
interacting entities. In the continuum model, the clusters are
treated as rings of uniform carbon density. Therefore, spacings
between the carbon atoms are uniform. In the discrete−
continuum model, the clusters possess the geometries obtained
from our electronic structure calculations. When the distance
and orientation dependence of the energetics are analyzed, the
geometries of the clusters remained the same. Detailed
electronic structure calculations are however expected to
reveal subtle variations in the geometrical parameters when the
rings are bound on graphene in the complexes. Therefore, in
order to assess the performance of the analytical approaches,
quantum chemical calculations based on electronic structure
theory are also performed. With an intention to compare the
energetics calculated using a hierarchy of levels of theory, we
performed computations using DFT and QM/MM ap-
proaches. The DFT approach, although more accurate, is
restrictive on the size of the model of polycyclic aromatic
hydrocarbon used to represent graphene. The QM/MM
approach, on the other hand, although less accurate, enables
us to consider much larger polycyclic aromatic hydrocarbon
models within a reasonable computational time. We believe
that such a detailed comparison of the energetics from a
hierarchy of theories can enable researchers to infer optimal
strategies to be adopted for modeling a given system. Results of
the analytical models are compared with data from the
computational approaches. For illustration purposes, one
representative example set for each approach, C_{n}−C_{96}H_{24}
complexes for the DFT approach and C_{n}−C_{216}H_{36} complexes
for the QM/MM approach are considered here. For more
details, we refer the readers to the Supporting Information
(Table S4 and Figures S3−S5). The optimized geometries of
the C_{n}−C_{96}H_{24} complexes obtained using the DFT approach
are shown in Figure 8. A comparison of the binding energies
and binding energies per carbon atom obtained using the
analytical, DFT, and QM/MM approaches is presented in
Figure 9. As can be seen from Figure 9, the total binding
energies increase with the increase in the ring size, whereas the
binding energies per carbon atom remain more or less the
same. Interestingly, the binding energies obtained using the
DFT approach reveal a zig-zag pattern with the increase in the
ring size. The C_{4n} rings are found to possess higher binding
energies than the C_{4n+2} rings. This feature is unique to the
DFT approach and is not captured by either the analytical
models or the QM/MM approach. The QM/MM approach
yields binding energies closer to the DFT data than the
analytical models, suggesting that they are more accurate than
the analytical approaches. The discrepancies in the computed
binding energy values of the analytical models from those of
the DFT results are to be expected because the models are
based on the Lennard-Jones potential and do not explicitly
account for the electronic structure of rings and graphene. In
contrast, the DFT results are based on one of the state-of-the-
art density functionals that is proven to be highly accurate for
describing noncovalent interactions. However, in view of the

Figure 8. Optimized geometries of various C_{n}−C_{96}H_{24} complexes computed using the DFT approach.

Figure 9. Comparison of the binding energies and binding energies per carbon atom (E_{ba}) in various carbon ring−graphene complexes obtained using the analytical and computational approaches.
fact that the analytical calculations can be performed at minimal computational cost, we attempted to fit the DFT binding energy data to the analytical expression of the derivative of the interaction energy (eq 3) for \( \phi = 0^\circ \). We note here that the interaction energy derivatives yield the minimum energy configurations. Such a fitting enabled us to arrive at the modified Lennard-Jones \( A \) and \( B \) parameters which are found to be 14.61 eV Å\(^6\) and 1003 eV Å\(^{-1}\), respectively. Subsequently, the binding energies are recalculated using the modified \( A \) and \( B \) parameters in the continuum approach, and the results are presented in Figure 9 as black traces. It is clear from the figure that the modified parameters yield the binding energy values that are much closer to the DFT data and can be employed for further investigations involving carbon ring–graphene and carbon ring–carbon nanotube systems. Indeed, one of the objectives of the analytical approaches based on the continuum approximation is to develop optimal model parameters that could be seamlessly adapted to various carbon-based systems for describing interactions with reasonable accuracy at a minimal computational cost.

Furthermore, we have studied the possibility of multiple ring adsorption on graphene. The strengths of binding of two \( C_{10} \) and two \( C_{18} \) rings on graphene in the parallel orientation (because parallel orientation is the most preferred orientation) are analyzed as representative examples. Herein, two configurations, namely, stacked and side-by-side configurations (Figure 10; optimized geometries of the complexes for \( C_{10} \) and \( C_{18} \) rings, Table S5) for some representative calculations performed at the QM/MM level that yield results qualitatively similar to those found from the continuum approach.

Finally, we comment on the relevance of this work in the context of current research on carbon clusters and graphene. Adsorption of various gas molecules and organic molecules on graphene was earlier investigated by several groups. Detection of individual gas molecules adsorbed on graphene further provided an impetus to this area. Recently, gas-phase spectroscopy experiments by Maier and co-workers have enabled detection of several of the carbon clusters. Vacuum-ultraviolet photolysis of methane at low temperature has also resulted in carbon clusters. Therefore, in this work, we have considered using graphene as a substrate for the adsorption of highly reactive monomeric carbon rings and studied the energetics for the adsorption process. Our investigation of the energetics is primarily based on the continuum approximation for carbon-based materials and has led to the prediction of optimal binding configurations (vertical positions and orientations) for the adsorption of various rings. Such configurations can be convenient starting points for more detailed quantum chemical calculations.

Further, we hope that the adsorption of tiny carbon clusters on graphene will soon be realized in experiments.

![Figure 10. Optimized geometries for the binding of two \( C_{10} \) rings in stacked and side-by-side configurations on graphene computed using the QM/MM approach.](Image)

| Table 8. Binding Energies, \( E_b \), for the Adsorption of Two \( C_{10} \) and Two \( C_{18} \) Rings on Graphene in the Stacked and Side-by-Side Configurations Obtained Using the Analytical Method |
|---|---|---|---|---|---|
| ring | configuration | \( E_b^{+} \) (eV) | \( E_b^{-} \) (eV) | \( E_b^{\pm} \) (eV) | \( E_b \) (eV) |
| \( C_{10} \) | stacked | 0.1517 | 0.4445 | 0.0422 | 0.6384 |
| | side-by-side | 0.0303 | 0.4445 | 0.4445 | 0.9193 |
| \( C_{18} \) | stacked | 0.2552 | 0.8001 | 0.0717 | 1.1271 |
| | side-by-side | 0.0416 | 0.8001 | 0.8001 | 1.6418 |

The energetics for the adsorption of the monomeric carbon rings, \( C_n (n = 10, 12, 14, 16, 18, 20, \text{and} 22) \), on graphene are studied using the continuum, discrete–continuum, and discrete models. In the continuum and discrete–continuum models, the graphene sheet is treated as an infinite plane of uniformly distributed carbon atoms. In the continuum model, carbon rings are treated as circular rings with uniform line density of carbon atoms, whereas in the discrete–continuum and discrete models, they are treated as discrete collections of carbon atoms whose position coordinates are obtained from electronic structure calculations. Further, graphene is represented by circumcicircumcoronene (\( C_{96}H_{24} \)) in the discrete model. Analyses of the interaction energies as a function of the vertical distances \( Z \) and the rotational angles \( \phi \) are performed in order to determine the preferred orientations, equilibrium positions, and binding energies for the adsorption of various monomeric carbon rings on graphene. A carbon ring is found to be adsorbed on graphene in three stages: the perpendicular configuration, the tilted configuration, and the parallel configuration, and the preferred orientation is the parallel configuration. We find that the effect of tilting is more pronounced for the larger carbon rings than that for the smaller carbon rings. Furthermore, the results from various models are compared with the computational data obtained using DFT and QM/MM approaches, highlighting the scope as well as the limitations of the analytical approaches. The analytical models that we have used are important both because of their low computational cost and ability to provide useful physical insights into the energetics of adsorption.
ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00378.

Binding energies per carbon atom ($E_{bb}$) evaluated using the continuum model; vertical offset distances for the atoms of C14 and C20 rings; carbon–carbon distances in various carbon rings; and comparison of the binding energies and the binding configurations obtained using various theoretical approaches (PDF)

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Notes
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