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Li@C_{60} complexes with amino acids: A theoretical analysis

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Abstract

In this work, we explore the ability of the Li@C_{60} fullerene to interact with amino acids at the DFT-BLYP/DND level of theory. The calculations suggest that the most favorable interactions of the fullerene is with arginine, leucine, and tryptophan which is related to the backbone structure of the corresponding amino acids. We propose correlations of the dissociation energies, HOMO/LUMO band gaps in relation to the computed quantum chemical behavior.
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Keywords: Amino acids; Fullerene; Interaction energies; Charge-transfer; BLYP

1. Introduction

Nanomaterials such as single walled carbon nanotubes (SWNT) carbon and fullerenes [1] are structures formed from networks of carbon atoms. These structures have several applications in electronics, materials science, chemistry and biochemistry which has been noted [2–7]. The graphene-based nanosystems are important in the study of drug delivery due to their stability from a chemical point of view [8]. In other works, the application of nanostructures in biochemical substance delivery has been shown to be a promising tool in biological applications [9–12].

To promote the surface properties of the fullerenes to be modified, a scheme to amelerioate charge-transfer must be devised. Metals ions are placed in fullerenes to elucidate these charge-transfer process between the encaged metal atom and C_{60}. These interactions can be of importance in the encapsulation of fullerene species [13] in structures that otherwise would not have an affinity for them. This is a topic of relevance in many applications that involve the solubility and reactivity of fullerenes. The metals lower the HOMO/LUMO gap of the complex which promotes its interaction with external species.

It is our assertion that charge-transfer effects could cause increased interactions with other materials (i.e. nanotubes, peptides, etc.). The dispersion of the charge throughout the guest material will cause the fullerenes to be insensitive to the applied electric field by the encapsulation of metals [14]. Other computations have shown that lithium (Li) transfers the majority of the electronic density of the metal to the surface of the fullerene [15a]. The metal ion increases its affinity to other molecular species capable of forming stronger and more specific chemical interactions [15b].

We also attempt to implement specialized techniques with metal ions to form biochemical attraction with amino acids and eventually peptides. Since the surface properties are modified by the charge-transfer, this can permit the fullerenes to form an attraction to molecules of biological interest that otherwise would not occur. This happens since the excess electron localized on the molecular surface of the fullerene can couple to amino acids and biomolecules to form strong van der Waals complexes.

Fullerenes are intrinsically hydrophobic and are insoluble in biological systems which makes them toxic. A simple route to allow fullerenes to participate in living systems is by functionalization of the system by hydrophilic moieties

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[16]. Generally, the functionalizations generally have local transformations that permits the nanosystems to maintain their physical properties, while reducing to a large extent the toxicity of carbon nanotubes (CNTs) and allowing for their safe use in biological systems. The impact of the interaction on the amino acid structure and its reactivity. There are scant studies on this problem [17,18] but further analysis is indeed relevant to modern research efforts.

There are experiments that have shown that dendritic poly(L-lysine) containing porphyrin–fullerene moieties [19] were synthesized. Others have reported theoretical calculations between the C_{60} fullerene and its derivatives with L-histidine [20b]. Their computations suggested relative stability of the complexes, primarily due to hydrogen bonding interactions with external polar chiral molecules. The work of Csizmadia [20a,20b] has truly demonstrated the efficacy of such approaches in the quantification of mutations at specific points. This has also been studied by Li and colleagues [20c,20d] that combine to show the usefulness of such approaches in biochemical applications.

This is further substantiated by other experimental studies that demonstrate the efficacy of functionalizing fullerenes with amino acid to increase their biological affinity [21–24]. Similar results reveal that synthesis of amino acid derivatives have been fabricated and seen to be soluble upon complexation [25–27]. Theoretical dynamics calculations [28] also show that the functionalization with peptides and amino acids can lead to fullerene-specific antibody interactions.

The computations described herein yield theoretical evidence for how metal encapsulation inside of fullerenes can enchance surface properties to improve biochemical activity. The primary significance in this manuscript deals with solvating fullerenes in biological environments. We will discuss the interaction of fullerenes with amino acids as a preliminary case of the ability of fullerenes to participate in biological systems and possibly in drug delivery. This can be of particular importance in causing toxic fullerenes to become favorable in living systems for various applications.

2. Computational methods

The quantum chemical computations in this work were carried out using the DMOL^3 [29] numerical-based density-functional computer software implemented in the Materials Studio Modeling 3.1 package from Accelrys Inc. Geometrical optimizations and frequency calculations were carried out with the BLYP general-gradient potential approximation in conjunction with the double-numerical plus diffusion basis set (all-electron core treatment) was employed (denoted as DND). Fine convergence criteria and global orbital cutoffs were employed on basis set definitions. Computations have shown that the methods used are ideal when studying C_{60} van der Waals interactions, and adequately account for BSSE effects and dispersion forces [30,31].

Calculations demonstrate that this basis set reduces the BSSE error and is ideal for calculations on molecules of this type. The amino acids used are all in the same chirality to ensure consistency in the structural representations. Presently, the dissociation energies (ΔE) for the complexes to determine their relative stability with respect to the fullerene–amino acid interactions:

$$\Delta E = E_{\text{Li@C60-Amino Acids}} - (E_{\text{Li@C60}} + E_{\text{Amino Acids}}).$$

This quantity is a measure of the stability of the complex however our calculations show that as this value increases entropy values decrease as a result of increased affinity for the fullerene surfaces. Therefore, if the complexation affinities are significant the amino acid will tend to localize strongly on the fullerene surface and the degrees of freedom will be reduced (causing changes in the entropy).

Hessian matrices were studied to ensure that the structures obtained are experimentally viable from the DFT computations performed in this work on the described systems. The reason for this is that the Hessian matrices were used to evaluate the vibrational frequencies of the studied complexes. If the number of imaginary frequencies was zero than we determined that the structure computed was indeed a minimum energy structure and not a transition state. The experimental relevance is that minimum structures should appear in the spectra obtained for such complexes if the Hessian matrices yield positive frequencies.

Another important concept to mention is that several competitive binding sites on the fullerene were considered but only lowest energy structures are retained. It is interesting to note that the minimal energy structures are those in which the amino acid occupies the region of the six and five membered ring junctions. In addition, we have also considered different minimum energy structures resulting from the modification of the position of the metal with respect to the fullerene cage to ensure that the structures were global minima.

Full correlation methods are ideal (i.e. HF, MP2, CCSD(T)) however, for systems of this size it not possible due to limitations of computational resources. Even on large scale supercomputers such calculations are cumbersome and time consuming. The DFT methods employed are capable in adequately describing van der Waals complexes as those shown in the present study. The presented calculations should be important for future experimental studies involving methodology for improving the solubility of fullerenes in biological systems.

3. Results and discussion

Table 1 presents the ΔR which is the off-center displacement of Li in the fullerene structure in Å, GAP^{AA} which is the HOMO/LUMO band gap of the amino acids, $\text{GAP}^{\text{C60–AA}}$ that is the HOMO/LUMO band gap of the C_{60}–amino acid complexes and finally ΔE is the dissociation energy. Also shown are the BLYP results reported for the fullerene–amino acid complexes without an endohedral metal atom