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Araştırma Makalesi / Research Article

Effect of the Al Doping on the Sensing Behaviour of Carbon Nanotubes Toward Carbazochrome: a Computational Study

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Keywords
Carbazochrome; Al doped CNT; Electron Localization Function (ELF); Computational Study

Abstract

In the current report, the interaction of Al-doped carbon nanotubes (CNT) with carbazochrome, an anti-hemorrhagic or hemostatic agent, was investigated with the M06-2X functional and 6-31G* basis set. The global index including frontier molecular orbital energies, hardness, softness, chemical Gibbs energies and some parameters and NLO properties of Carbazochrome, Al doped CNT and complexes formed between their were calculated and evaluated. Electron localization function (ELF) calculations were performed to validate the essence of the formed bonding model progress along the interaction. It is obtained that polarizability of the complex are bigger than those of Carbazochrome and Al doped CNT. According to the maximum electron flow index, the electrophilicity power is increased by increasing the chemical potential, the decreasing chemical hardness. All obtained complexes are exergonic and thus thermodynamically favorable

Al Doplu Karbon Nanotüplerin Karbazokroma Karşı Algılama Etkisi: Hesaplamalı Bir Çalışma

Anahtar kelimeler
Karbazokrom; Hesaplamalı Çalışma; Al doped CNT; Elektron Lokalizasyon Fonksiyonu (ELF)

Öz

Bu çalışmada, Al doplu karbon nanotüplerin (CNT)'nin anti-hemorajik veya hemostatik bir ajan olan karbazokrom ile etkileşimi, M06-2X fonksiyonel ve 6-31G* temel seti ile araştırıldı. Karbazokrom molekülü, Al doplu CNT ve aralarında oluşan komplekslerin sınır moleküler orbital enerjileri, sertlik, yumuşaklık, kimyasal Gibbs enerjisi gibi bazı parametreler ile NLO özelliklerini içeren global indeks hesaplandı ve değerlendirildi. Etkileşim boyunca oluşturulan bağ modeli ilerlemesinin özünü doğrulamak için elektron lokalizasyon fonksiyonu (ELF) hesaplamaları yapıldı. Kompleksin polarizebilitesinin Karbazokrom ve Al doplu CNT'den daha büyük olduğu elde edilmiştir. Maksimum elektron akış indeksine göre, artan kimyasal potansiyel ve azalan kimyasal sertlik ile elektrofilik gücü artar. Elde edilen tüm kompleksler ekzergoniktir ve bu nedenle termodinamik olarak uygundur.

1. Introduction

To ensure that drug side effects are minimized without affecting their essential pharmacophoric properties, the pharmaceutical industry has now switched to targeted drug delivery using nanotechnology (Duverger *et al.* 2014).

After its discovery in 1991 Iijima (1991), carbon nanotubes (CNTs) have attracted continued interest in pharmaceutical and biomedical applications (Monajjemi and Boggs 2013). CNTs, consisting of carbon layers with thin benzene rings wrapped in a continuous tubular structure, can be divided into two general categories according to their structure: single-walled (SWNTs) and multi-walled nanotubes (MWNTs). SWNTs consist of cylinders of a graphene sheet, whereas MWNTs contain several concentric

shells of cylindrical graphene sheets (Sinha and Yeow 2005).

NPs with absorption and/or light diffraction properties such as quantum dots, gold CNTs and ceramic NPs can be used not only as contrast agents for imaging but also for other biomedical purposes when functionalized (Huang *et al.* 2011). Additionally, the discovery of CNTs has opened up new therapeutic opportunities that have led to the development of innovative drug delivery or biosensor devices. CNTs have been recognized as promising delivery vectors for cancer diagnosis and chemotherapies due to their unique properties such as pH-dependent therapeutic unloading and long circulation time, as well as high loading capacity, efficient membrane transport, and chemotherapies (Monajjemi *et al.* 2013).

The use of density functional theory (DFT) has become widespread over the years in many branches of chemistry, in the study of the reaction mechanism, in the calculation of the electronic properties of different solvents, The relationship between the structures and photophysical properties of complexes (Odame 2018, Genç *et al.* 2021, Zheng *et al.* 2019).

Because experimental methods are more expensive and time consuming, computational methods can fill an important gap in this field and provide significant details about host-guest interactions between Carbon nanotubes and drug molecules.

Quantum mechanical calculations by using time-dependent DFT at B3LYP level 6–311G(d,p), 6–311+G(d,p), 6–311++G(d,p), 6–311++G(2d,2p), 6-311++G(3df,3pd) basis sets were performed to obtain some valuable information about the UV spectrum of the carbazochrome molecule in gas and solvent medium (ethanol, N, N-dimethylformamide, N, N-dimethylsulfoxide, water) and compared with experimental values (Genç *et al.* 2022). They reported that the adsorption of carbazochrome molecule on the Carbon nanotube by diverse functional groups performing Density-functional theory calculations and supplied significant data on structural features, adsorption energy, orientation and charge transfer between Carbon nanotube and Carbazochrome drug in Carbon nanotube / complexes of carbazochrome and according the percentage values of band gap of complexes with respect to the bare CNT, the CNT (4,0) can be used to detect Carbazochrome drug as an electrochemical sensor (Sayiner *et al.* 2022).

They studied adsorption properties of metformin (MF) drug onto pristine, Si- and Al-doped (5, 5) armchair single-wall carbon nanotubes SWCNTs using density functional theory (DFT) calculations at the B3LYP and ωB97XD methods with the standard 6–311 G** basis set and reported that high chemisorption can be achieved by using Al- and Si-doped SWCNTs (Hoseininezhad-Namin *et al.* 2017, Hazrati *et al.* 2016). It was reported that Al-doped SWCNT provides stronger adsorption, and the change in the energy gap of Si-doped SWCNT was more pronounced (Al-Sawaff *et al.* 2021).

The present work is mainly focused to examine the stability and binding afnity of carbazochrome molecule with Al-doped carbon nanotube. In order to determine the active site, the stability and adsorption, interaction and deformation energies were calculated and also and Frontier Molecular Orbital (HOMO, LUMO) calculations were implemented.

2. Material and Method

2.1 Computational method

Theoretical calculations of the interaction of carbazochrome and Al doped CNT were performed in the DFT framework with M062X functionals and 6-31G (d) basis set using the Gaussian 09 program package (Frisch *et al.* 2009). Adsorption energies of carbazochrome molecule via the unlike active sites on Al doped CNT were calculated using the

$$E = E_{complex} - \left(E_{carbazochrome} + E_{Al\ doped\ CNT}\right) \quad (1)$$

Where $E_{complex}$, E_{drug} and $E_{Al\ dopedCNT}$ are the energy of the complex, the free carbazochrome, and Al doped CNT. The natural fundamental set superposition error (BSSE) was used to correct binding energies.

interaction energy (Eint) and deformatıom energy are calculated

$$E_{inter} = E_{complex} - (E_{drug\ in\ complex} + E_{CNT\ in\ complex}) \quad (2)$$

and

$$E_{def} = E_{def-drug} + E_{def-CNT} \quad (3)$$

Deformation energy is called as the energy applied to change the molecule and its surface from its optimum configuration to the relaxed molecule-surface system. Hardness (η), electronegativity (χ), chemical potential (μ) and electrophilicity index (ω), nucleofugality, electrofugality, maximum electron flow parameters related to HOMO and LUMO energies were calculated using the

$$\Delta E = E_{LUMO-}E_{HOMO} \quad (4),$$

$$\mu = -\chi \cong \left(\frac{E_{HOMO}+E_{LUMO}}{2}\right) \quad (5),$$

$$\eta = \frac{E_{LUMO}-E_{HOMO}}{2} \quad (6),$$

$$\sigma = \frac{\eta}{2} \quad (7),$$

$$\omega = \frac{\mu^2}{2\eta} \quad (8),$$

$$\Delta E_n = \pm\frac{(\mu+\eta)^2}{2\eta} \quad (9),$$

$$\Delta E_e = \frac{(\mu-\eta)^2}{2\eta} \quad (10),$$

$$\Delta N_{ideal} = -\frac{\mu}{\eta} \quad (11),$$

The dipole moment, the averaged (isotropic) dipole polarizabilities (α), anisotropy polarizability (Δα), and total first static hyperpolarizability (Thanthiriwatte and De Silva 2002) are evaluated respectively as

$$\mu = \left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)^{1/2} \quad (12),$$

$$\alpha = \frac{1}{3}\left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right) \quad (13),$$

$$\Delta\alpha = \left[\frac{(\alpha_{xx}-\alpha_{yy})^2+(\alpha_{yy}-\alpha_{zz})^2+(\alpha_{zz}-\alpha_{xx})^2+6(\alpha_{xz}^2+\alpha_{xy}^2+\alpha_{yz}^2)}{2}\right]^{1/2} \quad (14),$$

$$\beta = \{(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2)\}^{1/2} \quad (15),$$

3. Result and Disscussion

For evaluating the adsorption of carbazochrome molecule onto the sidewall of Al-doped CNT seven configurations were picked up with respect to the seven different sites of the carbazochrome molecule (Figure 1). For each site, the related atom of carbazochrome molecule is pointed toward the doped aluminum atom in the nano tube to make a specific configuration and, each interaction model of carbazochrome with Al doped CNT (nanotube was fully optimized by DFT as mentioned earlier). The distances of the closest atom of adsorbed carbazochrome molecule onto the Al-doped nano tubes from the Al atom in the optimized models are given in Figure 1. For simlicity, we abbreviated the mentioned doped nano tubes with different size of carbazochrome as 1,2,3,4,5,6, and 7 respectively.

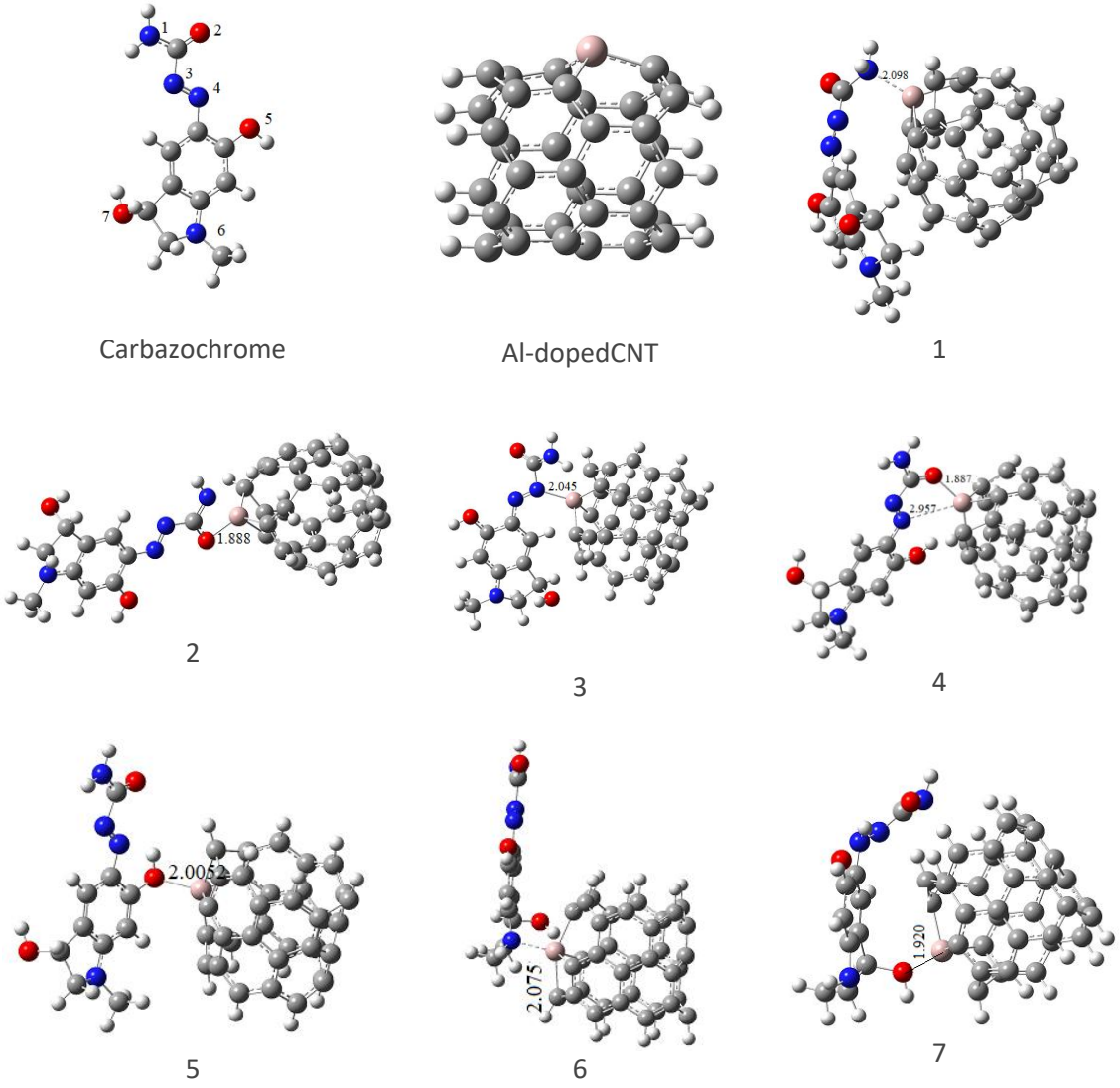


Figure 1. Optimized structure of studied complex

The equilibrium binding distance for complex1-complex7 formed between carbazochrome and Al-doped CNT is shown in Table 1. The calculated equilibrium binding distance between N1 of carbazochrome and Al atom of Al doped CNT for complex1 is 2.098 Å, the bond distance of O2-Al at complex2 is 1.889 Å, the bond distance of Al-N3 is 2.045 Å for complex3, the bond distances of O2-Al and N4-Al are 1.887 Å, 2.957 Å for complex4, the bond distance of O5-Al is 2.005 Å for complex5, the bond distance of N6-Al is 2.075 for complex6 and the bond distance of O7-Al is 1.759 Å for complex7. The Mulliken atomic charge of Al in Al doped CNT is less than that of complexes.

Analysis of the electron localization function (ELF) was used to further investigate the nature of the interaction. Electron localization function (ELF) is a method used to measure electron localization in atomic and molecular systems, the electron localization function is a key feature for understanding the nature of chemical bonds. While the interaction distance between Al and N atoms increases, ELF values decrease. The same trend is observed in the interaction between Al and O atoms (Lu and Chen, 2012).

Table 1. Calculated equilibrium binding distance between carbazochrome and Carbon nanotubes for the complex1-complex7.

Complexes	Atoms	Bond length(Å)	ELF	Mulliken charges(ē)		Atoms	Mulliken charges(ē)		From drug
				C NT_{Al}	Al charge in complex		charge in complex	Drug-free	Charge Flow
1	Al-N1	2.098	0.0762	0.346	0.378	N1	-0.876	-0.815	0.21831
2	Al-O2	1.889	0.0756		0.655	O2	-0.584	-0.482	-0.14065
	N1-H	2.385	0.0617			H	0.252	0.368	
	Al-N1	2.102	0.0716			N1	-0.766	-0.815	
3	Al-N3	2.045	0.0827		0.465	N3	-0.375	-0.339	0.18016
4	Al-O2	1.887	0.0611		0.503	O2	-0.566	-0.482	0.23531
	Al-N4	2.957	-			N4	-0.288	-0.227	
5	Al-O5	2.005	0.0589		0.387	O5	-0.742	-0.632	0.187486
6	Al-N6	2.075	0.0865		0.388	N6	-0.665	0.546	0.18349
7	Al-O7	1.759	0.100		0.530	O7	-0.633	-0.645	-0.15844
	O7-H	2.537	0.0293			H	0.212	0.414	

The calculated adsorption, interaction and deformation energies of complex1-complex7 are calculated and presented in Table 2.

The adsorption energy values of carbazochrome molecule in the interaction with Al doped Carbon nanotubes are calculated to be as -37.66, -43.46, -61,00, -40.43, -45.05 for complex1, complex3, complex4, complex5, complex6 $kcalmol^{-1}$, respectively. It was not considered complex2 and complex7 due to their large deformation energies.

Thermodynamic equilibrium constants of the reaction are calculated by placing the values of Gibbs free energy changes in the

$$K = exp\ (-\frac{\Delta G_{ads}}{RT})$$ equation (16).

In this formula, R denotes the ideal gas constant and T denotes the temperature. Among the studied complexes, complex4 has the largest K value.

Table 2. Adsorption, interaction and deformation energies for the formation of complex1-complex7 (kcal mol^{-1})

Complexes		SEZPE kcal.mol^{-1}	SETE kcal.mol^{-1}	SETEn kcal.mol^{-1}	SETFE kcal.mol^{-1}
1	E_{ads}	-37.66	-37.56	-38.16	-22.46
	E_{inter}	-41.51	-40.49	-41.09	-27.95
	E_{def}	3.85	2.93	2.93	5.49
2	E_{ads}	-73.72	-73.59	-74.19	-59.76
	E_{inter}	-280.57	-279.65	-280.25	-268.13
	E_{def}	206.85	206.06	206.06	208.37
3	E_{ads}	-43.46	-43.46	-44.05	-27.74
	E_{inter}	-43.67	-42.37	-42.96	-30.23
	E_{def}	0.21	-1.09	-1.09	2.49
4	E_{ads}	-61.00	-60.97	-61.56	-46.17
	E_{inter}	-57.02	-55.80	-56.39	-44.04
	E_{def}	-3.98	-5.17	-5.17	-2.13
5	E_{ads}	-40.43	-40.00	-40.60	-28.28
	E_{inter}	-25.43	-24.16	-24.76	-14.55
	E_{def}	-14.99	-15.84	-15.84	-13.73
6	E_{ads}	-45.05	-44.93	-45.52	-30.32
	E_{inter}	-43.21	-42.44	-43.03	-29.39
	E_{def}	-1.83	-2.49	-2.49	-0.94
7	E_{ads}	-119.41	-119.58	-120.17	-103.83
	E_{inter}	-275.23	-275.00	-275.59	-260.57
	E_{def}	155.82	155.42	155.42	156.75

SEZPE: Sum of electronic and zero-point Energies	SETE: Sum of electronic and thermal Energies
SETEn: Sum of electronic and thermal Enthalpies	SETFE: Sum of electronic and thermal Free Energies

The calculated thermal free energy order are complex1 (-22.46) < complex3 (-27.74) < complex5 (-28.28) < complex6 (-30.32) < complex4 (-46.17 kcal mol^{-1}). All obtained complexes are exergonic and thus thermodynamically favorable. The deformation energy of complex1 and complex7 is high due to one transferring one of the H from drug to the CNT.

Much of the theoretical chemistry regarding reactivity is based on the concept of Frontier Molecular Orbitals (FMO), specifically the Lowest unoccupied Molecular Orbital (LUMO) and the Highest Occupied Molecular Orbital (HOMO). The interaction between these orbitals generally allows a good description of the reactivity of reactions.

In a reaction between two molecules, species can act as a nucleophile which has a lower value of electrophilicity index. We consider two molecules A (carbazochrome) and B (Al doped CNT). If electron charge transfer (ECT) > 0, charge flow from B to A; and (ii) ECT < 0, charge flow from A to B. ECT is calculated by the

$ECT = (\Delta N_{max})_A - (\Delta N_{max})_B$ equation (17).

Where, A: ΔN_{max} for carbazochrome, B: ΔN_{max} for Al doped CNT. ECT were calculated as -1.512 and -1,304 (for beta and alpha electrons) for the carbazochrome and Al doped Carbon nanotube in gas phase means that electrons are transferred from the carbazochrome to the Al doped Carbon nanotube. Therefore, Al doped Carbon nanotube treats as electron acceptor and so carbazochrome treat as electron donor. So Al doped CNT has electrophilic behavior because the value of chemical potential of Al doped CNT (-3.497) is lower than that of carbazochrome (-3.825) (Sayiner *et al.* 2022) and also the value of electrophilicity index (4.563) is higher than that of carbazochrome (2.498) (Sayiner *et al.* 2022). ECT were calculated as -1.040 and -0,873 (for beta and alpha electrons) for the carbazochrome and Al doped complex in water phase and in octanol ECT was calculated as -1.128 and -0,956 (for beta and alpha electrons). Charge flowing from carbazochrome to the Al doped CNT in gas phase is the higher than those in solvent phase.

In quantum mechanics, the molecular orbital Ui is defined as the linear combination of applicable functions in the fundamental set.

$$\varphi_i(r) = \sum_a C_{a,i}\, \chi_a(r) \qquad (18).$$

Where $C_{a,i}$, χ_a are the molecular orbital coefficient and basis function. When orthonormality condition of spin orbital wavefunctions are inserted the Eq (18), this equation Eq(19)

$$\sum_a C_{a,i}^2 + 2\sum_a \sum_{b>a} C_{a,i} C_{b,i}\, S_{a,b} = 1 \quad (19)$$

was obtained. Where $S_{a,b}$ is an overlap matrix among basis functions. First term and second term represent local term denoting the net population of each basis function in orbital i and a cross term denoting the shared electrons between basis function pairs in orbital i (Lu and Chen 2012).

In the Mulliken analysis (Mulliken 1955), the cross terms are equally partitioned to the corresponding basis functions. So, the composition of basis function a in spin orbital i is defined as

$$\Theta_{i,a} = C_{a,i}^2 + \sum_{b\neq a} C_{a,i} C_{b,i}\, S_{a,b} \qquad (20).$$

The frontier molecular orbital theory was proposed by Fukui Kenichi. It was suggested that the reactivity of a molecule is determined by the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). In general, the smaller the energy difference between the HOMO of one molecule and the LUMO of another molecule, the greater the interaction between these two molecules. The HOMO and LUMO shapes of the carbazochrome molecule calculated in the gas phase are given in Figure. 2.

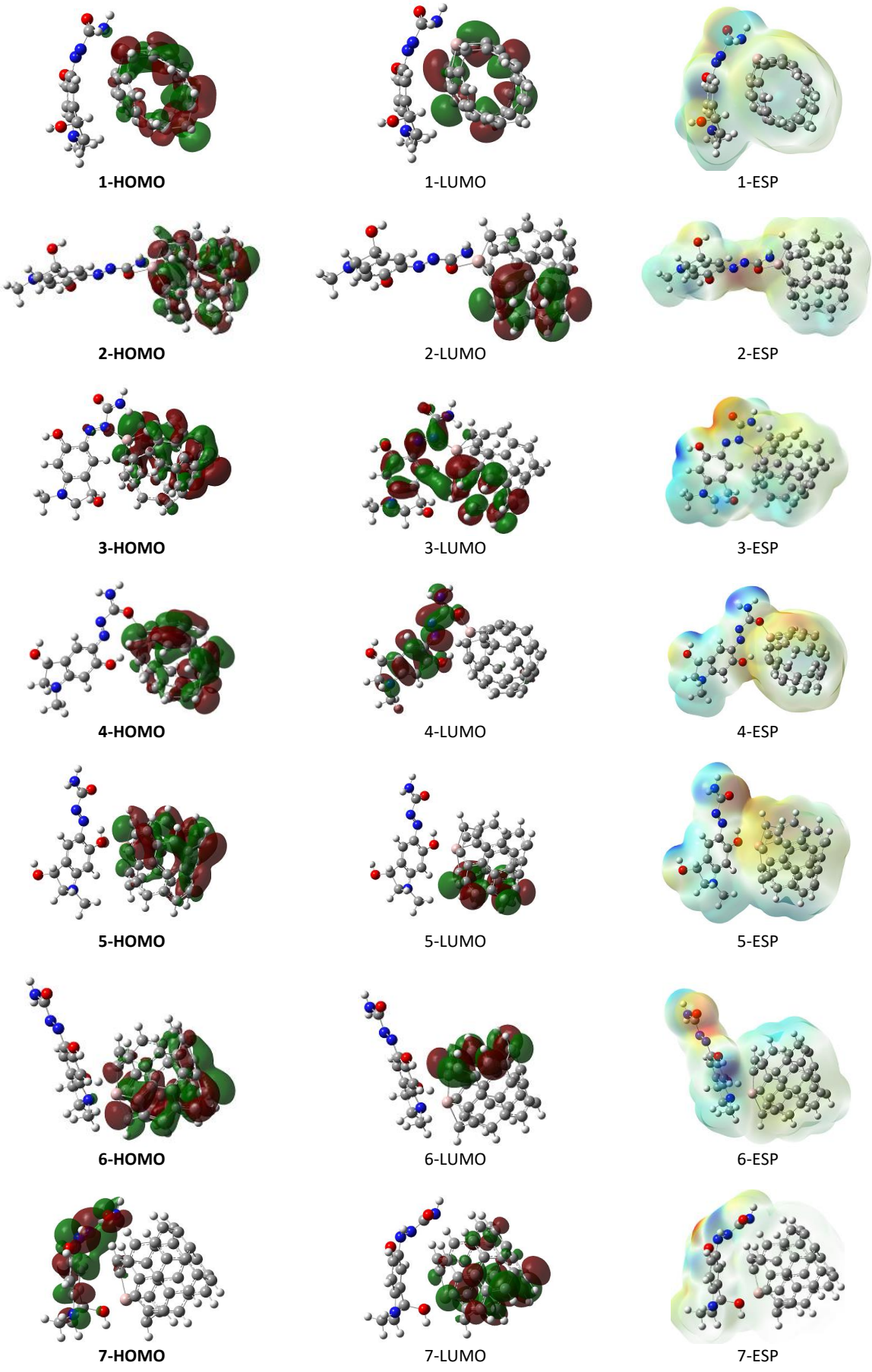


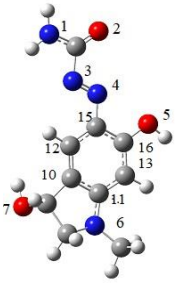
Figure 2. The shape of HOMO, LUMO and ESP of the studied complexes

HOMO and LUMO consist of Al doped CNT in complex1, complex2, complex5 and complex6, HOMO consists of Al doped CNT and LUMO consist of carbazochrome molecule for complex3 and complex4 and HOMO consists of carbazochrome and LUMO consists of Al doped CNT for complex7. Therefore, the atomic orbitals forming the HOMO and LUMO orbitals vary according to the bonding region. At same time, the electron density varies according to the binding site.

The contribution of atomic orbitals to the HOMO and LUMO orbitals for carbazachrome calculated according to the Mulliken molecular orbital composition is given in Table 3. HOMO consist of 23.36 % N6 and 10.17 % N3, and phenyl group. LUMO consist of N4 and N3 belonging to semicarbaziede group of carbazochrome and phenyl group of carbazochrome.

Table 3. Orbital composition analysis with partition

Atoms	HOMO	Atoms	LUMO
N6	23.36	O2	4.05
N3	10.17	N6	3.54
C10	14.99	N4	25.91
C11	6.08	N3	22.49
C13	5.35	C11	10.82
C15	23.23	C12	12.20
		C16	5.67
		C17	4.87



HOMO-LUMO energies and the parameters such as hardness (η), softness (σ), electronegativity (χ), the maximum amount of electronic charge transfer ΔN_{maks}, Chemical potential (μ) and electrophilicity index (ω), nucleofugality, electrofugality related to HOMO and LUMO energies of CNT and formed complex1-complex7 as reported considering Parr and Pearson interpretation (Pearson 1995, Pearson 1986) were calculated with M062X functional and 6-31g (d) basis set are presented in Table 4.

The alpha and the beta HOMO energy (E_{HOMO}) and the LUMO energy (E_{LUMO}) of the carbazochrome are -6.753eV, and -0.896eV. After adsorption of Carbazochrome on Al doped Carbon nanotubes, the HOMO energy of the complex1-complex7 increase to -5.581, -5.700, -5.532, -5.278, -5.536, -5.742, and -5.743 eV respectively. As seen when Carbazochrome is adsorbed on the Al doped CNT HOMO energy changes are noticeable.

Table 4. HOMO, LUMO energy, HOMO-LUMO energy gap, hardness (η), softness (σ), electronegativity (χ), Chemical potential (μ) and electrophilicity index (ω), nucleofugality (En), electrofugality (Ee) of CNT and complex 1-complex7 calculated with M062X functional and 6-31G (d) basis set.

	Parameters/complex	1	2	3	4	5	6	7	CNT
βorbital	E_{HOMO} (eV)	-5.581	-5.700	-5.532	-5.278	-5.536	-5.742	-5.743	-4.752
	E_{LUMO} (eV)	-1.827	-1.911	-1.804	-1.846	-1.862	-1.966	-1.766	-2.263
	ΔE (eV)	3.754	3.789	3.728	3.432	3.674	3.776	3.977	2.490
	η	1.877	1.894	1.864	1.716	1.837	1.888	1.988	1.245
	σ	0.266	0.264	0.268	0.291	0.272	0.265	0.251	0.402
	χ	3.704	3.805	3.668	3.562	3.699	3.854	3.755	3.507
	μ	-3.704	-3.805	-3.668	-3.562	-3.699	-3.854	-3.755	-3.507
	ω	3.655	3.822	3.610	3.698	3.725	3.934	3.545	4.941
	ΔE_n	0.889	0.964	0.873	0.993	0.944	1.024	0.785	2.056

α orbital	ΔE_e	8.297	8.574	8.210	8.118	8.343	8.732	8.294	9.071
	ΔN	1.973	2.009	1.968	2.076	2.014	2.041	1.888	2.818
	E_{HOMO} (eV)	-5.646	-5.673	-5.532	-5.335	-5.581	-5.758	-5.704	-4.837
	E_{LUMO} (eV)	-1.798	-1.886	-1.785	-1.842	-1.834	-1.935	-1.731	-2.157
	ΔE (eV)	3.848	3.787	3.748	3.493	3.747	3.823	3.973	2.680
	η	1.924	1.894	1.874	1.747	1.873	1.912	1.986	1.340
	σ	0.260	0.264	0.267	0.286	0.267	0.262	0.252	0.373
	χ	3.722	3.779	3.658	3.589	3.707	3.847	3.718	3.497
	μ	-3.722	-3.779	-3.658	-3.589	-3.707	-3.847	-3.718	-3.497
	ω	3.600	3.772	3.571	3.686	3.668	3.870	3.479	4.563
	ΔE_n	0.840	0.939	0.850	0.971	0.898	0.979	0.755	1.736
	ΔE_e	8.284	8.498	8.167	8.148	8.312	8.673	8.190	8.730
	ΔN	1.934	1.996	1.952	2.055	1.979	2.012	1.872	2.610

As a result, Excitation of complexes formed from the interaction of carbazochrome and Al-doped CNTs from HOMO to LUMO requires more energy. In order to understand the sensing mechanism of the Al-CNT to drug, the variation of ΔEg gap during the adsorption process is taken into account by the

$\Delta E_g\% = 100 * (\Delta E_2 - \Delta E_1)/\Delta E_1$ equation (20).

Where $\Delta E_1$and ΔE_2 are the values of the ΔE for Al doped CNT and complex, respectively.

According to the maximum electron flow index (ΔN), the electrophilicity power is increased by increasing the chemical potential, the decreasing chemical hardness. Having more electron deficiencies in the system makes the system more positive and therefore increases the probability of electron transfer to the system. Maximum electron flow indexes of carbazochrome is 1.306 and those for beta orbital for Al doped CNT is 2.818.

The dipole moment, polarizability, anisotropic polarizability and hyperpolarizability values of carbazochrome molecule, Al dolped Carbon nanotubes, complex1-complex7 molecules calculated with the M062X/6-31G(d) level in gas phase are shown in Table 5.

Table 5. The dipole moment, polarizability, anisotropic polarizability and hyperpolarizability values of carbazochrome, Al doped Carbon nanotubes, complex1-complex7 molecules calculated with the M062X/6-31g(d) level in gas phase.

Complex	μ D	α $10^{-24}cm^3$	Kappa	$\Delta\alpha$	β $10^{-30}cm^5esu^{-1}$
1	24.85	73.84	0.00170	15.69	21.54
2	26.73	80.82	0.05319	56.37	49.71
3	54.55	79.09	0.02410	38.16	35.81
4	23.22	80.86	0.01643	33.65	30.81
5	25.96	76.48	0.01729	31.81	27.53
6	2.62	74.83	0.01689	30.56	33.92
7	16.74	110.84	0.02704	61.45	83.52
Carbazochrome	8.63	56.23	0.00686	14.86	22.77
CNT	11.89	23.54	0.11460	24.19	25.42

a.u. (Bohr-electron) = 2.541765 Debye, Polarizability: (α) 1 a.u. = 0.148184709.$10^{-24}cm^3$;
First-hyperpolarizability (β): 1 a.u. = 8.639418.$10^{-33}cm^5esu^{-1}$

A dipole moment is an unequal distribution of charge in a compound and means that, the higher the dipole moment of a compound, the more polar the compound is. The dipole moment of complexes

except complex2 is bigger than that of carbaxochrome and Al doped CNT. Results shows that polarizability of the complex are bigger than those of Carbazochrome and Al doped CNT.

4. Conclusion

We used the additive aluminum (AlCNT) to improve the drug delivery properties of Carbon nanotube and reduce its toxicity. The adsorption energies of the carbazochrome molecule in interaction with doped Carbon nanotubes were calculated as -37.66, -43.46, -61.00, -40.43, -45.05 kcal mol^{-1} for complex1 and complex3-complex6, respectively.

ECT values were found as -1.512 and -1.304 (for beta and alpha electrons) means that electrons are transferred from the carbazochrome to the Al doped CNT. Therefore, aluminum doped Carbon nanotube treats as electron acceptor and so carbazochrome treat as electron donor. So Al doped CNT has electrophilic behavior because the value of chemical potential of Al doped CNT (-3.497) is lower than that of carbazochrome (-3.825) (Sayiner *et al.* 2022). and also the value of electrophilicity index (4.563) is higher than that of carbazochrome (2.498) (Sayiner *et al.* 2022). Their interaction or adsorption energies are in the chemisorption range, making them candidates for use in sensor technology and as drug delivery vehicles for medical applications.

5. References

Duverger, E., Gharbi, T., Delabrousse, E. and Picaud, F., 2014. Quantum study of boron nitride nanotubes functionalized with anticancer molecules. *Physical Chemistry Chemical Physics*, **16**, 18425-18432.

Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E. , Robb, M.A., Cheeseman, J.R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G.A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H.P., Izmaylov, A.F., Bloino, J., Zheng, G., Sonnenberg, J.L., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Montgomery, J.A., Peralta, Jr.J.E., Ogliaro, F., Bearpark, M., Heyd, J.J., Brothers, E., Kudin, K.N., Staroverov, V.N., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, J.C., Iyengar, S.S., Tomasi, J., Cossi, M., Rega, N., Millam, J.M., Klene, M., Knox, J.E., Cross, J.B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R.E., Yazyev, O., Austin, A.J., Cammi, R., Pomelli, C., Ochterski, J.W., Martin, R.L., Morokuma, K., Zakrzewski, V.G., Voth, G.A., Alvador, P., Dannenberg, J.J., Dapprich, S., Daniels, A.D., Farkas, Ö., Foresman, J.B., Ortiz, J.V., Cioslowski J. and Fox, D.J., 2009. Gaussian Inc., Wallingford CT.

Genç, F., Kandemirli, S.G. and Kandemirli, F., 2021. Theoretical B3LYP study on electronic structure of contrast agent iopamidol. *Acta Chimica Slovenica*, **68(2)**, 320-331.

Genç, F., Bsehen, H., Kandemirli, F., 2022. Quantum Chemical Studies of Carbazochrome Molecule. *Journal of the Chemical Society of Pakistan*, **44(2)**, 109.

Hazrati, M.K., Nasser, L., Hadipour, N.L., 2016. Adsorption behavior of 5-fluorouracil on pristine, B-, Si-, and Al-doped C60 fullerenes: A first-principles study, *Physics Letters A*, **380(7–8)**, 937-941.

Hoseininezhad-Namin, M.S., Pargolghasemi, P., Alimohammadi, S., Rad, AS. and Taqavi, L., 2017. Quantum Chemical Study on the adsorption of metformin drug on the surface of pristine, Si- and Al-doped (5, 5) SWCNTs. *Physica E:Low-dimensional Systems and Nanostructures*, **90**, 204-213.

Huang, H.C., Barua, S., Sharma, G., Dey, S.K. and Rege, K., 2011.Inorganic nanoparticles for cancer imaging and therapy. *Journal of Controlled Release*, **155(3)**, 344-357.

Iijima, S., 1991. Helical microtubules of graphitic carbon. *Nature*, **354**, 56–58.

Lu, T., and Chen, F. 2012. Multiwfn: A multifunctional wavefunction analyser. *Journal of Computational Chemistry,* **33(5)**, 580–592.

Monajjemi, M. and Boggs, J.E., 2013. The Journal of Physical Chemistry, **117(7)**, 1670.-1684.

Monajjemi, M., Najafpour, J. and Mollaamin, F., 2013. $(3,3)_4$ Armchair Carbon Nanotube in Connection with PNP and NPN Junctions: Ab Initio and DFT-Based Studies. *Fullerenes, Nanotubes and Carbon Nanostructures*, **21(3)**, 213-232.

Mulliken, R. S., 1833(1955). Electronic Population Analysis on LCAO–MO Molecular Wave Functions. I. *The Journal of Chemical Physics*, **23(10)**,–1840.

Odame, F., 2018. DFT Study of the Reaction Mechanism of N-(Carbomylcarbamothioyl) Benzamide. *Acta Chimica Slovenica*, **65**, 328–332.

Pearson, R.G., 1995. The HSAB Principle-more quantitative aspects. *Inorganica Chimica Acta*, **240(1-2)**, 93-98.

Pearson, R.G., 1986. Absolute electronegativity and hardness correlated with molecular orbital theory. *Proceedings of the National Academy of Sciences*, **83(22)**, 8440-8441.

Sayiner, H.S., Kandemirli, F., Dalgic, S.S., Monajjemi, M. , Mollaamin, F., 2022. Carbazochrome carbon nanotube as drug delivery nanocarrier for anti-bleeding drug: quantum chemical study. *Journal of Molecular Modeling*, **28(1)**, 1-15.

Sinha, N. and Yeow J.T., 2005. *IEEE Trans Nanobioscience*. **4(2)**, 180-95.

Thanthiriwatte, K.S., De Silva K.M.N.,2002. Non-linear optical properties of novel fluorenyl derivatives-ab initio quantum chemical calculations. *Journal of Molecular Structure: THEOCHEM,* **617(1-3)**, 169-175.

Z.H. Al-Sawaff, S. Senturk Dalgic, F.Kandemirli, 2021. Theoretical study of the adsorption of BMSF-BENZ drug for osteoporosis disease treatment on Al-doped carbon nanotubes (Al-CNT) as a drug delivery vehicle. *European Journal of Chemistry*, **12(3)**, 314-322.

Zheng, Z., Xiao-Han, Y., Zi-Wen, T., Han-Ru, X. , Kai, L. , Guang-Ying, C., Zheng-Rong, M., Shui-Xing, W., Zhi-Gang, N. and Gao-Nan, L., 2019. Synthesis and Characterization of High-Efficiency Red Phosphorescent Iridium(III) Complexes with 1-(4-(Trifluoromethyl)phenyl)isoquinoline Ligand. *Acta Chimica Slovenica*, **66(4)**, 978-986.