

Binding of Pollutant Aromatics on Carbon Nanotubes and Graphite

Anitha Ramraj and Ian H. Hillier*

School of Chemistry, University of Manchester, Oxford Road, Manchester M13 9PL, United Kingdom

Received February 8, 2010

The semiempirical PM3 method with dispersive corrections (PM3-D) is used to predict the interaction energy of a number of aromatic pollutants with a graphene surface and with carbon nanotubes. It is found that the dispersive interactions are dominant in determining the magnitude of the interaction and that electron transfer between the adsorbate and the surface is small. Good agreement is found between the calculated interaction energies and the experimental affinities measured in an aqueous environment.

1. INTRODUCTION

There is an increasing use of quantum chemical methods as a tool to aid an understanding of environmental problems at a molecular level. Quantitative structure–property relationships (QSPR) can be used to associate molecular structure with physicochemical properties and have been used to assess the environmental risk of potentially harmful substances. An alternative approach is to directly model precise chemical processes, particularly reactive or nonreactive interactions which are of direct environmental relevance. In both of these approaches, quantum mechanical (QM) methods can be valuable. For example, molecular descriptors of a range of organic pollutants have been calculated by different QM methods, and here semiempirical schemes have been found to be quite effective when compared to the more time-consuming density functional theory (DFT) approach.¹ We here describe calculations, based on a strategy of calculating the important interactions directly by QM methods, which are relevant to the question of the role of carbon nanotubes in determining the distribution of organic pollutants in the environment.

Carbon nanotubes (CNTs) are finding an increasing number of applications in many areas, such as biotechnology, due to their unique electronic, mechanical, and chemical properties, which are based upon the covalent or noncovalent attachment of species onto their walls. For example, there has been considerable interest in studying the interaction of purine and pyrimidine bases as well as aromatic amino acids with CNTs, since it has been found that various DNA sequence motifs can have specific interactions with CNTs and may, thus, provide a route for sorting a synthetic mixture of tubes into individual single-chirality components.² CNTs are particularly effective in adsorbing these, and other aromatic molecules, due to strong π – π stacking interactions. For this reason, the release of CNTs into the environment might affect the distribution of pollutants, particularly those having aromatic π -systems, and CNTs might also possibly be used for removing such contaminants. These considerations have prompted a discussion of the role of such π – π intermolecular interactions in soils and sediments³ and have also resulted in the experimental study of the adsorption of a variety of substituted aromatic molecules on both graphite and CNTs.

There have been two recent experimental reports of the adsorption of hydroxyl- and amino-substituted aromatics on CNTs.^{4,5} Such aromatic molecules are of interest in their own right, and also, since they may form part of larger biological systems. One finding was the particularly strong adsorption of hydroxyl-containing aromatics, which resulted in a discussion as to the nature of the interaction of these substrates with graphite and CNTs. Chen et al⁴ suggested that the enhanced adsorption of the phenolic compounds was due to π – π electron-donor–acceptor (EDA) interaction between the π -electron-rich aromatic ring(s) of the adsorbates and the π -electron depleted region of the surface. This explanation was challenged by Jiang et al⁶ who ascribed the enhanced interaction to the effect of oxygen on the adsorption. In a response to this comment, Chen et al⁷ argued that oxidative coupling was not a major mechanism for the enhanced adsorption. In addition to the EDA interaction, Lewis acid–base interaction was invoked to account for the strong adsorption of 1-naphthylamine, which Chen et al also reported. In a second study, Lin and Xing⁵ found that adsorption was enhanced both by an increase in the number of aromatic rings and by successive –OH substitution of phenol. Again the adsorption was discussed in terms of EDA interactions.

In view of these data, there is clearly a need for a fundamental study of the nature of the interaction between the adsorbate and the regular surface, particularly in order to see if additional mechanisms, other than adsorption, on the regular surface need to be invoked to explain the changes in adsorption affinities which have been seen.

It is now possible to carry out QM calculations to accurately predict the magnitude of these π – π stacking intermolecular interactions. In this paper we present such a computational study of the interaction of a range of hydroxyl-, amino- and chloro-substituted aromatic molecules with models of both graphene and CNTs. We use the following acronyms to label the adsorbate molecules which we shall consider: 1,3-dichlorobenzene (1,3-DCB), 2,4-dichlorophenol (2,4-DCP), naphthalene (NAPH), 2-naphthol (2-NATH), 1-naphthylamine (1-NALA), phenol (PH), 2-phenylphenol (2-PHPH), 1-naphthol (1-NATH), catechol (CT), and pyrogallol (PY); see Figure 1.

2. COMPUTATIONAL DETAILS

For molecular systems containing more than a few hundred atoms, QM calculations are now usually carried out using DFT,

* Corresponding author. Telephone: +44 161 275 4686. Fax: +44 161 275 4734. E-mail: ian.hillier@manchester.ac.uk.

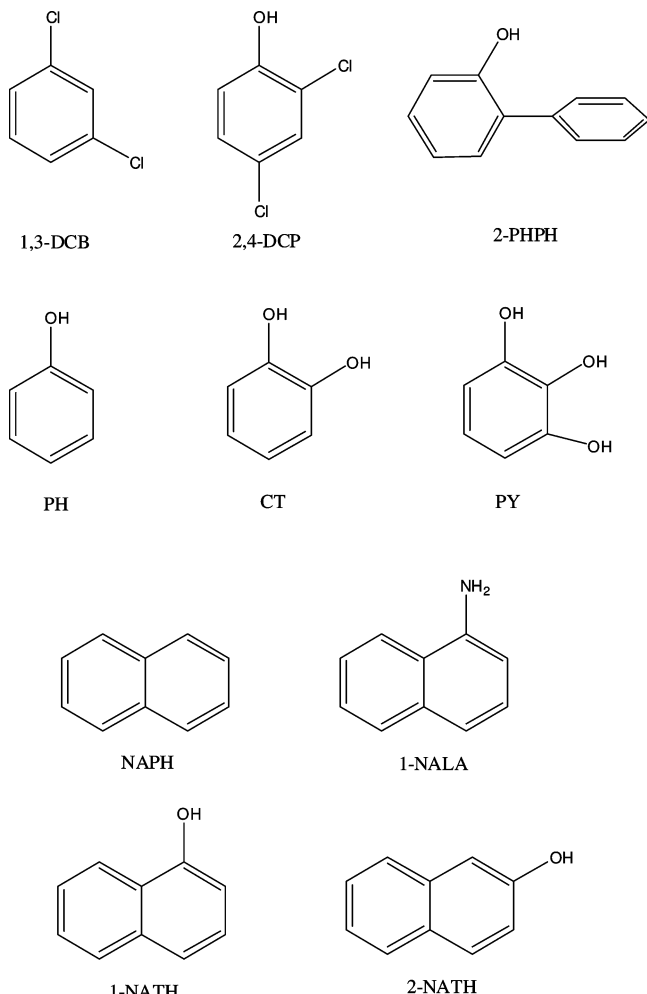


Figure 1. Aromatic pollutants.

which can potentially produce results of chemical accuracy, since these methods do include electron correlation effects, although somewhat approximately. DFT calculations of the adsorption of some small molecules, particularly purine and pyrimidine bases, on nanotubes have been carried out. These have modeled both the infinite periodic system and the nanotubes of finite length.^{8,9} However, the use of popular density functionals, such as BLYP and B3LYP, have generally seriously underestimated the magnitude of the intermolecular interactions because the important van der Waals dispersive forces, which are frequently responsible for the strong adsorption, are poorly modeled by these functionals.¹⁰ Newer functionals, particularly those developed by Truhlar and co-workers,¹⁰ have proved successful in describing short-range electron correlation but may be less successful for longer range correlation effects,¹¹ which can be important for modeling the adsorption of aromatics on extended delocalized systems.¹² The calculation of the important dispersive interactions from first principles using high-level (ab initio) QM methods would be desirable but is computationally prohibitive, except for quite small systems, so these cannot generally be used for modeling adsorption on carbon nanotubes. Semiempirical molecular orbital (MO) methods, such as AM1 and PM3, can, due to the approximations employed, model molecules having many thousands of atoms but do not include correlation effects explicitly, so that, like DFT methods, they are not suitable for modeling adsorption of small molecules on nanotubes.

A very effective way around this problem is to augment either DFT or semiempirical MO calculations with an empirical atom–atom dispersive term which has the usual R^{-6} dependence on the atom–atom separation. We refer to these two approaches as DFT-D and PM3-D, respectively, which have been fully discussed previously.^{13–15} In brief, a pairwise additive potential of the form C_6/R^6 is used to account for the long-range dispersion effects that are, in general, poorly described by semiempirical methods and by common density functionals. The dispersion corrected total energy (E_{Total}) is then given by

$$E_{\text{Total}} = E + E_{\text{disp}} \quad (1)$$

where E is the normal self-consistent DFT or semiempirical (PM3) energy, and E_{disp} is an empirical term containing the dispersion correction:

$$E_{\text{disp}} = -s_6 \sum_i \sum_{j>i} (C_6^{ij}/R_{ij}^6) f_{\text{dmp}}(R_{ij}) \quad (2)$$

Here, the summation is over all atom pairs, C_6^{ij} is the dispersion coefficient for the pair of atoms i and j (calculated from the atomic C_6 coefficients), s_6 is a scaling factor which is chosen to be 1.4, in line with the value used for the BLYP functional,¹³ and R_{ij} is the interatomic distance between atoms i and j . A damping function is used in order to avoid near singularities for small distances, given by

$$f_{\text{dmp}}(R_{ij}) = \frac{1}{1 + e^{-\alpha(R_{ij}/R_0 - 1)}} \quad (3)$$

where R_0 is the sum of the atomic van der Waals radii, and α is a parameter determining the steepness of the damping function. The atomic C_6 coefficients and the R_0 and α values as well as the combination rule for the composite C_6^{ij} coefficients are taken from the work of Grimme.¹³

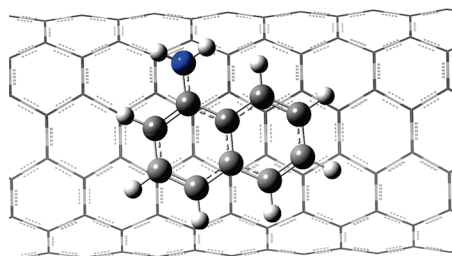
The DFT-D method has been implemented by us in Gaussian03,¹⁶ and the calculations reported here have used the BLYP functional with the TZV(2d,2p) basis, together with the values for the C_6 , R_0 , and s_6 parameters taken from the original parametrization of the DFT-D method.¹³ The semiempirical calculations reported herein were performed using our own local semiempirical program.¹⁷ The PM3-D method, which we have previously described,¹⁵ uses the semiempirical parameters for H, C, N, and O obtained by fitting to a database (S22)¹⁸ of weak complexes having the full range of important van der Waals interactions. We have recently reported the use of this semiempirical scheme to model the interaction of five DNA bases with both graphene sheets and CNTs. We find that the PM3-D method gives both structures and interaction energies which are very close to those given by the more time-consuming DFT-D method.¹² The PM3-D method predicts the order of the adsorption energies of the bases, guanine (G), adenine (A), thymine (T), and cytosine (C) on graphene to be $G > A > T > C$, with the values for T and C being within 1 kcal mol⁻¹. The corresponding experimental order in aqueous solution is $G > A > (T, C)$, with the positions of C and T being interchangeable.¹⁹ These results give us confidence that this approach can be used to study the interaction of aromatic pollutants with CNTs. A similar approach, in which the semiempirical PM6 method is augmented by dispersion and hydrogen-bonding correction terms, has subsequently been described.²⁰

The models used in the calculations reported here are finite clusters, rather than infinite periodic solids. To simulate the effect of infinite solids, we have used large clusters so that

Table 1. Structural Data (Å) for Complexes of Pollutants with –OH group on C96 and [6,6], [5,0] Nanotubes^a

	1-NATH	2-NATH	2-PHPH	2,4-DCP	PH	CT	PY
C96	3.32	3.32	3.68	3.35	3.30	3.31	3.30
[6,6]	3.43	3.40	3.70	3.25	3.24	3.23	3.15
[5,0]	3.13	3.15	4.01	3.15	3.16	3.17	3.08

^a Average distance of the pollutant heavy atoms from the root mean square (rms) plane through the central benzene ring of the graphene sheet or nanotube.

**Figure 2.** 1-naphthylamine on [6,6] carbon nanotube.**Table 2.** Structural Data (Å) for Complexes of Pollutants without –OH group on C96 and [6,6], [5,0] Nanotubes^a

	1-NALA	1,3-DCB	NAPH
C96	3.32	3.34	3.31
[6,6]	3.41	3.42	3.45
[5,0]	3.11	3.15	3.14

^a Average distance of the pollutant heavy atoms from the rms plane through the central benzene ring of the graphene sheet or nanotube.

the adsorbate is sufficiently far away from the edges of the adsorbent for size effects to be unimportant. Thus, we have studied the interaction of the aromatic pollutants with a large planar aromatic hydrocarbon, C₉₆H₂₄, to model a graphene surface or graphite. Previous calculations¹² have shown that the interaction energy of DNA bases changes by less than 1 kcal mol^{−1} when the size of the hydrocarbon is increased from C₅₄H₁₈ to C₉₆H₂₄, so that the hydrocarbon we have used is sufficiently large. Similarly, we have used 30 Å lengths of both [6,6] and [5,0] CNTs, which have 300 and 140 carbon atoms, respectively. We have studied the adsorption of the 10 pollutants, listed previously, with these model surfaces. The geometries of the intermolecular complexes were optimized at the PM3-D level, the starting structures having the center of the ring or the center of the bridging bond of the adsorbate molecule above one of the six equivalent central carbon atoms of the graphene sheet or nanotube. We have also taken these optimized structures and evaluated the interaction energies for the various adsorbates using the DFT-D method.

3. COMPUTATIONAL RESULTS

The results of our calculations are shown in Tables 1–4. A typical structure is shown in Figure 2. We first see that

Table 4. Interaction Energies (kcal mol^{−1}) for Complexes of Pollutants without –OH Group on C96 and [6,6], [5,0] Nanotubes

	model	1-NALA	1,3-DCB	NAPH
C96	PM3-D	−26.4 (−36.6)	−18.3 (−25.7)	−22.8 (−32.6)
	DFT-D//PM3-D	−22.7	−16.2	−19.6
[6,6]	PM3-D	−17.9 (−25.6)	−13.9 (−19.5)	−16.6 (−23.7)
[5,0]	PM3-D	−16.1 (−22.4)	−12.1 (−16.8)	−14.3 (−20.3)

^a Dispersion energy is given in parentheses.

the distance between the aromatic ring of the adsorbate molecule and the graphene or nanotube surface is similar for all the molecules studied, being in the range of 3.1–3.7 Å (Tables 1 and 2). The interaction energies (Tables 3 and 4) given by the DFT-D method are uniformly smaller than the PM3-D values, by ~2 kcal mol^{−1}, but the trends in these energies are the same for both models. In view of this, we have only calculated interaction energies for the nanotubes at the PM3-D level. A general conclusion of all these calculations is that the dispersive interactions are dominant, and in their absence, all of the intermolecular interactions would be repulsive. Furthermore, the trends in the interaction energies for the different adsorbates are the same for both the graphene sheet and the nanotubes, although the interactions are significantly smaller on the nanotubes than on the graphene sheet due to the surface curvature of the former. Similarly the interaction energy is smaller on the more curved [5, 0] than on the [6, 6] nanotube.

For all the adsorbents, we see that the largest interaction energies are for the group of molecules comprising naphthalene (NAPH) and its derivatives (1-NATH, 2-NATH, 1-NALA), with the value for 1-naphthylamine being the largest. For these molecules, both the attractive dispersive interactions and the remaining repulsive interactions are both greater than those of the smaller single ring systems, but the greater dispersive interaction outweighs the increase in the repulsive interaction, leading to a net increase in the interaction energy. The experimental work of Chen et al⁴ clearly shows the greater adsorption affinity on both graphite and CNTs of 1-NALA and 2-NATH compared to those of NAPH, 2, 4-DCP, and 1,3-DCB. This is in accord with the predictions of our calculations (Tables 3 and 4). These experimental data also suggest that the binding affinities increased in the order 1,3-DCB < 2,4-DCP < NAPH, which is also in agreement with our predicted order (Tables 3 and 4). We turn now to the data of Lin and Xing⁵ who studied the adsorption of a number of aromatic hydroxyl molecules on carbon nanotubes. They found that the sorption affinity of these species increased both with an increase in the number of aromatic rings and an increase in the number of hydroxyl groups, with the order of the affinities being PH < 2-PHPH < 1-NATH. Our calculations do predict that both 2-PHPH and 1-NATH have a substantially greater affinity than does PH. The PM3-D calculations predict that the affinity

Table 3. Interaction Energies (kcal mol^{−1}) for Complexes of Pollutants with –OH Group on C96 and [6,6], [5,0] Nanotubes^a

	model	1-NATH	2-NATH	2-PHPH	2,4-DCP	PH	CT	PY
C96	PM3-D	−24.5 (−34.9)	−24.6 (−34.9)	−24.1 (−31.8)	−19.4 (−27.5)	−15.8 (−22.4)	−18.0 (−24.6)	−19.8 (−26.8)
	DFT-D//PM3-D	−22.1	−22.4	−18.3	−17.8	−14.3	−16.5	−18.8
[6,6]	PM3-D	−17.3 (−24.8)	−17.8 (−25.4)	−17.8 (−23.0)	−14.4 (−20.5)	−11.7 (−16.6)	−13.1 (−17.9)	−13.8 (−19.1)
[5,0]	PM3-D	−15.0 (−21.3)	−15.5 (−21.8)	−15.5 (−19.3)	−13.0 (−18.2)	−10.2 (−14.0)	−11.1 (−15.3)	−11.8 (−16.0)

^a Dispersion energy is given in parentheses.

of 1-NATH and 2-PHPH will be very similar, with computed interaction energies being within $0.5 \text{ kcal mol}^{-1}$, whereas the DFT-D calculation on the C96 sheet does predict the affinity of 1-NATH to be significantly larger than that of 2-PHPH. For the series of hydroxyl molecules, both the PM3-D and DFT-D calculations predict the affinity to be in the order $\text{PH}(1\text{-OH}) < \text{CT}(2\text{-OH}) < \text{PY}(3\text{-OH})$, in agreement with experiment. For all adsorbates, we see that the variation in the interaction energy follows that of the dispersive interaction.

We have used a simple Mulliken population analysis to investigate electron transfer between the adsorbate and the surfaces. We find a small degree of electron transfer, of the order of $10^{-3} e$, from the adsorbate. However, there is no correlation between this quantity and the calculated interaction energy. Thus, these calculations do not support the suggestion that the degree of EDA is responsible for the variation in the interaction energy of the different adsorbates.

4. CONCLUSIONS

We have shown that the computationally attractive PM3-D method, which is some two orders of magnitude faster than DFT calculations, does yield relative adsorption affinities for a range of aromatic hydrocarbons on both graphene and CNTs, which are in accord with experiment. As with other π - π stacking interactions, we find that the dispersive interactions are dominant, and it is the increase in this quantity with the number of aromatic rings and the degree of -OH substitution that is responsible for the different binding affinities. In addition, we do not find any correlation between the interaction energy and the very small degree of charge transfer which our calculations predict.

Since it is computationally prohibitive to use high-level quantum chemical calculations to compute these dispersive π - π interactions, a more computationally effective approach, which nevertheless includes a proper description of the interactions, such as we have used here, is required. We would stress that these are essentially 'gas-phase' calculations employing an adsorbent, which lacks imperfections and other adsorbed species. Furthermore, we have not considered the role of solvent, which might be important in determining the adsorption affinities. However, in spite of these approximations, it is extremely encouraging that we have been able to correctly predict the relative affinities for a range of chemical structures. This suggests that the strength of the basic intermolecular interactions is indeed dominant in determining the strength of the adsorption. We have shown that the QM approach, which we have described herein, could be used to quickly screen a large number of pollutant molecules for adsorption on graphite and CNTs. It may also be used as the starting point for more sophisticated models should it prove necessary to include other effects, such as solvation, and surface imperfections.

REFERENCES AND NOTES

- (1) Puzyn, T.; Suzuki, N.; Haranczyk, M.; Rak, J. Calculation of quantum-mechanical descriptors for QSPR at the DFT level: Is it necessary. *J. Chem. Inf. and Model.* **2008**, *48*, 1174–1180.
- (2) Tu, X.; Manohar, S.; Jagota, A.; Zheng, M. DNA sequence motifs for structure-specific recognition and separation of carbon nanotubes. *Nature*. **2009**, *460*, 250–253.
- (3) Keilueit, M.; Kleber, M. Molecular-level interactions in soils and sediments: The role of aromatic π -systems. *Environ. Sci. Technol.* **2009**, *43*, 3421–3429.
- (4) Chen, W.; Duan, L.; Wang, L.; Zhu, D. Adsorption of hydroxyl- and amino- substituted aromatics to carbon nanotubes. *Environ. Sci. Technol.* **2008**, *42*, 6862–6868.
- (5) Lin, D.; Xing, B. Adsorption of phenolic compounds by carbon nanotubes: role of aromaticity and substitution of hydroxyl groups. *Environ. Sci. Technol.* **2008**, *42*, 7254–7259.
- (6) Jiang, J.; Pang, S.-Y.; Ma, J. Comment on 'Adsorption of hydroxyl- and amino-substituted aromatics to carbon nanotubes'. *Environ. Sci. Technol.* **2009**, *43*, 3398–3399.
- (7) Chen, W.; Duan, L.; Wang, L.; Zhu, D. Response to Comment on 'Adsorption of hydroxyl- and amino- substituted aromatics to carbon nanotubes'. *Environ. Sci. Technol.* **2009**, *43*, 3400–3401.
- (8) Rajesh, C.; Majumder, C.; Mizuseki, H.; Kawazoe, Y. A theoretical study on the interaction of aromatic amino acids with graphene and single walled carbon nanotube. *J. Chem. Phys.* **2009**, *130*, 124911–124916.
- (9) Gowtham, S.; Scheicher, R. H.; Pandey, R.; Karna, S. P.; Ahuja, R. First-principles study of physisorption of nucleic acid bases on small-diameter carbon nanotubes. *Nanotechnology* **2008**, *19*, 125701–125706.
- (10) Zhao, Y.; Truhlar, D. G. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* **2008**, *120*, 215–241.
- (11) Hohenstein, E. G.; Chill, S. T.; Sherrill, C. D. Assessment of the performance of the M05-2X and M06-2X exchange-correlation functionals for noncovalent interactions in biomolecules. *J. Chem. Theory. Comput.* **2008**, *4*, 1996–2000.
- (12) Ramraj, A.; Hillier, I. H.; Vincent, M. A.; Burton, N. A. Assessment of approximate quantum chemical methods for calculating the interaction energy of nucleic acid bases with graphene and carbon nanotubes. *Chem. Phys. Lett.* **2010**, *484*, 295–298.
- (13) Grimme, S. Accurate description of van der Waals complexes by density functional theory including empirical corrections. *J. Comput. Chem.* **2004**, *25*, 1463–1473.
- (14) Morgado, C.; Vincent, M. A.; Hillier, I. H.; Shan, X. Can the DFT-D method describe the full range of noncovalent interactions found in large biomolecules. *Phys. Chem. Chem. Phys.* **2007**, *9*, 448–451.
- (15) McNamara, J. P.; Hillier, I. H. Semiempirical molecular orbital methods including dispersion corrections for the accurate prediction of the full range of intermolecular interactions in biomolecules. *Phys. Chem. Chem. Phys.* **2007**, *9*, 2362–2370.
- (16) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *GAUSSIAN 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.
- (17) Mohr, M.; McNamara, J. P.; Wang, H.; Rajeev, S. A.; Ge, J.; Morgado, C. A.; Hillier, I. H. The use of methods involving semiempirical molecular orbital theory to study the structure and reactivity of transition metal complexes. *Faraday Discuss.* **2003**, *124*, 413–428.
- (18) Jurecka, P.; Sponer, J.; Cerny, J.; Hobza, P. Benchmark database of accurate (MP2 and CCSD (T) complete basis set limit) interaction energies of small model complexes, DNA base pairs, and amino acid pairs. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1985–1993.
- (19) Varghese, N.; Mogera, U.; Govindaraj, A.; Das, A.; Maiti, P. K.; Sood, A. K.; Rao, C. N. R. Binding of DNA nucleobases and nucleosides with graphene. *ChemPhysChem*. **2009**, *10*, 206–210.
- (20) Rezac, J.; Fanfrlik, J.; Salahub, D.; Hobza, P. Semiempirical quantum chemical PM6 method augmented by dispersion and H-bonding correction terms reliably describes various types of noncovalent complexes. *J. Chem. Theory Comput.* **2009**, *5*, 1749–1760.