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Non-Covalent Functionalisation of $C_{30}$ Fullerene by Pyrrole-$n$-Carboxylic Acid ($n = 2, 3$): Density Functional Theory Studies

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Abstract: For functionalisation of a representative $C_{30}$ fullerene nanostructure by pyrrole-$n$-carboxylic acid ($P_nCA; n = 2, 3$) their stabilities and properties were investigated based on density functional theory calculations. Parallel calculations were also done for $C_{60}$ fullerene as evidence for comparing the results. Non-covalent interactions are considered to make the functionalised structures. In contrast with the spherical shape of $C_{60}$, the shape of $C_{30}$ fullerene is elliptical; therefore, the functionalisation processes were done for both axial and equatorial elliptical positions ($AC_{30}$ and $EC_{30}$). The results indicated that both the positions of $C_{30}$ have almost equivalent chances to be functionalised by $P_nCA$; but functionalisation by $P_2CA$ is slightly more favourable than $P_3CA$, either for $C_{60}$. The illustrated molecular orbitals’ distributions indicated that the direction of charge transfer could be considered from $P_nCA$ counterparts to fullerene counterparts. The molecular properties indicated more reactivity for $C_{30}$ than for $C_{60}$ fullerene. Finally, the atomic scale quadrupole coupling constants indicated different roles for N and O atoms of $P_nCA$ in the functionalised models.

Keywords: Density Functional Theory (DFT); Fullerene; Functionalisation; Pyrrole-$n$-Carboxylic Acid.

1 Introduction

Since carbon nanotube were discovered [1], considerable efforts have been dedicated to create novel applications for the carbon-based materials, especially biological applications [2, 3]. Increasing water solubility is one of the methods to reduce or modify the initial toxicity of carbon nanostructures for applications in biological systems [4]. In this case, covalent and non-covalent functionalisation of carbon nanostructures by biological molecules could be considered as an important task [5, 6]. Nucleic acids, proteins, peptides and organic molecules are suitable candidates for either covalent or non-covalent functionalisation of carbon nanostructures [7, 8]. Moreover, functionalisation of carbon nanostructures could yield novel materials for applications in energy storages and conversions [9, 10]. The effects of functional counterparts on the electronic and structural properties functionalised counterpart could create novel properties for the new hybrid materials [11]. Based on electronic conductivities characters, the carbon nanostructures could be considered as metals or semiconductors, in which their bio-molecular functionalisation could create bio-compatibility for them to be used in life sciences and technologies [12]. Pyrrole and its derivatives in molecular or polymer forms are important compounds for applications in various fields ranging from industries to living systems [13–15]. Small molecular size and heterocyclic structure make pyrrole a good functional counterpart for the carbon nanostructures [16–18]. In addition, carboxylic acid derivative of pyrrole could yield structures for specific purposes because of the existence of keto-enol groups besides the original amine group in pyrrole-carboxylic acid structures [19–21]. Earlier studies indicated the possibility of functionalisation of carbon nanostructures by pyrrole-carboxylic acid [22].

Within this work, we investigated non-covalent modifications of a representative fullerene nanostructure by performing quantum chemical computations. Since the introduction of $C_{60}$ fullerene nanostructure [23], considerable efforts have been dedicated to characterise other fullerenes, in which experimental recognition of the
higher homologues of $C_n$ fullerenes ($n > 60$) were achieved more easily than the lower homologues ($n < 60$) [24]. It is worth noting that the pioneering $C_{60}$ fullerene is not suitable to employ in all applications because of the required electronic and structural properties for specific applications [25]. Therefore, it is still important to investigate the existence of other $C_n$ ($n \neq 60$) fullerene nanostructures. In this case, recognition of smaller $C_n$ fullerenes, especially ones smaller than $C_{40}$, has been mainly done based on computations either performed as a prior step to experiments or as an alternative procedure for studies of these important nanostructures [26]. Hence, as an advantage of computations, possibilities and properties for non-covalent functionalised models of a representative $C_{30}$ fullerene nanostructure by pyrrole-$n$-carboxylic acid ($P_n$CA; $n = 2, 3$) counterparts (Fig. 1) were investigated in this work based on density functional theory (DFT) calculations. To carry out the functionalisation processes, we considered two axial and equatorial positions for the elliptical $C_{30}$ fullerene ($AC_{30}$ and $EC_{30}$) to be functionalised as $P_n$CA@$AC_{30}$ and $P_n$CA@$EC_{30}$ structures (Fig. 1). Moreover, similar modifications were done for the $C_{60}$ fullerene nanostructure (Fig. 2) as evidence for comparing the results of $C_{30}$ modified structures. The DFT calculations were performed to evaluate the optimised structures (Figs. 1 and 2) and the corresponding molecular and atomic scales properties (Tabs. 1 and 2, Fig. 3). The results are discussed to reveal information about various aspects of the purposes of this work.

2 Computational Details

In this work, properties for singular and functionalised structures of $P_n$CA (pyrrole-$n$-carboxylic acid; $n = 2, 3$) and $C_{30}$ fullerene in axial and equatorial positions ($AC_{30}$ and $EC_{30}$) (Fig. 1) were investigated based on DFT calculations. Moreover, $P_n$CA functionalisations were done for the $C_{60}$ fullerene resulting in two $P_2$CA@$C_{60}$ and $P_3$CA@$C_{60}$ models (Fig. 2). First, all singular molecular structures ($P_2$CA, $P_3$CA, $C_{30}$ and $C_{60}$) were optimised to achieve the minimised energy structures. Second, functionalisations of elliptical $F$ in both axial and equatorial positions ($AC_{30}$ and $EC_{30}$) were done by each of $P_2$CA and $P_3$CA counterparts. As the $C_{60}$ fullerene has a spherical shape, two functionalised models of $P_2$CA@$C_{60}$ and $P_3$CA@$C_{60}$ were created. Next, the new models including $P_2$CA@$AC_{30}$, $P_3$CA@$AC_{30}$, $P_2$CA@$EC_{30}$ and $P_3$CA@$EC_{30}$ were optimised again to find
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The minimised energy structures. Subsequently, molecular properties were evaluated by the performed calculations for the investigated models (Tab. 1, Figs. 1–3). To ensure the validity of calculated energies, calculations based on the counterpoise theory were performed to check the basis set superposition error (BSSE) for the functionalised structures [27]. Total energies (\(E_T\)), BSSE correction energy (\(E_{\text{BSSE}}\)) and dipole moments (\(D_M\)) were directly calculated for the structures. As seen in Table 1, the values of BSSE corrections are almost negligible in comparison with total and binding energies. Interaction distances between two distinguished atoms of \(\text{PnCA}\) and fullerenes are designated by (\(D_{N\cdots\text{C}}\)) in the functionalised models to show the minimum distance of two molecular counterparts.

To obtain the values of binding energies (\(E_B\)) between \(\text{PnCA}\) and fullerene (F) counterparts, (1) is used:

\[
E_B = E_{\text{(PnCA@F)}} - E_{\text{(PnCA)}} - E_{\text{(F)}}
\]  

(1)

Energies for the highest occupied and the lowest unoccupied molecular orbitals (HOMO and LUMO) were calculated and their differences were evaluated as energy gap (\(E_G\)):

\[
E_G = E_{\text{LUMO}} - E_{\text{HOMO}}
\]  

(2)

Based on the HOMO and LUMO energies, the values of ionisation potential (\(I\)) and electron affinity (\(A\)) are evaluated using (3) and (4):

\[
I = -E_{\text{HOMO}}
\]  

(3)

\[
A = -E_{\text{LUMO}}
\]  

(4)

Mulliken electronegativity (\(\chi\)) is evaluated using (5):

\[
\chi = (I + A) \div 2
\]  

(5)

The chemical hardness (\(\eta\)) and softness (\(\sigma\)) are evaluated using (6) and (7):

\[
\eta = (I - A) \div 2
\]  

(6)

\[
\sigma = (2\eta)\div h
\]  

(7)

To examine the atomic scale properties, quadrupole coupling constants (\(C_{ij}\)) were evaluated for the N and O atoms of \(\text{PnCA}\) counterparts in both singular and functionalised models (Tab. 2). Along with this, electric field gradient (EFG) tensors were calculated and then converted to \(C_{ij}\) using (8), in which \(e\) is the electric charge, \(Q\) is the standard value of nuclear quadrupole moment and \(q_{zz}\) is the largest eigenvalue for the EFG components; \(|q_{xx}| \geq |q_{yy}| \geq |q_{zz}|\), and \(h\) is the Planck’s constant [28].
To illustrate the HOMO and LUMO distribution patterns (Fig. 3), time-dependent (TD-DFT) calculations were performed for each of the optimised structures. All computations of this work were done employing the CAM-B3LYP exchange-correlation functional and the 6-31++G** standard basis set as implemented in the Gaussian program [29]. Moreover, the keyword IOp(3/124 = 3) was included in the computations to include dispersion effects corrections for the interacting systems [30, 31].

3 Results and Discussion

In this work, we investigated stabilities and properties for the functionalised PnCA@C\(_{30}\) structures (Fig. 1) based on the evaluated computational parameters (Tabs. 1 and 2). To compare the obtained results of C\(_{30}\) models using evidence similar investigations were performed for the C\(_{60}\) fullerene structure to obtain results for the PnCA@C\(_{60}\) models (Fig. 2). After optimisations of the singular structure of 2- and 3-carboxylic acid derivatives of pyrrole (P2CA and P3CA) and the representative C\(_{30}\) fullerene (Fig. 1), the functionalised models were re-optimised to obtain the minimised energy structures. By the optimisation processes, two axial and equatorial orientations were obtained for the elliptical structure of C\(_{30}\) fullerene. Therefore, both orientations were considered as possible sites for occurrence of interactions between the PnCA and C\(_{30}\) counterparts. To address this point, four functionalised models were constructed including P2CA@AC\(_{30}\), P3CA@AC\(_{30}\), P2CA@EC\(_{30}\) and P3CA@EC\(_{30}\) structures, in which A and E designate the non-covalent functionalisation of axial or equatorial orientation of elliptical C\(_{30}\) (Fig. 1). The optimisation of C\(_{50}\) fullerene yielded only a spherical structure, in which two non-covalent functionalised P2CA@C\(_{60}\) and P3CA@C\(_{60}\) models were constructed for C\(_{60}\) (Fig. 2). Comparing the values of total energies (Tab. 1) indicates that the stability of the P2CA derivative of pyrrole is higher than the P3CA derivative. Parallel results are also seen for the functionalised models, in which the stabilities of P2CA@F are higher than that of P3CA@F in both C\(_{30}\) and

\[
C_{ij} (\text{MHz}) = e^{2}Q_{ij} \frac{\hbar}{2}
\]

(8)
fullerene (F) models. The values of N·–C interaction distances and binding energies are both supportive for the obtained trends by the total energies; shorter interaction distances and lower binding energies were observed for the P2CA@F models in comparison with P3CA@F models. Interestingly, the interacting distances for both P2CA@AC30 and P3CA@AC30 models are identical to those of P2CA@C60 and P3CA@C60 models indicating supportive elements for the investigated C60 model. It is important to note that the interactions between PnCA and F counterparts are non-covalent for both C30 and C60 models. In an earlier work, it was shown that the molecular interactions between uracil and small silicon carbide fullerene structures yielded covalent interactions for the silicon-rich fullerene models and non-covalent interactions for the carbon-rich fullerene models [32]. In another work, non-covalent interactions were recognised between vitamin C and C60 fullerene counterparts [33]. Indeed, several applications in biological systems, carriers for drug delivery systems, for example, are expected for carbon nanostructures, in which it is very important to recognise the characteristic behaviors of these materials [34, 35]. In this case, computational chemistry could provide bright information for the complicated nanostructures at the molecular/atomic scales.

Further examination of the results of Table 1 reveals that the values of each of ionisation potentials, electron affinities and energy gaps (I, A and Eg) are similar for the P2CA and P3CA counterparts. However, in the functionalised models, the F counterpart modulates them into values close to the values of each of the original F counterparts. Careful examinations of the values of Eg for C60 and C30 counterparts in singular or functionalised forms indicate that the reactivity of smaller F is more than that of the larger one, which is one of the reasons for the difficulties of the synthesis of small F nanostructures. Interestingly, the distribution patterns (Fig. 3) indicate that the HOMO distributions are almost identical for singular P2CA and P3CA models; however, the LUMO distributions are significantly different for the mentioned structures. The HOMO distributions are localised on the pyrrole ring for both P2CA and P3CA models whereas the LUMO distribution of P2CA is mainly localised on the whole structure and that of P3CA is only localised on the N-H amine group. For the functionalised models, the distribution patterns are mainly localised on the F counterparts as expected by the Eg values which were all close to the singular F counterparts. Parallel to the results of distribution patterns, the magnitudes of electronegativity (χ) (Tab. 1) also demonstrate that the direction of charge transferring is from PnCA to F counterparts. These achievements could be also very well approved by the magnitudes of chemical softness and hardness (η and σ); it is obvious that the charge transfer to the F counterpart is more achievable than to the PnCA counterpart. The magnitudes of dipole moments indicate that functionalisation could increase the polarity of F structure, which raise benefits for carbon structures to be dispersed in water media. The polarities for P3CA@F structures are more than for P2CA@F structures in both C30 and C60 models, which could be in agreement with lower stabilities of P3CA@F than P2CA@F functionalised structures. Moreover, the magnitude of dipole moment for C60 is zero remembering the spherical shape of the structure; however, it is a meaningful value for C30 remembering the elliptical shape of the structure. Additionally, it could be expected that the smaller F has more reactivity than the larger F, which has been mentioned above as one of the probable reasons of difficulties for their synthesis. Therefore, performing computational studies could be an advantage avoiding the complexity of experiments to characterise small F structures.

The atomic scale CQ (quadrupole coupling constant) properties for N and O atoms of PnCA counterparts in both singular and functionalised models approve the existence of interactions between the PnCA and F counterparts. The CQ properties are very sensitive to the electronic environments of atoms and they could detect any perturbations to this environment [36–38]. Indeed, the EFG tensors, which have arisen from the electronic sites of the quadrupolar nuclei, e.g. 14N and 17O with nuclear spin angular momentum greater than ½, could detect the perturbation effects to the electronic sites of atoms [39, 40]. The CQ properties are the experimentally measurable parameters, which are generated from the interactions of the nuclear quadrupole moment (Q) and the EFG tensors, (8) [28]. Examining the CQ properties (Tab. 2) indicates that the magnitudes for N atoms are all decreased in functionalised models in comparison with the singular PnCA models whereas the magnitudes for O atoms are increased in the same direction. As electronegativity of O is larger than N, it could be mentioned that the O atom adsorbs the electrons whereas the N atom releases the electrons during the molecular interactions. As indicated by the magnitudes for O atoms, O1 and O2 do not detect identical electronic environments; therefore, they behave different to each other. In this case, it could be recognised that the atomic scale properties are very much important to focus on the point to point of structural behaviors as could be seen by the CQ magnitudes.
4 Conclusion

We performed DFT calculations to investigate the stabilities and properties of PnCA@F functionalised models. The values of total energies, binding energies and interaction distances indicated that the P2CA@F models could be expected to be more stable than the P3CA@F models, in which the EC\textsubscript{30} and AC\textsubscript{30} models are almost in similar favorability. By the molecular properties for indicating the charge transfer, the F counterpart wins the chance to obtain the charges in the functionalised models as could be seen visually by the HOMO-LUMO distribution patterns. Comparing the results of C\textsubscript{30} models with C\textsubscript{60} indicate more reactivity of small F structures in comparison with the larger ones, which could be a probable reason of difficulties of their synthesis. The atomic scale C\textsubscript{Q} properties for PnCA counterparts also approved the interactions between the PnCA and F counterparts in the functionalised models revealing that the N atom plays the donor role and the O atom plays the acceptor role in the interacting systems.

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