

# Interaction of functionalized benzene molecules with carbon nanopores

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## Abstract

Benzene and its substituted analogs are considered hazardous because of their high risk to public health and the environment. Porous carbon materials are widely studied for their potential ability to act as a filter of carcinogenic materials. This study uses first-principles calculations to explore the selective adsorption of benzene and benzenes with substituents varying in electronegativity and size in a graphitic slit and (9,9) carbon nanotubes. The results show that the molecular adhesion energies are dependent on the bulkiness of substituent but are much less dependent on their electronegatives.

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## 1. Introduction

Porous carbon materials are used to absorb, separate and purify molecular mixtures in a variety of applications [1]. Organic molecules have been shown to have a particularly high affinity for the interiors of carbon pores [2,3]. Carbon nanotubes are a relatively new class of porous carbon material that have been under investigation for some time for gas storage [4,5] and the separation of molecular mixtures [6]. Membranes composed of carbon nanotubes have recently been synthesized and found to function well in molecular separations [7].

Benzene and many of its substituted analogues belong to a class of 188 compounds designated by the US Environmental Protection Agency [8] as ‘hazardous air pollutants,’ or ‘air toxics’ [9]. Exposure to these chemicals from sources such as chemical plants, oil refineries, and gas stations results after contact with contaminated air, foods, or water. Forty-five air toxics standards applying to 82 categories of major industrial sources have been issued thus far by the US EPA [9]. Given the in-

creasing stringency of these standards, new technologies for effective removal of these compounds are in demand.

In this Letter, we report the results of first-principles calculations that are used to study the effect of adding substituents to benzene on the adhesion energy to ideal graphitic slits and carbon nanotube (CNT) systems. This work presents a first basis for study of the effectiveness of carbon-based systems for removal of substituted benzene compounds in traditional and new nanoporous carbon materials.

## 2. Computational details

The approach followed in this study is density functional theory (DFT) [10–12] in the CASTEP program [13,14], where plane-waves and the ultrasoft pseudopotentials of Vanderbilt [15] are used to treat the electronic wave functions. The plane-waves in the calculation are expanded to a kinetic energy cutoff of 380 eV for all calculations unless otherwise specified. The exchange-correlation contribution to the total energy is calculated using the gradient corrected local density approximation of Perdew and Wang (GGA-PW91) [16–18]. One *k*-point at the gamma point of the unit cell is used in the majority of the calculations. The convergence criteria

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are at least  $5 \times 10^{-5}$  eV/atom for energy, the root-mean-square forces converge to at least 0.1 eV/Å, and atomic displacements between optimization steps are at least 0.001 Å. Finally, the finite system of atoms is treated as an infinite solid through the use of three-dimensional periodic boundary conditions.

The graphitic slit unit cell is made up of a single graphite sheet that contains 48 carbon atoms. The unit cell parameters are 12.77 Å and 9.88 Å in the planar directions and 14.00 Å in the direction of the surface normal. The graphitic slit is created when the unit cell is repeated in the direction of the surface normal, thus

creating a 14.00 Å-wide graphitic slit. Fig. 1a shows an example of a periodically repeated cell and illustrates how the slit is formed. As different molecules are added to the empty graphite unit cell, the distance between identical molecules in neighboring unit cells is reduced as the substitutions effectively make the benzene molecule longer in one direction. Fig. 1b, c illustrate how each molecule fits into the graphite unit cell.

The nanotube system consists of a (9,9) CNT with a diameter of approximately 12.3 Å. Each unit cell contains 144 carbon atoms that make up the walls of the CNT, which is 9.98 Å long but is effectively infinite

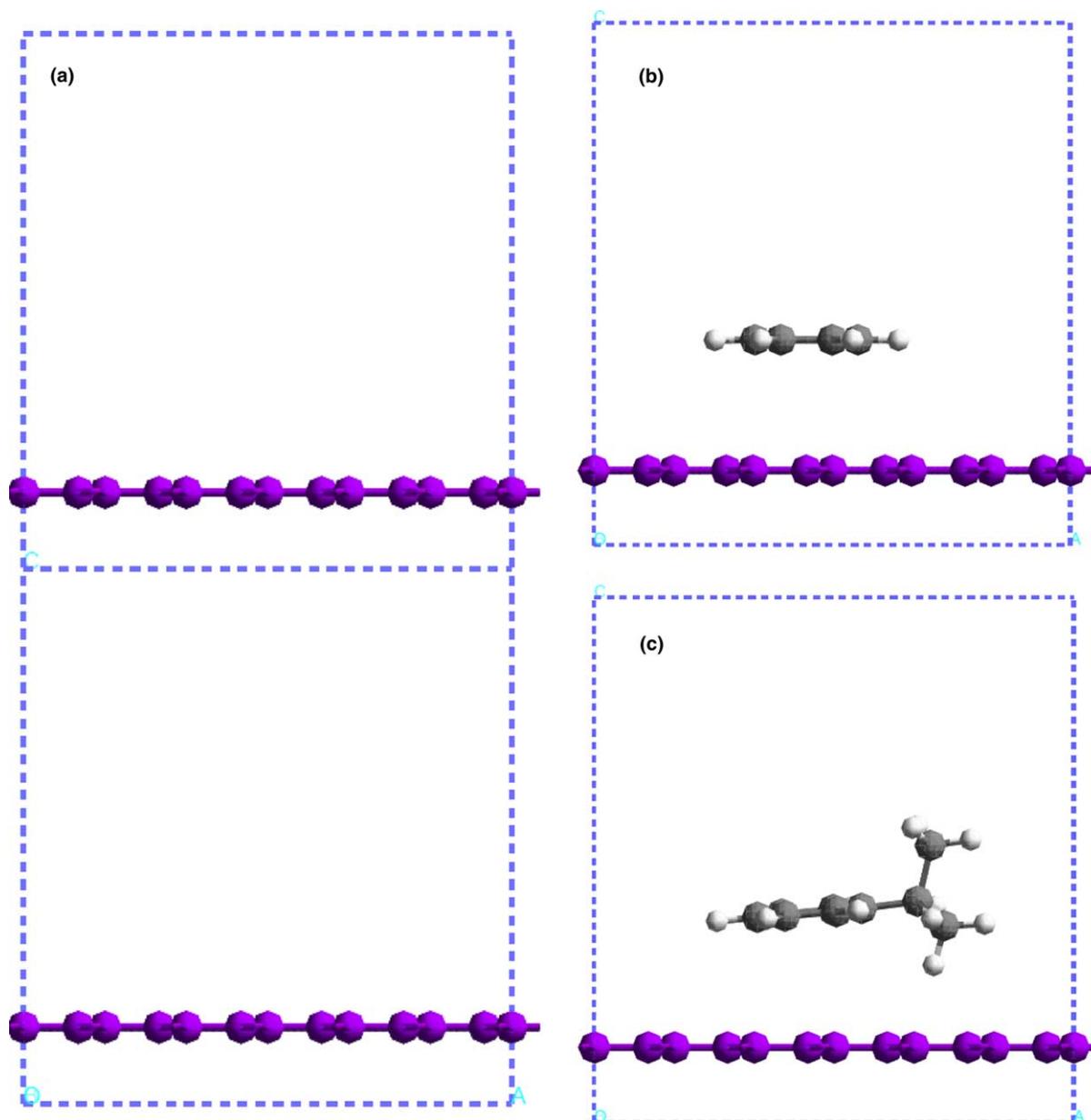


Fig. 1. (a) Snapshot of the carbon slit system used in this study. Two unit cells, indicated by the dashed lines, are shown for clarity. (b) Snapshot of the benzene molecule in the carbon slit (only one unit cell is shown). (c) Snapshot of the isopropylbenzene molecule in the carbon slit (only one unit cell is shown).

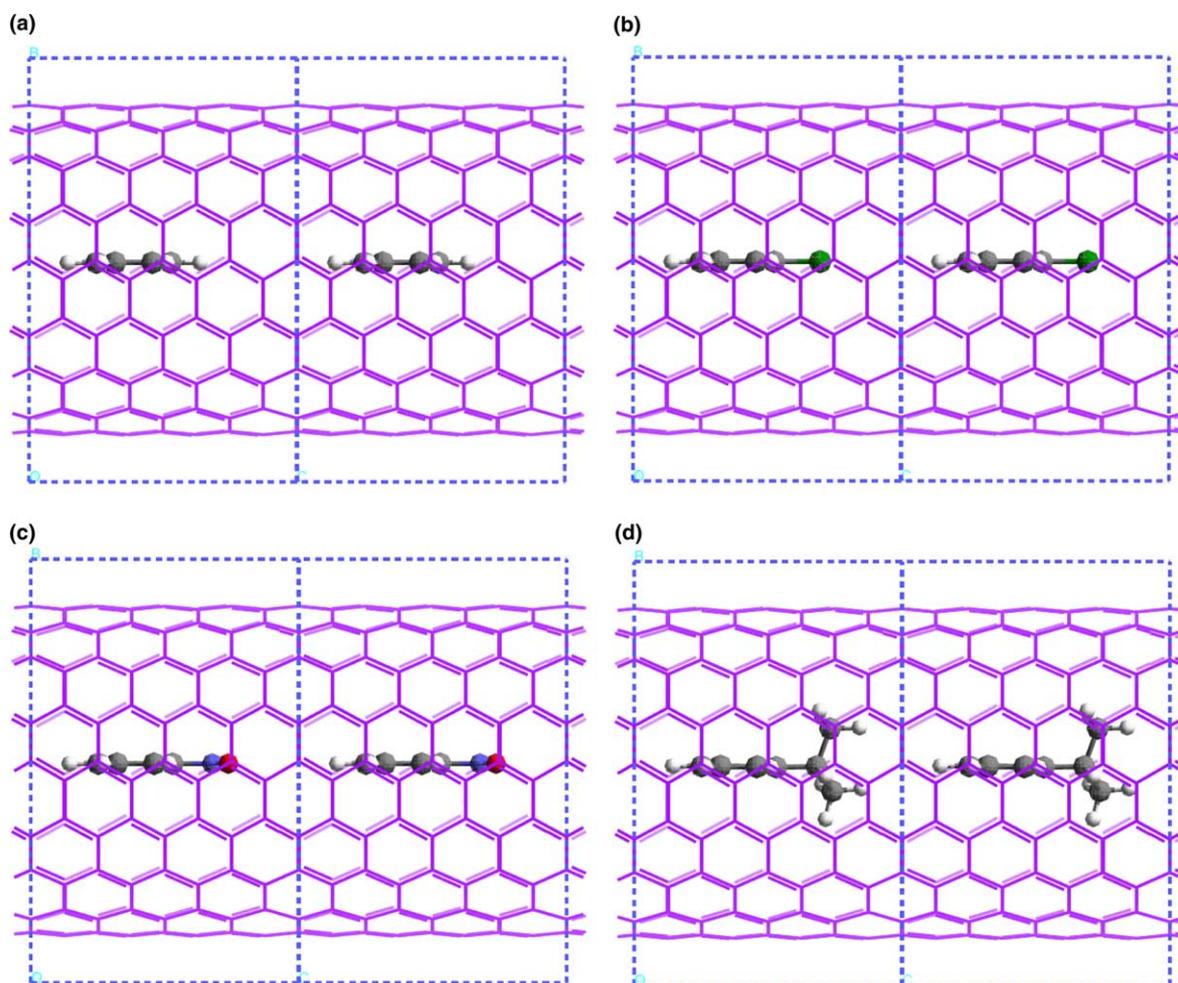


Fig. 2. Snapshots of: (a) benzene, (b) chlorobenzene, (c) nitrobenzene, and (d) isopropylbenzene in the (9,9) carbon nanotube. Two unit cells, indicated by the dashed lines, are shown in each case.

because of the periodic boundary condition in the direction of the CNT axis. The other lattice parameters are set such that the CNT and the periodic image of the CNT are about 3.5 Å from each other. This distance is roughly the nearest neighbor distance of CNTs in a bundle [17]. Fig. 2a–d show representative snapshots of the filled CNT unit cell.

### 3. Results and discussion

The absorption of four molecular species is considered in both the graphitic slit and the CNT systems. Unsubstituted benzene, the first species studied, serves as the base structure for comparison to benzene substituted with chloro- (–Cl), nitro- (–NO<sub>2</sub>), or isopropyl- (–C<sub>3</sub>H<sub>7</sub>) functional groups. The –Cl and –NO<sub>2</sub> groups represent two electronegative substituents, whereas the –C<sub>3</sub>H<sub>7</sub> group adds a bulky organic side group that renders this molecule non-planar. These molecules give a broad representation of electronic and steric character

of substituents onto an already carcinogenic benzene molecule and are intended to test the selectivity of the slit and CNT systems.

The molecules in this study are inserted into the carbon slits, and then an initial optimization is performed with a slightly lower plane-wave cutoff (310 eV) until convergence is reached. The lower cutoff is used for all the molecules in the study with the exception of nitrobenzene, for which only plane-wave cutoff values of 380 eV are used in all cases. The molecules are positioned 3.50 Å above the graphitic sheet and allowed to optimize their structure and position using the Broyden–Fletcher–Goldfarb–Shanno Hessian update method. During the optimization, the atoms in the graphite sheets making up the carbon slit are held fixed, and only the molecule is allowed to move.

Once the system structure is optimized, an additional series of calculations is performed to verify that the molecule is indeed in a minimum well in the potential energy surface. To do this, the positions of the molecules are stepped in small increments towards and away from

the graphite sheet in the direction of the surface normal. For these calculations the kinetic energy cutoff is increased to 380 eV for all systems so that all system energies are obtained from identical system conditions. Forces within the benzene molecules that are optimized with a 310 eV cutoff are monitored and found to be less than 0.1 eV/Å, which is smaller than the convergence criterion. To estimate the error in our calculation associated with freezing the molecules and the substrate, we allowed total relaxation of the molecules for several iteration steps. The energy differences between the frozen and optimized molecules are on the order of 0.0001 eV, confirming that there are no contortions to benzene in this shallow well that would lower the energy of the system.

A similar procedure is followed for the CNT system. Molecules are added to the center of the CNT and allowed to relax until convergence is reached. The large number of atoms in the CNT system makes the procedure of stepping through positions in the CNT for all molecules more computationally intensive than the graphite slit system. To increase computational efficiency, the length of the CNT is reduced to 7.48 Å, which decreases the molecule–molecule distance and increases the molecular density in the tube. Even though the reduction in CNT length reduces the molecule–molecule distance between neighboring molecules, the energy contribution caused by this increased interaction is subtracted out when the adhesion energy is calculated. Also, to make the calculations more accurate, the  $k$ -point spacing is reduced to a finer value of 0.05 Å<sup>-1</sup>, resulting in the use of two  $k$ -points. The molecules optimized with a 310 eV cutoff are evaluated with a 380 eV cutoff in this calculation.

The adhesion energy for the graphitic and CNT systems is calculated using the following expression:

$$E_{\text{Adhesion}} (\text{eV/molecule}) = E_{\text{Molecule} + \text{Slit/CNT}} - E_{\text{Slit/CNT}} - E_{\text{Molecule}}, \quad (1)$$

where  $E_{\text{Molecule} + \text{Slit/CNT}}$  is the converged total energy of the benzene or substituted benzene molecule in the graphitic slit system or CNT system,  $E_{\text{Slit/CNT}}$  is the converged total energy of the graphitic slit or CNT system by itself,  $E_{\text{Molecule}}$  is the converged total energy of the benzene or substituted benzene molecule in the same unit cell. Care was taken in calculating  $E_{\text{Slit/CNT}}$  and  $E_{\text{Molecule}}$  in that the graphite slit/CNT systems and the

molecules were left in the same positions in the unit cell as they were in the combined systems, which have been shown to have effects calculated total energies [19].

The calculated adhesion energies are summarized in Table 1. It can be seen that the effect of the substituents is negligible when the molecules are in the graphitic slit. All molecules studied are slightly more adherent in the CNT system than they are in the graphitic slit system, but there is very little difference in adhesion between different molecules, with the exception of isopropylbenzene. It was anticipated that some of the substitutions would enhance the adherence in the graphitic system while other substitutions would reduce the adherence of the benzene molecules. Surprisingly this is not found to be the case, as is shown in Table 1. Benzene with or without the substitutions adheres to approximately the same degree in the graphitic slit. This trend is also seen in the CNT system with the exception of isopropylbenzene (Fig. 2d). Within the CNT system, the isopropylbenzene adheres significantly better (almost twice as well) in comparison to all other molecules and to isopropylbenzene in the graphitic slit. This may be attributed to the non-planar nature of the isopropylbenzene molecule and its ability to interact with a larger portion of the inner walls of the (9,9) CNT.

Fig. 3 shows the adhesion energy as a function of distance above the graphite surface in the slit for benzene and nitro- and chlorobenzene. The equilibrium distances of the benzene and substituted benzene molecules are shown in all cases to be approximately 4 Å. This equilibrium distance was not achieved until after the molecule was ‘stepped’ towards and away from the geometry optimized position because of the shallow well in which the benzene molecule is located close to equilibrium. The adhesion energy behavior for isopropylbenzene is identical to that presented in Fig. 3 but is not included in the plot. This is true even though the other molecules considered were stepped up and down with the benzene ring parallel to the graphite sheet, while the isopropylbenzene relaxed to the angled position shown in Fig. 1c, and it was stepped towards and away from the graphitic slit wall in this orientation.

Fig. 4 shows the map of the adhesion energy surface for benzene in the CNT. The values were obtained with the shorter CNT and two  $k$ -points. Values of the adhesion energy calculated with a longer cell and one  $k$ -point in comparison to the shorter CNT and two  $k$ -points

Table 1

Table of adhesion energies of benzene and substituted benzene with a graphite slit and a carbon nanotube, as described in the text

Molecule	Graphitic slit adhesion energy (eV/molecule)	(9,9) Carbon nanotube adhesion energy (eV/molecule)
Benzene	-0.06101	-0.08726
Chlorobenzene	-0.06564	-0.09339
Nitrobenzene	-0.07784	-0.08437
Isopropylbenzene	-0.07626	-0.15244

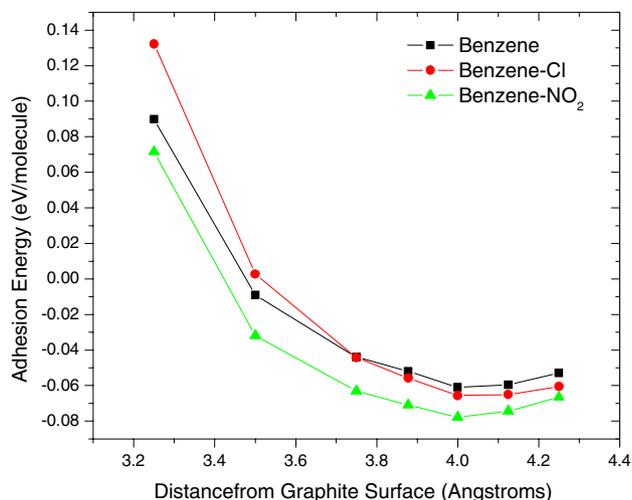


Fig. 3. Comparison of adsorption energies of substituted molecules in the graphite slit as a function of distance above the graphite.

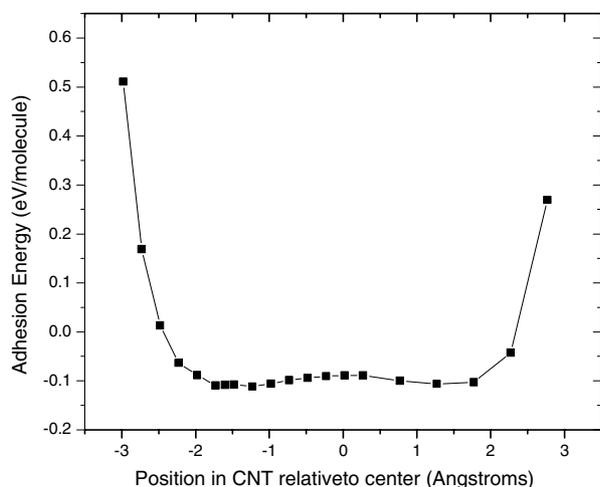


Fig. 4. Adhesion energy of benzene in the (9,9) carbon nanotube as a function of distance from the center of the tube.

differ by only 0.001 eV/molecule when calculated at the same points in their respective cells. It can be seen that the adhesion energy varies from the center of the tube to the center of the well, at a slight displacement from the tube center, by approximately 0.02 eV/molecule. The flat nature of the adhesion energy surface in the CNT allowed optimizations of the molecules to converge without finding the absolute minimum. This flat nature also means that the optimized values are essentially the same through most of the interior of the tube. It is clear that there is a large volume inside the CNT where the benzene molecules can be accommodated. Although there is little selectivity between which benzenes or substituted benzenes are incorporated into the nano-

tubes, there is still an energy benefit for the molecules to be on the inside of the tube.

#### 4. Conclusions

The calculations indicate that changing substituents on benzene molecules has a negligible effect on the interaction of the molecule with a graphitic slit or a CNT, unless the group is bulky and can interact with a larger fraction of the interior of the nanopore. Although the present results show that there is measurable adhesion between benzene-like molecules to graphite slits and CNTs, there is very little evidence of selectivity between different types of different aromatic molecules.

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