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Influence of phthalimide substitution on the interaction with carbon nanotube

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Abstract: The interaction energy of phthalimide and carbon nanotube calculated at SAPT0/6-31G* level is -17.37 kcal/mol. After the substitution of phthalimide with a hydroxyl group interaction was stronger (-18.64 kcal/mol) because of the larger dispersion followed by an increase in the molecular planar surface and an increased electrostatic term due to the additional electronegative oxygen atom. When a hexafluoroisopropyl group is used as a substituent (ph-6F/CNT), the molecule loses planarity and the dispersion term only slightly increases, but not enough to compensate for the unfavorable shift in the exchange interaction contribution. Thus, the resulting interaction energy in the ph-6F/CNT system is weaker (16.63 kcal/mol) than in the original ph/CNT system. Electrostatic contributions are also significant, with the largest value calculated for ph-OH/CNT (11.32 kcal/mol), because of the additional electronegative oxygen atom in the hydroxyl group. The other two systems, ph/CNT and ph-6F/CNT have electrostatic interactions of 10.14 and 10.05 kcal/mol, respectively. Exchange interaction is more repulsive for ph-OH (+26.60 kcal/mol) and ph-6F (+26.29 kcal/mol) systems than the ph/CNT (+24.86 kcal/mol).

Keywords: phthalimide, SAPT, quantum chemistry, carbon nanotube

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1. Introduction

Interactions of aromatic rings with other aromatic molecules are important for numerous fields from molecular recognition to catalysis [1]. Aromatic interactions have extensively been studied between two benzene molecules. The calculations for benzene dimer showed two low-energy geometries. In the first geometry, CH groups of one benzene molecule interact with the π system of the other by forming CH-π interaction and the interaction energy is -2.84 kcal/mol. In other geometries, two benzene molecules are parallel at offset 1.51 Å and the interaction energy is -2.73 kcal/mol. Although interactions between two benzenes show minima at lower offset values, in the crystal structure preferred parallel aromatic/aromatic interactions are at large offsets. At large offsets new minimum has been obtained at 4.53 Å with an interaction energy of 2.01 kcal/mol [2].

Here we analyze the interaction of substituted heteroaromatic systems with a planar non-polar carbon nanotube in order to better understand the interactions of aromatic rings.

2. Results

Interactions of phthalimide (ph) and phthalimide molecules substituted with hydroxyl (ph-OH) and hexafluoroisopropyl group (ph-6F) with carbon nanotube (CNT) sheet were investigated. Phthalimides (ph, ph-OH and ph-6F) were optimized at B3LYPD3/6-31G* level using Gaussian 09 program package and their geometries are presented in **Figure 1**.

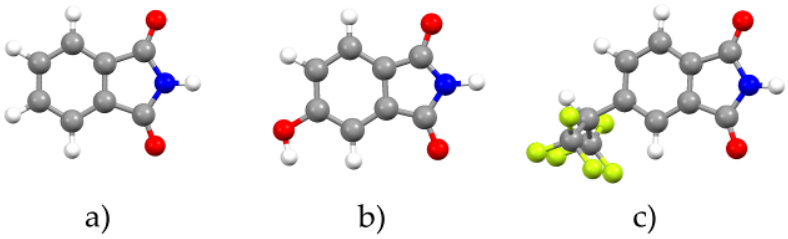
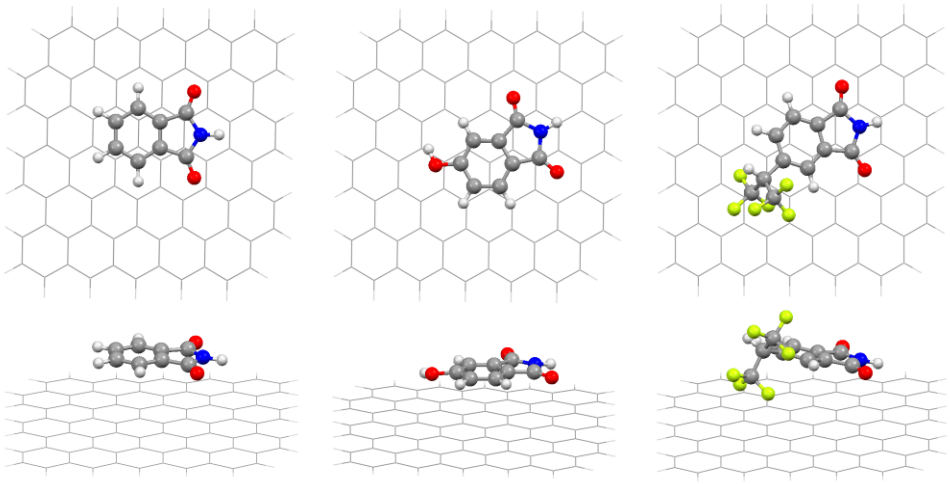


Figure 1. Optimized structures of phthalimide (ph) (a), and phthalimide substituted with hydroxyl (ph-OH) (b) and hexafluoroisopropyl (ph-6F) group (c).

Armchair (222,222) type CNT with a diameter of 30.1 nm was chosen and its atomic coordinates were obtained using VMD Nanotube builder plugin from which an approximately square curved sheet of 82 carbon atoms was cut out and saturated with 24 hydrogens to obtain a CNT sheet. Partial geometry optimization of each system consisting of one phthalimide and a CNT sheet was performed at B3LYPD3/6-31G* level with a frozen CNT sheet. The initial geometry used for optimization was with a phthalimide plane parallel to the CNT sheet. The optimized systems are shown in **Figure 2**.

Symmetry Adapted Perturbation Theory (SAPT) in the Psi4 program package was used for energy decomposition analysis in optimized systems at SAPT0/6-31G* level. Contributions to total SAPT0 energy (ΔE_{SAPT0}) are electrostatic (ΔE_{el}), exchange (ΔE_{ex}), induction (ΔE_{ind}), and dispersion (ΔE_{disp}) interactions. Normal distances (d) and SAPT energy decomposition results are presented in **Table 1**. Normal distance is calculated as the distance between the center of phthalimide C6 ring and a CNT sheet (**Figure 2**).



a) b) c)

Figure 2. Top and side views of ph/CNT (a), ph-OH/CNT (b), and ph-6F/CNT systems after geometry optimization.

After geometry optimization, ph and ph-OH stayed parallel to the CNT sheet with a normal distance of 3.38 and 3.30 Å (**Table 1**), but this is not the case in ph-6F/CNT system (**Figure 2**). In ph-6F/CNT system, normal distance value (3.86 Å) is larger because of the different position of the ph-6F molecule to the CNT sheet. One CF_3 and the NH group are oriented towards the CNT sheet (**Figure 2**). The atoms of ph-6F with the closest distances to the CNT are one fluorine atom with 2.81 Å and the hydrogen from the NH group with 2.82 Å.

Table 1. Normal distances d (Å) and decomposition of interaction energy ΔE_{SAPT0} at SAPT0/631G* level into electrostatic ΔE_{el}, exchange ΔE_{ex}, induction ΔE_{ind}, and dispersion ΔE_{disp} terms for optimized systems. All energies are in expressed in kcal/mol.

	d	ΔE_{el}	ΔE_{ex}	ΔE_{ind}	ΔE_{disp}	ΔE_{SAPT0}
ph/CNT	3.38	-10.14	+24.86	-2.73	-29.37	-17.37
ph-OH/CNT	3.30	-11.32	+26.90	-2.92	-31.31	-18.65
ph-6F/CNT	3.86	-10.05	+26.29	-2.70	-30.17	-16.63

After the substitution of the phthalimide with the hydroxyl group, the total interaction becomes stronger, while the substitution with hexafluoroisopropyl weakens the interaction (**Table 1**).

The largest contribution to the total SAPT0 energy is dispersion, which is interestingly very similar for all three systems. For ph and ph-OH, this contribution originates from the dispersion interactions of all atoms to the CNT sheet, which makes its value proportional to the molecule surface. This explains the larger ΔE_{disp} for phOH/CNT (-31.31 kcal/mol) than ph/CNT (-29.37 kcal/mol) (**Table 1**). On the other hand, the dispersion in ph-6F/CNT system is not equally distributed among ph-6F atoms because

of their different distances from the CNT sheet. Thus, ΔE_{disp} originates from the atoms closest to the CNT sheet and is calculated to be -30.17 kcal/mol which is interestingly very close to the values in ph/CNT and ph-OH/CNT systems.
Electrostatic contributions are also significant, with the largest value calculated for ph-OH/CNT (-11.32 kcal/mol), because of the additional electronegative oxygen atom in the hydroxyl group (**Figure 2**). The other two systems, ph/CNT and ph-6F/CNT have electrostatic interactions -10.14 and -10.05 kcal/mol, respectively (**Table 1**). Exchange interaction is more repulsive for ph-OH/CNT (+26.60 kcal/mol) and ph-6F/CNT (+26.29 kcal/mol) systems than the ph/CNT (+24.86 kcal/mol), because of the larger surface and smaller normal distance of the ph-OH, and because of the very small distance of some groups of the ph-6F to the CNT sheet (**Figure 2**). The induction term is relatively small in all cases, and values are very similar.

4. Conclusions

Interaction with CNT is strengthened after the substitution of phthalimide with hydroxyl group in ph-OH/CNT system, because of the larger dispersion interaction caused by the increase of the molecule planar surface and an increased electrostatic term caused by the additional electronegative oxygen atom. In the case of the hexafluoroispropyl substituted phthalimide (ph-6F/CNT), the molecule loses planarity, and the dispersion term only slightly increases, but not enough to compensate for the unfavorable shift in the exchange interaction contribution. Thus, the resulting interaction energy in the ph-6F/CNT system is weaker than in the original ph/CNT system.

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