

Full Length Research Paper

A study on the electronic and structural properties of fullerene C₃₆ and it's interaction with amino acid

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C₃₆ is the most important fullerene cage. In this paper, the structural properties of C₃₆ fullerene interacting with glycine radicals are analyzed through the density functional theory. The radical adsorptions result in modifications on the structural properties of the original fullerene. It was found out that the binding of glycine to C₃₆ generated a slightly unstable complex. This indicates that fullerene cages might be unable to form stable bindings to glycine radicals. These results are extremely relevant in order to identify the potential applications of functionalized C₃₆ as drug delivery systems.

Key words: C₃₆, glycine, density functional theory, formation energy, highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gap.

INTRODUCTION

With the discovery of C₆₀, the structure and stability of smaller fullerenes with less than 60 carbons have been studied experimentally and theoretically (Kroto, 1987; Guo et al., 1992; Mishra et al., 1999; Makurin et al., 2001; Grossman et al., 1998; Schultz et al., 2003; Breda et al., 2000; Gan et al., 2009; Malolepsza et al., 2009; Shi et al., 2008; Sun et al., 2005; Pattanayak et al., 2004; Song and Vaziri., 2006). A set of small fullerenes has been detected with the mass spectroscopic method and among them, only C₂₀ (Prinzbach et al., 2000) and C₃₆ (Zettle et al., 1998) have been observed.

The proposed synthesis of the fullerene C₃₆ by the arc-discharge method by Zettle et al. (1998) has attracted considerable attention, since fullerenes smaller than C₆₀ are considered to be highly strained due to the presence of fused five-membered rings. The pronounced strain energy will give rise to high reactivity, low stability and will make the determination and characterization difficult.

Recently, fullerene C₃₆ was studied by density functional theory (DFT) method (Chi et al., 2007; Estrada and Valladares, 2008). Malolepsza et al. (2007) compared the properties of C₂₀ to C₃₆. Kang (2006) calculated a series of endohedral C₃₆.

Nevertheless, current studies on fullerenes and their compounds mainly focus on large-size fullerenes. Systematic studies on small or middle-size fullerenes and non-isolated-pentagon-ring (IPR) fullerenes remain rare. There have been increasing interests in fullerenes potential applications in the field of chemical catalysis (Coq et al., 1998) and pharmaceuticals (Wilson et al., 1999), because of the particular properties possessed only by small-size carbon cages, like smaller curvature radius and higher chemical activity. However, experimental researches and practical applications of this sort of compounds are still limited by low yield and poor stability. Theoretical methods are therefore helpful in this field to discover some potential lead compounds with good properties and stabilities.

Glycine is the simplest of the 20 common amino acids and is often chosen as the simplest representative of a backbone unit of a protein. Therefore, glycine-C₃₆ complex can be chosen as a model for studying the chemical interaction between a protein and a fullerene nano-cage. Furthermore, glycine (or other amino acid)-fullerene derivatives are of special interest as biologically active compounds (Prato et al., 1993; Kiebe and Hirsch, 1994; Zhou et al., 1995).

In this paper, we select C₃₆ fullerene and it's interaction with glycine as objects of study. We investigate the of carbon cage structure toward the corrected single point

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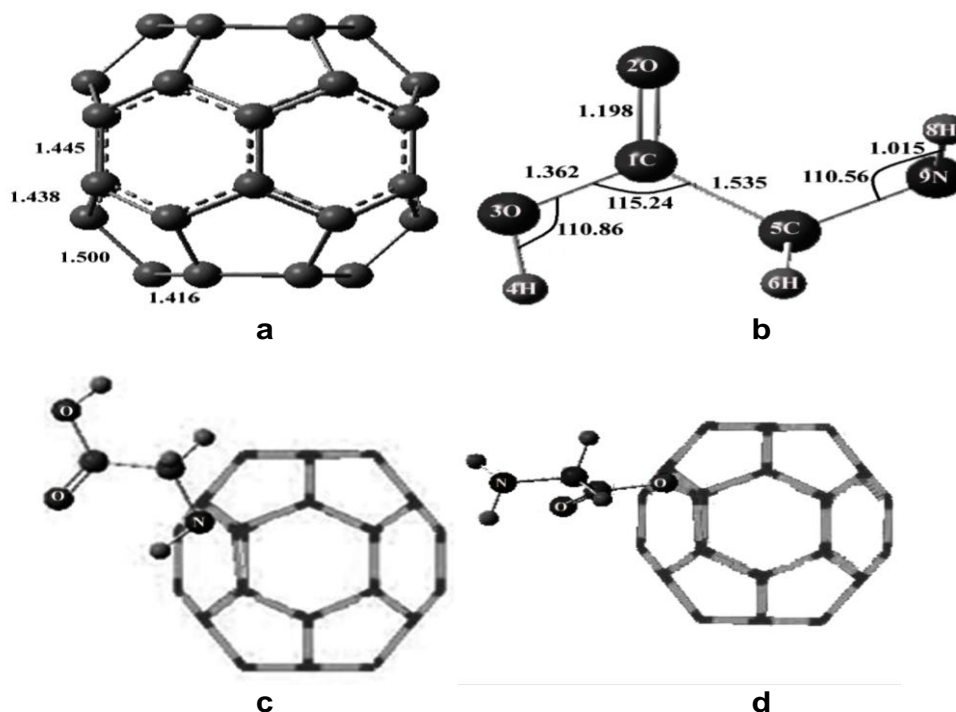


Figure 1. Relaxed atomic structures for (a) C_{36} , (b) glycine, (c) A and (d) B.

energy. The interactions between C_{36} and glycine were obtained for two active sites of glycine: the amino nitrogen (N) and the hydroxyl oxygen (O) sites.

COMPUTATIONAL METHOD

B3LYP has been proven to be a good method for the prediction of the fullerene structures (Hu and Ruckenstein, 2005, 2004). In this work, glycine and C_{36} were calculated using B3LYP method to geometry optimizations and energy calculations with the 6-31G* basis set for C_{36} and 6-311+G** basis set for glycine, separately. All calculations have been carried out using the Gaussian 98 program.

RESULTS AND DISCUSSION

Structures of glycine- C_{36} complexes

The D_{6h} triplet ground state and the corresponding D_{6h} singlet state are the two most stable structures in C_{36} (Jagadeesh and Chandrasekhar, 1999). There are no significant geometrical differences between them (Ito, 1999). In this letter, systematic calculations on the structures and electronic properties of singlet C_{36} species with D_{6h} symmetry are presented.

Ito et al. (1999) found out that both the six-membered and five-membered rings are aromatic. This is confirmed by our computed nucleus-independent chemical shift (NICS) value at the cage centers, that is, -23.40 ppm, and it is even more aromatic than C_{60} which has aromatic

six-membered rings and anti-aromatic five-membered rings, and therefore, is weak aromatic.

Due to the high symmetry, it has only four independent bond lengths, as shown in Figure 1. The structure of C_{36} obtained is in excellent agreement with the (Jagadeesh and Chandrasekhar, 1999).

As the simplest representative of a backbone unit in a protein, glycine has been widely studied (Tse et al., 1978). Its most stable structure, which we obtained using B3LYP/6-311+G**, is presented in Figure 1b. The geometric parameters of this structure are consistent with the literature (Tse et al., 1978). Furthermore, it is well known that a glycine molecule has three active sites, the amino nitrogen (N), the hydroxyl oxygen (O) and the carbonyl oxygen (O) sites. Therefore, it is expected for glycine to interact with the C_{36} via these three active sites. In order to examine the adsorption of a glycine on the C_{36} , two possible configurations, called [A] and [B], were selected: [A] denotes the amino nitrogen (N) and [B] the hydroxyl oxygen (OH) active sites. For the adsorption of the glycine molecule [A and B], one hydrogen atom was removed from the amine group with the nitrogen atom moving towards the C_{36} , labeled as [A] and one hydrogen atom was removed from one hydroxyl group, and then, the resultant oxygen atom approached the C_{36} , corresponding to the configuration labeled as [B].

The equilibrium geometries for the C_{36} , isolated glycine molecule and [A] and [B] are as shown in Figures 1a, b, c and d, respectively. Furthermore, the length of the C=C bond, which was saturated with the O of glycine, changed

Table 1. Total energies (E_{tot} in a.u.), relevant inter atomic distances and formation energies (E_f) for the glycine molecule, interacting with C_{36} at the ONIOM2 (B3LYP/6-311+G**: $B3LYP/6-31G^*$) methods.

Species	E_{tot} (a.u.)	E_f (eV)	Bond	Bond distance (Å)
A	-1655.16272296624	6.31	$C_{36}-N_{\text{gly}}$	1.475
B	-1655.16168594867	6.34	$C_{36}-O_{\text{gly}}$	1.462

Table 2. HOMO and LUMO energies (a.u.), and HOMO-LUMO energy separations ($\Delta E_{\text{H-L}}$ in eV) for the glycine molecule, interacting with C_{36} at the ONIOM2 (B3LYP/6-311+G**: $B3LYP/6-31G^*$) methods.

Species	HOMO	LUMO	$\Delta E_{\text{H-L}}$ (eV)
Glycine	-0.19962	-0.16198	1.024
A	-0.27662	-0.09977	4.812
B	-0.28098	-0.00345	7.552

from 1.437 to ~ 1.540 Å, indicating that the C=C double bond was transformed into a C-C single bond. Furthermore, the lengths of the other C-C single bonds also became longer (increasing from 1.453 to about 1.541 Å). As a result, there is an oval shape with a length of 5.943 Å and a width of 5.469 Å in [A] and [B] instead of length of 5.957 Å and a width of 5.439 Å in pure C_{36} . On the other hand, the binding between glycine and C_{36} also changes the structure of glycine. The lengths of the O-C bond of glycine become shorter (decreasing from 1.362 to 1.354 Å and from 1.362 to 1.357 Å, in [A] and [B], respectively). The length of the N-C bond of glycine does not have any change in [A] and [B] (It is 1.447 Å). The bond lengths of glycine exhibit only small changes during their binding to the C_{36} cage. In Table 1, the closest distances between C_{36} and Glycine radicals are listed.

Stabilities of glycine- C_{36} complexes

As shown earlier, glycine and C_{36} can form complexes by forming a new bond by breaking one of the original bonds of glycine. The new bond formation can increase the stability of the complexes, whereas the breaking of the original bond of glycine can decrease their stability. To evaluate the stability of glycine- C_{36} complexes, we calculated the energy of formation of a complex between the glycine and C_{36} molecules (glycine + C_{36} = glycine- C_{36}), by using the equation:

$$\Delta E = E_{\text{gly}-C_{36}} - E_{\text{gly}} - E_{C_{36}} \quad (1)$$

where E_{gly} , $E_{C_{36}}$ and $E_{\text{gly},C_{36}}$ are the energy values (obtained during the geometry optimization routine) of glycine, C_{36} and glycine- C_{36} complex, respectively. The results are listed as shown in Table 1. One can see that the formation of all two complexes (via the amino nitrogen and the hydroxyl oxygen active sites) increases the energy of the system by 6.31 and 6.34 eV,

respectively. This indicates that the binding of glycine to C_{36} is slightly unstable via its amino nitrogen and moderately unstable via its hydroxyl oxygen. Although, real proteins are much more complicated than glycine, all proteins contain amino nitrogen (N) and hydroxyl oxygen (O) active sites. Therefore, from the calculation results involving glycine, one can predict that proteins might not readily form stable bindings with C_{36} via their amino nitrogen (N) and hydroxyl oxygen (O) active sites. In other words, the C_{36} cage may have no permanent effects on the protein structure and function.

The electrons donated by a molecule in a reaction should be from its highest occupied molecular orbital (HOMO), while the electrons captured by the molecule should be located on its lowest unoccupied molecular orbital (LUMO). Furthermore, the atom, on which the HOMO mainly distributes, should have the ability for detaching electrons, whereas the atom with the occupation of the LUMO should gain electrons (Tang et al., 2009).

The HOMO-LUMO gap is traditionally associated with chemical stability against electronic excitation, with larger gap corresponding to greater stability. The HOMO-LUMO gaps of Kohn-Sham orbital calculated at B3LYP/6-311+G**: $B3LYP/6-31G^*$ level for A and B are 4.812 and 7.552 eV, show evident reductions in glycine (Table 2).

Conclusions

In this work, we have assessed the performance of the two layered ONIOM method to study chemical reactivity of C_{36} and glycine by computing the reaction energy. These calculations showed that the binding of glycine to C_{36} generated unstable complexes with destabilization energies of 6.31 and 6.33 eV via its amino nitrogen (N) and hydroxyl oxygen (O) active sites, respectively. Therefore, fullerene cages might be unable to form stable bindings to proteins via their active sites.

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