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Hydrogen storage capacity of $Mg@C_{120}$ system

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Abstract

The hydrogen storage capacity of single-walled and endohedrally Mg doped C_{120} composite system has been investigated theoretically by semiempirical quantum chemical treatment at the level of PM3 (RHF) type calculations. The structures are found to be stable but endothermic in nature. $(7H_2+Mg)@C_{120}$ structure has the smallest heat of formation value among the series of $(nH_2+Mg)@C_{120}$ molecules considered. Some structural and physicochemical data are also reported.

Keywords: Hydrogen storage; C_{120}; $(nH_2+Mg)@C_{120}$; PM3; Semiempirical

1. Introduction

Hydrogen storage has been a very attractive research subject in recent years, since hydrogen is thought to be the most clean and most powerful energy source of the future world. Compressed gas, liquefaction, metal hydrides and physorption are the four main techniques in use as well as under investigation for hydrogen storage [1–17]. Studies on the use of nanofibers, nanotubes and activated carbon as hydrogen storage material are still being developed [1–9, 11–15]. Carbon nanotubes and fibers are synthesized for various systems [18,19]. Storage of hydrogen in solid matrices serves the advantage of easier handling and safety whereas liquid storage needs low but constant temperature. On the other hand, in the case of compressed gas technique a very strong and bulky container will be necessary.

Carbon nanotubes have a larger capacity of hydrogen storage than ordinary activated carbon due to their hallow core and large surface area. Therefore, many scientists perform investigations on the hydrogen storage capacity of carbon nanotubes and nanofibers [6–9,20,21].

Hydrogen storage behavior of either metal doped or non-metal, fullerene and fullerene derivatives are also observed in the literature [22–25]. Endohedrally Be doped C_{120} system was studied by Türker et al. [25] and found to have a capacity of storing 15 molecules of hydrogen.

In the present study, the hydrogen storage capacity of single-walled and endohedrally Mg doped C_{120} ($Mg@C_{120}$) system has been investigated theoretically by semiempirical quantum chemical treatment at the level of PM3 type calculations.

2. Method

In the present treatise, the initial structure of the tube C_{120} was constructed starting from C_{60} [(5,6-fullerene-60-Ih) which was excerpted from the Hyperchem library [26]. The halves of C_{60} structure were suitably used as the caps of an armchair type tube having 10 benzenoid rings as the peripheral belt.

The geometry optimizations of all the structures leading to energy minima were achieved by using first MM+ and then, PM3 self-consistent field molecular orbital (SCF MO) [27,28] method at the restricted Hartree–Fock (RHF) level [29]. The optimizations were obtained by the application of the steepest-descent method followed by conjugate gradient methods, Fletcher–Reeves and Polak–Ribiere, consecutively (convergence limit of 4.18×10^{-4} kJ/mol (0.0001 kcal/mol) and RMS gradient of 4.18×10^{7} (kJ/m mol) (0:001 kcal/(A mol)). All these computations were performed by using the Hyperchem (release 5.1) and ChemPlus (2.0) package programs [26].

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3. Results and discussion

Endohedral doping method is the addition of an atom or ion into the interior hollow core of the fullerene molecule to form endofullerene [30]. Some theoretical studies on the endohedrally hydrogen and metal doped fullerenes were reported [22–24,31]. The accommodation of hydrogen in these cage like structures have not been solved yet, but theoretical approach for the stability of these type of molecules could be quite interesting.

In the present study, the hydrogen storage capacity of single-walled and endohedrally Mg doped C_{120} system has been investigated theoretically by semiempirical quantum chemical treatment at the level of PM3 (RHF) type calculations.

After the construction of the C_{120} tube as mentioned above, it is first endohedrally doped by Mg atom and then, geometry optimized (Fig. 1). Fig. 1 shows the side and the end views of the composite structure. As can be seen in Fig. 1, the Mg atom almost occupies the center of the capped tube. In Fig. 2 the three-dimensional electrostatic map of the $Mg@C_{120}$ structure is given. The dashed lines indicate the direction of the dipole moment.

The geometry optimized $Mg@C_{120}$ nanotube is then doped with $n \leq 13$ number of hydrogen atoms to obtain $(nH_2+Mg)@C_{120}$ ($n=6$–13) type structures. Fig. 3 shows the geometry optimized structures of the presently considered composite structures for $n=8$–10. Whereas the three-dimensional electrostatic maps of them are displayed in Fig. 4. Again the dashed lines indicate the direction of the dipole moment.

Table 1 shows some structural and physicochemical properties of the presently considered structures. As can be seen from the Table 1, the surface area and volume change irregularly from one molecule to another. Among the series, $Mg@C_{120}$ structure has the largest surface area. The dipole moments of the molecules also fluctuate irregularly. Of the structures considered $n=9$ and 12 number of hydrogen containing structures have the highest dipole moments. In each case the dipole moment of the structure is from somewhere on the surface to the center of the cage structure, which means that the Mg atom polarizes the composite structure. In Fig. 5 the three-dimensional charge density

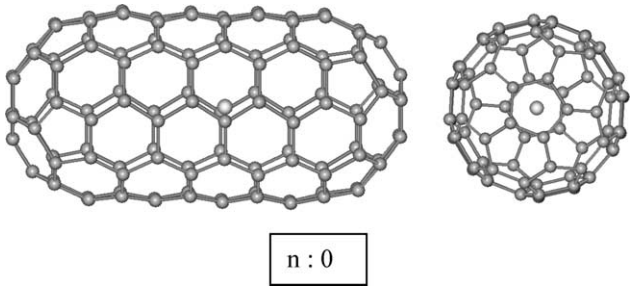

Fig. 1. The geometry optimized structure of the Mg doped C_{120} tube.

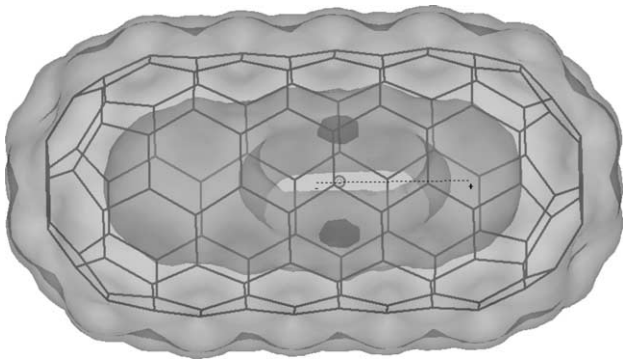

Fig. 2. Three-dimensional electrostatic map of $Mg@C_{120}$ system (dashed lines indicate the direction of the dipole moment).

maps for $n=0$, 8–10 are given. As can be seen from the Fig. 5 in all the structures Mg atom is negatively charged whereas the hydrogens possess positive, negative or zero charge development. A negatively charged Mg is a rare case but occurs when empty valance shell orbitals of the metal are occupied. In the present case π-orbitals of the tube structure should interfere with empty valance shell of Mg

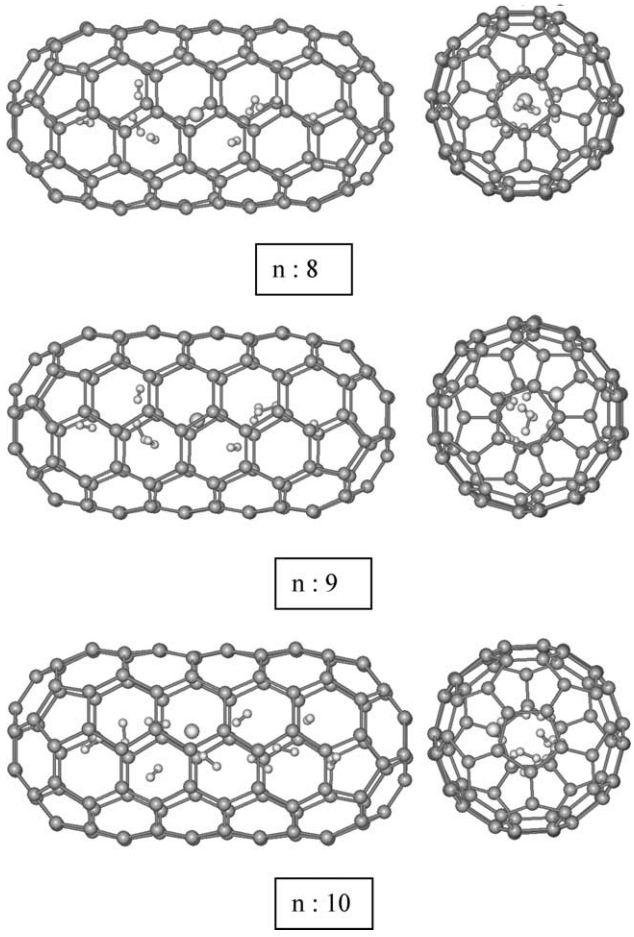

Fig. 3. The geometry optimized structures of $(nH_2+Mg)@C_{120}$ systems ($n=8$–10).