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Influence of Silicon Defects on the Adsorption of Thiophene-like Compounds on Polycyclic Aromatic Hydrocarbons: A Theoretical Study Using Thiophene + Coronene as the Simplest Model

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Physisorption and chemisorption processes of thiophene on coronene and 2Si-coronene have been studied using density functional theory and MP2 methods. These systems have been chosen as the simplest models to describe the adsorption of thiophene-like compounds on polycyclic aromatic hydrocarbons (PAHs). The calculated data suggest that the presence of silicon atoms in PAHs could favor their interaction with thiophene and similar compounds. Small stabilization energies have been found for several physisorbed complexes. The thiophene chemisorption on coronene seems very unlikely to occur, while that on 2Si-coronene leads to addition products which are very stable, with respect to the isolated reactants. These chemisorption processes were found to be exoergic ($\Delta G < 0$) in the gas phase and in the nonpolar liquid phase. The results reported in this work suggest that silicon defects on extended polycyclic aromatic hydrocarbons, such as graphite, soot, and large-diameter carbon nanotubes, could make them useful in the removal processes of aromatic sulfur compounds from oil hydrocarbons.

Introduction

Sulfur compounds are present in every stage of oil production and refining, and their removal processes have been the focus of extensive investigation. In addition, these compounds act as pollutants, and consequently, sulfur emissions to the environment are increasingly restricted. As a result, the oil industry is quite interested in eliminating sulfur compounds from hydrocarbons. Special attention is paid to aromatic sulfur-containing compounds, which are particularly difficult to remove. At the present time, the removal of such compounds is mainly performed by hydrodesulfurization, through reduction processes. However, alternative approaches to aromatic sulfur compound removal are always of interest. The use of extended carbon compounds such as graphite, soot, and carbon nanotubes might be one of those possible alternatives to eliminate these compounds from oil hydrocarbons.

Polycyclic aromatic hydrocarbons (PAHs) occur in many natural environments where carbon is present. They are implicated in soot formation, in hydrocarbon combustion, and in the formation of dust grains in the interstellar medium. Coronene ($C_{24}H_{12}$) is the smallest PAH having the essential structural elements of graphite. Therefore, theoretical models of graphite, soot, or carbon nanotube walls often employ PAH molecules as models representing a finite section of a carbon surface.

It is well-known that C and Si have completely different bonding characteristics, despite the fact that they are both in the fourth row of the periodic table and, accordingly, they have the same number of valence electrons. This happens because sp^2 hybridization is more stable for carbon while the silicon-preferable hybridization is sp^3. Starting from elementary clusters, carbon makes linear chains and planar structures, while silicon prefers 3-dimensional (3-D) formations. Even though the complete replacement of C with Si atoms in cage materials was due to fail from the beginning, partial substitution, which results in coexistence of C and Si atoms, is in principle possible. In 1999, the production of heterofullerenes containing up to 50% Si was achieved,[1,2] and in 2001 there was the first synthesis of silicon carbon nanotubes (SiCNTs).[3] The presence of Si atoms in extended carbon compounds should change their electronic properties and chemical behavior. Consequently, the study of the influence of silicon defects on these properties could be relevant to possible applications of such altered compounds.

In this paper, the adsorption (physisorption and chemisorption) of aromatic sulfur compounds on carbon surfaces has been modeled through the interaction of thiophene with coronene and 2Si-coronene. This model retains the chemistry of the systems of interest and allows performing relatively high-level calculations. The modeling of larger systems would exclude the possibility of performing frequency calculations to obtain thermodynamic corrections to energy.

Computational Details

The interactions of thiophene with coronene and 2Si-coronene have been modeled with the Gaussian 98[4] package of programs. Geometry optimizations have been performed using the hybrid density functionals B3LYP and BH and HLYP, in conjunction with the 3-21G* basis set. Frequency calculations were carried out for all the studied systems at the same level of theory, and the minima character of the modeled structure was identified by the number of imaginary frequencies (NIMAG = 0). Zero point energies (ZPE) and thermal corrections to Gibbs free energy at 298.15 K were included in the determination of the relative energies.

Bader topological analyses[5] of the B3LYP/3-21G* wave functions have also been performed to characterize the interactions in the physisorption products, and several critical points were found. The topological analyses were computed with the Aim2000 program.[6,7]

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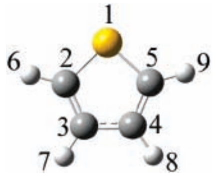

Figure 1. Atoms numbering in thiophene molecule.

The chemisorption reactions, involving 2Si-coronene, were additionally modeled at higher levels of theory to confirm the results. The geometries of the stationary points were fully optimized using the MP2 method with 6-31G* basis set. Frequency calculations were performed at the same level of theory. The energy values were improved by single point calculations using the same method and the 6-311+G* basis set. The Gibbs free energies were corrected a posteriori to convert them from gas phase to liquid phase, since the latter values would be more relevant to the removal processes of aromatic sulfur compounds from oil hydrocarbons.

Results and Discussion

Geometries and Molecular Orbitals. The atom numberings used through this manuscript, referring to different sites in thiophene molecule, are shown in Figure 1.

The frontier orbitals, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of thiophene, coronene, and 2Si-coronene, are shown in Figure 2. The plan view of the modified coronene has also been included in the figure. The frontier orbitals of the 2Si-coronene seem to be mainly located on the Si atoms and their neighbors, while these orbitals are more evenly distributed in coronene. As it can be seen in the figure, the silicon atoms cause the HOMO−LUMO 2Si-coronene gap to decrease about 0.7 eV, compared to that of coronene. 2Si-Coronene shows a higher HOMO (+0.27 eV) and a lower LUMO (−0.47 eV), which suggests a higher reactivity toward both electrophilic and nucleophilic reagents compared to coronene. Since the minimum interaction gap with thiophene would be that between the HOMO of thiophene and the LUMO of coronene or 2Si-coronene, the presence of the two silicon atoms favor this interaction by 0.47 eV (10.9 kcal/mol). These results suggest that the presence of silicon atoms in polycyclic aromatic hydrocarbons could favor their interactions with thiophene and similar compounds.

The fully optimized geometries of the physisorption products that were found to be formed between thiophene and coronene (**P-Ia**−**P-IVa**) and between thiophene and 2Si-coronene (**P-Ib**−**P-Vb**) are shown in Figure 3. The physisorption term has been used in this work to indicate those processes which do not involve any chemical bond formation but intermolecular interactions. Several conformations were tried for this kind of interactions. Starting geometries with the sulfur atom pointing to coronene and 2Si-coronene invariably evolved to one of those conformations showed in Figure 3. Configurations with thiophene parallel to coronene also evolved to one of those or to the addition products that will be discussed later.

Four physisorption products between thiophene and coronene were found. In all of them, the thiophene plane was found to be almost perpendicular to the coronene plane, with one or two of the hydrogen atoms in thiophene pointing toward coronene. **P-Ia** was found to be formed through the interaction between hydrogen atoms 7 and 8 in thiophene and the coronene sheet. The shortest C···H distance was found to be equal to 2.78 Å, while the other one was found to be equal to 2.95 Å. The interaction between hydrogens 6 and 7 in thiophene with the C atoms in the coronene sheet was found to be responsible for the **P-IIa** formation. The interaction distances were found to be almost identical and around 3.0 Å. Physisorption complexes **P-IIIa** and **P-IVa** are formed through interactions C···H7 (or H8) and C···H6 (or H9) with the coronene sheet, with distances of 2.51 and 2.58 Å, respectively.

Five physisorption products between thiophene and 2Si-coronene were found. **P-Ib** was found to be formed through the interaction between hydrogen atoms 7 and 8 in thiophene and the silicon atoms in 2Si-coronene, with interacting distances equal to 3.21 Å. The interactions between atoms 6 and 7 in thiophene with the Si atoms in 2Si-coronene led to the **P-IIb** formation. The interaction distances were found to be equal to 3.21 and 3.24 Å, for Si···H6 and Si···H7, respectively. The **P-IIIb** complex arises from the interactions between hydrogen atoms numbered as 7 and 8 and the C−C bonds in the central ring of the 2Si-coronene. The interaction distances between the corresponding H atoms and the center of the bond are 3.06 and 3.09 Å. This kind of interaction is also responsible for **P-IVb** formation; in this case the distances from the H atoms to the C−C bonds are 3.03 and 3.10 Å for H6 and H7, respectively. **P-Vb** was the only complex found with thiophene oriented

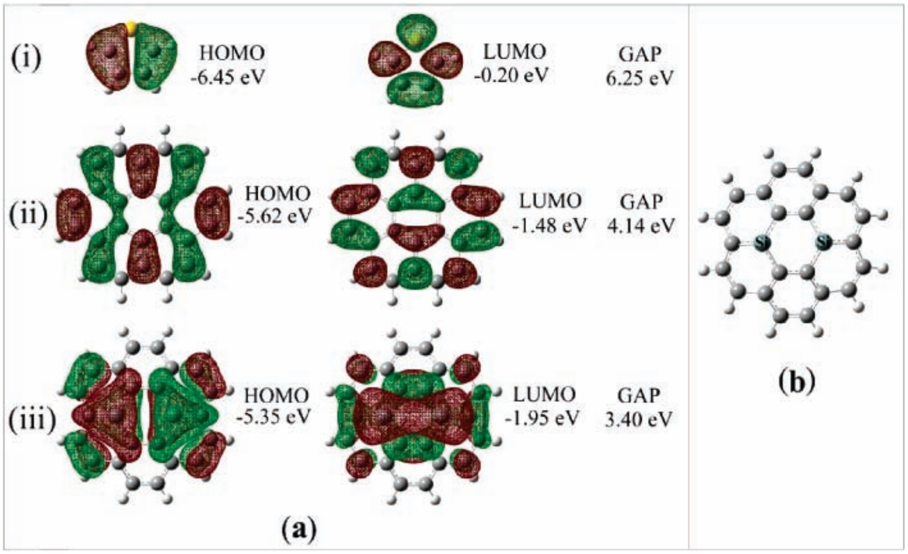

Figure 2. (a) Frontier orbitals of thiophene (i), coronene (ii), and 2Si-coronene (iii). (b) Plan view of 2Si-coronene.

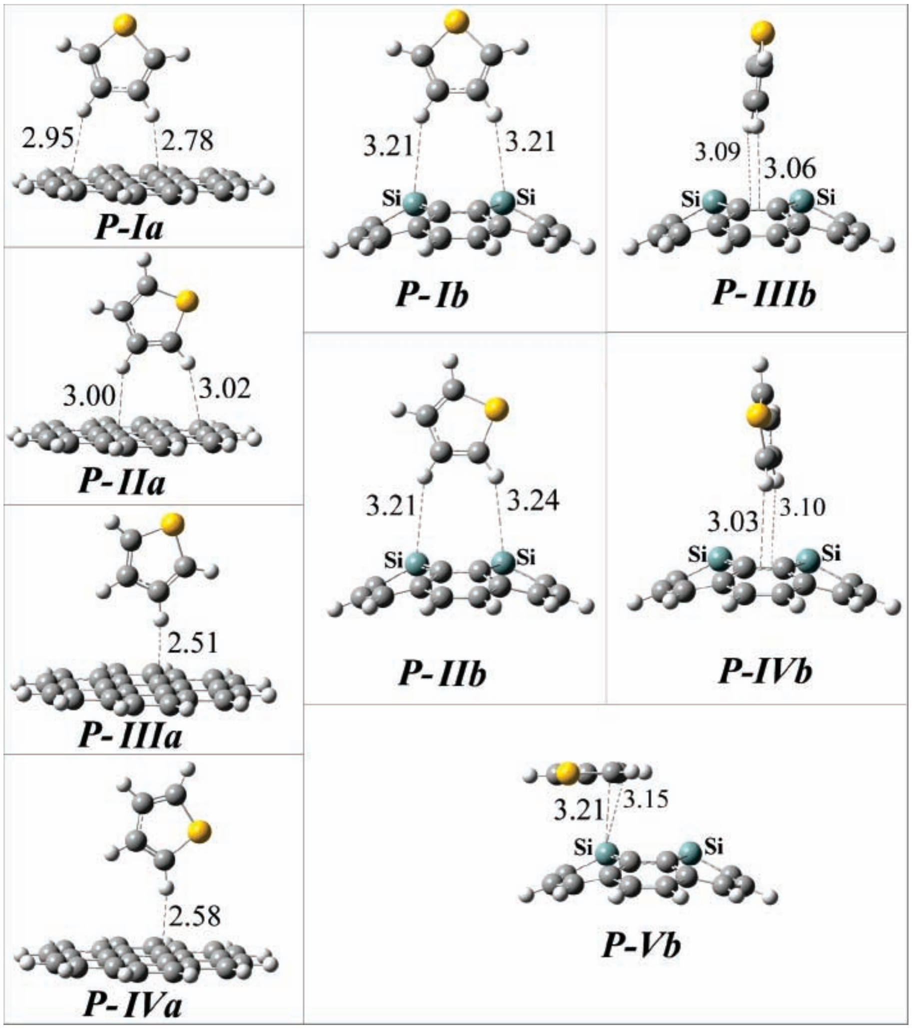

Figure 3. B3LYP/3-21G* fully optimized geometries of different physisorption products of thiophene on coronene and 2Si-coronene.

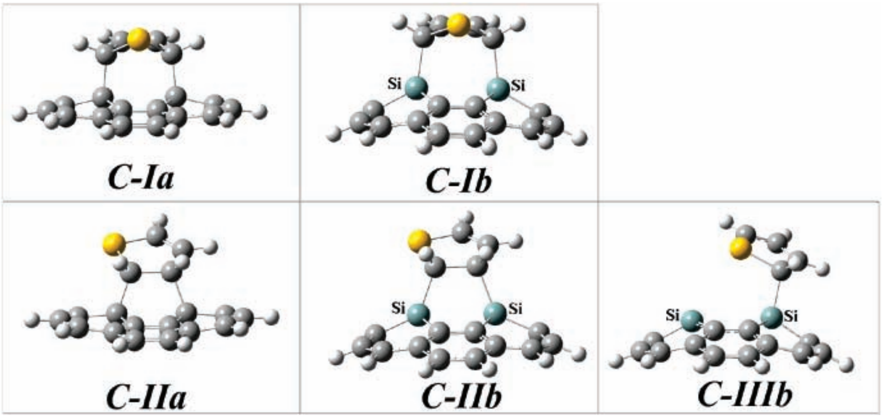

Figure 4. B3LYP/3-21G* fully optimized geometries of chemisorption products.

"parallel" to the 2Si-coronene molecule, with one of the silicon atoms pointing toward the center of the thiophene ring.

Figure 4 shows the fully optimized geometries of the chemisorption products that were found to be formed between thiophene and coronene (**C-Ia** and **C-IIa**) and between thiophene and 2Si-coronene (**C-Ib**−**C-IIIb**). The chemisorption term stands for those processes which involve chemical bond formation. These bonds are form through hybridization changes of the carbon atoms in thiophene and coronene (sp^2 to sp^3) and through expansion in the valence level of the silicon atoms in 2Si-coronene. **C-Ia** and **C-Ib** structures correspond to cycloaddition of thiophene through carbons 2 and 5, represented here as [2,5] to coronene and 2Si-coronene, respectively. This notation stands for the sites on thiophene involved in the addition process and should not be mistaken with the usual terminology $[n + m]$ that refers to the number of π electrons in each fragment of cycloaddition reactions. **C-IIa** and **C-IIb** structures correspond to cycloadditions involving thiophene carbons numbered as 2 and 3, [2,3]. The geometries obtained by B3LYP and BHandHLYP optimization are quite similar (Table 1). The two C−C(Si) bonds that arise from the chemisorption process are identical in **C-Ia** (**C-Ib**), while the C2−C(Si) bond is predicted

TABLE 1: Relevant Bond Distances (Å) in the Chemisorption Products

	d2[a]		d3[a]		d5[a]	
product	B3LYP	BH and HLYP	B3LYP	BH and HLYP	B3LYP	BH and HLYP
C-Ia	1.659	1.640			1.659	1.640
C-IIa	1.665	1.637	1.687	1.651		
C-Ib	1.950	1.932			1.950	1.932
C-IIb	1.941	1.915	1.955	1.924		
C-IIIb	2.191	1.912				

[a] d2, d3, and d5 represent distances between C2, C3, or C5, respectively, in thiophene and a C atom in coronene or an Si atom in 2Si-coronene.

TABLE 2: Characterization of the Critical Points Associated with the Physisorption Complexes

complexes	crit pt	$\rho(r)$	$-^2\rho(r)$
P-Ia	BCP	0.0063	−0.0061
	BCP	0.0047	−0.0045
	RCP	0.0033	−0.0034
P-IIa	BCP	0.0058	−0.0055
	BCP	0.0048	−0.0046
	RCP	0.0030	−0.0032
P-IIIa	BCP	0.0103	−0.0098
P-IVa	BCP	0.0090	−0.0085
P-Ib	BCP	0.0041	−0.0024
	BCP	0.0041	−0.0024
	RCP	0.0010	−0.0009
P-IIb	BCP	0.0041	−0.0024
	BCP	0.0039	−0.0023
	RCP	0.0011	−0.0010
P-IIIb	BCP	0.0044	−0.0032
	BCP	0.0039	−0.0034
P-IVb	BCP	0.0041	−0.0030
	BCP	0.0040	−0.0036
P-Vb	BCP	0.0134	−0.0059

to be shorter than the C3−C(Si) bond in **CIIa** (**C-IIb**). In addition, the coronene structure is quite distorted in **C-Ia** and **C-IIa** structures, which should cause a loss in the p-conjugation. Accordingly, it should not be expected that these addition products are energetically favored. On the other hand, the almost pyramidal configuration of silicon atoms in 2Si-coronene should facilitate the cycloaddition processes and the corresponding products should be energetically more favored than those involving coronene.

In addition, a possible chemisorption product with only the C2 atom bonded to one of the Si atoms was also modeled (**C-IIIb**) to study if the addition is feasible when the silicon defects do not occur in pairs. A proper bond was found, suggesting that the single anchored product could also contribute to the adsorption.

Topological Analysis. The topological analysis of the electronic charge density $\rho(r)$ and its Laplacian, $-^2\rho(r)$, is a powerful tool to describe the characteristics of bonds and interactions.[8,9] In particular, the critical points of $\rho(r)$, which present two negative curvatures and one positive curvature, identify the bonds in the molecule and will be denoted hereafter as bond critical points (bcp). The critical points with one negative and two positive curvatures are associated with the existence of a ring structure and will be denoted as ring critical points (rcp). The values of $\rho(r)$ and $-{}^2\rho(r)$ at these points provide quantitative information on the strength and nature of the bonding. Accordingly, topological analyses are very useful to characterize intermolecular interactions as those described above for thiophene physisorption on coronene and 2Si-coronene. The $\rho(r)$ and $-^2\rho(r)$ values of the different critical points found in the physisorption complexes are reported in Table 2. For all the studied complexes, at least one critical point was found, which confirms that the intermolecular interactions are meaningful. All the Laplacian values are negative, indicating that the electronic charge density is concentrated in the space region between the interacting molecules. All the values of the topological parameters are quite small, which means that these complexes are weakly bonded. The largest value of $\rho(r)$ corresponds to **P-Vb**, suggesting that it should exhibit the largest stabilization among the studied physisorption complexes.

TABLE 3: Energy (ΔE) and Gibbs Free Energy (ΔG) Changes Involved in the Adsorption Processes (kcal/mol)

	ΔE (ZPE)		ΔG_{298K}	
complex	B3LYP	BH and HLYP	B3LYP	BH and HLYP
P-Ia	−0.79	−1.73	6.27	5.17
P-IIa	−1.10	−1.85	6.87	6.03
P-IIIa	−0.72	−1.32	5.85	7.61
P-IVa	−1.01	−1.57	9.03	9.57
P-Ib	−0.80	−3.04	10.07	7.98
P-IIb	−0.73	−2.25	10.50	6.39
P-IIIb	−1.71	−6.29	4.70	3.44
P-IVb	−1.88	−2.11	8.80	8.02
P-Vb	−4.61	−2.34	6.21	6.72
C-Ia	86.65	90.99	99.61	104.34
C-IIa	67.07	71.23	79.51	84.11
C-Ib	−22.32	−26.13	−8.25	−12.01
C-IIb	−22.87	−25.06	−9.49	−11.67
C-IIIb	−6.10	−11.00	6.04	0.18

Energies. The energy changes (ΔE) involved in the thiophene physisorption and chemisorption on coronene and 2Si-coronene are reported in Table 3. The table shows the ΔE values, including ZPE corrections, and the change in Gibbs free energy (ΔG) involved in each process. The physisorption energies are quite small, as it should be expected from the topological analysis. The strongest interaction corresponds to complex **P-Vb**, which also agrees with the Bader analysis predictions. For all the other complexes the interaction energies are very small, with values which are of the same magnitude than the error of the calculation method, but even if these values were accurate, they do not support the physisorption mechanism as a viable way to anchor thiophene on extended carbon or carbon−silicon surfaces. All the physisorption processes were found to be endoergic, i.e., ΔG values >0, which definitively indicates that the complexes obtained that way are not stable enough to be considered as proper adsorption products. However, they could be short-lived intermediates leading to the formation of chemisorption products.

The cycloadditions of thiophene to coronene seem to be very unlikely to occur, since according to the results in Table 3, they are highly endothermic and endoergic. This result was expected on the basis of the fact that for the cycloaddition to occur the planarity of the coronene sheet must be breaking, which is a nonfavorable change due to the aromaticity of this compound. On the other hand, large stabilization energies involved in the thiophene cycloadditions to 2Si-coronene were found. The values of the stabilization energies due to the formation of **C-Ib** and **C-IIb** products were found to be similar, suggesting that [2,5] and [2,3] thiophene cycloadditions to 2Si-coronene should occur in almost equal proportions. In addition the cycloaddition processes were found to be exoergic. The ΔE and ΔG values associated with these processes are large enough to overcome any inaccuracy from the calculation method, which supports the reliability of the results. However, to be sure that these promising results of favorable additions to 2Si-coronene are not an artifact of the used methods, the level of theory was increase to get more accurate data for the energetic changes involved in the formation of **C-Ib**, **C-IIb**, and **C-IIIb**. For these channels we have extended the modeling to MP2 method. The quality of the basis set has also been increased to 6-31G* for geometry optimizations and frequency calculations. In addition, single point calculations have been carried out with 6-311+G* basis sets to improve the energy values.

Up to this point, all the reported results correspond to the gas phase, using the standard state of 1 atm, as calculated by the Gaussian program. However, since the purpose of this work is to propose a viable way to remove aromatic sulfur compounds from oil hydrocarbons, it seems logical to investigate if in the nonpolar liquid phase, where the actual process would take place, the associated ΔGs of reaction are going to remain negative. To accomplish that purpose the reference state has been changed from 1 atm to 1 M. Since K_P and K_C are related by

$$K_P = K_C(V_M)^{\Delta n} \tag{1}$$

where Δn stands for the mole change through reaction (i.e., $\Delta n = -1$ for bimolecular reactions), V_M represents the molar volume, and K_C and K_P are the equilibrium constants in concentration and pressure units, respectively, then

$$K_C = K_P V_M \tag{2}$$

$$\mathrm{e}^{-\Delta G^{1M}/RT} = e^{-\Delta G^{1atm}/RTV_M} \tag{3}$$

where R is the gas constant and T the temperature in K. From expression (3) it is evident that

$$\Delta G^{1M} = \Delta G^{1atm} - RT\ln(V_M) \tag{4}$$

This conversion lowers the ΔGs by 1.89 kcal/mol, for bimolecular reactions, at 298 K. In addition, the free volume correction to liquid phase proposed by Benson[10] has also been included. According to this approach, the ratio between the reactions in solution and in gas phase (r), in nonpolar solvents, is

$$r \cong \frac{n10^{(2n-2)}}{\mathrm{e}^{(n-1)}} \tag{5}$$

where n represents the total of reactants' moles (i.e., $n = 2$ for bimolecular reactions). Since the author previously assumed that

$$r \cong \frac{K_x^{\mathrm{sol}}}{K_x^{\mathrm{gas}}} \equiv \frac{\mathrm{e}^{-\Delta G^{\mathrm{sol}}/RT}}{\mathrm{e}^{-\Delta G^{\mathrm{gas}}/RT}} \tag{6}$$

the combination of expressions (5) and (6) easily leads to

$$\Delta G^{\mathrm{sol}} \cong \Delta G^{\mathrm{gas}} - RT\{\ln[n10^{(2n-2)} - (n-1)]\} \tag{7}$$

According to expression (7), ΔG^{sol} decreases by 2.96 kcal/mol for a bimolecular reaction, at 298 K, with respect to ΔG^{gas}. Table 4 shows the ΔG values obtained at the MP2/6-311+G*//MP2/6-31* level of theory for the standard state of 1 atm (ΔG^{1atm}) and for the standard state of 1 M (ΔG^{1M}) and includes Benson's free volume correction (ΔG^{1M+FV}). This approach has been successfully used before by Okuno[11] and Alvarez-Idaboy et al.[12] The ΔG values corresponding to the formation of **C-Ib**, **C-IIb**, and **C-IIIb** are all negative, indicating that the silicon defects do not need to be in pairs for the adsorption to occur. This seems to be an important finding, since it suggests that even if the silicon defects appear randomly, they would still lead to stable chemisorption products. In addition, the calculated data indicate that the major product would be that corresponding to thiophene [2,5] cycloaddition. As the values in the table show, the presence of a nonpolar liquid environment makes the chemisorption processes even more exoergic. This was expected since the packing effects of the solvent reduce the entropy loss associated with any addition reaction. Accordingly, it could be expected that extended polycyclic aromatic compounds with silicon defects may act efficiently as chemical traps for aromatic sulfur compounds in oil hydrocarbons.

TABLE 4: MP2/6-311+G*//MP2/6-31* Entropy Terms and Gibbs Free Energies Involved in the Chemisorption Reactions of Thiophene + 2Si-Coronene (kcal/mol)

compd	$-T\Delta S$	ΔG^{1atm}	ΔG^{1M}	ΔG^{1M+FV}
C-Ib	14.91	−21.93	−23.82	−26.78
C-IIb	13.81	−19.06	−20.95	−23.91
C-IIIb	7.53	−13.29	−15.18	−18.14

It seems worthy to emphasize the importance of considering Gibbs free energies of reaction to predict the viability of chemical processes. Unfortunately, it is a common practice to draw conclusions only on the basis of electronic energies, mainly in the gas phase, and with total disregard of the influence that entropic factors have on actual chemical processes. To illustrate the relevance of the entropy for the studied chemisorption reactions, values of the $-T\Delta S$ term have also been included in Table 4. As these values show, the entropy changes involved in the studied addition reactions are relative large and they must be taken into account. Logically, the entropy loss is larger for cycloadditions reactions (**C-Ib** and **C-IIb**) than for single additions (**C-IIIb**), where only one carbon−silicon bond is formed.

Since the higher level of theory lowers the values of ΔG, and so do the corrections made to convert the values from the gas phase to liquid nonpolar phase, it is possible that some physisorption processes could also lead to the formation of relative stable products. However, since in general physisorbed products are much less favored, they are not expected to significantly contribute to the overall adsorption process.

The differences in the cycloaddition processes to coronene and 2Si-coronene can be attributed to the hybridization, i.e., in carbon sp^2 hybridization (planar) is more stable while in silicon the preferable hybridization is sp^3 (pyramidal). The resulting difference in geometries seems to favor the thiophene addition to 2Si-coronene. These findings suggest that silicon defects on extended polycyclic aromatic hydrocarbons, such as graphite, soot, and large-diameter carbon nanotubes, could make them useful in the removal processes of aromatic sulfur compounds from oil hydrocarbons.

Since the planarity of pure carbon PAHs seems to prevent them from thiophene additions, small diameters nanotubes might also be an option for the removal processes of aromatic sulfur compounds. Therefore, the results reported in this paper support the previous findings of Gómez et al.,[13] who reported large stabilization energies for the dibenzothiophene + (7,7) and (10,5) open-ended carbon nanotubes. Further studies on the effect of silicon atoms in carbon nanotubes' capability to adsorb aromatic sulfur compounds seem to be the logical next step in this line of investigation. However, since the prices of carbon nanotubes are still relatively high, extended polycyclic aromatic hydrocarbons, with silicon defects, would be a better option for the removal processes of sulfur compounds, if only economic considerations are taken into account.

It seems relevant to point out that since the sulfur atom is not directly involved in the chemisorption reactions, the removal process proposed here would only apply to *aromatic* sulfur-containing compounds, which are just the focus of this research since they are especially difficult to remove from oil hydrocarbons. In addition, and according to the well-known fact that the presence of heteroatoms in aromatic compounds increases the site reactivity of the neighbor C atoms, the addition reactions studied here are also expected to be feasible for other heterocyclic compounds like furan or pyrrole. Furthermore, it should also be expected the reactivity order is pyrrole > furan > thiophene.[14] However, those reactions are not relevant to the purpose of this work.

Conclusions

Frontier orbital analysis suggests that the presence of silicon atoms in PAHs reduces the HOMO−LUMO gap, by raising the HOMO energy and lowering the LUMO energy. This should increase their reactivity toward both nucleophilic and electrophilic reagents.

According to the results obtained in this study, the chemisorption processes on 2Si-coronene are exoergic in the gas phase as well as in nonpolar liquid phase and could lead to thiophene [2,5] and [2,3] cycloaddition products, as well as single-anchored thiophene products. This suggests that there is no need for the silicon defects to be in pairs for the adsorption to occur.

The results presented here suggest that extended polycyclic aromatic hydrocarbons with silicon defects, such as graphite, soot, and large-diameter carbon nanotubes, could be useful in the removal processes of aromatic sulfur compounds from oil hydrocarbons, while pure carbon PAHs with negligible curvature are not.

Since the planarity of pure carbon PAH seems to prevent them from thiophene additions, small diameters nanotubes might also be an option for the removal processes of aromatic sulfur compounds. However assuming that the results reported here are correct, extended polycyclic aromatic hydrocarbons, with silicon defects, would be a better option, on the basis of price considerations.

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