Potential energy of H_2 inside the C_{116} fullerene dimerization: An atomic analysis

A.A. EL-Barbary [a], [b], *

[a] Physics Department, Faculty of Education, Ain Shams University, Cairo, Egypt
[b] Physics Department, Faculty of Science, Jazan University, Jazan, Saudi Arabia

ABSTRACT

DFT method has proved useful for its ability to provide an atomic analysis of the dimerization of fullerene molecules. Such atomic analysis may provide information that is not available by experimental methods. Here, the structures of possible three isomers of C_{116} fullerene dimerization obtained from two C_{58} fullerene cages have been optimized using DFT method at the B3LYP/6-31G(d,p) level of theory. The orientation of C_{58} fullerene and bond reorganization during the dimerization process have been studied. The transition structures and energy barriers between the three isomers are obtained. The potential energies of the H_2 molecule motion along and perpendicular to the axial dimer with possible rotational angles are calculated. Also, the ^{13}C NMR chemical shifts and electron density distribution have been applied to distinguish between the C_{58} fullerene cages and the three isomers of C_{116} fullerene dimerization. Our results show that the C_{116} fullerene dimerization could be considered to be good candidate for hydrogen storage.

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1. Introduction

The dimerization of fullerene molecules has been widely studied both experimentally and theoretically [1−10]. And yet for the large size of dimeric fullerenes the empirical calculations are mostly applied, however the ab initio calculations are seldom so far. The C_{120} dimer has been widely studied both experimentally and theoretically [1,8,10]. Although, the C_{116} dimer is most likely to obtain experimentally, the definitive data of individual dimeric fullerenes of C_{116} are seldom because of the isolation and characterization problems. Structural characterization plays an important role to understand the chemical and physical properties of dimeric fullerenes [6]. However there are only a few theoretical work on the structures of the possible isomers of the C_{116} dimer [3−5], more fewer on their energetic properties and nothing so far on their electronic properties, barrier energies and transition structures. Also, from previous theoretical and experimental studies it was reported that carbon materials possess a potential to be used as a high capacity and light-weight hydrogen storage material [11−24]. It is therefore important to establish the ability of hydrogen storage

in dimeric fullerenes through the study of H_2 potential inside the dimeric fullerenes.

In this paper, first, the three possible isomers of C_{116} dimer are created and are fully optimized. second, the energy barriers and transition structures between possible isomers of C_{116} dimer are obtained. Third, the electronic and spectral properties of the C_{58} cage and the three isomers of the C_{116} dimer are investigated. Finally, the H_2 potential energy inside the most stable isomer of the C_{116} dimer is studied, including the transitional and rotational motions of H_2 molecule.

2. Methodology

The C_{116} dimer forms by the combination of two C_{58} fullerene cages. The C_{58} fullerene cage is produced by a removal of C_2 unit with energy 5.2 eV [4] from C_{60} fullerene cage, creating one heptagon and two pentagons, (5-7-5) structure [25], see Fig. 1. The C_{58} fullerene cage is an open structure with four unsaturated carbon atoms, see Fig. 1. When the heptagon ring in one C_{58} fullerene cage faces the heptagon ring in the other C_{58} fullerene cage, the isomer I will be created. By rotating the top C_{58} fullerene cage of isomer I by 90° and bond reorganization, the isomer II will be produced. The same is true for isomer III, which is produced by rotating the top C_{58} fullerene cage of isomer II by 90° or by rotating the top C_{58} fullerene

* Physics Department, Faculty of Education, Ain Shams University, Cairo, Egypt.
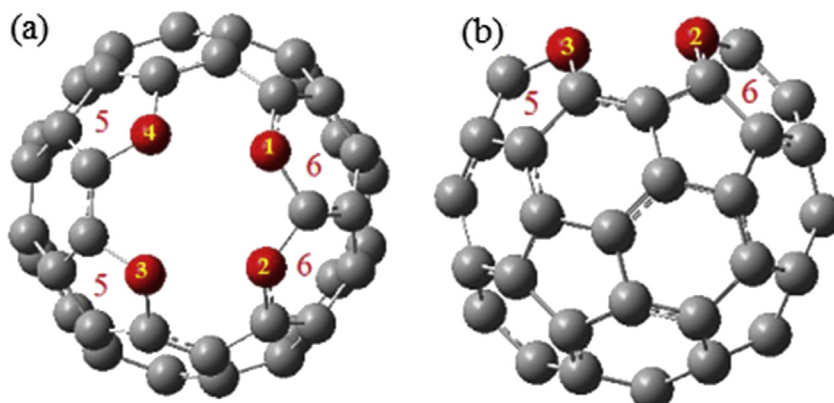E-mail address: ahla_eg@yahoo.co.uk.

Fig. 1. The structure of C_{58}(5-7-5) cage from a) top view and b) side view. The red color atoms refer to the carbon atoms that will be bonded during dimerization. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

cage of isomer I by 180° and bond reorganization. All obtained isomers are fully optimized and are performed with the density functional theory as implemented within G03W package [26–29], applying B3LYP exchange-functional [30,31] at basis set 6−31G(d, p). The ^{13}C NMR chemical shift is a sensitive method to the local environment allows to characterize the difference between the three isomers of dimer C_{116} fullerene cages. The optimization is applied using spin average. The ^{13}C NMR chemical shifts are sensitive to the choice of basis set and functions [32] and thus the ^{13}C NMR chemical shifts are calculated with respect to the calculated ^{13}C NMR chemical shifts of TMS (tetramethylsilane) at same basis set and functions. All the optimized geometric structures are confirmed with frequency calculations where all vibrational frequencies are found to be positive.

3. Results

3.1. Structure of C_{58} cage

If two adjacent atoms are removed from C_{60} cage, the C_{58} cage will be formed. The lower energy C_{58} cage possesses a large hole (seven member ring, C_{58}(5-7-5)) with a diameter of about 3.3A° [25], see Fig. 1. This large hole provides good place for dimerization.

3.2. Isomers of C_{116} dimer

The optimized geometries for three isomers of C_{116} dimer are shown in Fig. 2. Our calculations show that when two C_{58}(5-5-7) cages face each other through the heptagon member ring, the isomer I of C_{116} dimer is formed. Results in, two pentagon rings and one heptagon ring from each C_{58} cage were destroyed. The formed C_{116} dimer (called isomer I) possesses three parts, two of them are spherical and the third part connecting the two spherical parts is straight. The straight part consists of four holes, two holes with 10-member ring, one hole with 8-member ring and the last hole with 6-member ring, see Fig. 2(a,e). To obtain the other isomers of the C_{116} dimer, the top C_{58} cage is rotated with respect to the bottom C_{58} cage. By rotating the top C_{58} cage of isomer I by 90° the isomer II is produced. The straight part of isomer II consists of four holes, two holes with 9-member ring and the other two holes with 8-member ring, see Fig. 2(b,d). Finally, the isomer III of C_{116} dimer will be formed either by rotating the top C_{58} cage of the isomer I by 90° or the isomer II by 180°. The straight part consists of four holes, two holes with 10-member ring and the two holes with 7-member ring, see Fig. 2(c). In the three isomers, the carbon atoms in the straight regions connecting each other with bond length ~1.4 A°.

Fig. 3 shows the relative energy between two isolated C_{58} cages and the three isomers of C_{116} dimer. It is found that the energy of isomer I of the C_{116} dimer is lower in energy than the two isolated C_{58} cages by 4.84 eV, however the energy of isomer III of the C_{116} dimer is lower in energy than the two isolated C_{58} cage by 3.78 eV and higher in energy than the isomer I by 0.97 eV. Isomer II is the most stable isomer of the C_{116} dimer. The energy of isomer II is lower than the energy of the two isolated C_{58} cages, the isomer I and the isomer III by 5.03 eV, 0.19 eV and 1.16 eV, respectively.

Also, the energy barriers and transition structures between the three isomers of C_{116} dimer are investigated. From Fig. 4, the energy barrier between isomer I and isomer II of the C_{116} dimer is found to 19 eV and the energy barrier between the isomer II and isomer III is 20.3 eV. This means that the three isomers might be exist together and the converting one isomer to another is rare to happen due to the huge required energy barrier.

To distinguish between the three isomers of C_{116} dimer, both of the density states and ^{13}C NMR chemical shift has been studied. Fig. 5 shows the density of states and the energy levels of the three isomers of C_{116} dimer and are compared with C_{58} cage. The energy gaps of C_{58}, isomer I of C_{116} dimer, isomer II of C_{116} dimer and isomer III of C_{116} dimer are found to be 1.64 eV, 1.83 eV, 0.86 eV and 1.48 eV, respectively. Therefore, the energy gap is decreased when the isomer II and the isomer III are formed however it is increased when the isomer I is created, comparing with the energy gap of the C_{58} cage. To understand why the isomer I possesses the highest energy gaps (1.83 eV), however the isomer II possesses the smallest energy gap (0.86 eV), the HOMO and LUMO for both isomers are calculated. It is found that HOMO and LUMO for isomer I are 5.97 eV and 3.96 eV and for isomer II are 5.42 eV and 4.56 eV, respectively. For our reference, the C_{58} cage, the calculated HOMO and LUMO are found to be 5.87 eV and 4.23 eV, respectively. Therefore, one can report that the high energy gap of isomer I is due the shift of the LUMO far from the HOMO and for the isomer II both HOMO and LUMO are shifted towards each other, see Fig. 5.

The ^{13}C NMR chemical shifts of the C_{58} cage, and the three isomers of C_{116} dimer are listed in Table 1 and Fig. 6. The ^{13}C NMR chemical shifts of the C_{58}, isomer I, isomer II and isomer III possess continuous peaks starting from 134.8 ppm to 152.3 ppm, 124.6 ppm−149.8 ppm, 130.8 ppm−155.4 ppm and 119.9 ppm−152.5 ppm, respectively. The results show that the ^{13}C NMR chemical shifts can be applied to distinguish between the C_{58} cage and the three isomers of C_{116} dimer. The isomer I and Isomer III can be distinguished by their starting peak at 124.6 ppm and 119.9 ppm, respectively. However, for C_{58} cage and isomer II, the starting peak is at 134.8 ppm and 130.8 ppm, respectively. Also, The