

# Hydrogen Storage Inside a Toroidal Carbon Nanostructure C<sub>120</sub>: Density Functional Theory Computer Simulation

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Received 31 December 2009; accepted 2 March 2010

Published online 29 June 2010 in Wiley InterScience (www.interscience.wiley.com).

DOI 10.1002/qua.22711

**ABSTRACT:** Ab initio density functional calculations were performed for a toroidal carbon C<sub>120</sub> nanostructure. Hydrogen molecules,  $n = 1$ –15, were added inside the nanotorus and for each one of these systems a geometry optimization was obtained. The cohesive energy shows that these structures are energetically stable. For example, the binding energies are  $-34.95$  and  $-36.19$  Hartrees and the interatomic distances H–H are 0.753 and 0.772 Å for 1 and 14 molecules, respectively. Considering only molecular hydrogen, we have always seen so far weak physisorption into the C<sub>120</sub> nanotorus. There is no chemisorption until the number of hydrogen molecules are increased to 14. In this case, four hydrogen atoms are chemisorbed. With 15 molecules, there are 10 hydrogen atoms chemisorbed just at the inner nanotorus surface forming 10 H–C bondings with bond length close to that in methane. © 2010 Wiley Periodicals, Inc. *Int J Quantum Chem* 110: 2495–2508, 2010

**Key words:** hydrogen storage; DFT calculations; toroidal carbon nanostructure

## 1. Introduction

At the beginning of the 90's, a new carbon nanostructure with a toroidal shape was

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Contract grant sponsor: CONACyT.

Contract grant numbers: 25218, 57262.

proposed theoretically by Dunlap [1]. The geometry and topology of this new carbon form, also called nanotorus, was created from dangling bonds in a carbon nanotube. Carbon nanostructures and graphene materials are under study for nanoscale device applications. In this work, we study the C<sub>120</sub> nanotorus species, mainly as a hydrogen storage system. Besides the inherent hydrogen storage problems, the community looks

with effort for novel forms of H<sub>2</sub> storage. This interest is because hydrogen is a clean energy source and will play an important role to reduce the world consumption of hydrocarbons. Metal hydrides allow a greater hydrogen storage respect to other storage forms, such as compressed gas and liquefaction. Nanofibers materials constitute other possibilities under experimental and theoretical study. To our knowledge, this is the first time that a nanotorus is explored as a hydrogen storage system.

The nanotorus composed by 120 carbon atoms was built from 12 inequivalent carbon atoms as described by Ihara and coworkers [2]. We describe results as total and binding energies, electronic charge density, Mulliken population analysis and highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) energy gaps. The initial dimensions of the relaxed C<sub>120</sub> nanotorus are 4.159 and 11.740 Å for the inner and outer diameters, respectively. A transversal section of the nanotorus is close to a circle with diameter 4.623 Å. Adding hydrogen molecules inside the nanotorus cage causes the outer diameter to increase slightly, whereas the inner diameter decreases.

Some theoretical studies showed that this nanotorus may exhibit lower cohesive energy than fullerene C<sub>60</sub> so that both structures are considered as thermodynamically stable [3, 4]. On the other hand, Cho and Park [5] investigated the hydrogen storage behavior of Li-doped single-walled carbon nanotubes by means of density functional theory (DFT-) based calculations. Through Li-doping, it was found that two new adsorption sites for hydrogen molecule are created in addition to the inherent three adsorptive sites.

Lemi Türker and coworkers [6–8] studied the hydrogen storage on carbon nanotubes for the M@C<sub>120</sub> system, where M = (Be, Mg, and Se), with PM3 (RHF) type semiempirical quantum chemical calculations. The results indicate that all these systems are stable but endothermic in nature.

In this work, we present results of a DFT computational study of a C<sub>120</sub> carbon nanotorus, using Dmol<sup>3</sup> code [9, 10] as implemented in the Materials Studio package [11]. First of all, we analyzed the stability of the isolated C<sub>120</sub> nanotorus and also for each one of the *n*H<sub>2</sub>@C<sub>120</sub> systems with *n* = 1–15. As it occurs for carbon nanotubes, the nanotorus also has a peculiar texture and a large specific surface area. This characteristic suggested us to study the adsorption and storage of H<sub>2</sub> for this

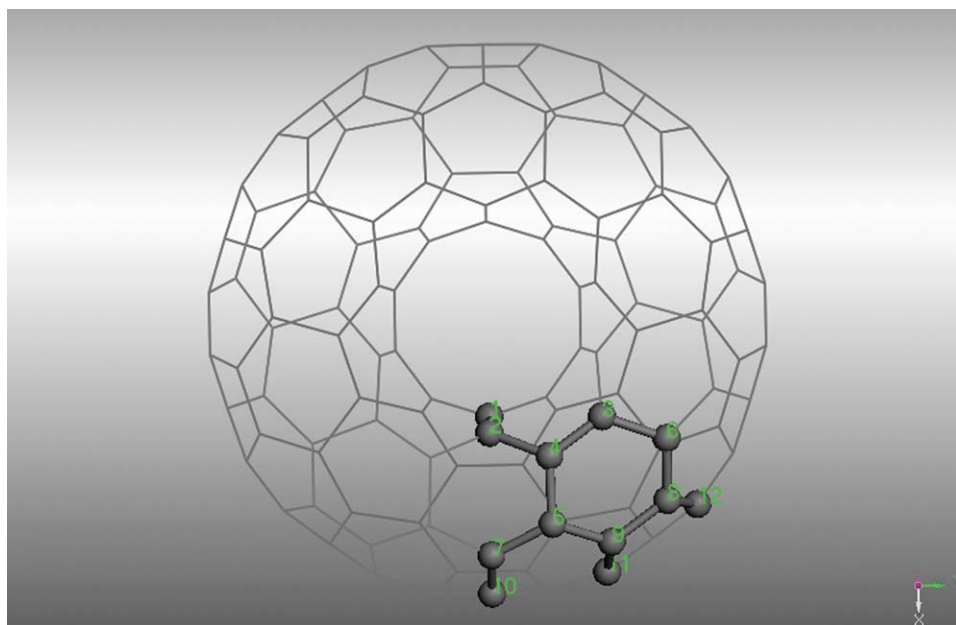
system. It is believed that carbon nanostructures, such as nanotubes and nanotorus will be widely used in technological new developments.

## 2. Method

To build the nanotorus we used the initial structure with only 12 carbon atoms, proposed by Ihara and coworkers [2]. The coordinates of the 120 carbon atoms of the nanotorus were obtained by successive five-fold rotations of this set of 12 atoms followed by a reflection and final rotation of  $\pi/5$  radians. The optimized structure for the nanotorus is shown in Figure 1. The numbers 1–12 identify the twelve initial carbon atoms. The generated structure is composed by 10 pentagonal, 40 hexagonal, and 10 heptagonal rings [12]. Five- and six-member rings on the nanotorus surface meet the isolated pentagon rule [13, 14]: “no two pentagons can touch, but are always surrounded by hexagons.” Panel a, b, and c in Figure 2 show, respectively, those rings.

The generalized gradient approximation of DFT, as proposed by Perdew and Wang (PW91) was used [15], just as implemented in the Materials Studio v.4.3 code. The Dmol<sup>3</sup> module was used to calculate, among others, total and binding energies, electronic charge density, HOMO–LUMO, and Mulliken population analysis. To calculate the interaction energies of the hydrogen molecules with the C<sub>120</sub> nanotorus, the DFT is complemented with a double numerical plus polarization basis set, (DNP). For occupied orbitals, two atomic orbitals are considered in the basis set. For C and H atoms polarization, *d*-function and *p*-function are used, respectively. The employed basis set has the advantage to be equivalent to the analytical basis set 6-31G\*\*. For the orbital cut-off distance and energy convergence, 4.3 Å and 10<sup>–5</sup> Ha were enough to obtain accurate results. Real frequencies were obtained for the isolated nanotorus. Once we could see this result, the hydrogen storage in the system was studied.

Table I contains the type of ring (pentagonal, hexagonal or heptagonal) for a pair of carbon atoms identified by their labels. For example, carbon atoms labeled 27 and 78 are neighbors in a pentagonal ring and the respective bond length is 1.458 Å, with a Mulliken bond order of 0.875, which makes difficult to assign either single or double bond character. As a reference, we have taken those characteristic values for the ethane



**FIGURE 1.** Optimized geometry of C<sub>120</sub> nanotorus. The numbers 1–12 identify the 12 initial carbon atoms. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

and ethene molecules, both, bond lengths and Mulliken bond orders. The C–C bond lengths are 1.523 and 1.369, for single and double bond, while Mulliken bond orders are 1.050 and 0.742, respectively. The average bond lengths are 1.460, 1.452, and 1.447 Å for the pentagonal, hexagonal and heptagonal rings, respectively.

Table II contains, for the pentagonal, hexagonal and heptagonal rings, the angle formed by three adjacent carbon atoms. For example, for atoms 27, 78, and 74, the angle is 105.7°. In a similar way as for the bond length, the average angle for each type of ring, pentagonal, hexagonal and heptagonal, is 107.4°, 119.1°, and 120.0°, respectively.

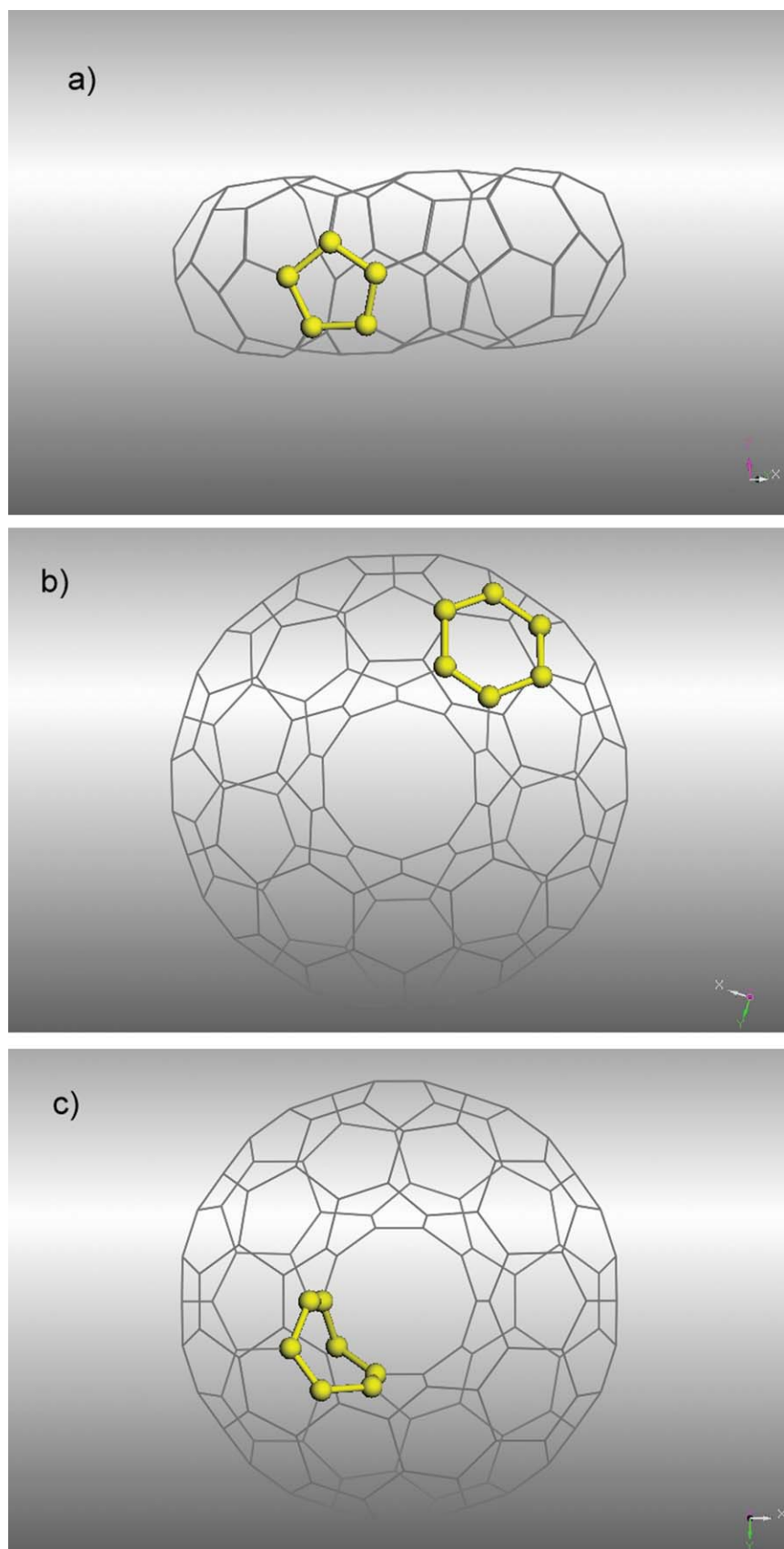
With the optimized C<sub>120</sub> nanotorus,  $n$  hydrogen molecules,  $n = 1$ –15, were added consecutively along a trajectory equidistant to all points around the inner surface of the nanotorus. The distance between adjacent hydrogen molecules was close to 1.2 Å. Then, optimization for that number  $n$  of molecules was done. In this way the final system contains fifteen hydrogen molecules.

### 3. Results

Once the energy  $-4573.616393$  Ha was obtained for the isolated and optimized C<sub>120</sub> nanoto-

rus, we begin the hydrogen adsorption study placing one hydrogen molecule inside the nanotorus in two different orientations, parallel and perpendicular to a nanotours radius axis. Optimizations for both initial configurations ended with the same final energy and orientation for the hydrogen molecule. The final configuration for 13, 14, and 15 hydrogen molecules are shown in Figures 3, 4, and 5, respectively. At the end of a geometry optimization, all the hydrogen molecules are nearly uniformly distributed and aligned along a trajectory equidistant to all points around the inner surface of the nanotorus.

The total and binding energies for the  $n\text{H}_2@\text{C}_{120}$  system are listed in columns 2 and 4 of Table III. Each row of the third column of Table III gives the energy difference for the system with  $n$  and  $n + 1$  hydrogen molecules. For example, the energy  $-1.1156$  Ha, corresponds to the energy difference for the systems with one and two H<sub>2</sub> molecules inside the nanotorus. The energy difference values changes slightly with  $n$ . The differences, between the pairs (13, 14) and (14, 15) are  $-1.0794$  and  $-1.1955$  Ha, respectively. The last value is even greater than for the isolated hydrogen molecule. As expected, that difference for the energy does not match with the energy for only one hydrogen molecule,  $-1.1691$  Ha, because the hydrogen molecules are not isolated, that is,



**FIGURE 2.** C<sub>120</sub>-optimized nanotorus system. The structure contains five-fold, six-fold, and seven-fold rings. Panel a, b, and c show, respectively, those rings. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

**TABLE I**  
**C—C bond lengths (Å) and Mulliken bond orders for pentagonal, hexagonal and heptagonal rings in the optimized C<sub>120</sub> nanotorus.**

C—C Atom label and ring-type			C—C bond lengths (Angstroms) and Mulliken bond orders		
Pentagon	Hexagon	Heptagon	Pentagon	Hexagon	Heptagon
27-78	33-35	91-104	1.458	1.457	1.440
			0.875	0.867	0.891
78-74	35-36	104-105	1.458	1.470	1.463
			0.846	0.917	0.814
74-75	36-32	105-92	1.470	1.458	1.417
			0.917	0.866	0.959
75-77	32-31	92-80	1.458	1.454	1.462
			0.845	0.813	0.811
77-27	31-30	80-79	1.457	1.417	1.439
			0.874	0.962	0.894
	30-33	79-40		1.454	1.456
				0.816	0.806
		40-91			1.456
					0.807
Average bond lengths			1.460	1.452	1.447

10 hydrogen atoms are adsorbed on the nanotorus for the 15H<sub>2</sub>@C<sub>120</sub> system. On the contrary, the obtained energies show both the interaction between hydrogen molecules themselves and with the carbon atoms of the nanotorus, changing in this way the binding energies. To compare those energies, we have also calculated the H<sub>2</sub>—H<sub>2</sub> and H<sub>2</sub>—C<sub>120</sub> repulsive energies as a function of the number of hydrogen molecules. The results are discussed ahead.

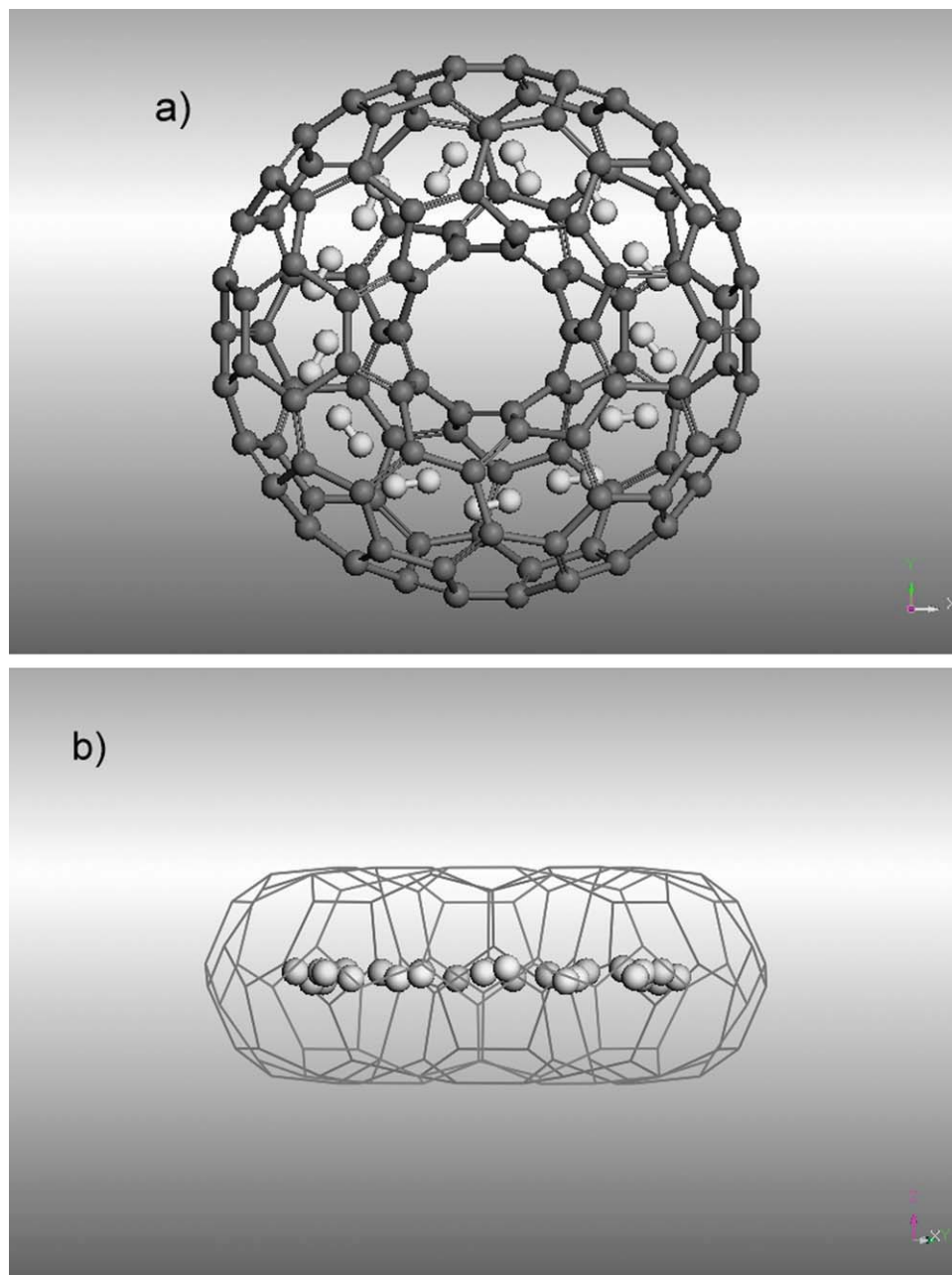
The H—H average distance (Å), average distance between adjacent H<sub>2</sub> molecules (Å), outer and inner diameter (Å) of the C<sub>120</sub> nanotorus with

$n = 1$ –15 hydrogen molecules are given in Table IV. It can be appreciated that the H—H bond length increases slightly from 0.753 to 0.772 Å, for  $n = 1$  and 14, respectively. In the final configuration for 15 hydrogen molecules, five of them are dissociated and the H—H distance is reduced up to 0.760 Å. The hydrogen atoms from H<sub>2</sub> dissociation form C—H bonds in the inner nanotorus surface.

In a similar way, the distance between adjacent H<sub>2</sub> molecules, 1.784 Å, for  $n = 2$ , is reduced to 1.286 Å, for  $n = 13$ . On the contrary, that distance is now increased to 1.516 Å, for  $n = 14$ , and

**TABLE II**  
**Angle (degrees), formed by three adjacent carbon atoms for the pentagonal, hexagonal and heptagonal rings in the optimized C<sub>120</sub> nanotorus.**

C—C—C Atom labels and ring type			Angle (degree)		
Pentagon	Hexagon	Heptagon	Pentagon	Hexagon	Heptagon
27-78-74	33-35-36	91-104-105	105.7	122.8	118.4
78-74-75	35-36-32	104-105-92	108.1	122.7	119.1
74-75-77	36-32-31	105-92-80	108.1	110.4	119.1
75-77-27	32-31-30	92-80-79	105.7	124.0	118.2
77-27-78	31-30-33	80-79-40	109.0	124.2	118.2
	30-33-35	79-40-91		110.4	123.7
		40-91-104			123.6
Average angle			107.4	119.1	120.0



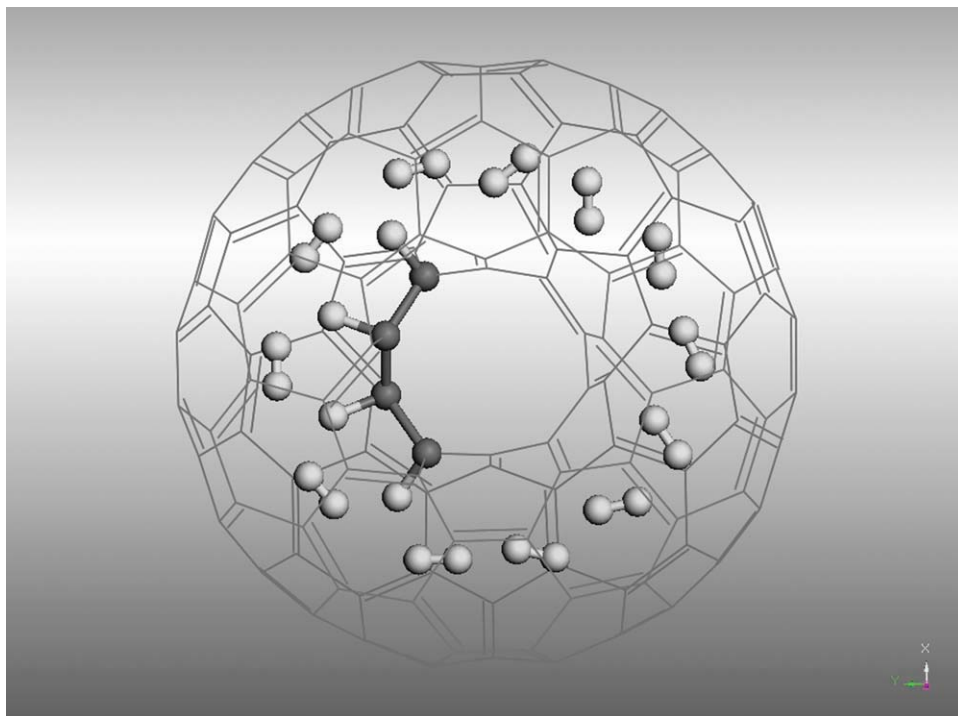
**FIGURE 3.** Panel a: Optimized geometry for 13 hydrogen molecules inside the  $C_{120}$  nanotorus. Panel b: Optimized geometry for 13 hydrogen molecules inside the  $C_{120}$  nanotorus. All the hydrogen molecules are on the middle plane of the nanotorus. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

1.849 Å, for  $n = 15$ . This behavior is because there are only 12 hydrogen molecules instead of 14. Two of them have been dissociated forming four C—H bonds. Correspondingly, five of the 15 molecules are dissociated yielding 10 C—H bonds and 10 nearly free hydrogen molecules. The average bond length C—H for both cases is 1.127 Å.

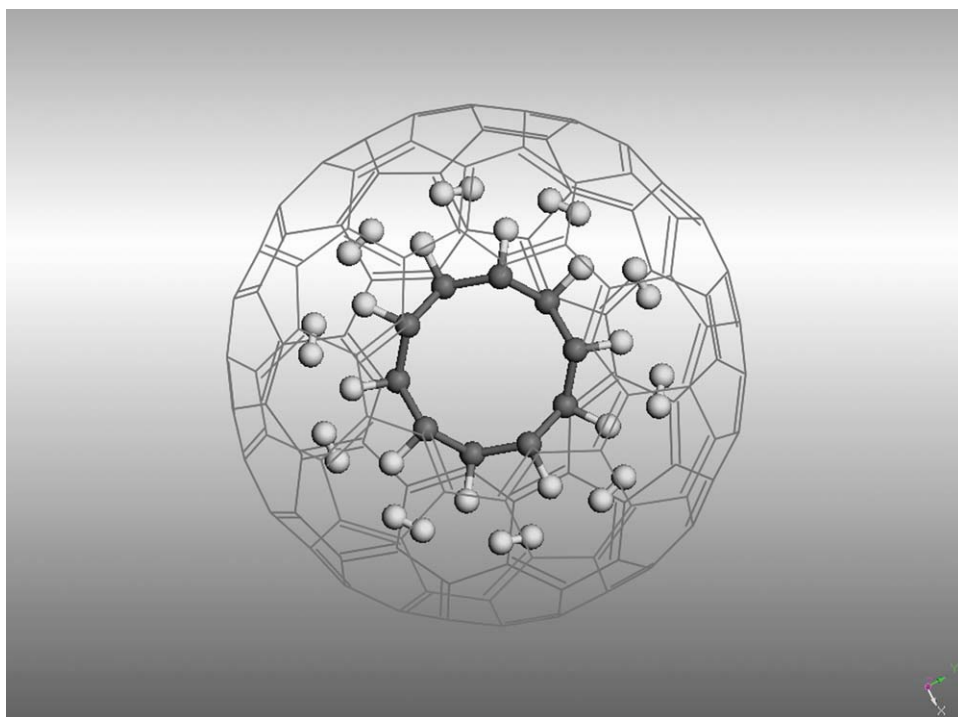
This value is close to the C—H bond length for the free methane molecule, 1.101 Å, determined from the same theoretical DFT approach.

The outer diameter of the  $nH_2@C_{120}$  system also increases from 11.856 Å for  $n = 1$  to 12.054 Å for  $n = 13$ . The diameters are 12.039 Å for  $n = 14$  and 12.060 Å for  $n = 15$ . This later value is a little





**FIGURE 4.** For the initially 14 H<sub>2</sub> molecules, this equilibrium configuration shows 12 molecules and two more dissociated yielding four C—H bonds. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**FIGURE 5.** For the initially 15 H<sub>2</sub> molecules, this equilibrium configuration shows 10 molecules and five more dissociated yielding 10 C—H bonds. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

**TABLE III**

**Total and binding energy (Hartrees) for the  $n\text{H}_2@\text{C}_{120}$  system, where  $n = 1-15$ , is the number of hydrogen molecules inside the nanotorus. The binding energy is the energy required to separate the individual atoms. All the binding energies in this table were calculated without the zero point energy correction.**

Number of $\text{H}_2$ molecules ( $n$ )	Total Energy (Ha)	$\Delta E$ (Ha)	Binding Energy (Ha)	$\Delta E$ (Ha)
0	-4573.616393		-34.834439	
1	-4574.731332	-1.1149	-34.948051	-0.1136
2	-4575.846976	-1.1156	-35.062368	-0.1143
3	-4576.961275	-1.1143	-35.175341	-0.1130
4	-4578.074100	-1.1128	-35.286840	-0.1115
5	-4579.185992	-1.1119	-35.397405	-0.1106
6	-4580.297870	-1.1119	-35.507956	-0.1106
7	-4581.409692	-1.1118	-35.618452	-0.1105
8	-4582.519339	-1.1096	-35.726772	-0.1083
9	-4583.627309	-1.1080	-35.833415	-0.1066
10	-4584.736371	-1.1091	-35.941150	-0.1077
11	-4585.776526	-1.0402	-35.979979	-0.0388
12	-4586.852112	-1.0756	-36.054239	-0.0743
13	-4587.907350	-1.0552	-36.108150	-0.0539
14	-4588.986713	-1.0794	-36.186186	-0.0780
15	-4590.182198	-1.1955	-36.380344	-0.1941

bit greater because there exists six additional C—H bonds for  $n = 15$  in comparison with  $n = 14$  case. Simultaneously, the inner diameter diminishes from 4.237 to 4.025 Å, whereas  $n$  changes from 1 to 13. The inner diameter is 4.079 Å for  $n = 14$ .

The gradual increase in the H—H bond length is due to the particular arrangement of the hydrogen molecules while increasing its number. Each time, the axes of all of the hydrogen molecules are reoriented in a way that allows the insertion of another one. Because of the number of

**TABLE IV**

**H—H average distance, average distance between adjacent  $\text{H}_2$  molecules, and outer and inner diameter of the  $\text{C}_{120}$  nanotorus with  $n$  hydrogen molecules. H—H = 0.755 (Å) for the isolated hydrogen molecule.**

Number of $\text{H}_2$ molecules ( $n$ )	H—H average distance (Å)	Average distance between adjacent $\text{H}_2$ molecules (Å)	Outer diameter (Å)	Inner diameter (Å)
0			11.740	4.159
1	0.753		11.856	4.237
2	0.756	1.784	11.877	4.296
3	0.758	1.681	11.874	4.280
4	0.758	1.662	11.873	4.238
5	0.760	1.621	11.879	4.096
6	0.761	1.648	11.939	4.148
7	0.760	1.668	11.949	4.224
8	0.764	1.679	11.961	4.273
9	0.766	1.659	11.966	4.274
10	0.765	1.710	11.967	4.004
11	0.766	1.477	12.003	3.965
12	0.770	1.340	12.043	4.012
13	0.770	1.286	12.054	4.025
14	0.772	1.516	12.039	4.079
15	0.760	1.849	12.060	4.201



**TABLE V**  
**HOMO-LUMO energies and energy gap for the  $n\text{H}_2@\text{C}_{120}$  system,  $n = 1\text{--}15$ .**

Number of H <sub>2</sub> molecules ( $n$ )	HOMO (eV)	LUMO (eV)	$\Delta E$ (eV)
0	-5.29	-4.22	1.07
1	-5.19	-4.24	0.95
2	-5.13	-4.27	0.86
3	-5.10	-4.30	0.80
4	-5.12	-4.33	0.79
5	-5.12	-4.36	0.76
6	-5.13	-4.41	0.72
7	-5.15	-4.44	0.70
8	-5.13	-4.48	0.65
9	-5.11	-4.49	0.62
10	-5.19	-4.52	0.67
11	-5.23	-4.52	0.71
12	-5.08	-4.57	0.52
13	-5.07	-4.61	0.46
14	-4.89	-4.77	0.12
15	-4.95	-4.75	0.20

hydrogen molecules increases, there is naturally a reduction in the distance between adjacent hydrogen molecules. The larger the number of hydrogen molecules also accounts for the simultaneous increase and reduction of the outer and inner diameter of the nanotorus, respectively. This general behavior is appreciated in the quantities given in Table IV. The exception for the cases  $n = 14, 15$  is because of the C–H covalent bonding as explained before.

It is well known that for large numbers of encapsulated hydrogen atoms, some of them become chemisorbed on the inner surface of the cage [16].

It has been seen that for the structures with  $n = 14$  and 15 hydrogen molecules, some hydrogen atoms form covalent bonds with the carbons of the nanotorus, as one can see from Figures 4 and 5. This agrees with the results of Koi and Oku [17, 18] and Dodziuk [19].

HOMO–LUMO and Mulliken population analysis were obtained simultaneously for each one of the  $n\text{H}_2@\text{C}_{120}$  systems for  $n = 1\text{--}15$ . Although increasing the number of hydrogen molecules, a reduction could be seen in the HOMO–LUMO energy gap until  $n = 14$ . The values are enlisted in Table V.

The spatial HOMO–LUMO distributions for the  $n\text{H}_2@\text{C}_{120}$  system with  $n = 13, 14$ , and 15 are shown correspondingly in Figures 6–8. There are

four and 10 C–H bonds for  $n = 14$  and 15 respectively; when compared with the  $n = 13$  case, where there is no C–H bond formation. Blue lobes show the positive and yellow lobes show the negative values of the wave function. The HOMO–LUMO isosurfaces plot suggests that C<sub>120</sub> nanotorus present wide regions of highest chemical reactivity.

The plot in Figure 8 demonstrates how the HOMO orbital is mainly localized at the C–H bonds.

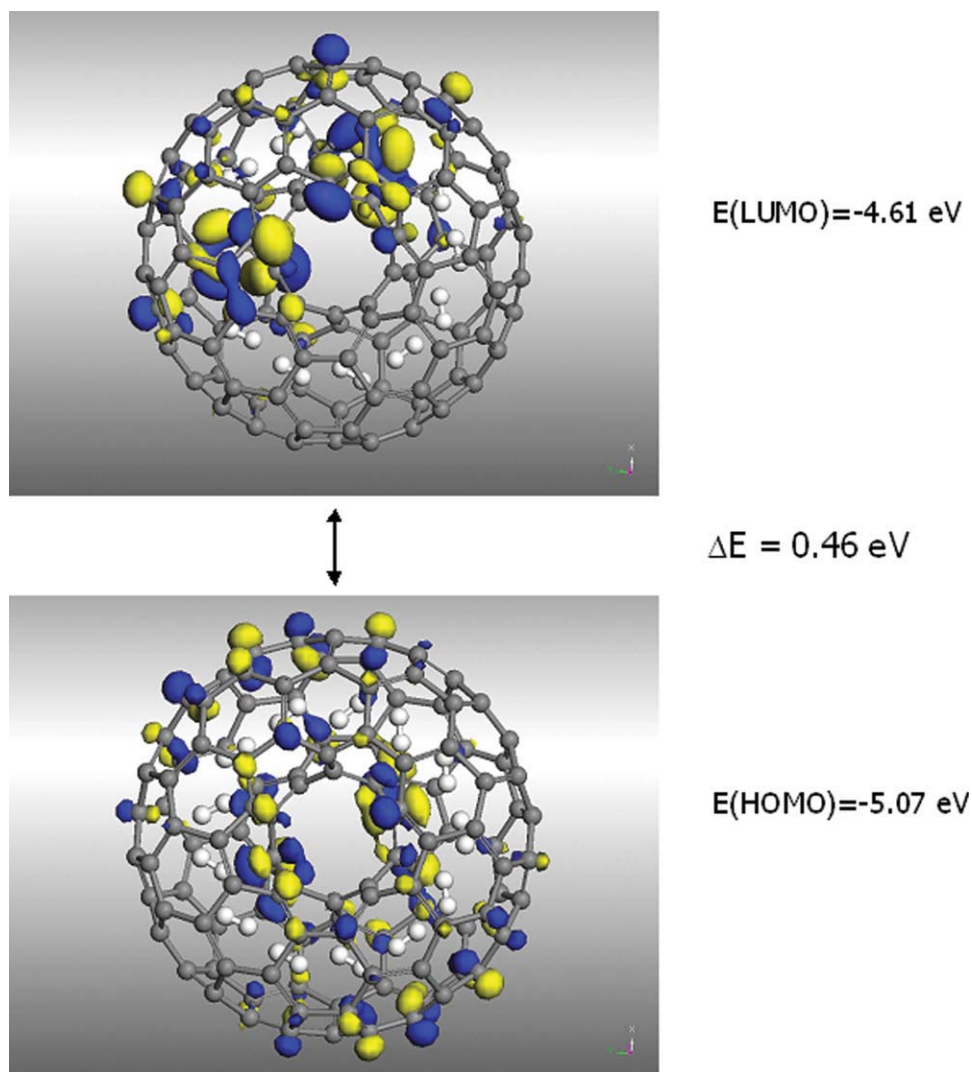
Without hydrogen molecules, the HOMO and LUMO energies are  $-5.29$  and  $-4.22$  eV, respectively, so that the pristine nanotorus exhibits a band gap of 1.07 eV. For comparison, Lusk and Hamm [20] have reported that the HOMO–LUMO gap of the C<sub>120</sub> nanotorus, 0.91 eV, is significantly smaller than the one, 1.5 eV, for fullerene (C<sub>60</sub>), signifying an increased reactivity for the nanotorus. We also obtained the same value, 1.5 eV, for the fullerene C<sub>60</sub>. Our results suggest that C<sub>120</sub> nanotorus and fullerene C<sub>60</sub> share roughly the same chemical reactivity.

The binding energy per atom or cohesive energy is obtained as  $-7.90$  eV for the C<sub>120</sub> nanotorus. As a point of comparison, we note that DFT calculations, done by Saito and Oshiyama [21], find a cohesive energy of  $-7.40$  eV for fullerene C<sub>60</sub>, using the LDA approach with the parameterized Ceperly–Alder potential. Our estimation for the binding energy for that fullerene is  $-7.99$  eV. A difference of 0.59 eV is obtained with respect to that of Saito and Oshiyama, mainly coming from the different DFT approaches. This means there is an agreement for the binding energy, independently of the number of the carbon atoms of the system, 60 or 120 for the fullerene or the nanotorus. A comparison of the DFT values for C<sub>120</sub> nanotorus and fullerene C<sub>60</sub> is a good indication of the relative stability of the two structures.

We have also calculated the average hydrogen binding energy  $E_b$ , defined as [22]:

$$E_b = (E_{\text{C}_{120}-n\text{H}_2} - E_{\text{C}_{120}} - N_{\text{H}}E_{\text{H}})/N_{\text{H}} \quad (1)$$

where  $N_{\text{H}}$  is the number of hydrogen atoms physisorbed inside the nanotorus.  $E_{\text{C}_{120}-n\text{H}_2}$  and  $E_{\text{C}_{120}}$  are the total energies of the hydrogenated nanotorus and corresponding pure C<sub>120</sub> nanotorus, respectively.  $E_{\text{H}}$  is the energy of an isolated hydrogen atom. Plot of this hydrogen binding energy,  $E_b$ , as a function of hydrogen atoms physisorbed inside the nanotorus is shown in Figure 9.



**FIGURE 6.** HOMO–LUMO for the  $n\text{H}_2@\text{C}_{120}$  system,  $n = 13$ . [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

It should be noted that according to the definition given in Eq. (1), the binding energy will be negative if the system is stable. The hydrogen binding energy for the nanotorus is observed to decrease in magnitude with increasing number of hydrogen atoms.

The experimental value for the binding energy of one H–H bond is of  $-4.51 \text{ eV}$ ; our calculated result for this energy  $-4.54 \text{ eV}$ , which is in excellent agreement.

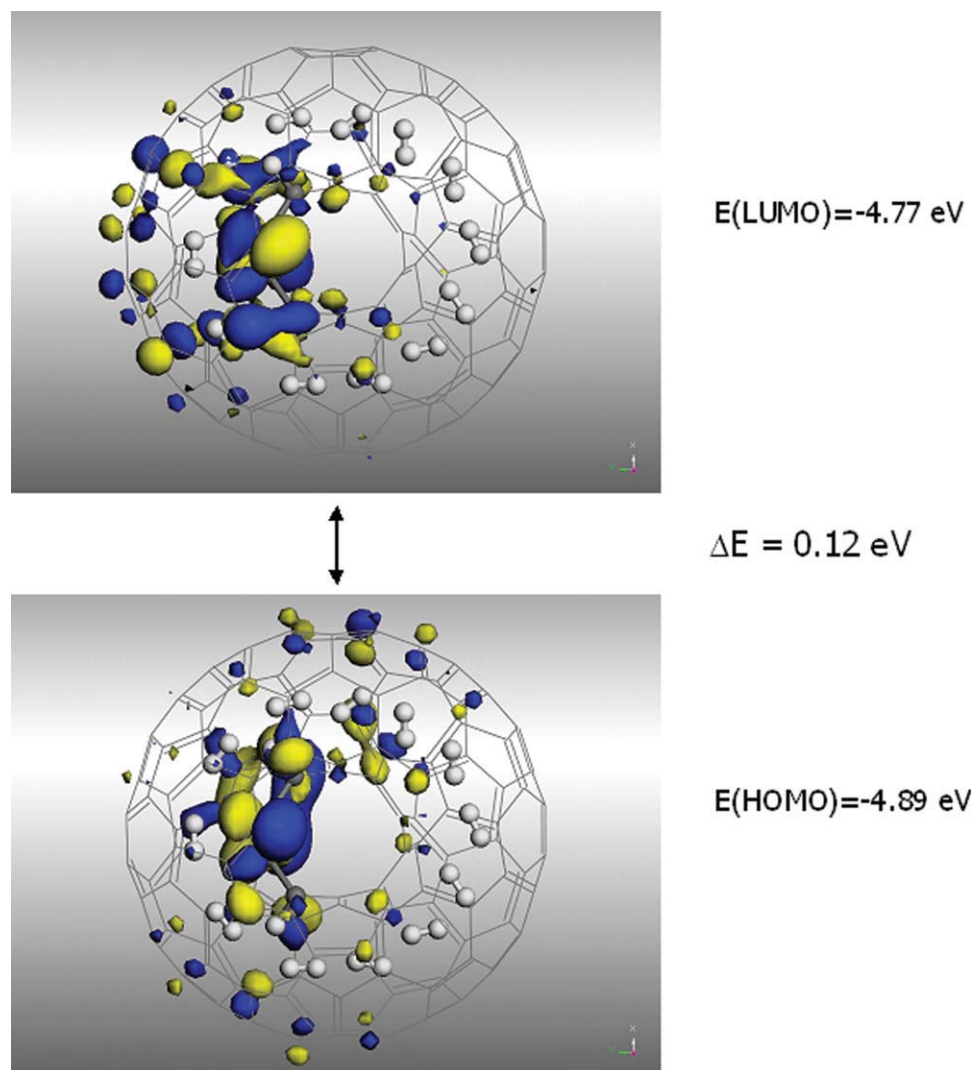
The binding energy  $E_b$  of the  $\text{H}_2$  molecule inside the nanotorus, as given by Eq. (1), is reduced by about  $2 \text{ eV}$ , compared with that of a gaseous  $\text{H}_2$  molecule. This is due to the repulsive forces between  $\text{H}_2$  molecules and between the

nanotorus wall and the  $\text{H}_2$  molecules, which in turn limit the maximum  $\text{H}_2$  storage capacity. Therefore, We calculated the corresponding  $\text{H}_2\text{--H}_2$  and  $\text{H}_2\text{--C}_{120}$  average repulsive energies given in Refs. 23, 24.

$$E_{\text{rep}}(\text{H}_2\text{--H}_2) = (E_{\text{total}}(\text{H}_n) - N_{\text{H}_2}E_{\text{H}_2})/N_{\text{H}_2} \quad (2)$$

and

$$E_{\text{rep}}(\text{H}_2\text{--C}_{120}) = (E_{\text{total}}(\text{H}_2\text{--C}_{120}) - E_{\text{total}}(\text{H}_n) - E_{\text{C}_{120}})/N_{\text{H}_2} \quad (3)$$



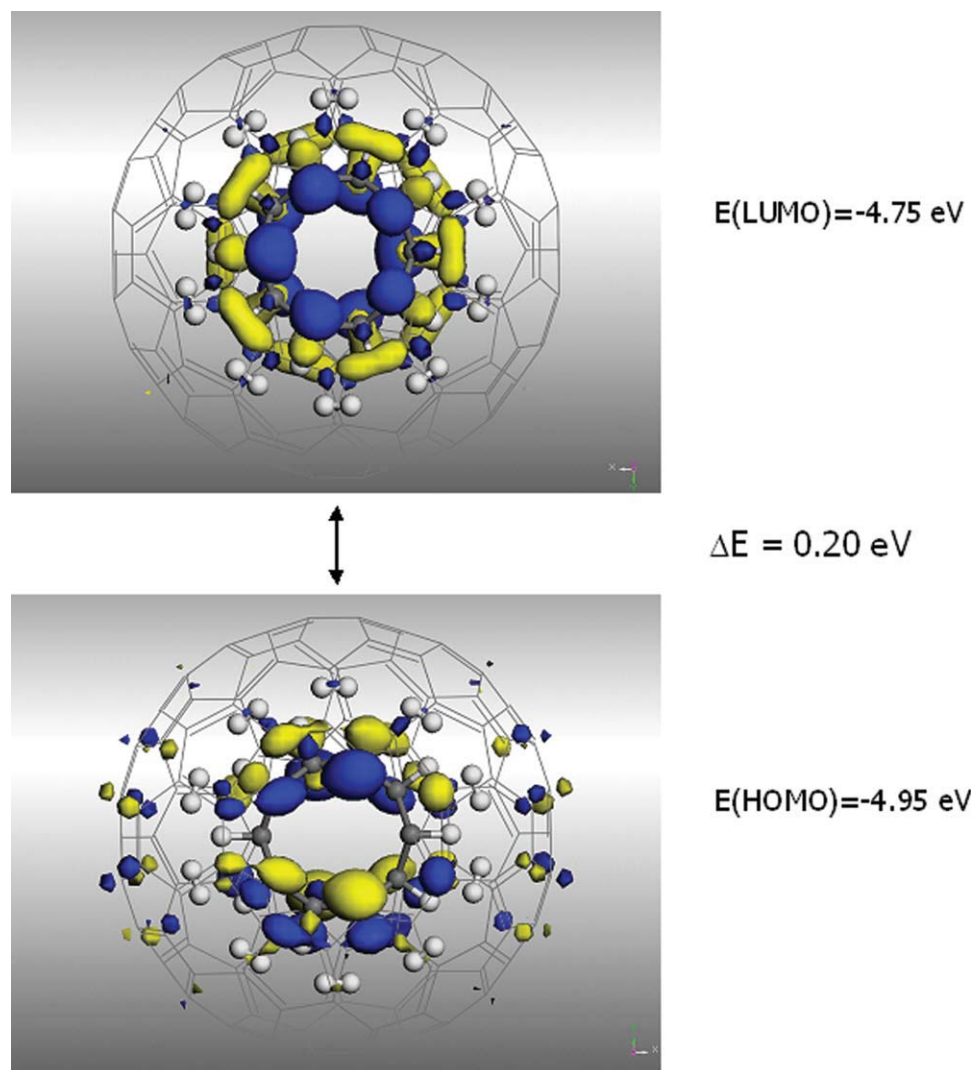
**FIGURE 7.** HOMO–LUMO for the  $n\text{H}_2@\text{C}_{120}$  system,  $n = 14$ . [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

where  $E_{\text{total}}(\text{H}_n)$  is the total energy of only the  $n$  hydrogen atoms in their final and equilibrium configuration in the entire system  $n\text{H}_2@\text{C}_{120}$ , that is, only the hydrogen atoms are considered at the equilibrium conformation of the molecular complex, for the calculation of this value in each system.  $E_{\text{H}_2}$  is the energy of a single  $\text{H}_2$  molecule encapsulated inside the  $\text{C}_{120}$  nanotorus, and  $E_{\text{C}_{120}}$  is the total energy of the  $\text{C}_{120}$  nanotorus alone.  $N_{\text{H}_2}$  is the total number of hydrogen molecules in the system, and  $E_{\text{total}}(\text{H}_2-\text{C}_{120})$  is the total energy of the system with  $N_{\text{H}_2}$  encapsulated hydrogen molecules.

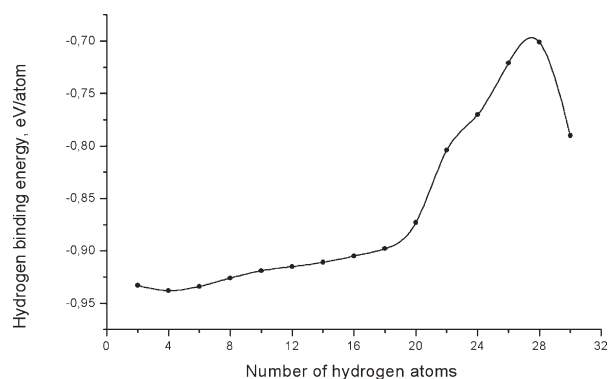
Figure 10 shows variation of  $\text{H}_2-\text{H}_2$  and  $\text{H}_2-\text{C}_{120}$  average repulsive energies with the number of  $\text{H}_2$  molecules confined inside  $\text{C}_{120}$ . The repulsive  $\text{H}_2-\text{H}_2$

energy is positive indicating repulsion between the 15  $\text{H}_2$  molecules, consistent with the results of Barajas-Barraza et al. [23], who showed that no negative repulsive energy between the  $\text{H}_2$  was observed at low uptake. As can be seen there is a pronounced change in the energy behavior as the number of hydrogen molecules is increased beyond  $n = 13$ .

The  $E_{\text{rep}}(\text{H}_2-\text{C}_{120})$  increases slightly until  $n = 10$   $\text{H}_2$  molecules. The increase is larger above 11 and even more so for 14 molecules. For  $n = 15$  molecules this energy is reduced; this is explained by the presence of 10 C–H bonds, and only 10 hydrogen molecules inside the nanotorus. The mean distance between adjacent  $\text{H}_2$  molecules is increased to 1.849 Å. Besides this, there is a weak



**FIGURE 8.** HOMO–LUMO for the  $n\text{H}_2@\text{C}_{120}$  system,  $n = 15$ . [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



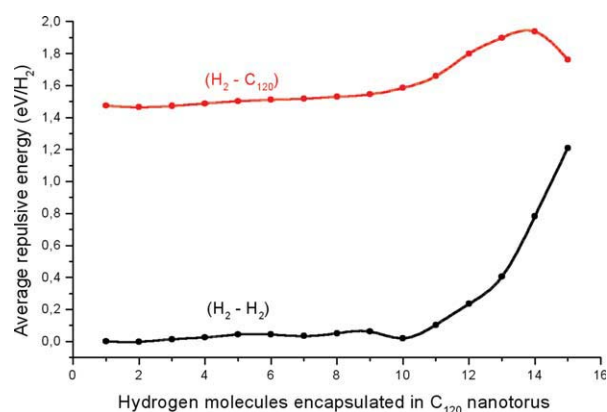
**FIGURE 9.** Hydrogen binding energy (eV/atom), for the  $n\text{H}_2@\text{C}_{120}$  system, as a function of the number of hydrogen atoms.

interaction between the 10 hydrogen atoms and the remaining 10  $\text{H}_2$  molecules. The average distance of one hydrogen molecule to the nearest hydrogen atom of the C–H bond is  $1.26 \text{ \AA}$ .

The charge density analysis has been done with the computer code AIM2000 v 1.0 [25]. For the middle point between the hydrogen atom of one C–H bond and the closer hydrogen molecule, the charge density is  $0.06 \text{ e}$ . In a similar way, the results are respectively  $0.28$ ,  $0.27$ , and  $0.26 \text{ e}$  for C–C, C–H, and  $\text{H}_2\text{--H}_2$  bonds.

Dmol<sup>3</sup> also allows the calculation of the Mulliken populations for all the studied systems. The Mulliken charges on the C atom and  $\text{H}_2$  molecules are shown in Table VI.





**FIGURE 10.** Variation of H<sub>2</sub>–H<sub>2</sub> and H<sub>2</sub>–C<sub>120</sub> average repulsive energies with the number of H<sub>2</sub> molecules confined inside the C<sub>120</sub> nanotorus. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

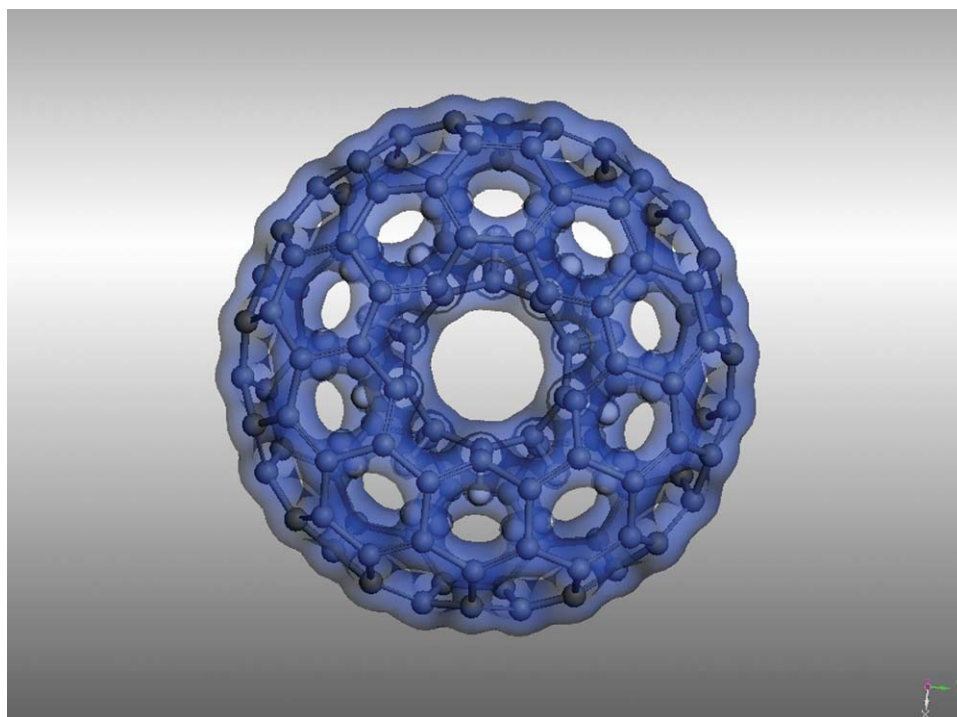
Mulliken charge analysis shows electron transfer occurs from the H<sub>2</sub> molecules to the nanotorus for all the systems. The average charge transfer to the carbon atoms increases with the number of hydrogen molecules. For only one hydrogen mol-

**TABLE VI**  
Average Mulliken charges of C atoms and encapsulated H<sub>2</sub> molecules.

Number of H <sub>2</sub> molecules ( <i>n</i> )	Average Mulliken charge (e)	
	C atoms	H atoms
1	–0.0004	0.0235
2	–0.0007	0.0235
3	–0.0013	0.0268
4	–0.0020	0.0299
5	–0.0026	0.0323
6	–0.0033	0.0335
7	–0.0037	0.0324
8	–0.0049	0.0370
9	–0.0058	0.0393
10	–0.0060	0.0360
11	–0.0064	0.0353
12	–0.0076	0.0381
13	–0.0094	0.0435
14	–0.0157	0.0673
15	–0.0191	0.0763

ecule the C atom gains 0.0004 e. For 15 H<sub>2</sub> molecules the charge becomes 0.0191 e.

The total charge density for the system with 15 H<sub>2</sub> molecules is shown in Figure 11. The final



**FIGURE 11.** Top view of the calculated total charge density of 15 H<sub>2</sub> molecules inside the C<sub>120</sub> nanotorus. The gray and dark-gray atoms are H and C, respectively. (Blue color isovalue = 0.748). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

equilibrium configuration for this case has a high symmetry distribution for all the atoms and in the charge density as well.

#### 4. Conclusions

By means of theoretical studies, the geometry optimization of all the systems  $n\text{H}_2@\text{C}_{120}$  with  $n = 1\text{--}15$ , were calculated. Among others, charge densities, HOMO–LUMO gap, Mulliken population analysis, binding and repulsive energies were discussed. The binding energy was calculated as function of the number of hydrogen atoms. It is found that for  $n = 14, 15$ , some hydrogen atoms can be chemisorbed on the inner surface of the carbon nanotorus; that is, they can form covalent C–H bonds. The variation for the average  $\text{H}_2\text{--H}_2$  and  $\text{H}_2\text{--C}_{120}$  repulsive energies with the number of  $\text{H}_2$  molecules confined inside the  $\text{C}_{120}$  nanotorus was calculated and discussed. All these results let us to conclude that hydrogen storage is possible in the  $\text{C}_{120}$  nanotorus, reaching up to now 2.05 wt %, for the system with  $n = 15$ , (10 hydrogen molecules and 10 hydrogen atoms). Other possibilities to increase the quantity of hydrogen bounded to the system are under study. The adsorption of more hydrogen molecules on the external surface of the nanotorus can increase the weight percent hydrogen uptake. These results will be reported shortly.

#### ACKNOWLEDGMENTS

Authors thank suggestions given by Dr. J. M. Martínez-Magadán.

#### References

1. Dunlap, B. I. *Phys. Rev. B* 1992, 46, 1933.
2. Ihara, S.; Itoh, S. *Phys. Rev. B* 1993, 47, 12908.
3. Avron, J.; Berger, J. *Phys Rev A* 1995, 51, 1146.
4. Setton, R.; Setton, N. *Carbon* 1997, 35, 497.
5. Cho, J. H.; Park, C. R. *Catalysis Today* 2007, 120, 407.
6. Türker, L.; Eroglu, I.; Yücel, M.; Gündüz, U. *Int J Hydrogen Energy* 2004, 29, 1643.
7. Türker, L.; Gümüş, S. *J Mol Struct (Theochem)* 2005, 719, 103.
8. Türker, L. *Int J Hydrogen Energy* 2007, 32, 1933.
9. Delley, B. *J Chem Phys* 1990, 92, 508.
10. Delley, B. *J Chem Phys* 2000, 113, 7756.
11. Dmol<sup>3</sup> in Materials Studio v4.3, Accelrys (USA).
12. Gapern, E. G.; Stankevich, I. V.; Chistyakov, A. L.; Chernozatonskii, L. A. *Full Sci Technol* 1994, 2, 1.
13. Kroto, H. W. *Nature* 1987, 329, 529.
14. Schmalz, T. G.; Seitz, W. A.; Klein, D. J.; Hite, G. E. *J Am Chem Soc* 1988, 110, 1113.
15. Perdew, J. P.; Wang, Y. *Phys Rev B* 1992, 45, 13244.
16. Pupyshova, O. V.; Farajian, A. A.; Yakobson, B. I. *Nano Lett* 2008, 8, 767.
17. Koi, N.; Oku, T. *Sci Technol Adv Mater* 2004, 5, 625.
18. Koi, N.; Oku, T. *Solid State Commun* 2004, 131, 121.
19. Dodziuk, H. *Chem Phys Lett* 2005, 410, 39.
20. Lusk, M. T.; Hamm, N. *Phys Rev B* 2007, 76, 125422.
21. Saito S.; Oshiyama, A. *Phys Rev Lett* 1991, 66, 2637.
22. Ponomarenko, O.; Radny, M. W.; Smith, P.V. *Carbon* 2005, 43, 1165.
23. Barajas-Barraza, R. E.; Guirado-Lopez, R. A. *Phys Rev B* 2002, 66, 155426-1.
24. Lee, S.; Lee, Y. *Appl Phys Lett* 2000, 76, 2877.
25. Biegler-König, F.; Schönbohm, J.; Bayles, D. *J Comp Chem* 2001, 22, 545.