Adsorption of Aromatic Amino Acids on Gallium Nitride Nanotubes - A Computational ONIOM Investigation

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Abstract:- **In this study, we have considered the interaction of aromatic amino acids (AAAs), i.e., Phenylalanine (Phen), Histidine (His), Tyrosine (Tyr), and Tryptophan (Trp), with different Gallium Nitride Nanotubes (GaNNTs). For optimization, we have used molecular mechanics (MM) method for GaNNTs and density functional theory (DFT) for aromatic amino acids respectively. We have investigated the interaction between AAAs and GaNNTs using ONIOM methods. We have found that aromatic amino acids are well encapsulated inside the wall of the GaNNTs. For different structures of GaNNTs chiral (10, 5), (12, 6) and armchair (10, 10), (12, 12) it has been found that the adsorption energy (E_{ads}) of all AAAs range from -24.058 to -60.907 kcal/mol.**

Keywords:- *Adsorption; DFT; QM/MM; ONIOM; AAAs; GaNNT.*

I. INTRODUCTION

Recently, nanostructures have received great interest for a wide range of applications due to their outstanding surface, structural and optical properties [1,2]. Even though there are different nanostructures, but nanotubes (NTs) exhibit unique properties because of the unidirectional curvature, large surface areas, and a high degree of shape anisotropy [3]. GaN has a direct and wide bandgap of 3.4 eV [4], which has generated promising interest over the last decade for its potential use in the field of future high performance, high-power optoelectronic devices, chemical and gas sensors, and in many areas of biological sciences [5,6]. Because of difficulties involved in the synthesis process, and scarcity of complete knowledge of physicochemical properties of these nanostructures, improvement in GaNNTs-based devices are limited.

Single-crystalline GaNNTs have been synthesized successfully using epitaxial casting method [7] and reported that the tubes have both an inner and outer surface to which organic molecules can readily adsorb, making the tubes to serve as nanoscale chemical sensors due to its transparent surface properties. The energy of GaNNTs depends on the chiral factor that is the main basis of stability of the nanotubes. The chiral configurations have higher energy while that have been lower in armchair configurations. The bandgap energy is also subjected to the chirality of the nanotubes [8]. Amino acids are biologically significant organic molecules for life and have different roles and functions in the body metabolism containing amine (-NH2) and carboxylic acid (-COOH) functional groups, which are important areas of research [9]. We have chosen AAAs inhibitor molecules in our current paper. Investigation on the adsorption of organic inhibitors like amino acids on metal and alloys and analysis of their chemisorption properties is a vital area of research that has experimental and theoretical importance in academic and industrial fields [10]. The adsorption of the inhibitor molecules depends on certain physical and chemical properties of the molecules, such as functional groups, aromaticity, surface area, steric factor, electronic structure of the inhibitor and the metal molecules, electron density, and the interaction energy between the inhibitor molecule and the metal surface [10,11].

In addition, DFT based theoretical methods have become attractive because they provide exact, and vital factors for small and complex molecules at a lower cost [12]. Quantum Mechanics - Molecular Mechanics (QM/MM) simulations can provide influential perceptions into molecular level on the adsorption of the inhibitor molecules on metal surfaces, and vital information, from which the interaction energy between them can be easily obtained [13]. Moreover, exciting information on the structures of adsorbed inhibitor amino acids onto metal surfaces of GaNNTs, and the adsorption energy between them can be obtained [13]. In this work we report on the adsorption energy, effective atomic contact energies (ACE), the desolvation free energies for interaction between aromatic amino acids and GaNNTs.

II. METHODS OF CALCULATIONS

In this work, the geometry optimization of AAAs (histidine, phenylalanine, tyrosine and tryptophan) were performed using DFT with the Becke's three-parameter hybrid functional using the Lee-Yang-Parr correlation functional theory B3LYP [14] and 6-31G (d,p) basis set. All geometry optimizations of GaNNTs (10, 5), (12, 6), (10, 10), and (12, 12) were performed using molecular mechanics (MM) under universal force field (UFF) theory [15]. For calculation of ACE molecular docking of the

AAAs to GaNNT was accomplished by PatchDock server [16]. Adsorption of aromatic amino acids (AAAs) on GaNNTs were carried out by QM/MM based ONIOM methods [17]. GaNNTs were considered as a high layer (DFT/B3LYP/6-31G(d,p)) and AAAs as a low layer (MM/UFF) in ONIOM method. All optimizations were completed using the Gaussian 09 program [18].

The energy required to adsorb for adsorbate AAAs on adsorbent GaNNTs is adsorption energy. In order to estimate the adsorption energy, E_{ads}, of aromatic amino acids to GaNNTa, we use the following equation:

$$E_{ads} = E_{GaNNTs-AAA} - (E_{GaNNT} + E_{AAA})$$

where $E_{GaNNTs-AAA}$ is the total energy of the fully geometry optimized GaNNTs-AAA complexes and the other two terms correspond to the energy of the GaNNT and aromatic amino acids independently relaxed respectively.

III. RESULTS AND DISCUSSIONS

We have optimized the geometry of the AAAs (histidine, tyrosine, tryptophan, and phenylalanine) and GaNNTs in the gas phase. The optimized structures of AAAs were depicted in Fig. 1.

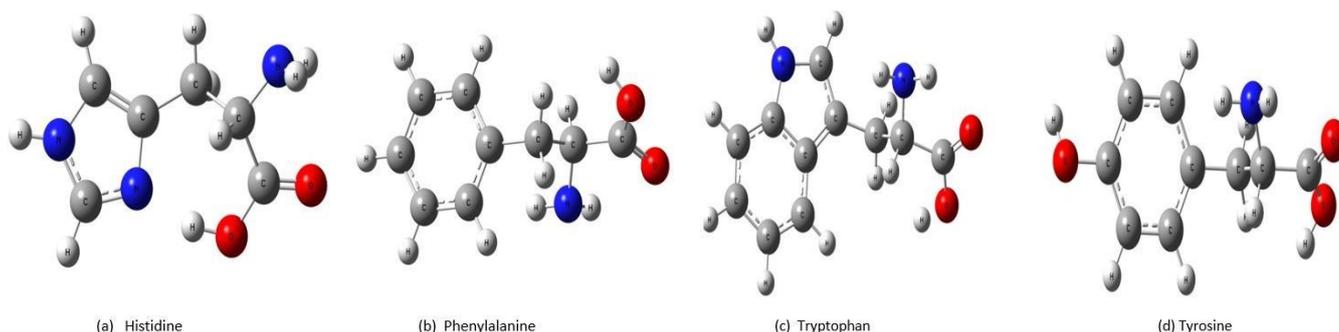(a) Histidine   (b) Phenylalanine   (c) Tryptophan   (d) Tyrosine

Fig 1:- Optimized structure of Aromatic amino acid (a) Histidine (b) Phenylalanine (c) Tryptophan (d) Tyrosine, indicating the atomic alignment the red circles are Oxygen (O), blue circles are Nitrogen (N), dark circles are Carbon (C) and white circles are Hydrogen (H) atom.

The optimized structures of GaNNTs armchair (10, 10) and (12, 12), and chiral (10, 5) and (12, 6) are displayed in Fig. 2. The locations of the atoms in the system are results due to optimization. The optimization result shows that there are buckling of N atoms towards

slightly outwards and the Ga atoms towards slightly inwards in Ga–N bonds in GaNNTs. The dangling bonds of surface-level atoms are the cause of buckling to reduce the surface energy and readjust bonding structure of the system, this result is similar to Lee's [19] experiment.

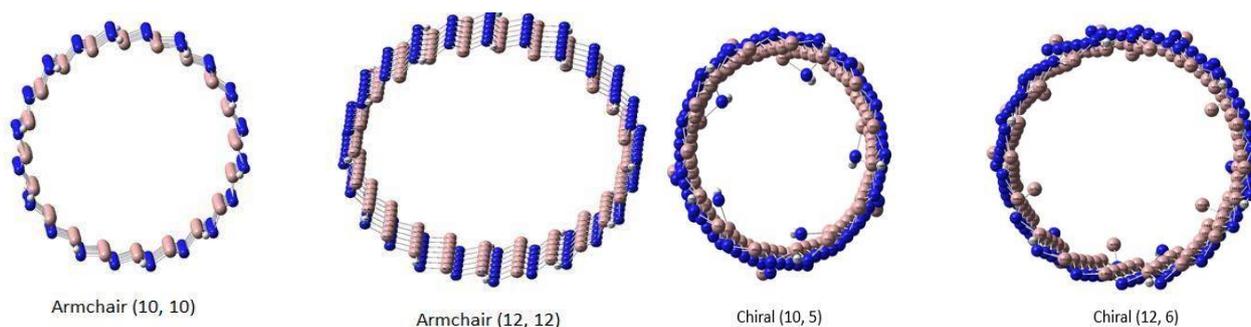Armchair (10, 10)   Armchair (12, 12)   Chiral (10, 5)   Chiral (12, 6)

Fig 2:- Optimized structure of GaNNTs.

Here we have used a very efficient PatchDock server which allows large-scale molecular docking experiments for structure prediction of protein-protein and protein-small molecule complexes [16]. We performed docking between receptor GaNNTs of four structure and ligand AAAs and their optimized structures are illustrated in Fig. 3. We calculated the bond distances of aromatic amino acids after adsorption on GaNNTs have shown in Table 1, the results

show that the selective bond length of amino acids is increased or decreased. In case of tryptophan, the bond length between C(3)-O(4) is 1.207 Å and C(7)-N(9) is 1.382 Å before interaction, but after interaction with GaNNTs chiral (10, 5) and armchair (10, 10) the bond distance of C(3)-O(4) are 1.259 Å and 1.260 Å and bond distance of C(7)-N(9) are 1.428 Å, and 1.431 Å respectively, which is greater than before.

Similarly, the bond distance between C(2)-C(5) is 1.555 Å before interaction, but after interaction with chiral (10, 5) and armchair (10, 10) the changed bond distances are 1.541 Å and 1.540 Å respectively. For the interaction between tryptophan and other GaNNTs, similar studies have been calculated. For phenylalanine, the bond length of C(3)-O(22) is 1.355 Å before interaction but after interaction with chiral (10, 5) and armchair (10, 10) of GaNNTs the bond distance of C(3)-O(22) are 1.396 Å and 1.395 Å respectively, which is larger than before. For the interaction between phenylalanine and other GaNNTs, similar studies have been calculated.
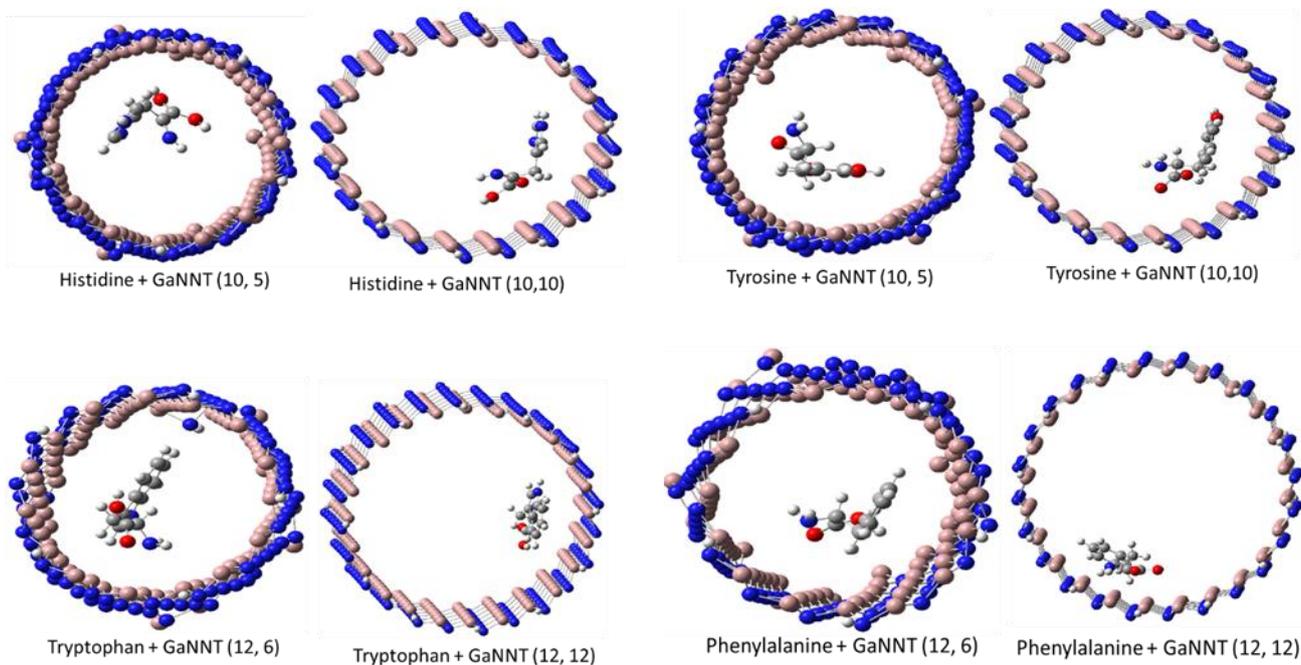

Fig 3:- Optimized structure of complexes AAAs and different GaNNTs.

Aromatic amino acids	Bonds between atoms	Distance in Å (before docking)	(10, 5)	(10, 10)	(12, 6)	(12, 12)
			Change in distance Å (after docking)	Change in distance Å (after docking)	Change in distance Å (after docking)	Change in distance Å (after docking)
Tryptophan	N(1)-C(2)	1.453	1.468	1.468	1.465	1.467
	C(3)-O(4)	1.206	1.259	1.260	1.259	1.260
	C(2)-C(5)	1.555	1.541	1.540	1.511	1.514
	C(7)-N(9)	1.381	1.428	1.431	1.429	1.428
	N(9)-C(10)	1.379	1.342	1.419	1.342	1.343
Histidine	C(8)-C(6)	1.377	1.325	1.324	1.324	1.325
	C(6)-N(7)	1.400	1.421	1.422	1.422	1.422
	C(2)-C(3)	1.553	1.514	1.508	1.508	1.508
	C(3)-O(19)	1.350	1.390	1.389	1.390	1.390
Phenylalanine	C(3)-O(22)	1.355	1.396	1.395	1.395	1.395
	O(4)-C(3)	1.206	1.259	1.260	1.260	1.260
	C(2)-N(1)	1.453	1.468	1.467	1.467	1.467
	C(9)-C(11)	1.396	1.398	1.398	1.398	1.398
Tyrosine	N(1)-C(2)	1.454	1.468	1.467	1.467	1.467
	C(3)-O(4)	1.206	1.260	1.260	1.259	1.260
	C(2)-C(5)	1.556	1.542	1.541	1.539	1.540
	C(10)-C(11)	1.398	1.405	1.405	1.405	1.405
	C(11)-O(12)	1.366	1.396	1.396	1.397	1.397

Table 1:- Change in bond distance between atoms for tryptophan, histidine, phenylalanine and tyrosine for (10, 5), (10, 10), (12, 6) and (12, 12) structures before and after docking.

The bond distance of C(3)-O(4) and C(3)-O(22) have increased because of the greater attraction between more electronegative oxygen of amino acid and electropositive Ga of GaNNT where C(3)-O(4) and C(3)-O(22) have a lower attraction. The C-C bond distances have been decreased because of the slight charge difference of carbon and gallium atom and less interaction between C and Ga atom.

We also investigated that the calculation indicates that there exhibit C-C a weak π-π interaction inside the aromatic amino acid. The change in bond distance of other aromatic amino acids (histidine and tyrosine) due to interaction with GaNNTs shows very similar readings that have been reported in Table 1. It is interesting to note that the amino acid molecules interact with the GaNNTs by both π−π and

CH…π type of interaction. In all the cases of the amino acids complexes, the oxygen atoms, the CH2 group and aromatic rings are oriented towards the GaNNTs inner wall and well encapsulated.

We calculated the electronic properties bandgap of aromatic amino acid using DFT calculation. The calculated band gap energy in eV is shown in Table 2. It has found that the bandgap energy of tryptophan is smaller (5.21 eV) and phenylalanine (6.27 eV) is greater. The order of bandgap energy Trp<His<Tyr<Phen. This is because phenylalanine and tyrosine both structure have benzene ring, on the contrary, there exist aromatic ring inside tryptophan and histidine. Therefore, the charge transfer between C-C is lower than the C-N bond is the cause of larger bandgap.

Aromatic amino acid	Bandgap in eV	ACE in (kcal/mol)			
		Chiral (10, 5)	Armchair (10, 10)	Chiral (12, 6)	Armchair (12, 12)
Tryptophan	5.21	-4.115	-3.746	-4.143	-3.642
Histidine	5.23	-2.422	-1.859	-2.336	-1.754
Tyrosine	5.80	-3.944	-3.370	-3.390	-3.208
Phenylalanine	6.27	-4.025	-3.388	-3.545	-3.302

Table 2:- Atomic contact energy (ACE) for the interaction of aromatic amino acids with different GaNNTs.

We have calculated the atomic contact energy which is the desolvation free energy shown in Table 2. The unit less ACE has transformed into unit Kcal/mol multiplying by 1/21 [20]. From Table 2 it is clear that the ACE is greater for every chiral nanostructure for each

aromatic amino acid and smaller for armchair nanostructures. We also found that the ACE is larger for tryptophan which has smaller bandgap. From Table 3, we have found a sequence of ACE varies as follows CHIRAL >ARMCHAIR.

AAAs	GaNNTs	Bandgap of GaNNTs and AAAs complexes in eV	E_{ads} in kcal/mol
Histidine	(10, 5)	4.523	-34.512
	(10, 10)	4.493	-25.166
	(12, 6)	4.516	-52.865
	(12, 12)	4.223	-24.058
Phenylalanine	(10, 5)	6.244	-38.368
	(10, 10)	6.307	-30.775
	(12, 6)	6.347	-57.855
	(12, 12)	6.279	-26.699
Tryptophan	(10, 5)	5.232	-43.188
	(10, 10)	5.176	-40.161
	(12, 6)	5.189	-59.684
	(12, 12)	5.177	-32.908
Tyrosine	(10, 5)	5.813	-39.956
	(10, 10)	5.818	-31.393
	(12, 6)	5.806	-60.907
	(12, 12)	5.821	-28.150

Table 3:- Bandgap energy of GaNNTs and AAAs complexes and adsorption energy of AAAs on GaNNTs.

The adsorption energy of AAAs on GaNNTs have been shown in Table 3. From the table, we see that the bandgap energy of AAAs has been changed due to interaction with the GaNNTs which carries significant results of adsorption of AAAs.

IV. CONCLUSIONS

In summary, we have studied the adsorption of hydrocarbons (aromatic amino acids) on gallium nitride nanotube using ONIOM method. The change in bond distances provides significant evidence for adsorption. The aromatic amino acids are well encapsulated with different GaNNTs. It has found that the bandgap of tryptophan is smaller (5.21 eV) and phenylalanine is greater (6.27 eV). The order of bandgap is Trp<His<Tyr<Phen. We also found that the ACE is larger for tryptophan which has smaller bandgap. The ACE is greater for each aromatic amino acid for each interaction with any chiral structure of GaNNTs. We have been found that there is a change in bandgap for each interaction of AAAs with the GaNNTs and the adsorption energy (E_{ads}) of all AAAs range from -24.058 to -60.907 kcal/mol. From this investigation, we recommend that GaNNTs can be a promising candidate for future biological sensors.

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