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

Abraham F. Jalbout *

Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, 04510 México D.F., Mexico

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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

* Tel.: +1 520 621 6761/+52 55 24 22 72; fax: +1 520 621 8047/+52 55 16 22 17.
E-mail address: ajalbout@u.arizona.edu

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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, GAP^{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

Table 1
Physical properties of the fullerene–amino acid complexes are shown

Group	System	ΔR[a]	GAP^{AA}	GAP^{C60-AA}[b]	ΔE	ΔE[c]
1	Gly	0.16	118.82	37.17	−11.1	−0.945
	Ala	0.40	117.26	37.58	−12.6	−0.220
	Val	0.06	115.97	36.90	−16.4	−0.187
	Leu	0.49	116.44	37.03	−18.5	−3.910
	Ile	0.11	115.62	37.33	−17.4	−0.801
2	Ser	0.03	116.25	37.45	−13.2	−0.554
	Thr	0.06	116.31	37.37	−16.0	−0.339
3	Cys	0.70	104.43	34.17	−20.9	−1.340
	Met	1.40	93.28	21.13	−21.2	−0.739
4	Asp	1.32	106.45	35.32	−27.8	−1.160
	Glu	0.06	107.04	20.65	−14.4	−2.360
	Asn	1.35	113.39	36.69	−18.7	−2.210
	Gln	0.15	108.60	35.27	−20.9	−1.960
5	Lys	1.33	107.07	28.54	−34.4	−0.766
	Arg	0.14	79.65	13.27	−30.2	−3.360
	His	0.27	90.08	20.19	−25.5	−1.990
6	Phe	0.24	109.95	36.95	−26.9	−0.795
	Tyr	0.04	98.50	21.96	−26.7	−2.220
	Trp	0.42	86.19	15.55	−34.2	−2.370
	Pro	0.22	116.89	32.51	−28.4	−0.595

In the table, ΔR is the off-center displacement of Li in the fullerene structure in Å, GAP^{AA} is the HOMO/LUMO band gap of the amino acids, GAP^{C60-AA} is the HOMO/LUMO band gap of the C_{60}–amino acid complexes and ΔE is the dissociation energy. The groups are arranged based on structural features (see text).

[a] The off-center displacement of Li in the isolated $Li@C_{60}$ system is about 1.18 Å.

[b] The HOMO/LUMO gap of the isolated $Li@C_{60}$ system is around 37.47 kcal/mol.

[c] DFT dissociation energies computed without the endohedral metal ion (see Ref. [32]).

[32]. In the majority of the cases examined the Mulliken charge is around 0.92 as computed with our DFT methods. It does not really matter what amino acid is considered this charge is maintained relatively constant. We demonstrated in previous works [15a] that the Li atom generally prefers to donate the excess electron density to the fullerene surface regardless of the environment in which it is placed. This makes it an ideal candidate for materials design and biochemical applications where the fullerene becomes insensitive to the externally applied field.

These structures in the table represent the following groups: Group 1 is amino acids with aliphatic R-groups (Gly, Ala, Val, Leu, IIe); Group 2 is non-aromatic amino acids with hydroxyl R-groups (Ser, Thr); Group 3 is amino acids with sulfur-containing-groups (Cys; Met); Group 4 is acidic amino acids and their amides (Asp; Glu, Asn, Gln); Group 5 is basic amino acids (Lys, Arg, His); and Group 6 is amino acids with rings (Phe, Tyr, Trp and Pro which is an imino acid but is grouped here).

The average improvement of the $Li@C_{60}$ complexes compared to the isolated fullerene case is −20.3 kcal/mol (the smallest improvement being for Glu and the largest for Val). In this case, the average improvement is the mean difference of the dissociation energy with and without metal insertion. The smallest improvement is the system for which metal insertion created minor changes in the ability of the fullerene to the amino acid. Selected geometrical parameters for the complexes are shown in Figs. 1 and 2, whereby bond lengths are in angstroms (Å) and bond angles in degrees (°). It must be pointed out that several positions of the metal were constructed to solidify the nature of the minimum energy structures. Fig. 1 displays the structural results of Groups 1, 2, 3 and parts of Group 4 (Asp, Glu). Fig. 2 presents the geometrical structures of Group 4 (Asn, Gln) and Groups 5 to 6.

3.1. Group 1: amino acids with aliphatic R-groups

Glycine (Gly) forms a simple interaction at around 4.0 Å and is stabilized by internal hydrogen bonding with a weak dissociation energy of −11.1 kcal/mol. This is attributed to the lack of specificity in its contact with the fullerene. Due to the small size of this system and higher degrees of rotational freedom this causes the energy of the resultant system to rise, and the specificity of C_{60} interactions to decrease.

The next amino acid that we will discuss is alanine (Ala) which has an off-center displacement of 0.4 Å of the Li atom. Upon complexation, the metal atom in this case tends to localize along the center of the fullerene cage. Fig. 1 shows that the intermolecular separation is about 4.6 Å with an internal hydrogen bond between the $–NH_2$ group and the OH group at about 1.88 Å that stabilizes the structure. As we can see the HOMO/LUMO gap of the amino acid is around 117.3 kcal/mol compared to 37.6 kcal/mol of the complexed species. The ΔE value of

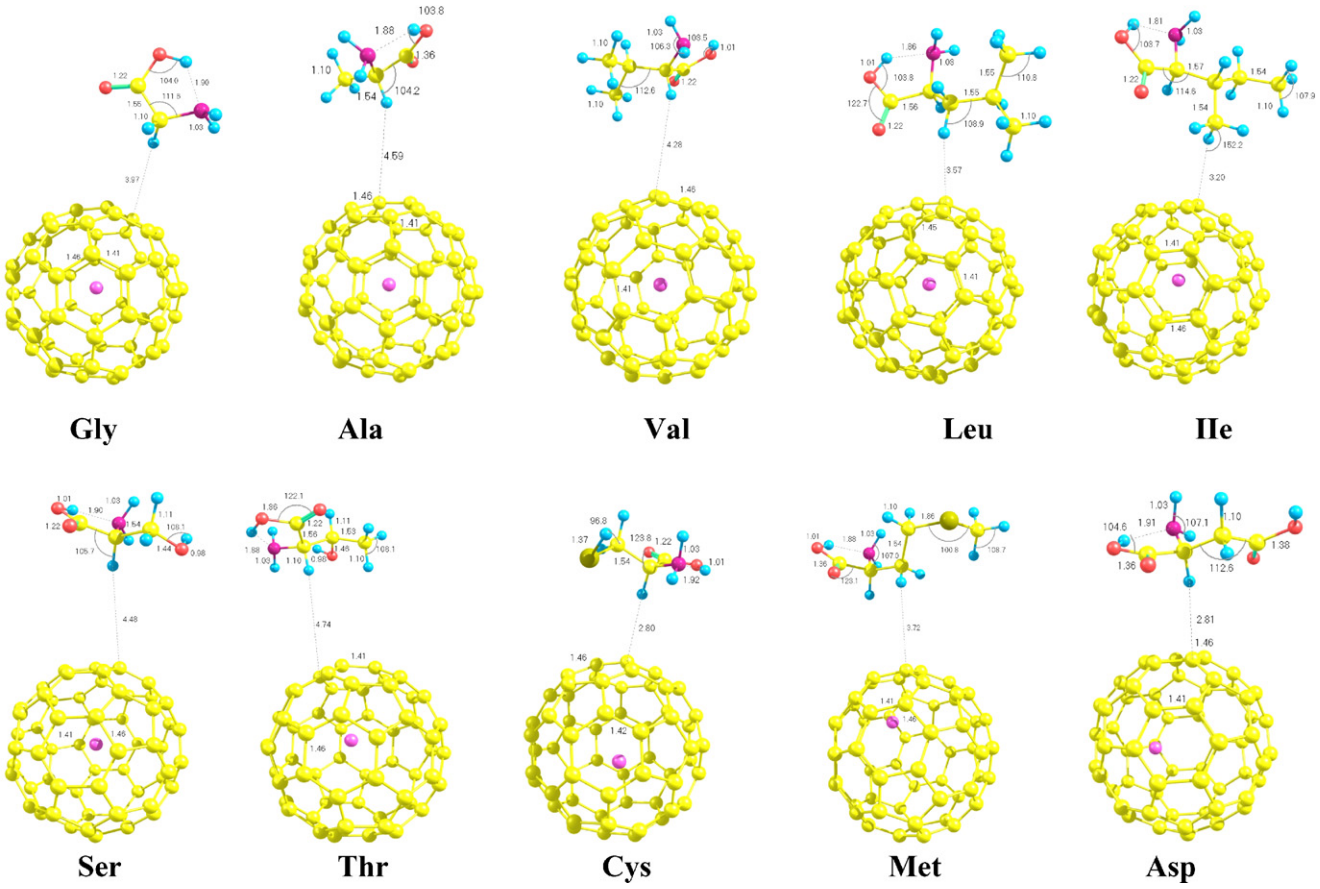

Fig. 1. Various geometrical parameters for the amino acid–C_{60} complexes, whereby bond lengths are in angstroms (Å) and bond angles in degrees (°). These structures represent the following groups: Group 1 is amino acids with aliphatic R-groups (Gly, Ala, Val, Leu, IIe); Group 2 is non-aromatic amino acids with hydroxyl R-groups (Ser, Thr); Group 3 is amino acids with sulfur-containing-groups (Cys; Met) and parts of Group 4 is acidic amino acids and their amides (Asp; Glu) the rest are in Fig. 2.

the complex without the metal is about −0.2 kcal/mol compared to the −12.6 kcal/mol with the metal atom. It is interesting to note that the placement of the metal ion greatly enhances the stability of the fullerene complexes with Ala.

In the valine (Val) case, we obtain a separation of about 4.3 Å with a larger HOMO/LUMO gap than Tyr and a smaller dissociation energy of −16.38 kcal/mol. While the latter case has a smaller dissociation energy it represents the highest improvement as a result of internal metal placement. This complex is stabilized by internal hydrogen bonding as is apparent from the dissociation energy values computed.

For the Leu structure we obtain a complex that has a similar intermolecular separation as IIe of about 3.5 Å with a larger off-center displacement (that can be due to the repulsion between the surface and the methyl group) with a dissociation energy of −18.5 kcal/mol. This again can be attributed to the repulsion and steric hindrance obtained from the free methyl rotor which couples to $–NH_2$ rotations a concept that will be explained in future works [34]. Isoleucine (IIe) has a minimal off-center displacement with a dissociation energy of −17.4 kcal/mol. The primary contact point is between the methyl group and the fullerene surface at a distance of about 3.2 Å.

This family exhibits interesting physical properties as we can see the differences in stabilities of Gly and Ala is due to the methyl group. In the latter species, the methyl group is electron withdrawing that permits an affinity for the fullerene surface. If we compare Val and Leu for example, the presence of the extra methyl groups as in Gly and Ala causes an increase in the dissociation energy. Rearrangement of the side chain in IIe causes a slight decrease in the dissociation energy when compared to Leu. This family shows that the side groups which posses aliphatic groups are indeed stable but have larger HOMO/LUMO gaps due to the organic nature of this group.

3.2. Group 2: non-aromatic amino acids with hydroxyl R-groups

Serine (Ser) has an intermolecular separation of around 4.5 Å which an off-center displacement of around 0.03 Å, with a dissociation energy of −13.2 kcal/mol that is significantly larger than the amino acid. For threonine (Thr), we obtain an intermolecular separation of around 4.7 Å with a

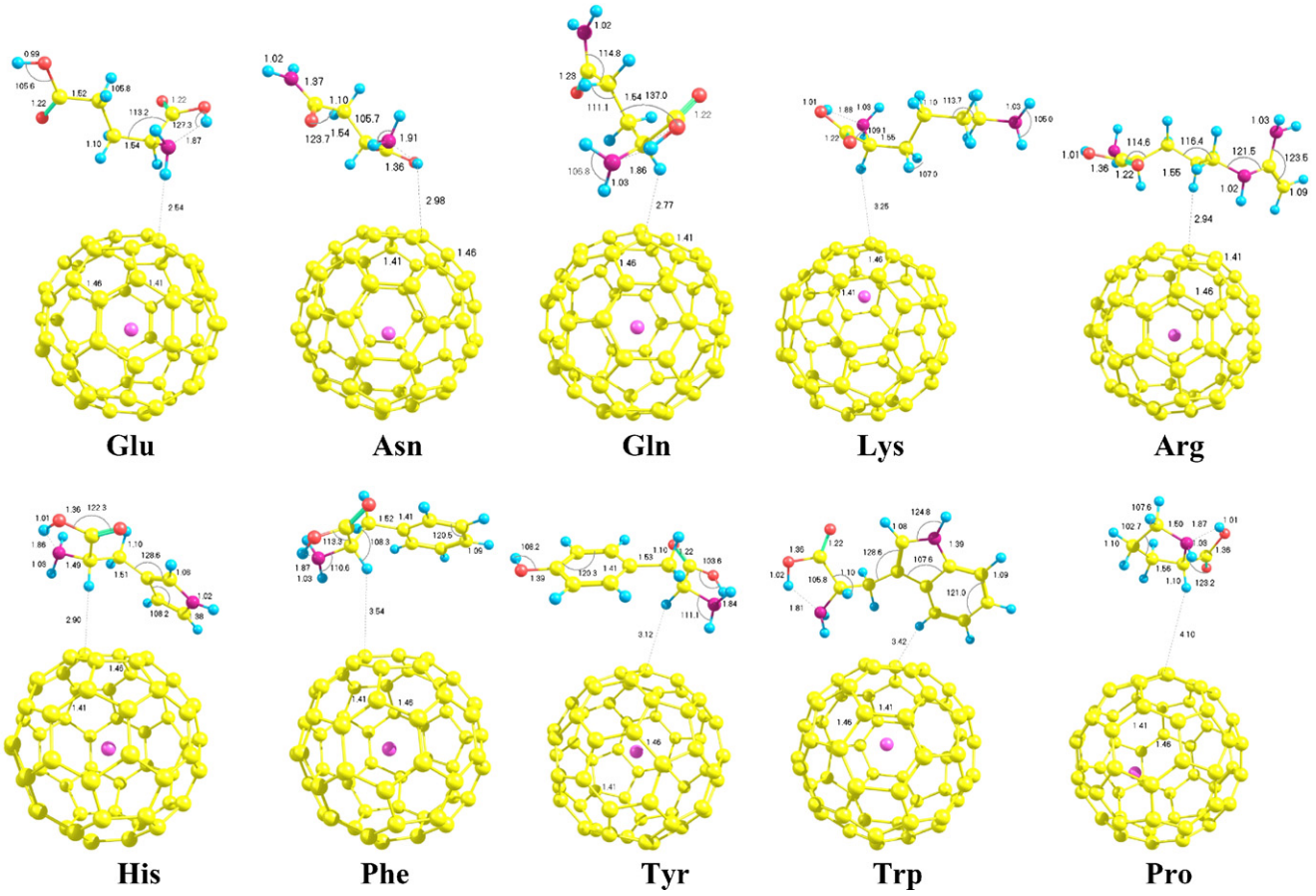

Fig. 2. Various geometrical parameters for the second set of amino acid–C_{60} complexes, whereby bond lengths are in angstroms (Å) and bond angles in degrees (°). These structures represent the following groups: the remainder of Group 4 is acidic amino acids and their amides (Asn, Gln); Group 5 is basic amino acids (Lys, Arg, His); and finally Group 6 is amino acids with rings (Phe, Tyr, Trp and Pro which is an imino acid but is grouped here).

minimal off-center displacement. The HOMO/LUMO gap is similar to Ser with a dissociation energy of about −16 kcal/mol which is larger than the value of −0.34 kcal/mol for the isolated non-metal case. The fact that Thr has a higher dissociation energy than Ser is the that the movement of the OH group causes distinct interactions with the fullerene surface. The placement of the OH group on the exterior reduces free degrees of rotational freedom and lowers the energy of the system which also is associated with a decrease in the HOMO/LUMO gap.

3.3. Group 3: amino acids with sulfur-containing-groups

Cysteine (Cys) has an intermolecular separation of 2.8 Å similar to Asp and is stabilized by both internal hydrogen bonding and a structure which maximizes contact with the fullerene surface. In this case, we calculate a dissociation energy of −20.93 kcal/mol and a HOMO/LUMO gap of 35.3 kcal/mol with an off-center displacement of 0.7 Å. Possibly the stabilization of the structure arises from the coupling of the Li atom with the thiol group which can lead to a lower system energy [33]. These metal ion–organic interactions have been shown to reduce the energy of molecular structures. Also, the bulky nature of the thiol group lowers the rotational degrees of freedom thereby reducing the energy of the system as well.

Methionine (Met) forms an interaction at about 3.7 Å with the fullerene surface. The structure is stabilized by internal hydrogen bonding with an off-center distortion of 1.4 Å and a HOMO/LUMO gap of about 21.3 kcal/mol. This structure has a dissociation energy of around −21.2 kcal/mol which is much larger than the isolated non-metal case. The latter case has a higher stability due to its more flexible nature of its side chain that permits increased interactions at more points with the fullerene surface.

3.4. Group 4: acidic amino acids and their amides

For aspartic acid (Asp) the off-center distortion of Li is larger but the intermolecular separation is smaller yielding a dissociation energy of about −27.8 kcal/mol (compared to the non-metal value of −1.16 kcal/mol). Therefore, the stability obtained in this complex arises in part from the metallic nature of the species upon metal insertion.

For the next case, glutamic acid (Glu), we can see that the intermolecular distance is 2.5 Å, and spans a face cap of the fullerene structure. The HOMO/LUMO gap of the

complex appears to suggest a stronger metallic nature of the complex and the dissociation energy is around −14.4 kcal/mol similar to that calculated for Asn as we will see. In any case, the metal ion tends to greatly increase the stability of the resulting structure. Interestingly, the placement of an extra –CH_2 group in this species in comparison to Asp causes the dissociation energy to increase. This can be attributed to steric crowding that causes unfavorable interactions with the fullerene surface.

Asparagine (Asn) has a significant off-center displacement of 1.35 Å which is similar to the isolated Li@C_{60} species that has a value of 1.18 Å. The dissociation energy is around −18.7 kcal/mol which is larger the non-metal case of −2.2 kcal/mol. It is evident from the figure that the contact with the fullerene structure is reduced which has a contact value at about 3.0 Å and larger dihedral angles with respect to the fullerene surface (the association with the fullerene occurs at a more inclined contact point).

Glutamine (Gln) has a small off-center displacement with a dissociation energy of about −20.87 kcal/mol and an intermolecular separation of 2.77 Å. While the interaction energy is significantly higher than the isolated non-metal case, it is reduced due to the fact that the backbone of Gln does not prefer to form extended interatomic interactions with the fullerene. Internal hydrogen bonding does stabilize the structure, but the lack of contact with the C_{60} molecule increases the energy of the complex. In this case, there is stability over the Asn case that permits more interaction at increased points of contact at the fullerene surface. Slight decreases in the HOMO/LUMO gap due to the composition of the side chain is apparent as we can see. The dissociation energies are similar to Group 3 values but the acidic nature of this group seems to resemble those of the aliphatic groups in Group 1.

3.5. Group 5: basic amino acids

Lysine (Lys) has a larger off-center displacement with a smaller HOMO/LUMO gap. The calculated gap reveals that the metal has changed the physical properties of the species studied and the complex exhibits a metallic nature. The dissociation energy of this structure is the largest among all species studied with a value of −34.4 kcal/mol compared to the isolated non-metal case of about −0.77 kcal/mol. The intermolecular separation is 3.3 Å in which its flexible backbone structure is stabilized by a network of hydrogen bonds. The internal stabilization by hydrogen bonding tends to lower the energy of the system and increase specificity with the fullerene cage due to its lack of internal rotations.

For the next structure, arginine (Arg) we can see that there is a smaller off-center displacement (ΔR) of around 0.14 Å with a smaller HOMO/LUMO gap of around 79.7 and 13.27 kcal/mol for the amino acid and the complex, respectively. The dissociation energy of the complex is around −30.2 kcal/mol compared to around −3.36 kcal/mol for the non-metal case. From the figure we can see that the intermolecular separation is around 2.9 Å, and the flexible linear backbone spans the fullerene structure. Internal hydrogen bonding also has a stabilizing effect of the energies of the species studied. Placement of the extra amino group in this case as compared to the previous example causes the dissociation energies to slightly decrease. This can be due to the presence of increased internal hydrogen bonding arrangements that causes it to loss some factor of stability with the fullerene species.

Next, we will explore histidine (His) which also has a minimal off-center displacement as Gly but has a lower HOMO/LUMO gap similar to Glu. The dissociation energy is −25.5 kcal/mol which is much larger than the non-metal case. We tried other configurations but this was the lowest energy structure obtained even after many attempts. This species is also basic and has a slightly lower dissociation energy when compared to Arg, that maybe attributed to the ring that causes steric hindrance.

3.6. Group 6: amino acids with rings

Phenylalanine (Phe) shows an intermolecular separation of 3.5 Å with a off-center distortion of 0.24 Å and a HOMO/LUMO gap of around 37 kcal/mol. The dissociation energy is around −26.9 kcal/mol which is much larger than the isolated non-metal case. Tyrosine (Tyr) has an intermolecular separation of around 3.1 Å that has a minimal HOMO/LUMO gap and a dissociation energy of about −26.7 kcal/mol. We can see that the phenyl ring interacts favorably with the fullerene surface to stabilize the molecular cluster. The extra OH group in Tyr has a minimal effect on the association energy due to the electron donating group of this group. This electron donating characteristic deeply affects the HOMO/LUMO gap as the table suggests.

Tryptophan (Trp) has an intermolecular separation of 3.4 Å with a larger off-center displacement than Thr which has a small HOMO/LUMO gap that results in a dissociation energy of −34.2 kcal/mol that is similar to the Arg case. Interestingly, the ringed systems tend to localize along the fullerene system to maximize interactions with the fullerene.

For the proline (Pro) system the ΔR system is minimal, with an intermolecular separation of around 4.1 Å. This structure has a non-aromatic ring but it is an imino acid by technical terms and shows similar dissociation energy values. The system is stabilized by internal hydrogen bonding with a dissociation energy of about −28.4 kcal/mol. The HOMO/LUMO gap of the complexed system is much smaller than the isolated amino acids which again suggests the importance of the metal ion. This structure although smaller is comparable to Trp due to the heterocyclic ring, but the dissociation energy is lower due to the non-aromaticity of Pro.

4. Conclusions

Physically speaking we have seen that when metals are encapsulated in fullerenes the charge-transfer to the surface increases. As mentioned previously if the metals donate a large portion of their electron density to the surface of the fullerene molecules, this can lead to favorable interactions with biological species. We have used Li due to the fact that this metal species has enhanced charge donor capabilities [15]. Currently, other metals are being computed but this serves as a benchmark for how metal encapsulation inside of fullerenes can improve specificity and reactivity with biological components. The most significant improvement has been observed for Lys, Tyr, and Trp which has been discussed in the above sections.

From an analysis of the groups we have shown that certain important trends can be observed for each classification. As we can see the presence of a thiol group (Group 3) and basic amino acids (Group 5) leads to increased dissociation energy. This is due to the fact that they have intrinsic abilities to donate solvate excess electron density on the fullerene surface. While the role of charge-transfer by Li has not been solidified by this work we can assume that the excess electron density on the fullerene surface donated by Li needs to be solvated by a basic agent. The thiol groups have unique abilities to deal with this density as a result of their HOMO/LUMO gaps.

From the data, we presented we observe that the HOMO/LUMO gap decreases upon complexation. The reason for this is attributed to the fact that the fullerene posesses metallic properties that when coupled to the endohedral Li atom causes the gap to decrease. This permits for the increased reactivity of the newly formed $Li@C_{60}$ complex that can increase its binding affinity to the amino acids. Therefore, it serves as an example of how the metal can allow for the biochemical activity of otherwise toxic compounds. The concept of charge-transfer in these systems as well as the nature of bonding mechanism will be the focus of future studies in our group.

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