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DFT/NBO Analysis of Interaction between 4-hydroxycoumarin and Single Walled Carbon Nanotubes in Pistachio

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A R T I C L E I N F O

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A B S T R A C T

Fruits, vegetables, oils, coffee, nuts, and tea contain coumarin. The scientific attraction of coumarins is attributed to their pharmacological activity. In this study, density functional theory (DFT) calculations were performed in the B3LYP/6-31G(d) level of theory to evaluate the potentialities of single-walled carbon nanotubes (SWCNT) as a carrier for 3-acetyl-6-methyl-4-hydroxy-coumarin. The natural bond orbital (NBO) analysis suggested that the functionalized nanotube plays the role of an electron donor and 3-acetyl-6-methyl -4-hydroxy-coumarin molecule acts as an electron acceptor at the SWCNT -coumarin complex. Variations of density and dipole moment values of coumarin after interaction were studied. Also, the frontier orbital energies, HOMO-LUMO gap, chemical hardness (η), electrophilicity index (ω), charge transferred (ΔN_{max}) and chemical potential (μ) were computed. Pure coumarin is less conductive and smoother than SWCNT -coumarin. Our results show efficient coumarin loading with the interaction energy of -1.19 eV. NBO analysis shows that the occupied orbitals in the coumarin and the unoccupied orbitals in the nanotube overlap.

Introduction

Nuts contain phenolic compounds that are good for health (Cheniany *et al.*, 2013; Jahanbani *et al.*, 2016). Phenolic compounds of nut crops are divided into flavonoids, lignans, stilbenes, coumarins, tannins and phenolic acids etc. (Alasalvar *et al*., 2020; Sharifkhah et al., 2020; Jahanbani *et al.*, 2018; Alasalvar *et al*., 2015; Alasalvar *et al*., 2011; Arriagada *et al*., 2018). Coumarin (2H-1-benzopyran-2-one) is a plant-derived natural product that has pharmacological properties such as anticancer, anti-inflammatory, antiviral, anticoagulant, antiadipogenic, antibacterial, antifungal, antioxidant, antihypertensive, antituberc ular, anticonvulsant, and antihyperglycemic (Bhagat *et al*., 2019; Pereira *et al*., 2018; D. Pantarotto *et al*., 2004; N. Etminan *et al*., 2016; Balasubramanian *et al*., 2006; Pantarotto *et al*.,2004). Many of the natural coumarins isolated from plants have been found in microorganisms. These compounds are found in coffee, tea, vegetables, seeds, fruits and wine nuts (Romer et al., 2009). The anti-cancer and anti-inflammatory properties of coumarin derivatives are also related to their antioxidant properties. (Witaicenis et al. 2012).

When the coumarin ring is absorbed by the CNT, the resulting compounds may have interesting and unprecedented properties. In addition, the biological activity of both rings increases (Sandhu, et al. (2014). Such compounds are used in the development of various new and unique coumarin-based therapeutic agents. Carbon nanotubes (CNTs) (Iijima *et al*. 1993) are described as hollow cylinders formed that classified into

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single-walled, double-walled and multi-walled. They have interesting properties and unique structure (Tiwari *et al*. 2012). CNTs can be loaded with drugs by forming stable covalent bonds. They can enhance the cellular uptake of therapeutic molecules by interacting with the cell membrane. Several studies have done on anticancer drugs – CNTs (Huang *et al.*,2011; Saikia *et al*., 2010; Wang *et al*.,2013). Recently (Khorram *et al*., 2017) theoretical calculations performed on the interactions of Carmustine with functionalized single-walled carbon (Ewend *et al*., 2007).

It is importance, evaluating of coumarins properties and applications. The present work indicates the results of quantum chemical calculations (Frisch *et al*. 2010) on the electronic and structural properties interaction coumarin with covalent functionalization single-walled carbon nanotube. This work has made endeavors to investigate the interaction between a nanotube and 3-acetyl-6-methyl -4-hydroxy- coumarin.

Materials and Methods

Geometrical optimizations and thermodynamic parameters calculations were done by Gaussian 09 software (Becke *et al*. 1993). The calculations of systems contain C, O, and N atoms described by the standard 6-31G(d) basis set. Geometry optimization was performed utilizing with the Becke, three parameters, Lee-Yang-Parr method (B3LYP) (O'Boyle *et al*. 2013). All NMR analysis have been performed using 6-31G(d) basis set and the B3LYP level.

The GIAO methods was used to calculate the isotropic NMR shielding at the B3LYP /6-31G(d) of theory. Interaction energy (ΔE) are calculated due to the difference between the total energies of adducts with the sum of the components:

$$\Delta E = E_{CNT/coumarin} - [E_{coumarin} + E_{CNT}] \qquad (1)$$

Where ΔE is the interaction energy, $E_{CNT/coumarin}$ the complex energy, $E_{coumarin}$ the energy of coumarin component, E_{CNT} the energy of SWCNT component.

DFT-based chemical reactivity and stability descriptors which are chemical softness (S), electrophilicity (ω) and chemical hardness (η), electronic chemical potential (μ), were calculated as defined in equations 2-5 according to Koopmans theorem:

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{V(r)\eta} \qquad (2)$$

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_{v(r)I} \qquad (3)$$

$$S = I/2\mu \qquad (4)$$

$$\omega = \mu^2/2\eta \qquad (5)$$

Results

As it can be seen in Fig. 1, coumarin has sites to interact with the selected nanotube. Fig. 1(a, b) presents the structures of 3-acetyl-6-methyl -4-hydroxy-coumarin and SWCNT -coumarin. Their selected geometrical parameters are given in Table 1. Absolute energy values of these molecules, amounts of HOMO and LUMO energies, dipole moment (μ), ionization potential (I), electron affinity (A), Energy gap and Chemical potential (μ), Global electrophilicity (ω) ΔNmax Dipole Moment (debye) are gathered in Table 2.

The higher LUMO–HOMO energy gap, the greater stability and the lower reactivity of the chemical species. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) in coumarin, SWCNT -coumarin SWCNT are shown in Fig. 2

One important question is what is the energy level of the orbitals. This can be shown and investigated by using the DOS spectra calculations. Fig. 3 illustrates the DOS of the CNT models calculated using the Gauss Sum 3.0 (Frisch *et al*., 2009; Lacy *et al*. 2005) Program package.

Nuclear magnetic resonance (NMR) chemical shieldings and quadrupolar couplings are used to check the electronic state of matter. The values of the isotropic shielding are shown in Tables 3 and 4. NBO calculation shows the O-bonding contribution in the compounds. A filled bonding orbital can act as a donor and an antibonding orbital can act as acceptor. These interactions can strengthen and weaken bond. Table 5 shows the hybridation coefficient of bonds involved in formation of SWCNT –coumarin.

Table 1. Selected geometrical parameters for 3-acetyl-6-methyl -4-hydroxy-coumarin(C) and SWCNT -coumarin (NC)in B3LYP/6-31G(d) levels of theory (distances in angstrom and angles in degree).

Compounds	O_{63}– C_{26}	O_{63}- C_{57}	O14- C8	H15-O14	C26 - O_{63}- C_{57}	H15 - O_8– C_{14}
C	-	-	1.3186	0.9996	-	110.5025
NC	1.4228	1.3545	-	-	126.6753	-

Discussion

Energetic aspects

We have found that the interaction energy of the compound coumarin over the CNT nanotube has negative value about −1.19 eV, therefore reaction is exothermic.

Dipole moment

The dipole moment values of coumarin and SWCNT - coumarin are listed in Table 2. It can be found, the dipole moment values are increased in SWCNT - coumarin in compared to coumarin. Dipole moment has a direct relationship with solubility in water and a substance with higher dipole moment is more soluble in polar solvents. Hence, it can be deduced that the solubility of SWCNT - coumarin is better than pure coumarin.

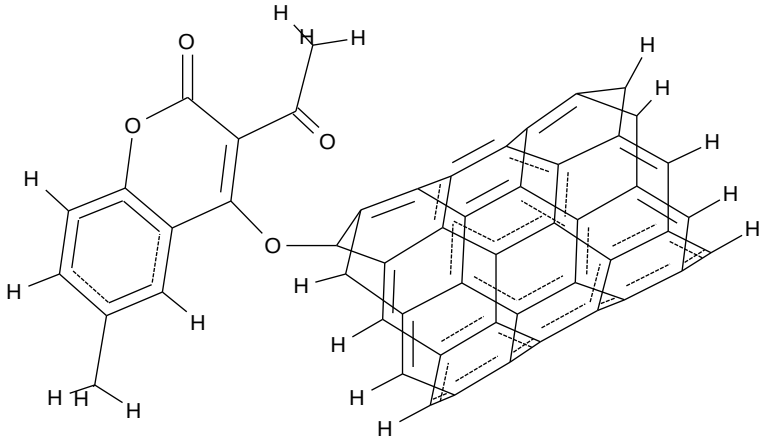

Fig. 1. The structure of optimized SWCNT- 3-acetyl-6-methyl -4-hydroxy- coumarin

Electronic structure

The energy gap between the frontier orbitals (highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are significant properties in numerous chemical processes. The band gap is a good parameter for investigating the conductivity and reactivity of a compound. The energy values of the HOMO (E_{HOMO}) and LUMO (E_{LUMO}) reveals the electron donating and electron accepting

characters of molecule, respectively. It has been explored in numerous investigations that the HOMO-LUMO gap may be a significant stability index of the molecules. Exploring of the frontier orbitals is useful to illustration whether the reaction is possible or not and the relative thermal stability of an individual molecule in the gas phase. High HOMO–LUMO gap directly related to the high stability of compounds so these compounds are less reactive in chemical reactions.

It can be found, the HOMO and LUMO energy levels increase, and the HOMO–LUMO gap of SWCNT - coumarin is decreased compared to the single coumarin. Energy gap has a direct relationship with the electronic conductivity. Indeed, the materials with lower HOMO–LUMO gap show better conductance than the substances with higher HOMO–LUMO gap values and in this research, the electronic conductivity of SWCNT - coumarin is lower than pure coumarin. Thus pure coumarin is less conductive than SWCNT -coumarin.

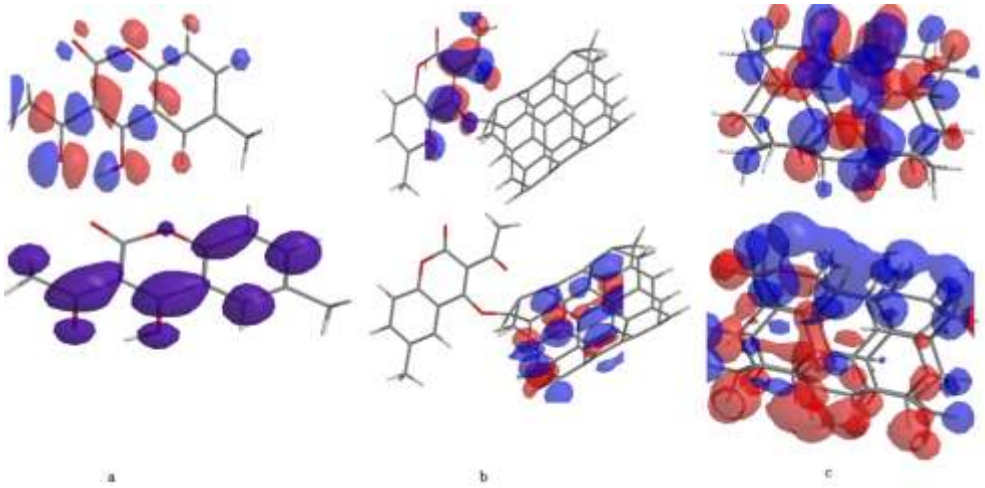

Fig.2 . HOMO and LUMO molecular orbitals and HOMO- LUMO Gap (HLG) of(a) coumarin, (b) SWCNT -coumarin (c) SWCNT

Next variable is chemical hardness which can estimate the softness of a molecule. In other words, a hard molecule has a large HOMO-LUMO gap and a soft molecule has a small HOMO-LUMO gap. As it is obvious from the table, the chemical hardness of coumarin has decreased remarkably from 0.1925 (eV) to 0.1025. So, after binding to nanotube, the structure of coumarin has become more chemically smoother (Fig. 2).

In an electrophilic-nucleophilic system, the electrophilic power of a compound is called electrophilicity index. In this study, electrophilicity index and maximum amount of electronic charge index were also calculated. A compound with higher electrophilicity index demonstrates more electrophilicity.

ΔNmax parameter is the maximum electrical charge that a system can accept. A positive ΔNmax indicates that the system acts as an electron acceptor. But a negative ΔNmax value indicates that the system likes to lose its electrons and acts as an electron donor. As it can be observed from the table, the electrophilicity and ΔNmax of coumarin has enhanced significantly after its attachment to the studied nanostructure. In other words, its affinity for accepting electron has defused dramatically.

Therefore, electronic properties of the coumarin is sensitive to interaction with CNT nanotube.

An important question is what is the energy level of the orbitals.

Density of states (DOS)

The band structure and DOS provide adequate information regarding the conductivity of the CNT structures as well as more complex geometric and electronic configurations. A conductor is a material with a half-filled energy band but it may be a very poor conductor if there are very few unfilled orbitals available close to the frontier orbitals (chemical potential).

Table 2. The calculated amounts of HOMO and LUMO energies, dipole moment (μ), ionization potential (I), electron affinity (A), Energy gap and Chemical potential (μ),Global electrophilicity (ω) ΔNmax Dipole Moment (debye) with the B3LYP/6-31G(d) basis set.

Chemical properties	nanotube	coumarin	NT-Coumarin
Dipole Moment (debye)	1.1078	4.395	5.4178
E_{HOMO}/au	-0.218	-0.336	-0.224
E_{LUMO}/au	-0.014	0.047	-0.019
Energy gap	0.204	0.383	0.205
Chemical Hardness (eV)	0.102	0.1915	0.1025
Chemical Potential(μ)	-0.116	-0.1445	-0.1215
ΔNmax(eV)	1.1372	0.7545	1.1853
Global electrophilicity (ω)(eV)	0.066	0.0545	0.072
Absolute energy (au)	-1511.2954	-755.5035	-2265.6021

Table 3. Isotropic shift, for 13C and 1H NMR of coumarin (C) SWCNT -coumarin (NC)using GIAO method at B3LYP/6-31G(d)

structure	Atom number	$\sigma_{isotropic}$
C	$_{15}$H	19.2925
NC	$_{26}$C	138.8855
C	$_{14}$O	228.617
NC	$_{63}$O	259.4065
C	$_{8}$C	43.7207
NC	$_{57}$C	56.3288

Table 4. Isotropic shifts in ppm for coumarin (C) SWCNT -coumarin (NC) using GIAO method at B3LYP/6-31G(d)

structure	Atom number	ppm (δ)
C	1C	107.005
NC	$_{50}$C	107.315
C	$_{2}$C	108.509
NC	$_{51}$C	107.04
C	$_{3}$C	90.7787
NC	$_{52}$C	94.1249
C	$_{4}$C	131.767
NC	$_{53}$C	129.587
C	$_{5}$C	95.2744
NC	$_{54}$C	95.9669

C	$_{6}$C	117.226
NC	$_{55}$C	115.226
C	$_{8}$C	156.935
NC	$_{57}$C	143.657
C	$_{12}$C	79.5704
NC	$_{61}$C	87.9685
C	$_{9}$H	6.3069
NC	$_{58}$H	6.3685
C	$_{10}$H	6.8530
NC	$_{59}$H	6.8145
C	$_{7}$H	7.4597
NC	$_{56}$H	7.4737
C	$_{13}$O	161.4
NC	$_{62}$O	161.851
C	$_{14}$O	93.6795
NC	$_{63}$O	62.5282
C	16O	363.205
NC	$_{64}$O	385.779
C	$_{18}$O	456.659
NC	$_{66}$O	624.153

According to GIAO calculations performed after interaction of 3-acetyl-6-methyl -4-hydroxy- coumarin molecule on the functionalized nanotube, the iso value of the NMR shielding tensor for ^{1}H nucleus change, which changes the electrostatic properties of these nucleus (see Tables 4). It is worth mentioning that the electrostatic properties of nuclei are mainly dependent on the electronic density around them. Therefore, coumarin interaction affects the electrical density of all nucleus. The studies have shown that due to the increased magnetic field in the ring of nano-carrier nanotube-coumarin, the amount of (isoσ) in the nano-carrier hydrogens is lower than that of the coumarin hydrogens and, on the other hand, their δ is increased. Thus, the benzene ring in the coumarin - carrier is more reactive than the benzene ring in the coumarin alone.

NBO calculation shows the C or O-bonding contribution in the compounds. The donor-acceptor interactions can strengthen and weaken bond. Interaction with the antibonding pair as the acceptor will weaken. To strengthen the bond, interaction with the bonding electron pair is necessary.

Strong electron delocalization in a best Lewis structure will also show up as donor-acceptor interaction.

Table 5. Hybridation coefficient of bonds calculated by NBO method in B3LYP/6-31G(d) level.

Compounds	Bond	Hybridation coefficient of bond orbitals	Contribution of p orbital in σ bond
C	O_{14}- C_{8}	σ=0.5796 ($SP^{2.96}$) $_{8}$C+0.8149 ($SP^{1.75}$) O_{14}	1.5668
NC	O_{63}- C_{57}	σ=0.5673 ($SP^{3.10}$) $_{57}$C+0.8235 ($SP^{1.85}$) O_{63}	1.6410

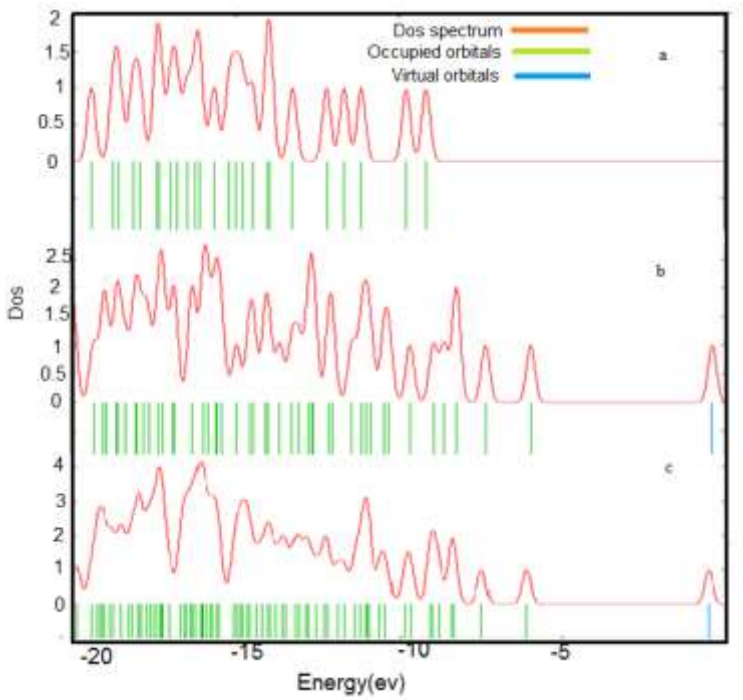

Fig. 3. The total densities of states (DOS) for the coumarine (a) nanotube(b) and SWCNT -coumarin (c)

Conclusions

Natural coumarins have broad pharmacological properties and many chemists consider them as new therapeutic agents.(Sanches *et al.*,2018; Fernández *et al.*,2000; Hrobonˇová *et al*., 2013). It is important to know about the electronic properties of coumarines. For this reason, we studied the interaction between between 3-acetyl-6-methyl -4-hydroxy- coumarin and an armchair nanotube was invetigated. We found that coumarin could strongly be adsorbed on C-SWCNT. According to the obtained results, the process of the coumarin interaction on the external surface of the functionalized nanotube is exothermic and studied configuration is stable. It seems C-SWCNT can be used for determination of coumarin especially by conductometric titration method because this technique is based on the alterations that occur in the conductivity of the system [34]. Moreover, NBO analysis indicated that coumarin molecule can be adsorbed on the nanotube surface with a charge transfer from the nanotube to the coumarin molecule. In SWCNT -coumarin, the hyperconjugation effect can be observed. The calculation of the DOS spectrum provided important information on the conduction properties of the structures. It is suggested that coumarin is adsorbed on the nanotubes and thus a common aromatic system is created between them and facilitate charge transfer between neighboring nanotubes which causes the improvement of sensor response.

The obtained results from ΔNmax and ω shows that there is the strong interaction of C-SWCNT and coumarin. It can be concluded that electrophilicity value of C-SWCNT is greater than coumarin and C-SWCNT acts as a Lewis acid due to its high affinity for accepting the electron.

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