Calculating Structural, Electronics Structures, Electronic Properties and IR Spectra of Pentacene Molecule

Dhia Hamdi Al-Amiedy
Physics Dept.,
College of Science for Women
Univ. of Baghdad, Iraq
amiedy48@gmail.com

Zeyad Adnan Saleh
Physics Dept,
College of Science
Al-Mustansriyah Univ, Iraq

Rajaa Khedir Al-Yasari
Physics Dept
College of Science
Univ. of Karbala, Iraq

Abstract: *A theoretical has been carried out of calculating molecular structure parameters of pentacene molecule ($C_{22}H_{14}$) and effects adding of fluoride atoms situed in different positions was performed by using Density Functional Theory (DFT). The substituent effect on the structure of molecule and electronic structures for the position variation of the fluoride substituent's in the pentacene molecule were carried out. The optimized structure ,electronic states, total energies , energy gaps(2.090 -2.195 eV), ionization potentials (5.057 -5.264 eV), electron affinities(2.967 -3.068 eV), chemical potential, hardness, softeness, electrophilictity, and IR spectrum were calculated. The results showed an decrease in energy gaps and increases in the electronic properties.*

Keywords: *DFT, Ionization potential, electron affinity, energy gap, and IR spectrum.*

1. INTRODUCTION

Aromatic compounds are important in industry and play roles in the biochemistry of all living things[1]. Where's solar cells and photovoltaic [2], thin film from grazing-incidence x-ray [3],and field effect transistor [4].

Many studies on cyclic oligomers have been reported both experimentally and theoretically are discussed in terms of reorganization energy [5], in the substituent effects of studied the geometric and electronic properties for polythiophines and cynothiophene oligomers as a prototype of an organic conducting polymer using Ab Intio and DFT[6],they showed that the cyanogroup generally reduced the bond gap with variation of the substitution position.

Pentacene is a polycyclic aromatic hydrocarbon consisting of five rings linearly-fused benzene rings. This highly conjugated compound is an organic semiconductor [7], 6,13-Bis(4-propylphenyl) pentacene was synthesized and characterized. The structures of the products that were obtained during the reaction steps were identified vai FT-IR and NMR spectroscopy and elemental analysis. The compound was found to be soluble in organic solvents like chloroform, dichloromethane, and toluene[8]. The fluoride atoms substituent effect were examined on pentacene molecule in different positions. In present work ,density functional theory has been performed in order to study the electronic properties of the pentacene fluoride molecules beside determine the effects of the substituent atoms.

2. COMPUTATIONAL DETAILS

The Density Functional Theory (DFT) methods has been carried out using the Gaussian 09 programs [9]. For the molecular properties of the pentacene molecules using the standard 6-311G(d,p) basis set . The lowest energy structures of the species conformational analysis of the molecules had been performed using . The vibrational wave number assignments were used by combining the results in the Gauss view 5.08 programs [9].

Theory with the same basis set had been used to perform the geometry optimization by using B3LYP density functional [10], beside the harmonic vibrational . The hybrid functional B3LYP were used for calculation the electronic properties of the molecule such as electronic states, ionization potentials , and energy gaps[11]. In the DFT partitions, the electronic energy such as $E = E_T + E_V + E_J + E_{XC}$, where E_T (kinetic energy), E_V (electron nuclear attraction) and E_J (electron-electron repulsion) terms respectively. The electron correlation is taken into account in DFT the exchange correlation term E_{XC}, which includes the exchange energy arising from the ant symmetry of the quantum mechanical wave function and the dynamic correlation in the motion of individual electrons; it makes DFT dominant over the conventional Haretrr-Fock (HF) procedure[12].

The geometry optimized structures are obtained by restricted closed-shell formalism and without any symmetry restriction , and vibrational analysis for each structure does not yield any imaginary frequencies, which indicates that the structure of each molecule corresponds to at least a local minimum on the potential energy surface[13].

In this investigation , electronic potential (IP) ,electron affinities (EA), chemical potential (μ) (the negative of electronegativity (χ)), hardness (η), softness (S) ,electrophilic index (ω) were calculated. The ionization potential is calculated as the energy difference between the energy of the molecule derived from electron-transfer (radical cation) and the respective neutral molecule; $IPv = E_{cation} - E_n$. The EA was computed as the energy difference between the neutral molecule and the anion molecule: $EA = E_n - E_{anion}$ [14]. The highest occupied molecular orbital (HOMO) and the lowest Unoccupied Molecular Orbital (LUMO) energy were also used to estimate the IP and EA in the framework of Koopmans, theorem: $IP = -\varepsilon_{HOMO}$ and $EA = -\varepsilon_{LUNO}$ [15].
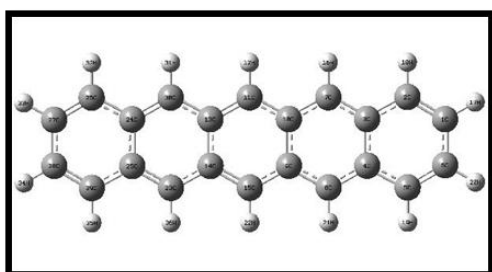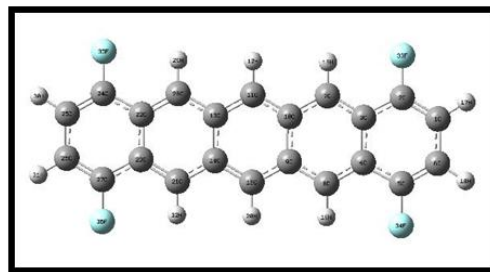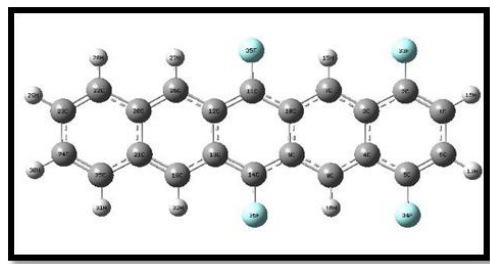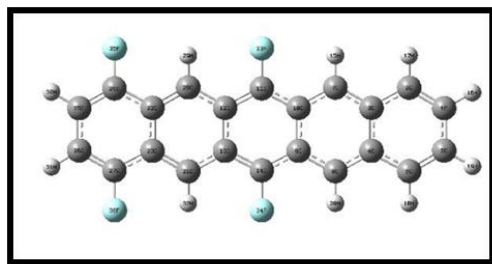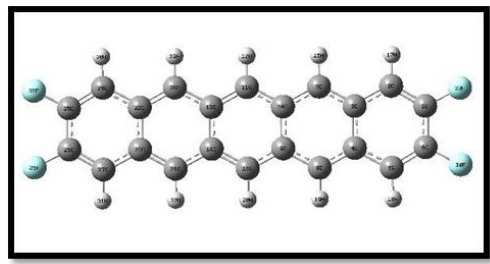

1(pentacene)

2(2,5,24,27-pentacene fluoride)
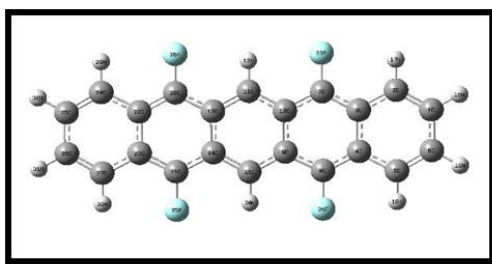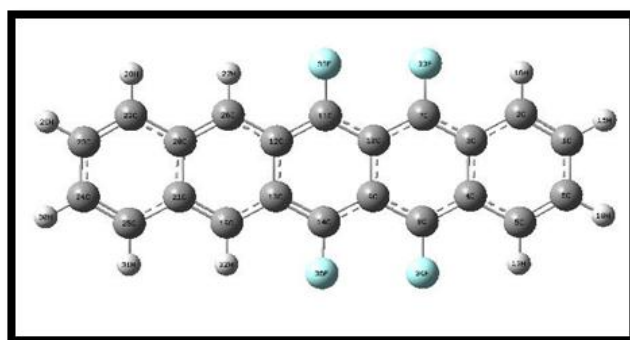

3(7,8,21,28-pentacene fluoride)

4(2,5,11,14-pentacene fluoride)

5(11,14,24,27-pentacene fluoride)

6(1,6,15,16-pentacene fluoride)

7(7,8,11,14-pentacene fluoride)

Figure1. *The optimized structures of pentacene fluoride molecules*

Within the framework of DFT ,one of the global quantities is chemical potential (μ), which is measures the escaping tendency of an electronic cloud, and equals the slope of the energy versus N(number of electrons) curve at external potential v(r)[16]:

$$\mu = \left[\frac{\partial E}{\partial N}\right]_{v(r)} \cdots \qquad (1)$$

Using difference approximation to chemical potential gives,

$$\mu \approx -\chi = -(IP + EA)/2 \qquad (2)$$

The chemical hardness has been calculated by the density functional theory as the second derivative of electronic energy with respect to the number of electrons N,for a constant external potential v(r)[17]:

$$\eta = \frac{1}{2}\left[\frac{\partial^2 E}{\partial N^2}\right]_{v(r)} = \frac{1}{2}\left[\frac{\partial E}{\partial N}\right]_{v(r)} \cdots \qquad (3)$$

Using difference approximation to chemical hardness gives,

$$\eta = (IP - EA)/2 \qquad (4)$$

For insulator and semiconductor ,hardness equal to half of the value of the energy gap which equal to (ε_{HOMO}-ε_{LUMO}), and the softness is given by the following relative as [18]:

$$s = \frac{1}{2\eta} = \left(\frac{\partial^2 N}{\partial E^2}\right)_{v(r)} = \left(\frac{\partial N}{\partial \mu}\right)_{v(r)} \cdots \qquad (5)$$

Electrophilicity index is a measure of energy lowering due to maximal Electron flow between donor and acceptor. Electrophilicity index (ω) is defined as [18].

$$\omega = \frac{\mu^2}{2\eta} \qquad (6)$$

3. RESULTS AND DISCUSSION

3.1 Molecular Geometry

The optimized structure parameters of molecules calculated by using DFT –B3LYP levels with the 6-311G (d,p) basis set are listed in table 1 in accordance with the atom numbering scheme shown in figure (1). Table (1) shows the values of bond lengths and angles for (1-7) molecules.

From the theoretical values, we can find that most of the optimized bond length are small difference while bond angles are between (116.948^o and 121.529^o)

Table1. *Optimized geometrical parameters of pentacene molecule, R(A^o) bond length ,A(^{o}) bond angles.*

Molecules	Bond length	Our data (A^o)	Bond angles	Oure data (^{o})
1	R(C1 = C2)	1.362	A(C2-C3-C7)	122.301
	R(C1-C6)	1.431	A(C2-C1-C6)	120.564
	R(C2 – C3)	1.434	A(C3-C7-C10)	121.972
	R(C3 – C4)	1.453	A(C2-C1-H17)	120.186
	R(C2 – H18)	1.085	A(C7-C3-C4)	119.332
2	R(C1= C2)	1.355	A(C2-C1-C6)	119.583
	R(C1 – C6)	1.430	A(C1-C2-F33)	119.983
	R(C2– F33)	1.352	A(C2-C1-H17)	119.767
	R(C2 – H17)	1.082	A(C23-C27-F36)	116.948
	R(C24-C25)	1.355	A(C22-C28-C29)	119.378
3	R(C1 = C2)	1.362	A(C2-C1-C6)	120.851
	R(C1 – C6)	1.430	A(C3-C7-F33)	118.690
	R(C7 – F33)	1.354	A(C1-C2-H17)	1.21.090
	R(C2 – H17)	1.082	A(C22-C24-C29)	118.421
	R(C24-C25)	1.361	A(C22-C28-F36)	118.730
4	R(C1 = C2)	1.355	A(C2-C1-C6)	119.608
	R(C1 – C6)	1.430	A(C1-C2-F33)	120.002
	R(C1– H16)	1.082	A(C1-C6-H17)	120.650
	R(C2–F33)	1.351	A(C22-C23-C29)	120.186
	R(C24-C25)	1.361	A(C13-C14-F36)1	118.103
5	R(C1=C2)	1.362	A(C2-C1-C6)	120.614
	R(C1–C6)	1.431	A(C10-C11-F33)	118.056
	R(C1 –H16)	1.084	A(C1-C2-H17)	120.675
	R(C11–F33)	1.353	A(C22-C28-C29)	119.832
	R(C24–C25)	1.355	A(C26-C27-F36)	120.027
6	R(C1 = C2)	1.353	A(C2-C1-C6)	121.183
	R(C1 – C6)	1.43	A(C2-C1-F33)	121.529
	R(C1 – F33)	1.343	A(C1-C2-H17)	119.390
	R(C2 – H17)	1.083	A(C22-C28-C29)	119.368
	R(C24 – C25)	1.353	A(27-C26-CF36)	121.565
7	R(C1 – C2)	1.362	A(C2-C1-C6)	120.8211
	R(C1–C6)	1.430	A(C22-C23-C29)	120.186
	R(C2 – H16)	1.081	A(C10-C7-F33)	118.789
	R(C7– F33)	1.349	A(C1-C2-H16)	121.107
	R(C24– C25)	1.361	A(C13-C14-F36)	116.975

Represent original pentacene molecule.

1. Denoted (2,5,24,27-pentacene fluoride molecule)

2. Denoted(7,8,21,28 –pentacene fluoride molecule)

3. Represent(2,5,11,14-pentacene fluoride molecule)

4. Denoted(11,14,24,27-pentacene fluoride molecule)

5. Denoted (1,6,25,26-pentacene fluoride molecule)

6. Denoted (7,8,11,14-pentacene fluoride molecule)

3.2 Energies

The Pentacene molecule has energy gap (2.25 eV), HOMO (-4.8598 eV), and LUMO(-2.6560) . table (2) shows the values of the total energy and symmetry of the studied molecules. The total energy for all study molecules as a linear function of fluoride atoms number which added to the molecule.

It is clear that from table (2),the total energy for all pentacene fluoride molecules is approximately the same which refer that the total energy is independent of the position of the fluoride radical in the ring, and   the symmetry of study molecules, the molecules (1,2,3,5,6)is planar with inversion centerand have D_{2h} symmetry (high symmetry),while molecules (4,7) is planar with rotation axis and have C_{2v} symmetry (high symmetry).

The substitution of fluoride atoms (electron withdrawing) causes increasing in the value of HOMO and slight increase of the value of LUMO energy, beside decreasing the value of energy gap therefore ,the presence of substituent decreases the energy gaps (Eg) which improves the conductivities which enhances the solubilities of these molecules. This effect of the fluoride atoms was the largest in molecule no. 6 with energy gap of (2.245 eV).

Figure (2) shows the HOMO and LUMO energies of pentacene fluoride molecules   figure (3) shows the energy gaps of pentacene fluoride molecules.

Table 2. *Total energy and symmmetry for pentacene molecules.*

molecule	Total Energy(a.u)	Symmetry
1	-846.989	D_{2h}
2	-1244.045	D_{2h}
3	-1244.044	D_{2h}
4	-1244.044	C_{2V}
5	-1244.044	D_{2h}
6	-1244.032	D_{2h}
7	-1244.032	C_{2V}
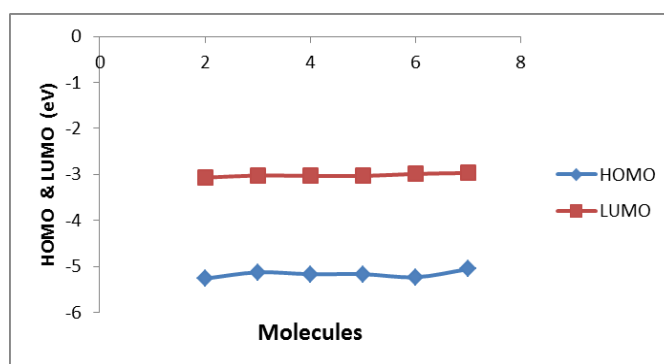
Figure(2). *HOMO and LUMO values as a function of positions of fluoride atoms added to in pentacene molecule.*
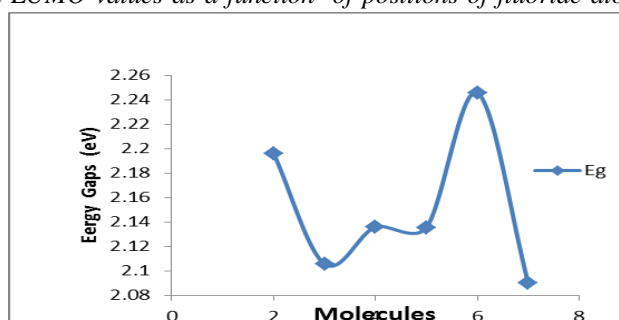
Figure (3). *Energy gaps values asa function of positions of fluoride atoms added pentacene molecule.*

3.3 Some Important Variables.

The B3LYP functional has been used in a high efficient in order to calculate the electronic properties for the organic studied molecules, such as ionization potentials (IP),electron affinities (EA),electronegativity (χ) ,absolute hardness(η),absolute softness(S), electrophilic index(ω) , which displayed in table (3) for each variable are computed by two different ways: The first being energy –vertical method is based on the differences of total electronic energies when an electron is added or removed in accordance with the neutral molecule. The second is based on the differences between the HOMO and LUMO energies of the neutral molecule and is known as orbital –vertical (Koopmans᾽ theorem).

The calculated properties for each variable shown in table (3) which reveal that these pentacene fluoride compounds have a tendency to capture electrons instead of donating them. The ionization potential of the pentacene fluoride molecules is greater than that for the original molecule, but the (1, 6, 25, 26-pentacene fluoride) molecule has the largest value of ionization potential, this indicates that the pentacene fluoride molecule needs high energy to become cation comparing with the others molecules. The strength of an acceptor molecule is measured by its EA which the energy released when adding one electron to LUMO. An acceptor must have a high EA, adding the radical to the ring leads to increasing the ability of the electron affinity for the molecule, EA of molecule 2 is the largest, as we see in table (3).

Table3. *The electronicproperties for molecules . a- energy-vertical method and b-orbital-vertical method.*

Molecules	IP(e V)	EA(eV)	X(e V)	η (e V)	S(e V)	ω (e V)
1	6.126[a]	1.417[a]	3.771[a]	2.354[a]	0.212[a]	3.020[a]
	4.859[b]	2.656[b]	3.757[b]	1.101[b]	0.453[b]	6.408[b]
2	6.509[a]	1.827[a]	4.168[a]	2.340[a]	0.213[a]	3.711[a]
	5.264[b]	3.068[b]	4.166[b]	1.097[b]	0.455[b]	7.904[b]
3	6.369[a]	1.787[a]	4.078[a]	2.290[a]	0.218[a]	3.629[a]
	5.127[b]	3.022[b]	4.074[b]	1.052[b]	0.474[b]	7.885[b]
4	6.412[a]	1.797[a]	4.105[a]	2.307[a]	0.216[a]	3.651[a]
	5.167[b]	3.031[b]	4.099[b]	1.068[b]	0.468[b]	7.868[b]
5	6.412[a]	1.797[a]	4.105[a]	2.307[a]	0.216[a]	3.651[a]
	5.167[b]	3.031[b]	4.099[b]	1.067[b]	0.468[b]	7.870[b]
6	6.479[a]	1.771[a]	4.125[a]	2.353[a]	0.212[a]	3.615[a]
	5.232[b]	2.987[b]	4.110[b]	1.122[b]	0.445[b]	7.523[b]
7	6.301[a]	1.738[a]	4.019[a]	2.281[a]	0.219[a]	3.540[a]
	5.057[b]	2.967[b]	4.012[b]	1.045[b]	0.478[b]	7.703[b]

Few interesting observations have been made from the results that are shown in table (3) obtained through the energy –vertical and orbital- vertical methods. The EA computed from the energy of the (LUMO) are higher for all study molecules than that of the energy –vertical method. The IP which results from the HOMO is smaller for all studied molecules than that of the energy –vertical method. The two results obtained by the calculation of electronegativity and electrophilicities also agreed very well with the deference in the result. This could be the reason for the low hardness values obtained from the orbital-vertical method than from the energy-vertical method. Koopman᾽s theorem neglects the relaxation effect by using the frozen-orbital approximation. However, this error is frequently compensated by the oppositely directed error was due to the electron correlation effect, beside neglect in the Hartree-Fock (HF) method. Therefore, the Koopmans᾽ theorem is a crude but useful and fast approach [17]. The behavior of electronegtivity, softness and electrophilic index for the studied molecules shows a large

magnitude than those for the original ring, except 6 molecule is low, adding the atoms (such as F) give the molecule more softness. The calculated values of softness and electrophilic index by using orbital-vertical method higher than energy-vertical method, while the calculated values of electronegtivity and hardness by using orbital- vertical method are lower than energy-vertical method.

3.4 IR Spectra

The IR spectra of (1-7) molecules are shown in the figure (4). The harmonic vibrational frequencies were calculated for study molecules by using   B3LYP level with 6-311G (d,p) basis set. The (C- H) stretching vibrations of aromatic molecules shown in the region (2900-3250) cm^{-1} while the region (3100-3250) cm^{-1} was for asymmetric stretching whereas (2900-3100) cm^{-1} for symmetric stretching modes of vibration [19].

The frequencies values of pentacene molecule at (3188.28 and 3189.46) cm^{-1} . The aromatic molecules frequency has both in-plane (1100 – 1700) cm^{-1} and out-of-plane (below 1000 cm^{-1}) [20]. While (C – H) bending vibrations, for in-plane vibration for B3LYP method were 1144.18 cm^{-1} and 1376.7cm^{-1} .Whereas out-of-plane (C – H) deformation vibrations were 746.98 cm^{-1} and 876.85 cm^{-1}.

It is clear from figure (4) that the IR spectra for pentacene fluoride molecules enhanced new peaks in the vibration modes due to existing of stretched bond such as (C- F) , (C- H),and (C= C)   For (2-7) molecules, the stretching of (C- H) had been observed with the range (3191.17–3212.87) cm^{-1} ,while the (C- F) stretching observed within the region ranged (1136.97-1509.36) cm^{-1} and the stretching of (C= C) bond shown at the region range (1535.22 – 1601.08) cm^{-1}.

Figure4: *Calculated IR spectra of study pentacene molecules*
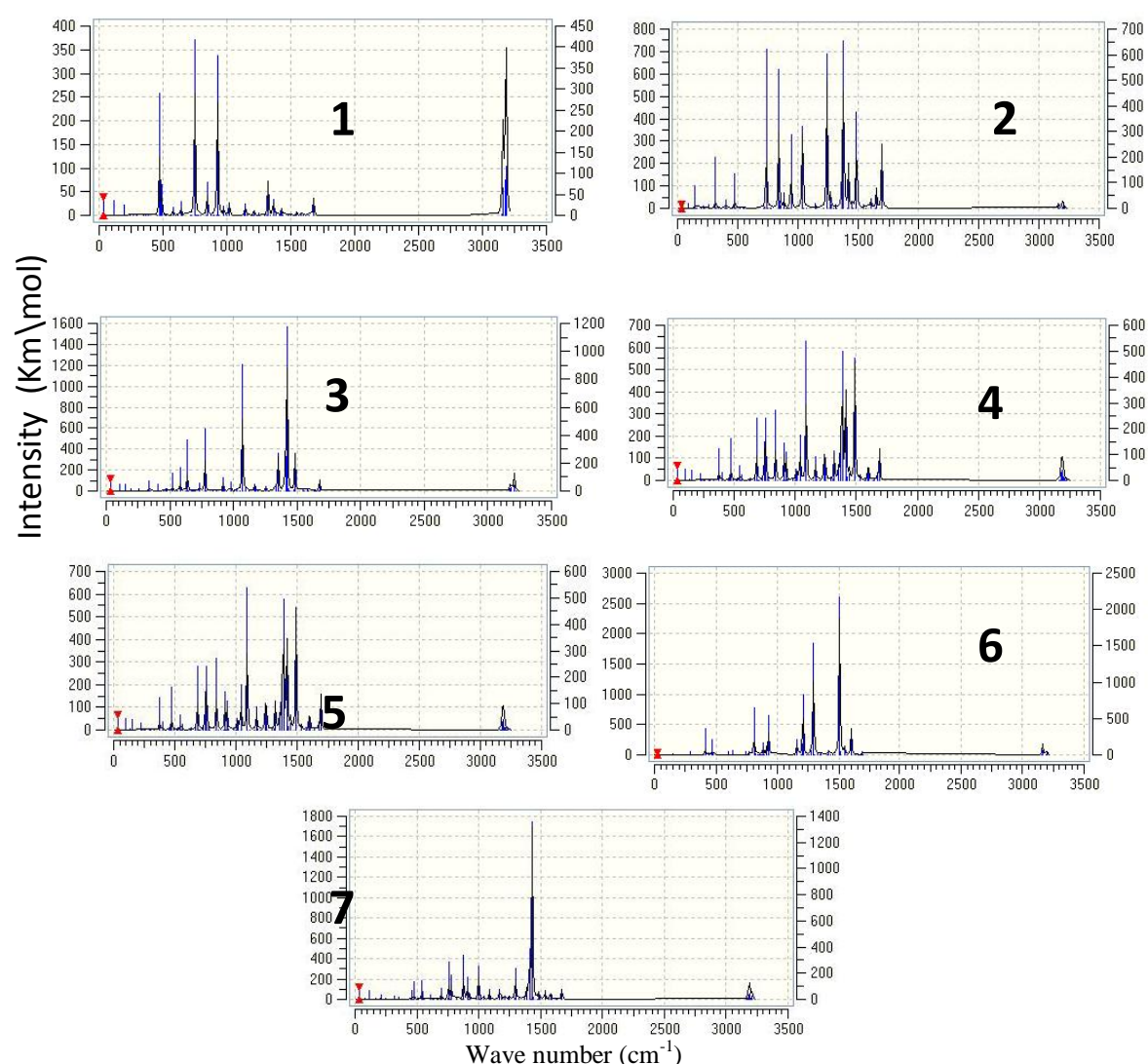
4. CONCLUSION

The calculated electronic properties such as ionization potential, electron affinity, electronegativity, hardness, softness and electrophilic index by using energy-vertical method and orbital-vertical method, mentioned the following conclusions :

The optimized bond length are small difference while bond angles showed approximately 120°.

The total energies for pentacene fluoride did not dependent on the position of the fluoride radical in the ring substitution while fluoride atoms causes increasing energy.

The substituents of atom fluoride causes increasing HOMO and slight increasing LUMO and decreases the energy gap of the molecules , and a small energy gap means small excitation energies of manifold of the exited states.

The electronic properties (IP,χ ,η) were calculated by using energy-vertical method are larger than orbital –vertical method, while (EA,S,ω) calculated by using energy-vertical method are less than orbital –vertical method.

IR spectra calculation shows that when adding the fluoride atoms leads to increasing the vibrational mode ,and highest wave numbers of stretching vibration

REFERENCES

[1] R. Morrison and R .Boyd , Organic Chemistry ,6th Edition, New York University,(2007).

[2] A. Gorodetsky ,M. Cox, N. Tremblay , Z. Kymissit , and C. Nuckolls ,Chem. ,Mater. ,4090 - 4092,(2009) .

[3] D. Nabok ,P. Puschnig ,and C. Ambrosch ,Phys. ,Rev. ,B76, 235322-235326(2007).

[4] S.Schaur , Electrochemical Doping of Organic Field- Effect Transistors to Improve Contact Resistances , Johannes Kepler, University Linz , Juni, (2010) .

[5] S. Duhm, S. Hosoumi, I. Salzmann, A. Gerlach, M. Oehelt, B. Wedl, T. Lee, F. Schreiber, N. Koch, N. Ueno, and S. Kera, Phys., Rev., B 81, 045418- 045424, (2010).

[6] T.Demisse, Computatioal Investigation of Phlenyl Ssubstituted Poly Thiophenes ,Addis Ababa, Ethlopla, (2007).

[7] S., Seo, Structural and Electronic Properties of Pentacene at Organic-Inorganic Interfaces, University of Wisconsin- Madison, (2010).

[8] E. Choi, H. Kim, J. Park, and J. Kim, J., of Inform., Displ., 1598-0316,(2009).

[9] M.Frisch,G.Trucks,H.Schlegel,G.Scuseria,M.Robb,J.Cheeseman,G.Scalmani,V.Barone,B.M ennucci,G.Petersson,H.Nakatsuji,M.Caricato,H.Hratchian,A.Izmaylov,J.Bloino,G.Zheng,J.S onnenberg,M.Hada,M.Fhara,K.Toyota,R.Fukuda,J.Hasegawa,M.Ishida,T.Nakajima,Y.Honda ,O.Kitao,H.Nakai,T.Vreven,J.Montgomery,J.Peralta,F.Ogliaro,M.Bearpark,J.Heyd,E.Brother s,K.Kudin,V.Staroverov,R.Kobayashi,J.Normand,K.Raghavachari,A.Rendell,J.Burant,s.lyen gar,J.Tomasi,M.Cossi,N.Rega,J.Millam,M.Klene,J.Knox,J.Cross,V.Bakken,C.Adamo,J.Jara millo,R.Gomperts,R.Stramann,O.Yazyev,A.Austin,R.Cammi,C.Pomelli,J.Ochterski,R.Marti n,K.Morokuma,V.Zakrzewski,G.Voth,P.Salvador,J.Dannenberg,S.Dapprich,A.Daniels,O.Far kas,J.Foresman,J.Ortiz,J.Cioslowski, and D.Fox, Gaussin an 09 ,Rev.,A.,02,(Gaussian Inc.,PA, Wallingford ,CT.,(2009).

[10] M. Cossi and V. Barone, J., Chem., Phys., 115, 4708- 4717, (2001).

[11] N. Seidy and S. Ghammamy, Curr., World Environ., 7, 221-226, (2012).

[12] W.Demtroder , Atoms,Molecules and Photons ,Springer ,(2005).

[13] D. Lehnherr and R.Tykwinski, Mater., 3, 2772 -2800,(2010).

[14] C. Zhan, J.Nichols ,and D.Dixon , J., Phys.,Chem., 107, 4184 -4195 ,(2003).

[15] C. Swartz, S. Parkin, J. Bullock, J. Anthony, A. Mayer, and G. Malliaras, Org., Lett., 7, 3163-3166, (2005).

[16] B.Nickel, M.Fiebig, S.Schiefer ,M.Gollner, M.Huth, C.Erlen,and P.Lugli ,Phys., Stat., Sol., 3,526-533,(2008).

[17] M.Oftadeh, S.Naseh, M.Hamadanian, Computational and Theortical Chemistry, 20, 966-978, (2011).

[18] J.Gersten ,The Physics and Chemistry of Materials ,John Wiley & Sons New York, (2001).

[19] A.Perry, M.Martin ,J.Nibler, A.Moki, A.Weber, and T.Blake, J., of Mole., Spectr., 276-277,(2012).

[20] M.Gazyous, A.Sacuto, G.Horowitz, Ph. Lang ,A.Zimmers, and P.Lobo ,Phys., Rev., B70,081309-0813013, (2004).

AUTHORS' BIOGRAPHY

Name: Prof.Dr. Dhia Hamdi Al-Amiedy

Date of Birth: 30/10/1948
Specialization: Molecular Physics
Work Address: Physics Department, College of Science for
                        Women, University of Baghdad.
E-mail: amiedy48@gmail.com
Scientific Certification:
Ph.D. in Molecular Physics, (1979.University of Keele, U.K

Name: Assist. Prof.Dr. Zeyad Adnan Saleh
Date of Birth: 30/12/1958
Specialization: Molecular Physics
Work Address: Physics Department, College of Science ,
Al-Mustansiryah University
E-mail: zeyad_saleh1958@yahoo.com
Scientific Certification: Ph.D. in Molecular Physics, (2005).College of Science,Baghdad,Iraq

Name: Assist. Lect. Rajaa Khedir AL-Yasari
Specialization: Molecular Physics
Work Address: Physics Department, College of Science ,
University of Karbala, Iraq.
E-mail: ralyasarair@gmail.com
Scientific Certification:
M.Sc. in Molecular Physics, (2010).College of Science for Women, Baghdad, Iraq