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Exploring Adsorption of Water and Ions on Carbon Surfaces using a Polarizable Force Field

Patric Schyman and William L. Jorgensen*

Department of Chemistry, Yale University, New Haven, Connecticut 06520-8107

Abstract

Graphene, carbon nanotubes, and fullerenes are of great interest due to their unique properties and diverse applications in biology, molecular electronics, and materials science. Therefore, there is demand for methods that can accurately model the interface between carbon surfaces and their environment. In this letter we compare results for complexes of water, potassium ion, and chloride ion with graphene, carbon nanotube, and fullerene surfaces using a standard non-polarizable force field (OPLS-AA), a polarizable force field (OPLS-AAP), DFT, and *ab initio* theory. For interactions with water, OPLS-AA with the TIP3P or TIP4P water models describes the interactions with benzene (C₆H₆) and coronene (C₂₄H₁₂) well; however, for acenes larger than circumcoronene (C₅₄H₁₈) and especially for C₆₀, the interaction energies are somewhat too weak and polarization is needed. For ions interacting with carbon surfaces, inclusion of polarization is essential, and OPLS-AAP is found to perform well in comparison to the highest-level quantum mechanical methods. Overall, OPLS-AAP provides an accurate and computationally efficient force field for modeling condensed-phase systems featuring carbon surfaces.

Keywords

polarization; graphene; carbon nanotube; buckyball; fullerene; acene; arene

Carbon-based materials, such as graphene, carbon nanotubes (CNTs), and fullerenes have attracted much interest due to their unique chemical properties and wide range of possible applications. Greater knowledge of the interface between carbon surfaces and adjacent water molecules and ions is important for further understanding and development of related biological, electrochemical, and energy conversion systems.^{1–4} Molecular dynamics and Monte Carlo statistical mechanics simulations with force fields have frequently been used to model condensed phase systems;^{5–8} however, the seemingly simple carbon surfaces can be expected to present challenges. In the most common classical force fields, the central carbon atoms of graphene, CNTs, and fullerenes are uncharged so they do not participate in Coulombic interactions. If the force field also does not explicitly treat polarization, substantial inaccuracies can be expected, especially for interactions with ions. However, multiple approaches do exist for inclusion of polarization effects, for example, by using fluctuating atomic charges, inducible dipoles, or Drude oscillators;⁹ the benefits of such approaches have been noted in many contexts.^{9–15} For reference, quantum mechanical treatments of the interaction of carbon surfaces with ions and small molecules are also possible. Density functional theory (DFT) calculations can now be performed on realistic models, however, accurate treatment of the dispersion energy has been controversial and requires corrections.¹⁶ In the *ab initio* realm, MP2 calculations with even mid-sized basis

*Corresponding Author: william.jorgensen@yale.edu.

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sets are still too costly for routine calculations for large complexes, and they can overestimate two-body dispersion energies.¹⁷ Though DFT and *ab initio* calculations have been applied recently to examine interactions of water molecules and ions with benzenoid surfaces,^{18–27} such approaches remain challenging in the context of modeling liquids or solids containing CNTs, fullerenes, or graphene with extensive configurational sampling. With this goal in mind, we set out to test the accuracy of the non-polarizable OPLS-AA force field and its polarizable relative, OPLS-AAP, for describing the interactions of water and ions with carbon surfaces.

Complexes with Water

OPLS-AA is a standard non-polarizable force field with fixed, atom-centered charges.⁷ In OPLS-AAP, inducible dipoles are added on non-hydrogen atoms, and they are determined by the response to the electric field from the fixed charges.^{13–15} Further details are provided in the methods section. With OPLS-AA, carbon atoms without attached hydrogens in neutral π -systems have no partial charge, so they only interact with their surroundings via Lennard-Jones potentials. Though this treatment includes dispersion interactions, polarization effects are expected to become progressively more significant with increasing dipolar or ionic character of the adsorbents.

The adsorption of a single water molecule on benzenoid surfaces has previously been studied in detail.^{18–27} The most favorable orientation of a water molecule normally has the oxygen above the ring centroid and the two hydrogen atoms facing the surface, as in Figures 1 and 2. However, for the complex with benzene, the most favorable water orientation has one of the hydrogen atoms pointing toward the center of the ring (Figure 1). The present results are summarized in Table 1 for the acenes and in Table 2 for the CNT models and C₆₀. In addition to the force field results, we have carried out ω B97X-D/6-31+G(d,p) DFT calculations, which include dispersion corrections, and single-point MP2/6-311G(d,p) calculations using the ω B97X-D geometries. Results from previous higher-level calculations including presumably definitive CCSD(T) results are also included in Table 1.

The OPLS-AA results in Table 1 with both the TIP3P and TIP4P water models are in good agreement with the CCSD(T) interaction energies for benzene and coronene (C₂₄H₁₂). In these two cases, addition of polarization with OPLS-AAP leads to overestimation of the attraction by ca. 1 kcal/mol. However, for the larger systems, C₅₄H₁₈ and C₉₆H₂₄, OPLS-AAP yields better agreement with the DFT-SAPT and CCSD(T) results, which are converging near –3.0 kcal/mol.^{22,26} It is also apparent that the present ω B97X-D and MP2 calculations overestimate the binding; counterpoise (CP) corrections are necessary, especially for the MP2 results,¹⁸ to bring the energetic predictions into reasonable accord with the best values. It should be noted that in Table 1 the CP corrections were calculated for benzene and coronene, and the corrections for the larger systems were approximated to be the same as for coronene. The CP correction is expected to increase slowly with growing system size; the corrected interaction energies for C₅₄H₁₈ and C₉₆H₂₄ are lower limits. Computation of accurate interaction energies for such systems is clearly challenging with DFT and *ab initio* methods.

The quantum mechanical results for the systems in Table 1 concur that the optimal separation between the water oxygen and the π -plane is roughly invariant at 3.3 Å. The OPLS-AA results also converge to this value, while the OPLS-AAP prediction is about 0.1 Å too short. However, the energy surfaces near the equilibrium distance are almost flat; an increase in the separation by 0.1 Å raises the energy by only 0.05 kcal/mol with the force fields. For the water-benzene complex, an experimental value for R_e has also been reported as 3.33 Å from microwave spectroscopy in 1993.²⁹ In addition, there is an experimental

result for the binding energy of the benzene-water complex from two-photon resonant ionization measurements;³⁰ the value of -2.44 ± 0.09 kcal/mol is in accord with the OPLS-AA and CCSD(T) values after a 1.0 kcal/mol correction is made for the change in vibrational zero-point energy.¹⁸ It may be noted that the OPLS-AA model for benzenoid hydrocarbons and the benzene/water results in Table 1 were first reported in 1990.³¹

Turning to Figure 2 and Table 2, the introduction of curved carbon surfaces is investigated. The orientation of water on C_{60} has been discussed previously.^{24,32} The preference is for interaction with a hexagonal rather than pentagonal ring, and there is indication in aqueous solution that a lone pair on the oxygen atom is oriented towards the surface.³² The latter preference may not apply in the gas phase where the weak C_{60} -water interaction is not competing with water-water hydrogen bonding. In view of the computed preference for the acene-water complexes to have hydrogens oriented towards the surface, further examination was pursued. The OPLS-AA and OPLS-AAP optimized interaction energies for TIP4P water in the up orientation with the hydrogen atoms pointing away from C_{60} are -1.04 and -1.41 kcal/mol, respectively, and the corresponding values for the down orientation are -1.05 and -1.52 kcal/mol. Thus, the preference for the down orientation is slight. The interaction energies are also considerably less attractive than for the acenes. This is expected since the curvature of C_{60} leads to diminished contact with adsorbents. Nevertheless, the 0.5 kcal/mol difference in optimal interaction between the OPLS-AA and OPLS-AAP models is significant and will lead to greater ordering of water molecules around C_{60} with the inclusion of the polarization.¹¹ The computed optimal contact distances are again similar at about 3.3 Å for OPLS-AAP and ω B97X-D in Table 2.

The computed interaction energies with the graphene or CNT models are more attractive than for the fullerene since constructive Coulomb interactions occur between the charged atoms on the periphery and the water molecule. For example, in the $C_{54}H_{18} \dots H_2O$ case (Table 1), the intermolecular Coulomb interactions contribute 1.04 of the 2.68 kcal/mol net attraction with OPLS-AA. In Table 2, the OPLS-AAP results find a 2.07 kcal/mol enhancement of the interaction energy in going from $C_{60} \dots H_2O$ to the $C_{48}H_{24} \dots H_2O$ surface case (-3.59 kcal/mol), which is in accord with the ω B97X-D and MP2 differences of 2.06 and 1.43 kcal/mol. The interaction becomes less favorable for surface interaction with the central ring of the larger $C_{84}H_{24} \dots H_2O$ system (-2.89 kcal/mol), since the surface atoms with non-zero charges are farther from the water molecule. The listed ω B97X-D and MP2 interaction energies are exaggerated since CP corrections are needed. The average of the CP corrections for the complexes of water with benzene and coronene is ca. 2 kcal/mol in Table 1. If this difference is applied to the ω B97X-D and MP2 interaction energies in Table 2, the results fall into good agreement with the OPLS-AAP values.

The $C_{48}H_{24}$ model is the smallest cylindrical fragment for a (6,6) CNT, which, in turn, is the smallest nanotube that can accommodate an internal water molecule.^{33,34} Thus, in addition to the surface arrangement, the water molecule was also optimized inside the CNT models (Figure 2). It is expected that both the Coulomb and polarization effects are enhanced for the interior water molecule since it is proximal to more surface atoms than in the external complexes. Indeed, the interaction energies for the confined water molecule are more attractive by roughly 2 kcal/mol (Table 2). There is only a small difference, 0.3 kcal/mol, between the OPLS-AAP results for the $C_{48}H_{24}$ and $C_{84}H_{24}$ systems suggesting that further extension of the nanotube will have modest effects. At -5 to -6 kcal/mol, the interaction energies for the interior water molecules are similar to those for hydrogen bonds.⁷ In summary, to this point, the present findings have illustrated the diversity of interactions for these model systems and that the polarizable force field reproduces well the expectations based on the highest level quantum mechanical results.

Complexes with K⁺

The effects of explicit inclusion of polarization are expected to be substantial for interactions with ions. Analogous complexes were modeled with the water molecule replaced by a potassium or chloride ion. The ions were also initially positioned above the ring centers and then the geometries were fully optimized. As shown in Table 3, the OPLS-AAP interaction energies for the acene-K⁺ complexes are in good agreement with the ω B97X-D and MP2 results and with previous observations of cation... π -systems.³⁵ The CP corrections are again smaller for the ω B97X-D calculations than with MP2. CCSD(T) calculations have also been performed on the C₆H₆...K⁺ complex yielding an interaction energy of -16.5 kcal/mol and an R_e of 2.9 Å,³⁶ which are in excellent agreement with the OPLS-AAP results. The presented results show that cations can be adsorbed strongly on benzenoid surfaces reaching an attraction of more than 30 kcal/mol for C₅₄H₁₈...K⁺, and even stronger binding is found for K⁺ in the interior of the nanotube models. For the K⁺ complexes, polarization contributes up to 20 kcal/mol to the interaction energy for the acenes and ca. 25 kcal/mol inside the nanotubes. The OPLS-AAP, DFT, and MP2 results are somewhat disparate for the C₄₈H₂₄ CNT model with OPLS-AAP finding relatively weaker binding on the exterior and stronger binding in the interior. Considering all of the results to this point, it is unclear which of these computational methods is more accurate. However, it appears safe to conclude that the true interaction energies are -25 ± 5 and -40 ± 5 kcal/mol for the surface and interior geometries. The K⁺ ion inside the (6,6) CNT model is positioned near the center. The sum of the vdW radii of carbon and potassium ion is 4.45 Å, which is close to the 4.15 Å radius of the C₄₈H₂₄ nanotube. Thus, it is possible that the wavefunction methods are picking up some repulsive orbital overlap leading to the weaker interior binding than from OPLS-AAP.

For the C₆₀ fullerene, the interactions with K⁺ are weaker than for the acenes or CNT models. This can again be attributed to the greater curvature of the surface and diminished polarizability. With OPLS-AA, the only attractive interaction comes from the $1/r^6$ term in the Lennard-Jones potential. However, polarization is found to add about 12 kcal/mol to the attraction, similar to the case for benzene. With counterpoise corrections estimated from the acenes, the ω B97X-D and MP2 results are indicating an interaction energy of about -15 kcal/mol for the C₆₀-K⁺ complex, while OPLS-AAP yields -12 kcal/mol.

Complexes with Cl⁻

The results for the complexes with Cl⁻ are listed in Table 4. There have been previous discussions concerning whether aromatic hydrocarbons can form stable π -complexes with anions.³⁷ For benzene, the consensus is that there is no attractive interaction between chloride ion and the π -system of benzene.^{38,39} In cases of favorable anion... π interactions with substituted benzenes, the binding has been assigned to charge-dipole interactions between the anion and the dipole of the substituent.³⁹ However, for larger acenes, anions can form π -complexes in view of the enhanced polarizability.^{28,40} The present OPLS-AAP and ω B97X-D results agree well with each other and with these views, while the non-polarizable force field fails to find the attractive interactions with the larger acenes. Overall, the attractive interactions are much weaker than for complexes with potassium ion, reaching only -8 kcal/mol for the chloride complex with C₉₆H₂₄ compared to ca. -30 kcal/mol with K⁺. For OPLS-AAP, this can largely be attributed to the switch from repulsive to attractive Coulombic interactions with the outermost carbon atoms.

It should be noted that Shi et al. recently studied closely related complexes of C₈₄H₂₄ with halide ions.²⁸ Their computed interaction energies are -16.3, -7.7, and -6.0 kcal/mol for the complexes with F⁻, Cl⁻, and Br⁻ using ω B97X-D/6-31+G(d,p) with CP corrections. The

corresponding OPLS-AAP results for the present complexes with $C_{96}H_{24}$ are reasonably similar at -13.2 , -8.2 (Table 4), and -7.5 kcal/mol. With the 6-31+G(d,p) basis set Shi et al. found the CP correction to only be 0.5 kcal/mol for the Cl^- complex with $C_{84}H_{24}$, thus we did not pursue CP corrections for Table 4.

For $C_{60}...Cl^-$, the OPLS-AAP and $\omega B97X-D$ interaction energies are in good accord near -12 kcal/mol, though the distance to the surface is 0.3 Å longer with the force field, 3.5 vs. 3.2 Å. For the $C_{48}H_{24}$ CNT model, attempted optimizations of the Cl^- on the outer surface led to migration of the chloride ion to form $Cl...H-C$ hydrogen bonds with the edges. Thus, the chloride ion was constrained to move normal to the surface in the direction of R_e (Figure 2) during subsequent OPLS-AAP optimization. The OPLS-AAP interaction energy for the $C_{48}H_{24}...Cl^-$ complex is only -2.33 kcal/mol, while for the larger $C_{84}H_{12}$ model there is strengthening to -5.06 kcal/mol. The non-polarizable force field fails to find energy minima for these π -complexes owing to Coulombic repulsion between the charged carbon atoms and the anion. The results for the complexes with the Cl^- near the center of the CNT models are varied. For $C_{48}H_{24}$, the OPLS-AAP approach finds a well-bound anion (-13.07 kcal/mol), whereas the $\omega B97X-D$ and MP2 results predict a weaker interaction (-7.04 and -1.88 kcal/mol). The MP2 results are not expected to be accurate for the anionic complexes since diffuse functions were not included in the basis set.

In summary, it is important to have a force field that can describe well the interactions between adsorbents and carbon surfaces for use in wide-ranging molecular dynamics and Monte Carlo modeling of interesting materials. From the present results, it is clear that a non-polarizable force field such as OPLS-AA, Amber or CHARMM is not appropriate in this regard. However, the simple polarizable force field OPLS-AAP can accurately describe interactions between water and larger acenes using either the TIP3P or TIP4P water models. The polarizable force field is essential for interactions with ions and it is found to reproduce well trends from the DFT and MP2 calculations. The remaining, principal quantitative uncertainties center on the strengths of interactions for ions on the inside of the nanotube models. This is difficult to resolve with high-level DFT and *ab initio* calculations owing to the computational demands. Overall, OPLS-AAP emerges as a viable force field for simulations of carbon surfaces in condensed phases. The timing differences for the methods used here are, of course, striking. Even for the largest systems, the geometry optimization with OPLS-AAP using the *MCPRO* or *BOSS* programs⁴¹ did not take more than a few seconds on a 3 GHz processor. This can be compared to the more than one week needed for a single point calculation on the $C_{96}H_{24}$ model with the $\omega B97X-D$ method. It may also be noted that the polarizability for carbon ($\alpha_C = 1.0 \text{ Å}^3$) used here was a default value from earlier work.¹⁴ Given reliable reference data, α_C could be refined for specific systems. E.g., for C_{60} , increasing α_C to 1.2 Å^3 enhances the OPLS-AAP interaction energies for the K^+ and Cl^- complexes to -15.11 and -12.65 kcal/mol, respectively, which improves the agreement with the $\omega B97X-D$ results of -16.68 and -12.65 kcal/mol (Tables 3–4).

COMPUTATIONAL METHODS

The DFT and MP2 calculations were carried out using the Gaussian 09 program.⁴² The hybrid density functional $\omega B97X-D/6-31+G(d,p)$,⁴³ which includes empirical dispersion corrections, was used for geometry optimizations and to calculate the interaction energies. This method was also featured in a recent, extensive study of anions interacting with benzenoid surfaces.²⁸ Subsequently, MP2/6-311G(d,p) energies were obtained from single-point calculations on the $\omega B97X-D$ geometries.^{44–47}

The corresponding calculations with the OPLS-AA⁷ and OPLS-AAP^{13–15} force fields were carried out with the *MCPRO* program.⁴¹ The OPLS-AA parameters for aromatic

hydrocarbons were used;³¹ specifically, carbon atoms with attached hydrogen atoms have a partial charge $q_C = -0.115$ e and Lennard-Jones parameters $\sigma_{CC} = 3.55$ Å and $\epsilon_{CC} = 0.07$ kcal/mol, while the corresponding parameters for the hydrogen atoms are $q_H = +0.115$ e, $\sigma_{CH} = 3.55$ Å, and $\epsilon_{CH} = 0.07$ kcal/mol. All other carbons are uncharged Lennard-Jones particles with $\sigma_{CC} = 3.55$ Å and $\epsilon_{CC} = 0.07$ kcal/mol. Standard OPLS-AA parameters were used for chloride ion, potassium ion, and TIP3P and TIP4P water.^{48,49}

The polarizable OPLS-AAP force field is obtained from OPLS-AA by adding inducible dipoles, $\mu_i = \alpha_i E^q_i$, which are calculated for each non-hydrogen atom i in the presence of the electric field E^q_i generated by the permanent charges. The polarization energy is then given by $E_{\text{pol}} = -(1/2) \sum \mu_i \cdot E^q_i$. For aromatic carbon atoms, α_C was assigned as 1.0 Å^3 .¹⁴

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Figure 1. Modeled complexes of water with acenes. For complexes with potassium and chloride ions, the ions were located in the same manner as the oxygen atom of the water molecule. R_e indicates the distance between the surface and the adsorbent.

Figure 2.

Modeled complexes of water with CNT fragments and C_{60} . Water and ions were placed above the centroid of six-membered rings as indicated. R_e indicates the distance between the surface and the adsorbent.

Table 1

Interaction Energies and Ring Center–O Distances for Acene-Water Complexes^a

Acene	OPLS-AA TIP3P	OPLS-AA TIP4P	OPLS-AAP ^b	ωB97X-D	MP2	DFT-SAPT ^c	CCSD(T)
	ΔE (kcal/mol)						
C ₆ H ₆	-3.79	-3.80	-4.41	-4.32 (-3.73)	-4.61 (-2.59)	-3.16	-3.2 ^{de}
C ₂₄ H ₁₂	-3.67	-3.52	-4.03	-5.47 (-3.64)	-5.16 (-2.41)	-3.05	-3.35 ^e
C ₃₄ H ₁₈	-2.74	-2.68	-3.22	-5.44 (-3.60) ^f	-5.71 (-2.96) ^f	-2.93	
C ₉₆ H ₂₄	-2.26	-2.24	-2.78	-6.12 (-4.28) ^{fg}	-2.68 ⁱ	-3.0 ^h	-3.1 ⁱ
	R_c (Å)						
C ₆ H ₆	3.09	3.10	3.04	3.32		3.36	3.38 ^d
C ₂₄ H ₁₂	3.23	3.24	3.15	3.26		3.36	3.30 ^e
C ₃₄ H ₁₈	3.30	3.30	3.21	3.25		3.36	
C ₉₆ H ₂₄	3.32	3.32	3.22	3.22 ^f			3 ^j

^aValues in parentheses include counterpoise corrections.

^bUsing TIP4P.

^cRef. 22.

^dRef. 21.

^eRef. 23.

^fEstimated CP correction from coronene.

^gSingle-point calculation using the OPLS-AAP geometry.

^hEstimated for graphene; uncertainty is ±0.15 kcal/mol.

ⁱRef. 26, calculated for graphene.

Table 2
Interaction Energies and Ring Center–O Distances for Fullerene and CNT–Water Complexes

Complex	OPLS-AA TIP3P	OPLS-AA TIP4P	OPLS-AA ^a	ωB97X-D	MP2
ΔE (kcal/mol)					
C ₆₀	-1.03	-1.05	-1.52	-3.62	-3.99
<i>Surface H₂O</i>					
C ₄₈ H ₂₄	-3.12	-3.03	-3.59	-5.68	-5.42
C ₈₄ H ₂₄	-2.54	-2.44	-2.89	-	-
<i>Interior H₂O</i>					
C ₄₈ H ₂₄	-4.75	-4.92	-5.87	-8.20	-7.37
C ₈₄ H ₂₄	-4.48	-4.55	-5.54	-	-
R_e (Å)					
C ₆₀	3.37	3.37	3.27	3.34	-
<i>Surface:</i>					
C ₄₈ H ₂₄	3.35	3.35	3.30	3.22	-
C ₈₄ H ₂₄	3.28	3.28	3.23	-	-
<i>Interior:</i>					
C ₄₈ H ₂₄	3.17	3.22	3.13	3.36	-
C ₈₄ H ₂₄	3.70	3.70	3.49	-	-

^aUsing TIP4P water.

Table 3Interaction Energies and Ring Center Distances for Complexes with K⁺

	OPLS-AA	OPLS-AAP	ωB97X-D	MP2
Acene				
	ΔE (kcal/mol)			
C ₆ H ₆	-8.03	-17.21	-18.17 (-17.9) ^a	-19.46 (-17.11)
C ₂₄ H ₁₂	-12.35	-28.74	-26.17 (-25.28)	-23.10 (-19.91)
C ₅₄ H ₁₈	-11.35	-29.78	-29.92 (29.03) ^b	-31.80 (-28.61) ^b
C ₉₆ H ₂₄	-9.76	-28.94	-32.06 (-31.17) ^{bc}	-
R_e (Å)				
C ₆ H ₆	3.08	2.77	2.92	
C ₂₄ H ₁₂	3.19	2.76	2.85	
C ₅₄ H ₁₈	3.38	2.80	2.82	
C ₉₆ H ₂₄	3.55	2.81		
Fullerene or CNT				
	ΔE (kcal/mol)			
C ₆₀	-0.06	-11.86	-16.68	-19.32
<i>Surface:</i>				
C ₄₈ H ₂₄	-7.31	-19.84	-26.17	-28.85
C ₈₄ H ₂₄	-7.94	-23.80	-	-
<i>Interior:</i>				
C ₄₈ H ₂₄	-20.51	-45.14	-37.50	-35.37
C ₈₄ H ₂₄	-19.35	-52.17	-	-
R_e (Å)				
C ₆₀	4.41	2.90	3.27	
<i>Surface:</i>				
C ₄₈ H ₂₄	3.40	2.97	2.80	
C ₈₄ H ₂₄	3.33	2.78	-	
<i>Interior:</i>				
C ₄₈ H ₂₄	3.87	2.83	4.15	
C ₈₄ H ₂₄	3.99	3.09	-	

^aValues in parentheses correspond to CP corrected energies^bEstimated CP correction from coronene.^cSingle-point calculation using the OPLS-AAP geometry.

Table 4Interaction Energies and Ring Center Distances for Complexes with Cl⁻

	OPLS-AA	OPLS-AAP	ωB97X-D	MP2
Acene				
	ΔE (kcal/mol)			
C ₆ H ₆	0.00	0.00	0.00	0.00
C ₂₄ H ₁₂	0.00	-1.10	-1.18	0.00
C ₅₄ H ₁₈	5.69 ^a	-5.02	-4.92	-3.94
C ₉₆ H ₂₄	5.05 ^a	-8.18	-7.68 ^b	-
	R_e (Å)			
C ₆ H ₆	-	-	-	-
C ₂₄ H ₁₂	-	3.60	3.22	-
C ₅₄ H ₁₈	5.39	3.48	3.32	-
C ₉₆ H ₂₄	3.88	3.42	3.42	-
Fullerene or CNT				
	ΔE (kcal/mol)			
C ₆₀	-2.53	-10.78	-12.65	-15.15
<i>surface:</i>				
C ₄₈ H ₂₄	0.00	-2.33	-	-
C ₈₄ H ₂₄	0.00	-5.06	-	-
<i>confined:</i>				
C ₄₈ H ₂₄	8.87 ^c	-13.07	-7.04	-1.88
C ₈₄ H ₂₄	5.54 ^c	-25.56	-	-
	R_e (Å)			
C ₆₀	3.85	3.47	3.18	-
<i>surface:</i>				
C ₄₈ H ₂₄	-	3.84	-	-
C ₈₄ H ₂₄	-	3.53	-	-
<i>confined:</i>				
C ₄₈ H ₂₄	3.86	3.86	4.12	-
C ₈₄ H ₂₄	3.98	3.98	-	-

^a Local π-minima.^b Single-point calculation using the OPLS-AAP geometry.^c Angle and dihedral constraints were applied to keep the Cl⁻ inside the CNT model.