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ADSORPTION MECHANISM AND STRUCTURAL INVESTIGATION OF DOPED C_{60} FULLERENES WITH PENTYLAMINE

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ABSTRACT

Interaction mechanisms of doped fullerenes and various types of molecules have been paid increasing attention. In this research, adsorption mechanism, structural and electronic properties, natural bond orbital (NBO) analysis between pentylamine (pa) and doped (Si or Al) C_{60} fullerenes were investigated by density functional theory (DFT). Results of bond order and binding energy (E_b) suggest that a chemisorption occurs between nitrogen atom of pa and silicon or aluminum atoms of doped fullerenes, the complexes yielded with higher E_b value in water media and the system of AlC_{59}…pa in water was found as having the highest E_b value.

Keywords: Adsorption mechanism, Doped C60 fullerene, NBO, DFT

1. INTRODUCTION

Nanoscience has found an important place for itself in many fields. One current field is production of drug delivery systems with fullerene nanocage [1-3]. Fullerene incorporated drug systems have been examined with an increasing popularity due to their low toxicity and less side effects [1-3]. Further, it is possible to change some properties such as molecular stability and conductivity by doping fullerenes [4]. Pentylamine has been used as solvent or raw material in the synthesis some compounds including dyes, emulsifiers and pharmaceutical products [5]. It was also employed in the search of the treatment of urge urinary incontinence [6]. In 2001, Qiao and coworkers reported UV/Vis absorption, fluorescence spectra and dynamic study on interactions of C_{60} with eight kinds of aliphatic amines, such as diethylamine, triethylamine, tri-n-amylamine, propylethylamine, n-butylamine, n-heptylamine, dodecylamine and ethylenediamine [7]. They showed that charge transfer interactions of C_{60} with aliphatic amines are much stronger than that of C_{60} with aromatic amines and products can all emit a strong fluorescence at the relatively shorter wavelength around 519 nm.

Recently, interactions between nanocages and ligands have become an important subject and they can be used together as drug delivery agent and sensor [8-12]. In these studies, structures of doped C_{60} fullerenes with drug molecules as 1-formylpiperazine, amphetamine or favipiravir were investigated by DFT. In the present work, the adsorption mechanism of pa with doped C_{60} fullerenes with silicon and aluminum atoms have been investigated by the B3LYP functional with 6-31G(d) basis set in gas and water environments for the hope of better understanding and possible future applications of amines and doped fullerene complex systems. From the quantum mechanical findings, the structural and spectroscopic discussions were reported here.

2. CALCULATIONS

All computations were performed with the Gaussian 09 in gas phase and water media [13]. Multiwfn program was also included to find out Wiberg bond index (WBI) and Fuzzy bond order (FBO) and to gain more understandings in the nature of bonding [14]. The DFT method was used to optimize the

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investigated clusters as seen in Figure 1. The functional used was B3LYP and the basis set for all atoms was 6-31G(d). Frequency computations based on the same geometry optimization method were used to confirm the nature of the stationary points. No imaginary frequencies were encountered. Calculations of E_b, frontier molecular energy gap (E_g), geometrical parameters, NBO, harmonic wavenumber and NMR shift were performed.

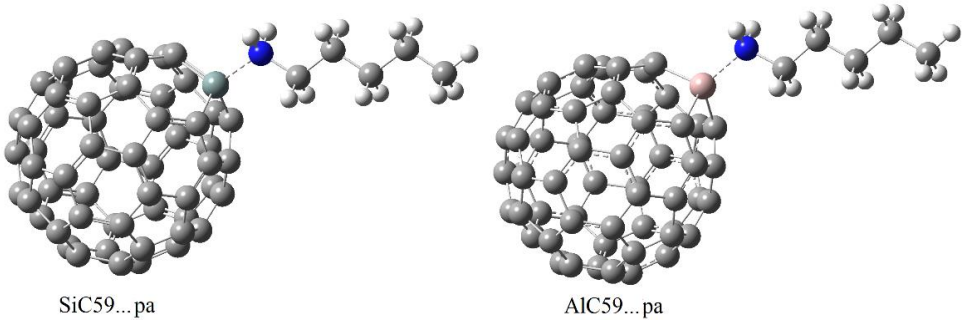

Figure 1. Optimized structures of the investigated complexes

3. RESULTS AND DISCUSSIONS

Interaction site and bonding properties of pa and doped fullerenes were analysed based on NBO calculations (Table 1). Regarding the results of NBO analyses, it is clear that effective interaction site for pa is the nitrogen atom.

Table 1. NBO analyses of the investigated structures

Structure	Atom	Valence number	Mulliken charge	NBO charge	FBO	WBI
Gas						
AlC_{59}	Al	3.321	0.395	1.642	-	-
SiC_{59}	Si	3.604	0.344	1.286	-	-
Pa	N	2.766	-0.704	-0.888	-	-
SiC_{59} + pa	N	2.983	-0.746	-0.940	0.925	0.652
	Si	4.065	0.539	1.896		
AlC_{59} + pa	N	2.955	-0.792	-0.969	0.844	0.645
	Al	3.565	0.377	1.663		
Water						
AlC_{59}	Al	3.210	0.501	1.735	-	-
SiC_{59}	Si	3.608	0.360	1.303	-	-
Pa	N	2.740	-0.749	-0.915	-	-
SiC_{59} + pa	N	3.025	-0.761	-0.958	0.987	0.734
	Si	4.012	0.632	1.936		
AlC_{59} + pa	N	2.989	-0.803	-0.989	0.892	0.705
	Al	3.500	0.462	1.708		

Results of E_b examinations given in Table 2 show that AlC_{59}…pa has the highest E_b values in both gas and water. It was also observed that SiC_{59}…pa and AlC_{59}…pa systems by introducing water become more stable compared to gas phase. Binding energies lie in the range of 30-52 kcal/mol addressing a possible chemisorption [15]. Results of solvent energy (E_s) mean that Si-compound is more soluble than Al-compound by 2.47 kcal/mol. Proper distances are required to build a chemical bond between two atoms [16]. Bond distances of Si…N and Al…N in gas and water were found as 1.95 / 1.90 Å and 2.02 / 1.99 Å, respectively. It was seen that upon introduction of water as solvent these distances were decreased and E_b energies were increased.

Furthermore, NBO results can describe acceptor-donor interactions [17]. In Table 1, it is seen that Mulliken and NBO charges suggest the formation of acceptor-donor couples between Si/Al and N atoms in the examined complexes. FBO and WBI can be used to evaluate the degree of covalent bonding [18]. In the current work, when the calculated these indexes are examined in Table 1, it is seen that covalent bond characters between Si/Al and N atoms increase from gas to water media in compliance with E_b values for the complexes.

Table 2. Energies (kcal/mol) of the investigated structures

Structure	B3LYP/6-31G(d)		
	E_b (gas)	E_b (water)	E_s
Pa	-	-	-2.90
SiC_{59}	-	-	-1.01
SiC_{59} + pa	-30.17	-41.44	-15.18
AlC_{59}	-	-	-3.91
AlC_{59} + pa	-45.86	-51.76	-12.71

At the presence of pa, the conductivity of the Si-/Al-doped C_{60} increases due to the reduction of E_g values by about 4/5% and 10/8% in gas phase and water correspondingly. Chemical hardness and electrophilicity index are the indicators of chemical stability and reactivity. As values of E_g and chemical hardness for both complexes decreased from gas to water phase calculations offering the least resistance to charge transfer in water phase, the reverse was observed for electrophilic behaviour of these complexes as seen in Table 3.

Table 3. Electronic properties (eV) of the investigated structures

Structure	HOMO	LUMO	E_g	Chemical Hardness	Electrophilicity Index
Gas					
C_{60}	-5.985	-3.227	2.758	1.379	7.692
SiC_{59}	-5.818	-3.649	2.169	1.085	10.330
AlC_{59}	-5.377	-3.119	2.258	1.129	7.992
SiC_{59} + pa	-4.673	-2.587	2.086	1.043	6.317
AlC_{59} + pa	-4.748	-2.598	2.150	1.075	6.275
Water					
C_{60}	-5.868	-3.109	2.759	1.380	7.302
SiC_{59}	-5.687	-3.517	2.170	1.085	9.760
AlC_{59}	-5.254	-3.017	2.237	1.119	7.645
SiC_{59} + pa	-4.768	-2.805	1.963	0.982	7.304
AlC_{59} + pa	-4.892	-2.834	2.058	1.029	7.251

The frequency shifts in NMR and IR for N, Si or Al atoms and asymmetric or symmetric NH_2 stretching vibrations, respectively, were also performing to support interactions between nitrogen of pa and Si or Al atoms of fullerene cages. For the NMR and IR results given hereby belong to the water and gas phase, respectively. The relative chemical shifts of ^{29}Si and ^{27}Al nuclei changed around 86 ppm and 122 ppm from SiC_{59} and AlC_{59} to SiC_{59}…pa and AlC_{59}…pa whereas ^{15}N relative chemical shifts changed around 24 ppm and 7 ppm for SiC_{59}…pa and AlC_{59}…pa correspondingly as comparing with free pa. Turning to IR data, asymmetric / symmetric NH_2 stretching wavenumbers were decreased about 52 / 38 cm^{-1} and 31 / 15 cm^{-1} for Si- and Al-complex correspondingly. These results also indicate the possible formation of chemical bonding between Si or Al and N atoms due to chemisorption.

4. CONCLUSIONS

Binding energy values of pa to the Si- and Al-doped fullerenes suggest that doping of fullerene nanocage enhances the interaction mechanism and alters the structural, chemical and electronic properties of the complexes. When the Si- and Al-doped fullerenes interact with pa, the complexes become more stable leading E_b energies lie in the range of chemisorption. Investigated complexes become more stable in water media when compared to gas phase computations. AlC_{59}…pa in water is found as the most stable while SiC59…pa is more soluble than Al-complex. NBO, NMR and IR analyses also suggest a possible bonding between Si or Al atoms of the doped fullerene cages and nitrogen atom of pa. Findings of the current research can be useful for better understanding possible future applications of amines and doped fullerene complex systems.

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