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Investigation of Electronic Sensing and Spectroscopy Behavior of di-oxide Pyrimidine As Breast Cell using Density Functional Theory

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Abstract

This study deals with the investigation of the electronic sensing and spectroscopic behavior for the di-oxide pyrimidine as one type of Breast cancer cell and it is adduct di-oxide fluorine pyrimidine. The stationary state energy, electronic states, forbidden energy and some electronic variables were theoretically calculated by employing density functional theory using Gaussian 09 package of programs. The results showed that the di-oxide pyrimidine with presence of Fluorine has high electronic sensing and it is more chemically active to interacts with the surrounding. The presence of Fluorine in the structure has no effect on the vibration modes of the di-oxide pyrimidine but has high effect on the excitation energy can occur for the Breast cancer cell, the di-oxide pyrimidine with Fluorine has high sensing property than the di-oxide

Key words: DFT, Breast, Medical Physics, Pyrimidine, Energy Gap and Polarizability

الخلاصة

هذه الدراسة تتعامل مع تقييم التحسس الألكتروني والسلوك الطيفي لثنائي أوكسيد البايريمادين لأحد أنواع خلايا سرطان الثدي ومشتقاتها ثنائي أوكسيد فلورايد البايريمادين فمستوى الطاقة الثابت والحالات الألكترونية والطاقات الممنوعه وبعض الأهتزازات الألكترونية حسبت نظريا" بواسطة نظرية كثافة الدالة بواسطة برامجيات الحزمة الكاوسية 09 بينت النتائج ان ثنائي اوكسيد البايريمادين وبوجود الفلور يملك اعلى استشعار الكتروني وكذلك يكون اكثر فعالية كيميائية للتفاعل مع المحيط

أن أضافة الفلور للتركيب لا يؤثر على موديلات الأهتزاز ل البايريمادين لكنه ذو تأثير كبير على الطاقة المهيجة التي قد تحدث لخلايا سرطان الثدي .أن ثنائي اوكسيد البايريمادين مع الفلور يكون اعلى خصائص استشعارية من ثنائي الاوكسيد نفسه.

الكلمات المفتاحية: DFT, الثدي, الفيزياء الطبية , البايريمادين, فجوة الطاقة, الأستقطابية

Introduction

While breast cancer is often referred to as one disease, there are many types of breast cancer [Jemal *et al.*, 2007]. All breast cancers start in the breast, so they are alike in some ways, but they differ in others. Invasive breast cancer has spread from the original site (either the milk ducts or the lobules) into the surrounding breast tissue. It may have spread to invasive breast cancer is invasive ductal carcinoma. It starts in the ducts of the breast (the tubes that carry breast milk to the nipple). Invasive lobular carcinoma is the next most common type.[Ferranti *et al.*, 2000]. It occurs in the lobules (the sacs in the breast that produce milk). [Gülsün *et al.*,2003]. There are less common types of invasive breast cancer that tend to have a good prognosis (outcome). They are: Mucinous (colloid) carcinoma, Papillary carcinoma and Tubular carcinoma[Tabar *et al.*,2004; Haka *et al.*,2002].

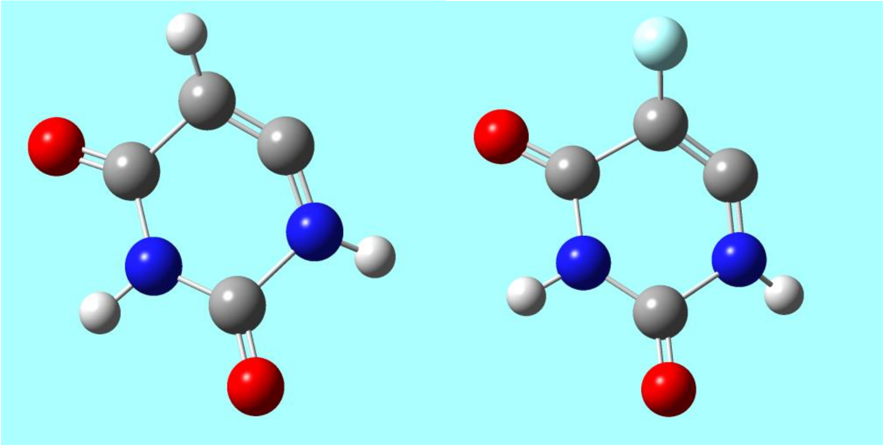
Aromatic compounds are important in industry and play key roles in the biochemistry of all living things [Kroto *et al.*,1985; Hirsch *et al.*,2005]. There are many organic materials show useful field effect transistor performance, which can be characterized by their carrier mobility and on/off current ratios [Died Erich *et al.*, 1991; Buhl *et al.*,2001]. Many studies on cyclic oligomers have been reported both experimentally and theoretically [Kratchmer *et al.*, 1990; Richter *et al.*, 1997], in [Taylor *et al.*,1993] the substituent effects of oligomers such as oligothiophene, oligopyrrole and oligofuran are discussed in terms of reorganization energy. Also, [Pope *et al.*,1993] studied the geometric and electronic properties for cynothiophene oligomers as a prototype of an organic conducting polymer using ab initio and DFT [Howard *et al.*,1991], they showed that the cyano group generally reduced the band gap with variation of the substitution position.

II Theory

Full relaxation of the di-oxide pyrimidine as one type of Breast cell and it is adduct di-oxide fluorine pyrimidine were performed with Berny optimization algorithm in which the calculation of the energy derivatives with respect to nuclear coordinates are done analytically, in redundant internal coordinates [Ellis *et al.*,2000; Yu *et al.*,1998]. The gradient corrected density functional methodology was employed Becke's three-parameter adiabatic connection (B3) hybrid exchange functional were used in combination with the Lee-Yang-Parr correlation functional B3LYP. The B3LYP functional contains a linear combination of exact HF exchange, Slater exchange and Becke gradient-corrected exchange [Brabec *et al.*,2002]. The standard 6-31G basis set of DZP quality was used for orbital expansion to solve the Kohn–Sham equations in all cases. **[**Schlegel, 1982] The LUMO-HOMO energy gap for the studied structures in this study was calculated at the same level of theory [Becke, 1988; Lee ,1988].

III Results and Discussion

Figure 1 represents the relax structures of di-oxide pyrimidine and it is adduct. The standard orientations are represented by the optimized coordinates in Angstrom (A^0) for all atoms in the two structures and listed in Table 1. Table 2 illustrates the optimized parameters of these molecules included bonds in Angstrom (A^0) and angles in degree calculated from DFT-B3YLP/6-31G. As seen in Tables 1 and 2, the bonds are change due to the presence of fluorine atom in place of hydrogen atom. This change comes from the linear combination atomic orbitals-molecular orbitals.



di-oxide pyrimidine

di-oxide fluorine pyrimidine

Figure 1: The relaxed structures of di-oxide pyrimidine and its adduct using DFT- B3LYP/6-31G

Table 1: The standard orientation of the di-oxide pyrimidine and it is adduct

Atom	**di-oxide pyrimidine**			**Atom**	**di-oxide fluorine pyrimidine**		
	X	**Y**	**Z**		**X**	**Y**	**Z**
1C	1.247583	-0.3826	0.071873	**1C**	-1.6082	0.125324	0.142828
2C	-0.02272	1.610284	-0.03240	**2C**	0.142128	-1.44795	-0.35793
3C	-1.21453	1.182518	0.277919	**3C**	1.155839	-0.64048	-0.05259
4C	-1.29223	-0.32711	-0.06328	**4C**	0.805902	0.841747	-0.20407
5H	1.857221	1.503234	-0.85214	**5H**	-1.78648	-1.74578	-0.95455
6H	-1.98423	1.624084	0.898373	**6H**	-0.83670	2.011491	0.262934
7H	-0.03533	-1.96571	0.082491	**7O**	1.629480	1.731424	-0.32263
8O	-2.33650	-0.93881	-0.18872	**8N**	-0.56922	1.044956	0.081451
9N	-0.01664	-0.94861	0.040691	**9N**	-1.12213	-1.23409	-0.36599
10N	1.147886	1.122515	-0.22201	**10O**	-2.77929	0.314588	0.379155
11O	2.328392	-0.92084	0.140719	**11F**	2.298632	-0.95352	0.562431

Table 2: The optimized parameters of the di-oxide pyrimidine and it is adduct

di-oxide pyrimidine				**di-oxide fluorine pyrimidine**			
Bond	**A^0**	**Angle**	**(^{0})**	**Bond**	**A^0**	**Angle**	**(^{0})**
C = C	1.303	**C–C=C**	108.24	**C = C**	1.331	**C–C=C**	112.98
C - C	1.594	**C=C=N**	138.15	**C - C**	1.530	**C=C=N**	130.61
C - N	1.422	**C=N-H**	125.65	**C - N**	1.388	**C=N-H**	124.03
C =N	1.282	**N–C=O**	129.41	**C =N**	1.282	**N–C=O**	120.75
C - H	1.082	**C=C-H**	130.72	**C - F**	1.335	**C=C-F**	127.96
N - H	1.022	**C–N-C**	129.88	**N - H**	1.024	**C–N-C**	129.71
C = O	1.209	**C–C=O**	123.87	**C = O**	1.209	**C–C=O**	124.22

Calculated Energies

The calculated energies of the studied structures are the total energy ET, ionization energy IE, electron affinity EA, electronegativity X. IE and EA are calculated according to the vertical orbital theorem or so called Koopmans theorem. These calculations are carried out by performing B3LYP/6-31G level of density functional theory. Table 3 shows the results of the calculated energies of the di-oxide pyrimidine and it is adduct.

Table 3 : The calculated energies of the di-oxide pyrimidine and it is adduct from DFT-B3LYP/6-31G.

Structure	**ET(eV)**	**IE(eV)**	**EA(eV)**	**X(eV)**
di-oxide pyrimidine	-11256.118	13.693	10.274	11.983
di-oxide fluorine pyrimidine	-13954.925	13.869	10.879	12.374

From table 3, the total energy of di-oxide fluorine pyrimidine is less than the total energy of the di-oxide pyrimidine. The total energy was decrease with adding the Fluorine atom in place of hydrogen in the di-oxide pyrimidine structure, this result is a reflection of the binding energy of the structure in which the Fluorine has atomic number more than the hydrogen. The calculated values of ionization energy and electron affinity of the two structures showed that the constructed molecular orbitals from the linear combination of atomic orbitals are arrays due to absence and presence Fluorine atom in the structure. The di-oxide pyrimidine has low values of IE and EA in comparison with the di-oxide fluorine pyrimidine structure. Adding the F atom in place of H atom increased the IE and EA of the di-oxide pyrimidine. That means the di-oxide pyrimidine without Fluorine needs low energy to become cation. These results are global properties and they are not coming from the frontier molecular electronic states . The higher value of EA of the di-oxide fluorine pyrimidine structure gave it high ability to acceptance an electron from the surrounding. The large value of electronegativity of the di-oxide fluorine pyrimidine makes from this structure more chemically active in comparison with the di-oxide pyrimidine without Fluorine, that means this structure has a large escaping tendency. This result may come from the high value of the electronegativity of Fluorine [3.98 eV] comparing with hydrogen [2.20 eV].

Electronic States

Table 4 shows the high occupied molecular orbital energy E_{HOMO}, lower unoccupied molecular orbital energy E_{LUMO} and the forbidden energy gap E_g of the di-oxide pyrimidine and di-oxide fluorine pyrimidine structures calculated from the B3LYP/6-31G density functional theory calculations. The addition of Fluorine atom in place of hydrogen in the di-oxide pyrimidine has effect on both HOMO and LUMO energies. The results showed that the energy gap of the di-oxide pyrimidine was decrease with the addition of Fluorine atom, the variation of the forbidden energy gap is about 0.429 eV, this variation indicates that the energy gap of di-oxide pyrimidine will be soft with the presence of atoms of high electronegativity.

Table 4 : The E_{HOMO}, E_{LUMO} and E_g of the di-oxide pyrimidine and it is adduct from DFT-B3LYP/6-31G.

Structure	E_{HOMO}(eV)	E_{LUMO}(eV)	Eg(eV)
di-oxide pyrimidine	-13.693	-10.274	3.419
di-oxide fluorine pyrimidine	-13.869	-10.879	2.99

Molecular Polarizability

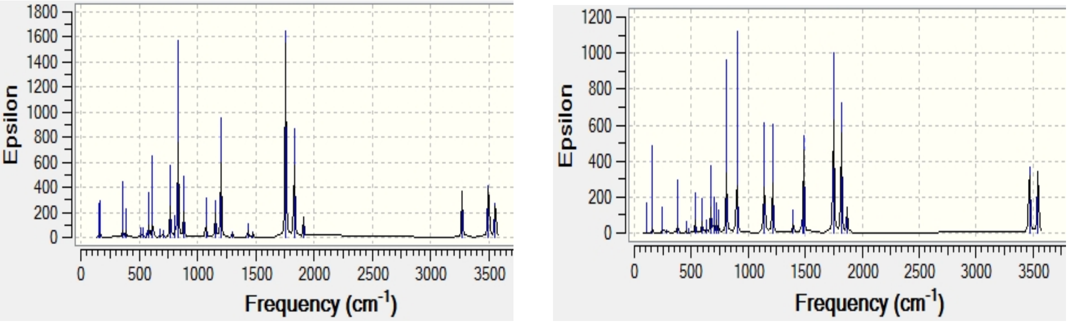
Table 5 illustrates the calculations of total dipole moment in Debye and Polarizability in a. u of the di-oxide pyrimidine and di-oxide fluorine pyrimidine structures. This table showed that the addition of Fluorine atom to the di-oxide pyrimidine changes the charge distribution and, therefore, effects on the electric dipole moment of the di-oxide pyrimidine. This effect corresponds to the point group symmetry for each structure. The calculated average Polarizability and its components α_{zz}, α_{yy} and α_{xx} in table 5 refers to that the new di-oxide fluorine pyrimidine has large value of Polarizability in comparison with the reference di-oxide pyrimidine structure and that an indication to this structure is more reactive in charge transform with the surrounding media. The reason of this may a result of the presence of F atom of high electronegativity in the terminal end of the ring.

Table 5: The calculated total dipole moment and Polarizability of the di-oxide pyrimidine and it is adduct from DFT-B3LYP/6-31G.

Structure	Total D.M (Debye)	Polarizability(a.u)			
		α_{xx}	α_{yy}	α_{zz}	α_{ave}
di-oxide pyrimidine	3.947	23.446	57.128	85.829	55.467
di-oxide fluorine pyrimidine	3.796	25.443	59.737	87.183	57.454

Spectra Properties

Figure 2 shows the infrared IR spectra of the di-oxide pyrimidine and di-oxide fluorine pyrimidine structures, For di-oxide pyrimidine structure, the stretching mode of N-H bond was observed at (3499.44 - 3557.97) Cm^{-1} and the bending of N-H bond was observed at (1433.55 – 1477.28) Cm^{-1}, the stretching of C-H bond was observed at 3276.04 Cm^{-1}, while the stretching of C-H bond was observed at (1758.43 – 1831.82) Cm^{-1}. The stretching of C – C bond is below 800 Cm^{-1}, while the stretching of C-O bond was observed at (17558.43 – 1831.82) Cm^{-1} For di-oxide fluorine pyrimidine structure, the stretching mode of N-H bond was observed at (3469.85 - 3546.14) Cm^{-1} and the bending of N-H bond was observed at (1396.20 – 1488.60) Cm^{-1}, the stretching of C-F bond was observed at 1135.23 Cm^{-1} and the bending C-F bond is at 285.33 Cm^{-1}, while the stretching of C-O bond was observed at (1748.68 – 1817.47) Cm^{-1}. The stretching of C – C bond is below 810.20 Cm^{-1}. The results mean that the presence of Fluorine atom has approximately no effect on the vibration modes of the bonds of the di-oxide pyrimidine because it has electronic structure like the hydrogen.

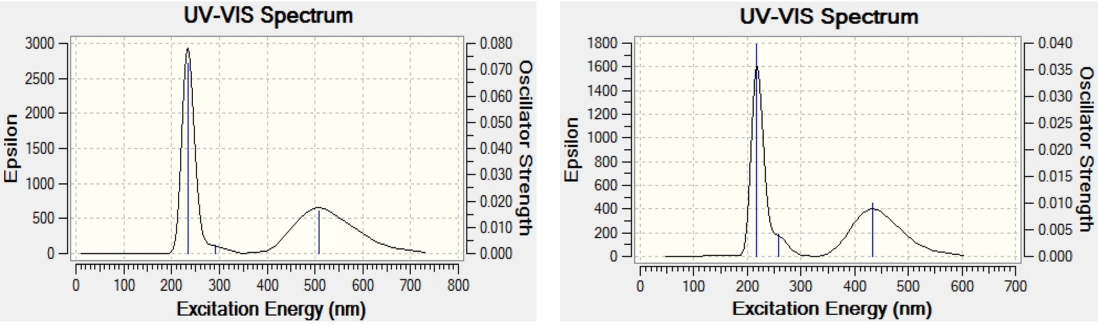


di-oxide pyrimidine

di-oxide fluorine pyrimidine

Figure 2: The IR-Spectra of di-oxide pyrimidine and its adduct using DFT-B3LYP/6-31G

Figure 3 shows the influence of the addition of Fluorine atom in the di-oxide pyrimidine on the absorption energy of the structure, as we see in mentioned Figures, the excitation energies for the di-oxide pyrimidine are at (245 and 505) nm correspond to oscillation strength of the maximum peaks 0.075 and 0.017, respectively. Adding the Fluorine in place of hydrogen reduced the strength of the oscillation to 0.035 and 0.010 correspond to 220 nm and 440 nm. That means the di-oxide pyrimidine became more reactive with Fluorine atom in comparison with di-oxide pyrimidine, and this result agree with the result of the electronic states of the di-oxide pyrimidine. The di-oxide fluorine pyrimidine has electronic sensing properties more than the di-oxide pyrimidine.



di-oxide pyrimidine

di-oxide fluorine pyrimidine

Figure 3: The UV-Vis of di-oxide pyrimidine and its adduct using DFT-B3LYP/6-31G

Conclusions

The total energy of the di-oxide pyrimidine was decreased with adding the Fluorine in place of hydrogen atom in the di-oxide pyrimidine. Adding the Fluorine to the di-oxide pyrimidine leads to change both the HOMO and LUMO energies, therefore, reduced the energy gap of the structure, but this decrease of energy gap may depends on the location of added atom in the structure. This results is a sign of constructing molecular structure has electronic sensing properties. The di-oxide pyrimidine has low values of IE and EA in comparison with the di-oxide fluorine pyrimidine structure. Adding the F atom in place of H atom increased the IE and EA of the di-oxide pyrimidine, the di-oxide pyrimidine without Fluorine needs low energy to become cation. The higher value of EA of the di-oxide fluorine pyrimidine structure gave it high ability to acceptance an electron from the surrounding. The new di-oxide fluorine pyrimidine has large value of Polarizability in comparison with the reference di-oxide pyrimidine structure and that an indication to this structure is more reactive in charge transform with the surrounding media. The presence of Fluorine in the structure has no effect on the vibration modes of the di-oxide pyrimidine but has high effect on the excitation energy can occur for the di-oxide pyrimidine, means the di-oxide pyrimidine with the Fluorine has high sensing property than the di-oxide pyrimidine.

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