Investigation of H2 Physisorption on Corannulene (C20H10), Tetraindenocorannulene (C44H18), Pentaindenocorannulene (C50H20), C60, and Their Nitrogen Derivatives

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The hydrogen storage capacities of the recently synthesized tetraindenocoranulene C$_{44}$H$_{18}$ and pentaindeno-corannulene C$_{50}$H$_{20}$ have been investigated and compared with those of corannulene and C$_{60}$. The results for the physisorption of a single H$_2$ on the concave side indicate that the adsorption energies (E_{ads}) for tetraindenocorannulene and pentaindenocorannulene are very similar, 2.9 and 3.0 kcal/mol, respectively. The later values are slightly larger than that estimated for corannulene, 2.4 kcal/mol, and about half of the encapsulation energy of H$_2$ in C$_{60}$, 5.4 kcal/mol. The differences in adsorption energies can be explained considering the dipole moments of the molecules. For C$_{50}$H$_{20}$ and C$_{44}$H$_{18}$ they are very similar, 4.0 and 3.7 Debye. However, it is much smaller in corannulene, 2.0 Debye, which explains the lower E_{ads} observed for the later polyarene. The E_{ads} presents a different behavior on the electron-poor convex side; they are nearly identical for all of the molecules considered. The interaction energies on the convex side, determined for corannulene, tetraindenocorannulene, pentaindenocorannulene, and C$_{60}$, are 1.2, 1.1, 1.1, and 1.2 kcal/mol, respectively. The hydrogen storage capabilities are discussed in terms of the results obtained for the sandwich complexes between pentaindenocorannulene with benzene or corannulene. As a by product, we estimated the complexation energies for the benzene–pentaindenocorannulene and corannulene–pentaindenocorannulene pairs as 6.0 and 8.3 kcal/mol, respectively. Finally, we replaced some carbon atoms in corannulene and pentaindenocorannulene with nitrogen atoms. The adsorption energies were increased; C$_{16}$N$_4$H$_{10}$ has nearly the same adsorption energy as the much larger pentaindenocorannulene. In the case of pentaindenocorannulene, the introduction of six nitrogen atoms (12% of carbon atoms replaced) increases the adsorption energy, about 0.2 kcal/mol. The present results showed that the introduction of a small number of nitrogen atoms can increase the adsorption energy in carbon structures without increasing the weight of the material too much, but the increment seems to be strongly dependent on the position of the nitrogen atoms.

1. Introduction

Carbon structures have a tremendous potential in hydrogen storage[1-17] technologies. Their major advantages are the high volumetric and gravimetric densities. However, there is a serious drawback: it is very difficult to easily adsorb and desorb H$_2$ at ambient temperatures because the physisorption energies are too low and the chemisorption energies are too high.[1-10] For those reasons, several routes have been explored to reach the DOE targets at ambient temperature, for density and volume, 6.5 wt % and 62 Kg/m^3, respectively. The results obtained for hydrogen storage on nanotubes are somewhat contradictory: while some reports claim hydrogen storages of 1%, other investigations yield results as a high as 10%.[1-8,14-17] These differences are probably due to the different states of the nanotubes employed by the researchers. It is well known that unpurified carbon nanotubes have metallic nanoparticles, which may enhance the hydrogen adsorption, and capped ends that do not allow the entry of molecular hydrogen. However, purified nanotubes may have uncapped ends and more defects that facilitate H$_2$ storage. The situation is even more complicated if we consider that electric arcs gives carbon nanotubes that have more defects than HiPco carbon nanotubes.[18] Therefore, new alternatives to store H$_2$ in carbon nanostructures have been

proposed. Some of them involve the use of carbon nanoscrolls,[13] fullerenes, and fullerenes passivated with transition metals.[10-12] In the present work, we explore the hydrogen storage capacities of the recently synthesized geodesic polyarenes, pentaindecorannulene (C$_{50}$H$_{20}$) and tetraindecorannulene (C$_{44}$H$_{18}$).[19] The interest is twofold: First, because of the curvature of these two polyarenes the results may shed light on the interaction between H$_2$ and other carbon nanostructures. It is important to note that the carbon atoms of the central pentagon in pentaindenocorannulene have POAV[20-21] angles that are larger than those observed in C$_{60}$, 12.4° versus 11.6°, respectively. Second, considering the large volume available inside the cavity of pentaindenocorannulene, it may be possible to store H$_2$ molecules inside, if suitable molecules are designed to cover the open area of the polyarene. The results are compared with those obtained for curved graphenes by Okamoto and Miya-moto[22] and by Scanlon et al.[23] We also investigated a different route to increase the electronic density of the polyarenes. We replaced some carbon atoms with nitrogen atoms. As a by product, we have corroborated that the LSDA[24,25] density functional gives results that are similar to those obtained at the MP2 level for the interaction between H$_2$ and curved carbon nanostructures such us C$_{60}$[26] and corannulene.[22,23] We want to stress that it is not the purpose of the present investigation to accurately estimate the noncovalent interactions between H$_2$ and

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the carbon structures selected. However, it is expected that the information obtained here may help to improve the hydrogen storage capabilities of these fascinating curved graphenes, that one day may provide a different route to the rational synthesis of fullerenes.[27]

2. Methods

It is well known that most of the density functionals available present serious problems to describe noncovalent interactions. However, it has been demonstrated that, in some cases, because of a fortuitous error cancellation, LSDA can give reasonable results for physisorption energies. A proof of that is the vast number of landmark articles published in the present journal that use LSDA approximation. We have selected the LSDA implementation in Gaussian 03[28] SVWN5 (LSDA)[24,25] and not the default SVWN1 because the former gives slightly better results. The SVWN1 parametrization overestimates the phys-isorption energies with respect to SVWN5. For example, by employing the 6-31G*[29] basis set we find that the interaction energy between H_2 and benzene is 1.8 kcal/mol if we choose SVWN5, and 1.9 kcal/mol with SVWN1. As expected, the differences increases when the system is bigger, being close to 0.2 kcal/mol for the interaction energy between H_2 and corannulene. Tight thresholds were employed in all geometry optimizations. The basis set selected for the DFT calculations was the 6-31G* basis set.[29] The SCF tight threshold was used in the LSDA single-point calculations. We performed compara-tive tests between the fine grid (75 302) 75 radial shells and 302 angular points per shell and the ultrafine grid (99 590). The results indicated that the use of the ultrafine grid changed the interaction energies by less than 0.02 kcal/mol. Therefore, the fine grid was selected. In the case of the H_2 and benzene interaction, some comparative tests were performed: MP2 and CCSD(T)[30] levels in conjunction with Dunning's augmented correlation consistent basis sets.[31,32]

It is well known that physisorption energies must be corrected by basis set superposition error. For that purpose, we used the counterpoise correction suggested by Boys and Bernardi in 1970.[33]

3. Results and Discussion

3.1. Assessment of SVWN5 (LSDA). There is substantial evidence that most of the available density functionals cannot describe noncovalent interactions properly.[34] The clearest example is the B3LYP[35,36] functional, which predicts repulsive curves for the dimmers of the noble gases. However, there is some evidence that performance of LSDA, as well as some functionals developed by Zhao and Truhlar,[34] for noncovalent interactions are superior to most of the available density functionals.

Before employing LSDA to study the interactions between H_2 and the polyarenes, we performed some comparative calculations. The smallest system that can be used as a model for the later interaction is the H_2−benzene complex. At the MP2/aug-cc-pVDZ and CCSD(T)/aug-cc-pVDZ levels of theory, we have estimated that the interaction energy between H_2 and C_6H_6 as 0.87 kcal/mol. The later result is in good agreement with the value suggested by Zhou et al.[5] at the CCSD(T)/cc-pVTZ//MP2/6-311+G** level of theory, 0.87 kcal/mol. At the SVWN/6-31G* level, the interaction energy is 1.8 kcal/mol. The results are somewhat disappointing: SWVN5 overestimates the inter-action energy by a factor of 2. We decided to perform additional tests with larger curved π systems. Okamoto and Miyamoto[22] and Scanlon et al.[23] determined the interaction energy between

corannulene and H_2. The hydrogen molecule was located on the concave side and perpendicular to the five-member ring. At the MP2/6-311G(d,2p)[22] and MP2(Full)/6-311++(3df,2p)//MP2(Full)/6-31G(d)[23] levels of theory, the interaction energies obtained were 3.05 and 2.81 kcal/mol by Okamoto et al.[22] and Scanlon et al.,[23] respectively (both results are BSSE uncor-rected). The SVWN5/6-31G(d) estimation, for the same con-formation, is 2.4 kcal/mol after BSSE correction (2.9 kcal/mol without it). The later value is lower than the MP2 result, but as we have noticed above the MP2 values reported in refs 22 and 23 were not corrected by BSSE. Thus, we expect that the true ab initio results are closer to the LSDA estimation. The distance between H_2 and corannulene is 2.3, 0.7, and 0.5 Å larger than that estimated by Okamoto et al.[22] and Scanlon et al.,[23] respectively. Another comparison was performed for corannu-lene. In the new configuration, the H_2 is still perpendicular to the pentagon, but now it is located on the convex side of corannulene. The binding energy at the SVWN5/6-31G* level is 1.2 kcal/mol after BSSE correction, in reasonable agreement with the MP2(Full)/6-311++G(3df,2p) estimation of Scanlon et al.,[23] 1.38 kcal/mol (without BSSE correction). Again, as explained for the adsorption on the concave side, the true MP2 result is expected to be smaller because of the lack of BSSE.

Finally, we studied the encapsulation of H_2 inside a C_{60} molecule. Slanina et al.[26] determined the encapsulation energy of the endohedral fullerene $H_2@C_{60}$ as 2.36, 6.94, and 6.07 kcal/mol at the MP2/6-31G**, MP2/6-311G**, and MP2/6-311(2d,-2p) levels of theory respectively (all values are BSSE corrected, the uncorrected values are 3.99, 8.63, and 10.62 kcal/mol, respectively). Our estimation at the SVWN5/6-31G* level of theory is 5.4 kcal/mol (BSSE corrected), which is in very good agreement with the values obtained by Slanina et al.[26] The basis set superposition error is about 1 kcal/mol; the uncorrected value is 6.3 kcal/mol. Thus, the basis set superposition error for SVWN5 is not as important as that for ab initio calculations. It is important to remark that, in general, the MP2 predictions slightly overestimate the binding energies of the noncovalent interactions. Indeed, Sinnokrot and Sherrill[37] determined that for the benzene dimer the differences between the MP2/aug-cc-pVDZ* and CCSD(T)/aug-cc-pVDZ* interaction energies were 1.5, 0.76, and 1.9 kcal/mol for the sandwich, T-shaped, and parallel displaced conformations, respectively. In the case of the SH_2 benzene complex,[38] the differences between the MP2/aug-cc-pVTZ and CCSD(T)/aug-cc-pVTZ estimations were 0.83 kcal/mol, (−3.47 and −2.64 kcal/mol, respectively). Therefore, considering the evidence exposed by the Sherrill group[37,38] we can expect that the values obtained for the $H_2@C_{60}$ complex, by Slanina et al.[26] are slightly larger than those we would obtain if the CCSD(T) is employed, reducing the difference with the encapsulation energy estimated at the SVWN5/6-31G* level of theory.

The results presented above showed that when the size and curvature of the system is increased from benzene to corannu-lene and C_{60} the interaction energy of the curved π system with H_2 at the SVWN5 level becomes in better agreement with the ab initio computations. Thus, taking into account the size of the systems investigated, pentaindecorannulene ($C_{50}H_{20}$) and tetraindecorannulene ($C_{44}H_{18}$),[19] we can expect reasonable results for the interaction energies between them and H_2, and for the sandwich complexes that we created to mimic C_{60}. We want to stress that it is not the purpose of the present investigation to accurately estimate the noncovalent interactions with H_2, but the information obtained can help us to estimate the hydrogen storage capabilities of these curved graphenes.

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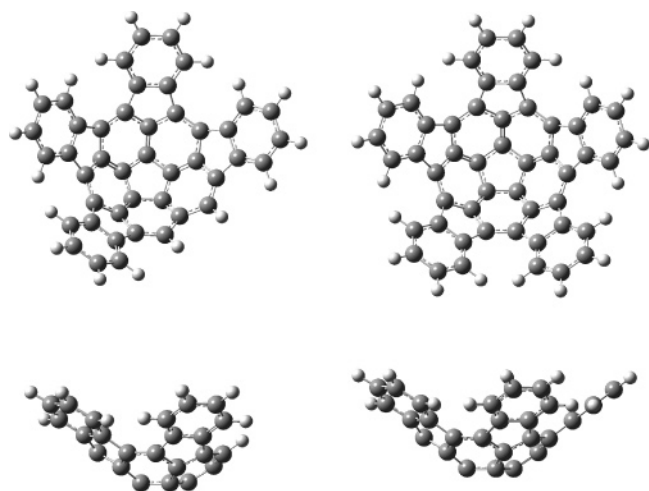
Figure 1. Two views of tetraindenocorannulene (left) and pentainde-nocorannulene (right).

3.2. Interaction between Pentaindecorannulene and Tetraindecorannulene with H$_2$. Pentaindecorannulene has 6 pentagons and 10 hexagons, whereas tetraindecorannulene has 5 pentagons and 9 hexagons as we can appreciate in Figure 1. Considering the similar area of both molecules, we expect nearly equivalent interaction and slightly larger energies than those determined for corannulene. Indeed, we found that the binding energies at the SVWN5/6-31G* level of theory are 3.0 and 2.9 kcal/mol for pentaindecorannulene and tetraindecorannulene, respectively. The basis set superposition error is larger than that observed for corannulene and closer to that determined for the encapsulation of H$_2$ in C$_{60}$. The BSSE correction is 2.3 kcal/mol for pentaindecorannulene and tetraindecorannulene. In both cases, the H$_2$ is oriented perpendicular to the central pentagon, 2.4 Å above.

The interaction energies obtained can be compared to those determined for corannulene. In the case of C$_{20}$H$_{10}$, the interaction energy in the same configuration was determined as 2.4 kcal/mol at the SVWN5/6-31G* level of theory, 0.6 kcal/mol lower than that determined for pentaindecorannulene. The later result was expected if we consider the dipole moments of the three molecules. They are 4.0, 3.7, and 2.0 D for pentaindenocorannulene, tetraindenocorannulene, and corannulene, respectively. Thus, the larger dipole moments increase the Van der Waals interaction between H$_2$ and the polyarene. On the basis of energetic considerations, for a single H$_2$, the values determined for the larger polyarenes seem more suitable for H$_2$ storage. However, the interaction energies of pentaindenocorannulene and tetraindenocorannulene are much lower than that estimated for C$_{60}$, 5.4 kcal/mol. Thus, to achieve greater interaction energies we considered as a next step the formation of sandwich complexes between pentaindecorannulene and two molecules, benzene and corannulene.

As a first step to investigate sandwich complexes, we determined the interaction energies for the adsorption of H$_2$ on different positions. We considered the convex side of the polyarenes, above the central pentagon. The E_{ads} are very similar, 1.2, 1.1, and 1.1 kcal/mol for corannulene, tetraindecorannulene, and pentaindenocorannulene, respectively. Thus, the adsorption energies on the convex side are much smaller than those determined on the concave side, about three times lower for tetraindecorannulene and pentaindenocorannulene. This behavior can be explained if we consider that the convex side of the polyarenes is electron-poor and the concave side is electron-rich.[40] We have checked the later hypothesis performing
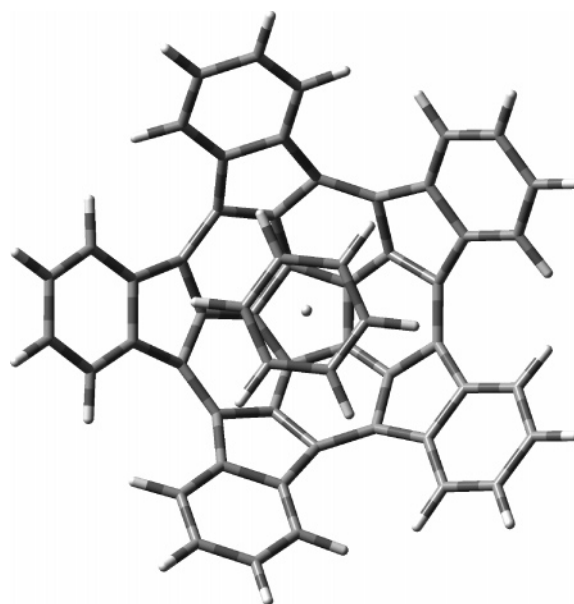
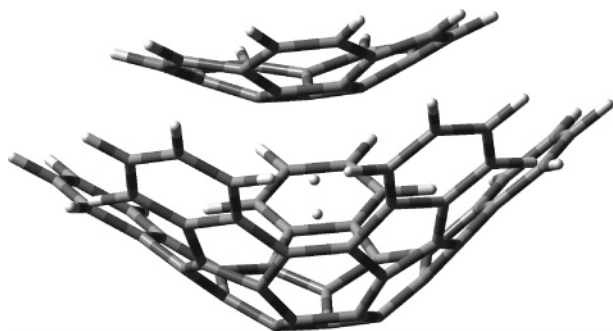**Figure 2.** Top view of the benzene$-$H$_2$$-$pentaindenocorannulene complex.

additional calculations for H$_2$ physisorption over C$_{60}$. Four positions were considered, over a pentagon, hexagon, 66 CC bond, and 56 bond. The interaction energies obtained were 1.0, 1.2, 0.9, and 0.9 kcal/mol, respectively, showing again that the physisorption on the convex side is not strongly dependent on the adsorption site. In the case of pentaindenocorannulene, we considered a different position for the adsorption of H$_2$. The hydrogen molecule is located on the convex side and above the CC bond that connects two pentagons, 2.7 Å above both carbons. The physisorption energy is slightly larger than that observed for the adsorption on the convex side over the pentagon, 1.3 kcal/mol, at the SVWN5/6-31G* level of theory.

With the aim of understanding how the adsorption energy varies with the position on the concave side, we have investigated two more adsorption sites of pentaindenocorannulene. First, we placed the H$_2$ over the most negatively charged carbon atoms, that is, those that are bonded to hydrogen atoms, and the physisorption energy obtained is 1.2 kcal/mol, almost three times lower than that above the central pentagon. The second, and final site considered, was over a carbon atom that connects two pentagons. The interaction energy is 1.1 kcal/mol. The later value shows that the physisorption energy obtained at the center of the pentagon is not obtained over the complete surface area of the polyarene.

In the final test performed, we placed two hydrogen molecules over the central pentagon, one on the concave side and other in the convex side. The interaction energy obtained was exactly the sum of the interaction energies of the individual H$_2$ molecules. Thus, we can expect only a small diminution of the interaction energies when several H$_2$ are physisorbed over these polyarenes, mostly because of repulsion between the H$_2$ molecules.[22]

3.3. Encapsulation of H$_2$ in Sandwich Complexes of Pentaindecorannulene, with Benzene Corannulene and Pentaindenocorannulene. Several attempts have been made to use C$_{60}$ to store H$_2$, but it has been very difficult to open and close C$_{60}$. Very interesting results have been obtained by Murata et al.[39] that synthesized H$_2$@C$_{60}$ in more than 100 mg quantities by closure of a 13-membered ring. However, the procedure is far from being scalable for large hydrogen storage. Therefore, we have considered the possibility of encapsulating molecular

Figure 3. Side view of the corannulene−H$_2$−pentaindenocorannulene complex.

hydrogen inside sandwich complexes of pentaindenocorannulene and other conjugated hydrocarbons[22,40] such us benzene and corannulene. Corannulene and pentaindenocorannulene have the advantage of being a curved π system; thus, we can benefit from the concave convex interactions that these molecules exhibit. According to Kawase and Kurata,[41] the bowl stacking begins to appear for C$_{26}$H$_{12}$ diindenocrysene, so we may expect strong concave convex interaction for pentaindenocorannulene and corannulene. Indeed, the large contact area of pentaindenocorannulene facilitates self-assembling. It is important to note that Kawase and Kuwata[41] clarified that the concave−convex interaction is not so important for self-assembling. It is more important to have a wide contact area, and that is the case of pentaindenocorannulene; but even if corannulene and pentaindenocorannulene do not self-assemble spontaneously, the ordering can be induced performing some halogen substitution on corannulene or pentanindenocorannulene.[41]

The smallest system for which we studied the π complexation is benzene. In Figure 2, we show the structure of the complex. We fixed the geometries of pentaindenocorannulene, H$_2$, benzene, and the H$_2$−pentaindenocorannulene distance. With these constraints, we varied the benzene−H$_2$ distance until the largest interaction energy was observed. The maximum interaction was obtained at a distance of 2 Å between benzene and H$_2$, and the binding energy at the SVWN5/6-31G* level is 13.3 kcal/mol without BSSE correction. To understand the interaction in the benzene−H$_2$−pentaindenocorannulene complex, we determined the interaction energy of the benzene−pentaindenocorannulene complex without H$_2$. At the SVWN5/6-31G* level of theory the interaction energy is 8.5 kcal/mol, a value that is lowered to 5.4 kcal/mol if BSSE corrections are included. Considering the later estimation, and the assessment performed for LSDA as well as the BSSE corrections for the interaction between H$_2$−benzene (0.4 kcal/mol), H$_2$−pentaindenocorannulene (2.3 kcal/mol), and benzene−pentaindenocorannulene, we estimate that the real interaction energy is between 6 and 8 kcal/mol, which is ideal for H$_2$ sorption and desorption at ambient temperature. The later value is larger than the encapsulation energy in C$_{60}$. Thus, even if it is possible to open and close C$_{60}$ selectively to store H$_2$, the formation of the sandwich complexes seems to be more favorable. As a by product, we have estimated that the optimal interaction energy between pentaindenocorannulene and benzene is 10.5 kcal/mol without BSSE correction and 6.0 kcal/mol with BSSE correction, which corresponds to a separation of 1.75 Å between the benzene plane and the plane that contains the central pentagon of pentaindenocorannulene. We expect the real distance between benzene and pentaindenocorannulene to be longer by at least 0.3 Å because LSDA has a strong tendency to underestimate bond distances. It is important to note that higher-level calculations are mandatory to correct these raw estimations of the benzene−pentaindeno-
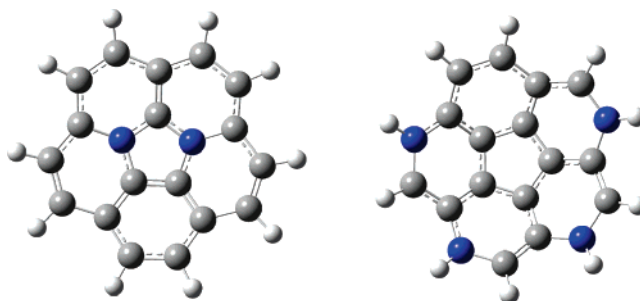
Figure 4. Top view of the N-substituted corannulenes C$_{18}$N$_2$H$_{10}$ (left) and C$_{16}$N$_4$H$_{10}$ (right).
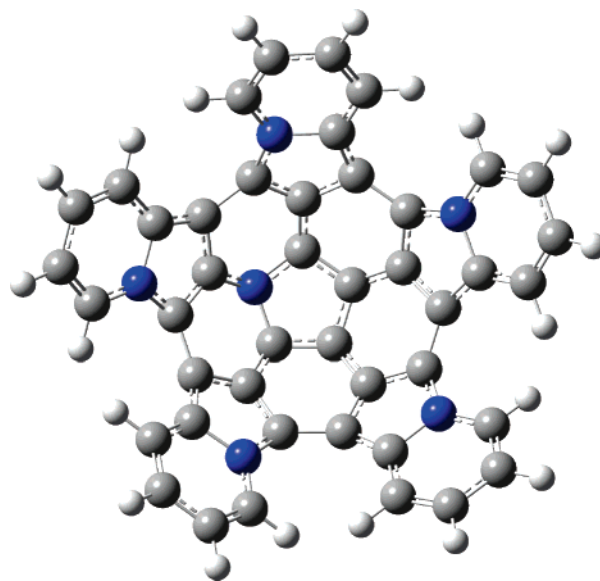
Figure 5. Top view of the N-substituted pentaindenocorannulene C$_{46}$N$_4$H$_{20}$.

corannulene interactions. The inclusion of a single H$_2$ increases the intermolecular separation by 0.2 Å, with a diminution of the interaction energy between the two π systems of about 2−3 kcal/mol, but a total energy gain of about 4−5 kcal/mol because of H$_2$ complexation.

The next system considered to cap pentaindenocorannulene is corannulene, which we present in Figure 3. The procedure to determine the interaction energy is similar to the benzene case; we optimized the corannulene−H$_2$ separation and kept the other structural parameters fixed. The optimum location of the corannulene unit is 2.75 Å above H$_2$, (5.15 Å above pentaindenocorannulene). The interaction energy is 17.4 kcal/mol at the SVWN5/6-31G* level, larger than that observed for benzene, reflecting the strong interaction between these two π systems, when the electron-rich concave side of pentaindenocorannulene interacts with the electron-poor convex side of corannulene. We expect that after BSSE (2.3 kcal/mol for pentaindenocorannulene−H$_2$, 0.52 kcal/mol for corannulene−H$_2$, corannulene−pentaindenocorannulene) and overbinding corrections, the real interaction would lie between 7 and 9 kcal/mol. Thus, the present results seem to be very promising for H$_2$ storage because the small physisorption energy of H$_2$ over carbon structures can be increased by adding the stacking interaction. It is important to note that we expect a diminution of the stacking energy due to the adsorption of H$_2$ molecules between the aromatic molecules. However, the interactions can be increased performing some halogen substitution in the polyarenes. As a by product, we have performed a raw determination of the stacking energy between pentaindenoc-

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TABLE 1: Adsorption Energies of H₂ One the Structures Investigated (kcal/mol)

system	position	E_{ads}
benzene	center	1.8
corannulene	concave, over pentagon	2.4
	convex, over pentagon	1.2
2N-corannulene[a]	concave, over pentagon	2.6
4N-corannulene[b]	concave, over pentagon	2.9
tetraindenocorannulene	concave, over central pentagon	2.9
	convex, over central pentagon	1.1
pentaindenocorannulene[c]	concave, over central pentagon	3.0
	concave, over C bonded to hydrogen	1.2
	concave, over C between 2 pentagons	1.1
	convex, over central pentagon	1.1
	convex, over CC bond between 2 pentagons	1.3
6N-pentaindenocorannulene	concave, over central pentagon	3.2
C₆₀	endohedral, center	5.4
	exohedral, over pentagon	1.0
	exohedral, over hexagon	1.2
	exohedral over 66 bond	0.9
	exohedral over 56 bond	0.9
benzene−pentaindenocorannulene	over pentagon	between 6 and 8[d]
corannulene−pentaindenocorannulene	over pentagon	between 7 and 9[e]

[a] Two carbon atoms were replaced by N atoms according to Figure 4. *[b]* Four carbon atoms were replaced by N atoms according to Figure 4. *[c]* Six carbons were replaced by N atoms according to Figure 5. *[d]* The estimated value lies between 6 and 8 kcal/mol. *[e]* The estimated value lies between 7 and 9 kcal/mol.

orannulene and corannulene. At a separation identical to that observed in the pentaindenocrannulene−H₂−corannulene complex, it is 14.4 without BSSE correction and 6.9 kcal/mol with BSSE correction, about 1 kcal/mol larger that that obtained for pentaindenocorannulene−benzene. The interaction energy is increased to 8.3 kcal/mol if the separation between both aromatic molecules is relaxed. Molecular mechanics calculations, similar to those performed on refs 22 and 40, would be desirable to shed light on this problem. A simple calculation reveals that in order to reach the 6.5 wt % storage required by the DOE 26 hydrogen molecules should be adsorbed for each pentaindeno-corannulene−corannulene pair.

3.4. Nitrogen Substitution. It is well known that an increment of the electronic density in carbon nanostructures facilitates hydrogen adsorption because the binding energies are increased. The most-recent examples include the introduction of alkali atoms or ions, such as lithium doping[40] or electrochemical methods.[42] In the present work, we considered the possibility of replacing some carbon atoms with more-electronegative elements.[43−46] The synthesis of N-substituted corannulenes has proven to be very difficult as demonstrated by Tsefrikas et al.[43] However, Sastry and co-workers,[44−46] employing theoretical calculations and homodesmic reactions, have suggested that substitutions at appropriate sites impart stability to the bucky-bowl framework. In the present work, we selected nitrogen to increase the electron density of the polyarenes because it has a size similar to that of carbon and also because of the lone pair of electrons that it has. It is important to note that it is not the focus of the present work to discuss the stability of the N-substituted bukybowls but to analyze the effect of the substitution on the adsorption energy of molecular hydrogen.[47] We substituted two and four nitrogen atoms in corannulene, as shown in Figure 5. The adsorption energies were increased 0.2 and 0.5 kcal/mol, respectively, very significant considering the small weight increment introduced by nitrogen. Preliminary calculations indicated that the interaction energy is strongly dependent on the position of the nitrogen atoms because it changes the dipole moment of the bowl. For example, the dipole moment of the 4N-substitued corannulene is 5.3 D at the PBE/6-31G* level, and that of the 2N-substitued corannulene is only 0.3 D.

Finally, we substituted six nitrogen atoms in pentaindenoc-orannulene, and the E_{ads} increased from 3.0 to 3.2 kcal/mol. Therefore, if the physicochemical properties and stability of the polyarenes are not dramatically changed by the introduction of a small number of nitrogen atoms (10% in the case of C₅₀H₂₀) then the hydrogen storage capabilities of these structures can increase significantly, in particular for corannulene. Further work is being carried out with the anions and the N-derivatives of pentaindenocorannulene, because it is very easy to introduce negatives charges in them via electrochemical methods.

4. Conclusions

We have investigated the hydrogen storage capacities of the recently synthesized tetraindenocoranulene and pentaindenoc-orannulene and compared them with those of corannulene and C₆₀. The results for the physisorption of a single H₂ on the concave side indicated that the adsorption energies (E_{ads}) for tetraindenocorannulene and pentaindenocorannulene are very similar, 2.9 and 3.0 kcal/mol, respectively. The later values are slightly larger than that estimated for corannulene, 2.4 kcal/mol, and about half of the encapsulation energy of H₂ in C₆₀, 5.4 kcal/mol. However, the E_{ads} presents fewer differences for the physisorption on the convex side. The interaction energies determined for corannulene, tetraindenocorannulene, and pen-taindenocorannulene are 1.2, 1.1, and 1.1 kcal/mol, respectively. The present results seem to be very promising for H₂ storage because the small physisorption energy of H₂ over carbon structures can be tuned by adding the stacking interaction and hydrogen bonding if terminal fluorine chlorine atoms are included. It is well known that fluorine forms very strong H bonds and that chlorine atoms increase the interaction energies between curved π systems.[41] As a by product, we estimated the complexation energies between benzene−pentaindenoc-orannulene, corannulene−pentaindenocorannulene, and pen-taindenocorannulene−pentaindenocorannulene as 6.0 and 8.3 kcal/mol respectively.

Finally, we replaced some carbon atoms in corannulene and pentaindenocorannulene with nitrogen atoms. The adsorption energies were increased 0.2 and 0.4 kcal/mol if two and four atoms are introduced in corannulene, respectively. Thus, C₁₆N₄H₁₀ has the same adsorption energy as the much larger

pentaindenocorannulene. In the case of pentaindenocorannulene, the inclusion of six nitrogen atoms (12% of carbon atoms replaced) increases the adsorption energy about 0.2 kcal/mol. The present results showed that the introduction of a small number of nitrogen atoms can increase the adsorption energy in carbon structures without increasing the weight of the material, but the increment seems to be strongly dependent on the position of the nitrogen atoms. Extensive calculations are necessary to identify the best sites for nitrogen substitution on these polyarenes.

References and Notes

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(47) The stability of the N-substituted polyarenes will be discussed in a future work that is in preparation. Preliminary PBE/6-31G* calculations indicated that all the 2N-substituted corannulenes are stable minima at the HEP and the 4N-substituted corannulene investigated in the present work is also a minimum with real frequencies.