

Electronic Properties, IR and NMR Spectra of Pentacene and Some of Derivatives

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Introduction

Pentacene (C₂₂ H₁₄) is a polyaromatic hydrocarbon that consisting of five linearly-fused benzene rings, is one of the most promising materials has density (1.3 gm/cm³) and melting point >300 C° sublimates at 372 C° [1]. Pentacene is a popular organic semiconductor material, being widely used in the studied of organic thin film transistors, organic light emitting diodes (OLED), or organic solar cells and (OFET) due to a very high hole mobility of up to 55 cm²/Vs[2,3]. Many studies has been carried out to calculate electron properties, IR spectra, and NMR spectrum. Ionization potential, electron affinity, electronegativity, hardness to atoms and organic molecules by using DFT method[4]. Synthesis, properties, IR and NMR spectrum of 6,13-Bis(4-propylphenyl)pentacene[5]. Electronic properties, IR spectra and Raman spectra investigation of 2-chloro-5-nitrobenzyl alcohol[6]. Synthesis of Naphthalene

Abstract

The optimization structure, electronic properties such as ionization potential, electron affinity, electronegativity, hardness, and electrophilic, IR spectra, and NMR spectroscopy are calculated of pentacene and tetrachloropentacene molecules with substitution chloride for hydrogen atoms in difference positions, study NMR spectrum is very important in medicine application. The calculated ionization potential(6.126 eV) and electron affinity (1.417eV) of these molecules are in a good agreement with experimental values. All properties are calculated by using Gaussian program 09 and Gaussian view 5.08 program using density function (DFT) method with basis set B3LYP/6-311G (d,p), While NMR spectrum is computed by using ChemBioDraw program.

Keywords:

Electronic properties; ionization potential; electron affinity; electronegativity; hardness; electrophonic; IR spectra; NMR spectra

calculation the electronic properties such as ionization potentials, electronic states and energy gaps[12].Figure (1) shows the geometric optimization of pentacene molecules in the gas phase by using DFT method. E_{HOMO} the energy of the highest occupied molecular orbitals, while E_{LUMO} the energy of the lowest unoccupied molecular orbitals. Ionization potential (IP) and electron affinity (EA) in the framework of Koopmans' theorem have been calculated by using the following equations[13].

$$IP = -E_{HOMO}, EA = -E_{LUMO}$$

While the electronegativity (χ) has been calculated by using the following equation [15].

$$\chi = - (IP + EA) / 2 \quad \dots\dots(1)$$

Whereas the hardness (η) is defined as [14].

$$\eta = (IP - EA) / 2 \quad \dots\dots\dots(2)$$

The softness (S) and electrophilic (W) by the following equations [14].

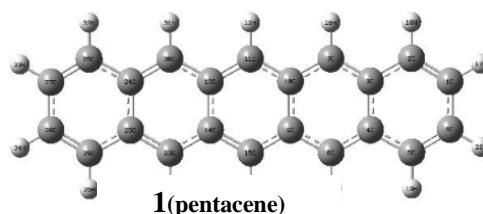
$$S = 1/2 \eta \quad \dots\dots(3)$$

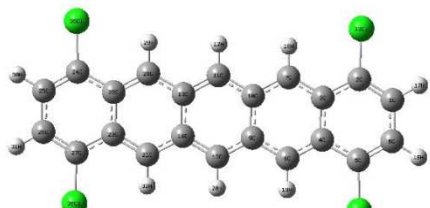
$$W = \chi^2 / 2 \eta \quad \dots\dots(4)$$

Dimide Based N-type Organic Semiconductors[7].The Effect of Atom Size on Electronic Properties of Organic Semiconductors for N-Channel Field Effect Transistors[8].Mid-infrared Waveguiding on Silicon-and-Sapphire[9].

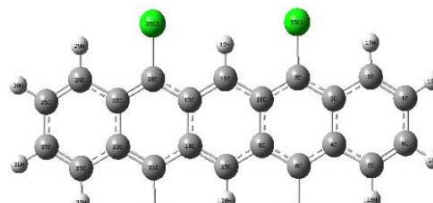
Method

All computational are calculated by using Gaussian 09 and Gaussian view 5.08 program [10],The DFT partitions the electronic energy as $E = E_T + E_V + E_J + E_{XC}$, where, E_T , E_V and E_J are the electronic kinetic energy, the electron nuclear attraction and the electron-electron repulsion terms, respectively. The electron correlation is taken into account in DFT via the exchange correlation term E_{XC} , which includes the exchange energy arising from the antisymmetry of the quantum mechanical wavefunction and the dynamic correlation in the motion of individual electrons; it makes DFT dominant over the conventional HF procedure[11]. the geometric optimization of pentacene and tetrachloropentacene molecules have been performed with DFT method using the B3LYP/6-311G(d,p) level in the gas phase and B3LYP/ 6-311G basis set,The hybrid functional B3LYP has shown to be highly successful for





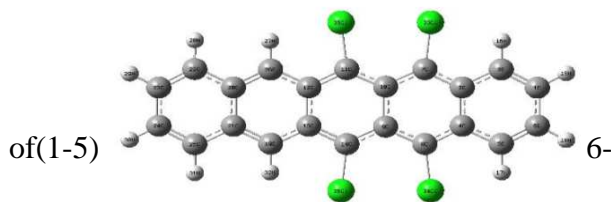
2(1,4,8,11-tetrachloropentacene)



3(5,7,12,14-tetrachloropentacene)



4(2,3,9,10-tetrachloropentacene)



5(5,6,13,14-tetrachloropentacene)

Table :Optimized geometrical parameters of (1-5) pentacene molecules, R(A°) bond lengths,(A°) bond angles.

Molecules	Bond length	Our data (A°)	Previous study[15]	Bond angles	Our data (°)
1	R (C 1 = C 2	1 . 3 6 2	1 . 3 7	A (C 2 - C 3 - C 7	1 2 2 . 3 0 1
	R (C 1 - C 6	1 . 4 3 1	1 . 4 3	A (C 2 - C 1 - C 6	1 2 0 . 5 6 4
	R (C 2 - C 3	1 . 4 3 4	1 . 4 4	A (C 3 - C 7 - C 10	1 2 1 . 9 7 2
	R (C 3 - C 4	1 . 4 5 3		A (C 2 - C 1 - H 17	1 2 0 . 1 8 6
	R (C 2 - H 18	1 . 0 8 5		A (C 7 - C 3 - C 4	1 1 9 . 3 3 2
2	R (C 1 = C 2	1 . 3 5 9		A (C 2 - C 1 - C 6	1 2 0 . 3 3 9
	R (C 1 - C 6	1 . 4 2 5		A (C 1 - C 2 - C 133	1 1 8 . 5 7 7
	R (C 2 - C 133	1 . 7 5 8		A (C 2 - C 1 - H 17	1 2 0 . 2 4 6
	R (C 2 - H 17	1 . 0 8 1		A (C 23 - C 27 - C 136	1 1 9 . 4 0 3
	R (C 24 = C 25	1 . 3 5 8		A (C 22 - C 28 - C 29	1 1 9 . 2 5 8
3	R (C 1 = C 2	1 . 3 6 0		A (C 2 - C 1 - C 6	1 2 0 . 5 1 7
	R (C 1 - C 6	1 . 4 2 5		A (C 3 - C 7 - C 133	1 1 9 . 1 1 9
	R (C 7 - C 133	1 . 7 6		A (C 1 - C 2 - H 17	1 2 0 . 2 0 9
	R (C 2 - H 17	1 . 0 8 0		A (C 22 - C 24 - C 29	1 1 8 . 3 5 8
	R (C 24 = C 25	1 . 3 6 0		A (C 22 - C 28 - C 136	1 1 9 . 1 3 2
4	R (C 1 = C 2	1 . 3 6 0		A (C 2 - C 1 - C 6	1 2 0 . 2 5 3
	R (C 1 - C 6	1 . 4 3 9		A (C 1 - C 2 - C 133	1 1 9 . 4 3 8
	R (C 1 - H 16	1 . 0 8 2		A (C 1 - C 6 - H 17	1 1 9 . 4 9 8
	R (C 2 - C 133	1 . 7 4 7		A (C 22 - C 28 - C 29	1 1 9 . 4 8 8
	R (C 24 = C 25	1 . 3 6 0		A (C 13 - C 14 - C 136	1 1 9 . 4 6 6
5	R (C 1 = C 2	1 . 3 5 9		A (C 2 - C 1 - C 6	1 2 0 . 1 7 7
	R (C 1 - C 6	1 . 4 2 1		A (C 10 - C 7 - C 133	1 2 3 . 0 2 6
	R (C 1 - H 16	1 . 0 7 7		A (C 1 - C 2 - H 16	1 1 9 . 3 3 3
	R (C 11 - C 133	1 . 7 6 4		A (C 22 - C 23 - C 29	1 2 0 . 1 2 4
	R (C 24 = C 25	1 . 3 6 1		A (C 13 - C 14 - C 136	1 1 2 . 8 3 6

311G method for(1-5) pentacene molecules. It is clear from table(2) that the substitution of a chloride atoms for hydrogen lead to slight increasing the values of HOMO and decreasing LUMO, and decreasing of IP while increasing of EA with the substitution, because adding the radical to the ring leads to increasing the ability of the EA for the molecule, the 5pentacene molecule has high EA equal (3.3200eV), 1-molecule has IP(6.126eV) and EA(1.417eV) in a good agreement with the experimental values (6.589eV) and (1.39eV), respectively [16]. The values of χ , S and W are increasing. The behavior of χ , S and W for the studied molecules shows the magnitude large than these for the original ring, the calculated values indicates that the substituted pentacene molecules more softness than the original pentacene molecule, since the chloride atom has borderline softness behavior. This could be the same reason for the low hardness values obtained from this method. Therefore, the Koopmans's theorem is a best useful and fast approach.

Table (2): HOMO, LUMO, and Electronic properties (IP, EA, χ , η , S, and W) measured in eV for (1-5) pentacene molecules using DFT with B3LYP/6-311G(d,p) basis set.

Molecules	HOMO(eV)	LUMO(eV)	IP (eV)	EA(eV)	χ (eV)	η (eV)	S(eV)	W(eV)
1	- 4 . 8 5 9	- 2 . 6 5 6	6.126[15]	1.417[15]	3.771	2.354	0.212	3 . 0 2 0
2	- 5 . 4 2 4 7	- 3 . 2 5 3 3	5 . 4 2 4 7	3 . 2 5 3 3	4.3390	1.0857	0.4605	8 . 6 7 0 5
3	- 5 . 3 7 8 7	- 3 . 3 1 9 7	5 . 3 7 8 7	3 . 3 1 9 7	4.3492	1.0295	0.4856	9 . 1 8 6 8

Results and discussion

1- Molecular geometry

Figure (1) shows the gas phase optimized structure parameters calculated by DFT-B3LYP method with the 6-311G(d,p) basis set. The geometric parameters of (1- 5) pentacene molecules are listed in the table (1). From this table and figure(1) show the values of bond length (C – C) for 1- pentacene molecule in a good agreement with theoretical previous study[15], and the substitution of a chloride atoms for hydrogen lead to decreasing the bond lengths of C – H, C-C, and C-Cl, while it is observed that the C-Cl bond length in all the chloride atoms approximately at (1.747Å and 1.764 Å), in 5 pentacene molecules found the substitution causes Obstruction vacuum, therefore this molecule has high bond length equal to (1.764Å). All angles in pentacene chloride ring (C – C – C angles) are approximately 120°.

2-Electronic properties

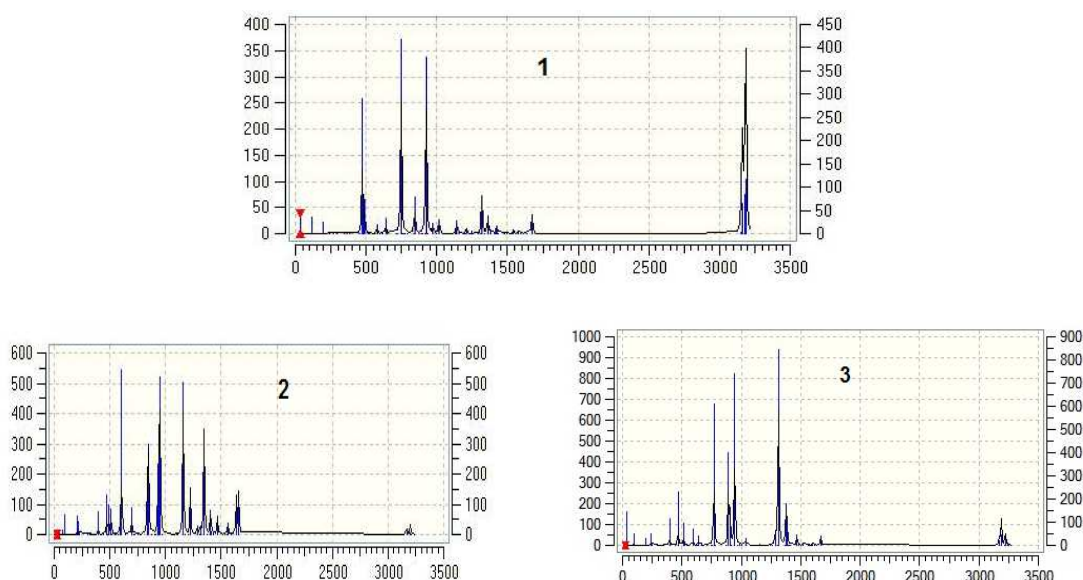
Table (2) show the values of HOMO and LUMO, and electronic properties (IP, EA, χ , η , S, and W) computed by using DFT/ B3LYP 6-

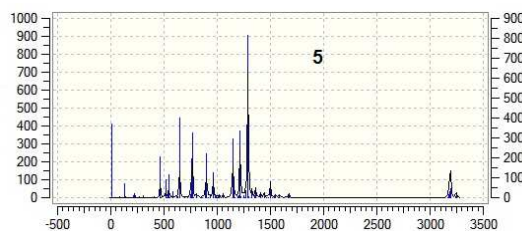
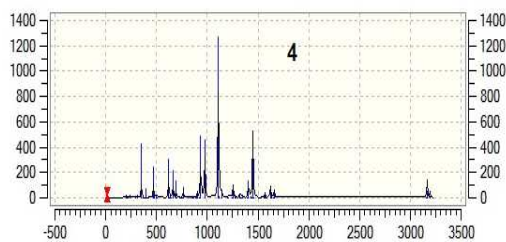
4	- 5 . 3 8 0 1	- 3 . 2 2 8 0	(5 . 3 8 0 1	3 . 2 2 8 0	4.3041	1.0760	0.4646	8.6079
5	- 5 . 2 9 3 3	- 3 . 3 2 0 0	(5 . 2 9 3 3	3 . 3 2 0 0	4.3066	0.9866	0.5067	9.3990

1672.42– to 1678.95) cm^{-1} . The (C – C – C) out-of-plane bending occurs in the region (from 647.193 – to 1303.36) cm^{-1} . The (C – Cl) stretching vibrations of the (2-5) pentacene molecules occur in the region (from 1110.16- to 1313.5) cm^{-1} . While the wagging vibrations of it, observed as a weak bands at the range (from 332.75- to 501.29) cm^{-1} . Also the scissoring vibrations of the (C-Cl) bonds, observed as a weak bands at the range (from 186.24 - to 317.96) cm^{-1} . Finally the rocking vibrations of (C-Cl) bonds, observed as a weak bands at the range (from 148.67 - to 301.33) cm^{-1} , these modes of chloride atoms have low vibration, because the chloride has high electronegativity and high mass.

3- IR spectra

The IR spectra of (1-5) pentacene molecules are shown in figure (2). The harmonic vibrational frequencies are calculated using B3LYP level using the 6-311G(d,p) basis set, the substitution hydrogen for chloride atoms lead to vibrational modes. For pentacene molecules, the (C – H) stretching studied in the region (3188.46–3211.58) cm^{-1} . The in-plane bending vibrations are calculated at the range (from 1144.81– to 1483.58) cm^{-1} . The out-of-plane (C–H) bending vibrations are found in the region (from 746.98 – to 809.30) cm^{-1} . And the (C– C) stretching vibrations are occurred in the region (from 1434.03– to 1538.2) cm^{-1} . So a (C = C) bond stretches at a higher frequency at the range (from





Wave number cm^{-1}

Figure(2): Calculated IR spectra of (1-5) pentacene molecules using B3LYB /6-311G(d,p) method .

and 11 it is clear the peaks and lines dark, because chemical shift and the mutual influences between nuclei that cause the growth of some spectral lines at the expense of other. The 4-molecule has low chemical shift compare with other pentacene molecules of at (7.86 – 8.31) ppm, and has low chemical shift of carbon at (125.2 – 131.8) ppm. That is referring to the H^1 NMR and C^{13} NMR spectrum depended on the position of substituted atom in the ring of molecule.

In 5 molecule found Obstruction vacuum, therefore, this molecule has chemical shift for carbon equal to (128.2-130.1) ppm and chemical shift for hydrogen equal to (7.39-8.52) ppm. Also There is another effect is the ring current effect absorb in aromatic compound the circuit current through the molecule cause long-term.

4- NMR spectrum

A calculated H^1 NMR and C^{13} NMR had been carried out by using ChemBioDraw Program, shown in figure (3-12). The effect of diamagnetic shielding is the most important factor on the chemical shift which, leads to shielding the nucleus for the magnetic field and the magnetic field which achieve greater resonance conditions. It is clear from figures (3-12) that the substitution effect of chloride atoms in pentacene molecule on H^1 NMR and C^{13} NMR spectrum, the substitution hydrogen for chloride atoms causes to increase the H^1 NMR and C^{13} NMR spectrum for (2-5) tetrachloropentacene molecules . Because the chloride atoms have higher electro negativity than hydrogen, and the electron density around the chloride atoms is high, this lead to high diamagnetic shielding. In figures 3,7,8

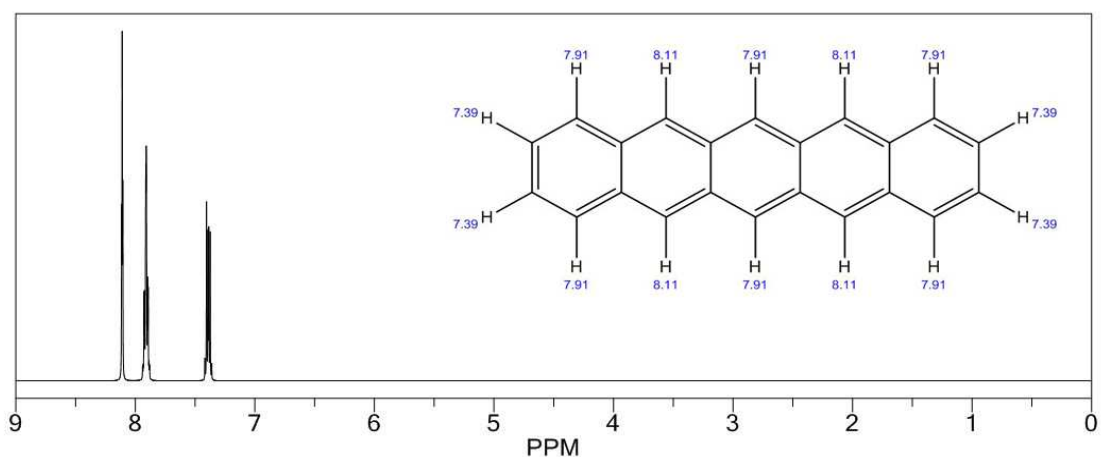


Figure (3): Calculated ^1H NMR of 1- pentacene molecule by using ChemBioDraw program

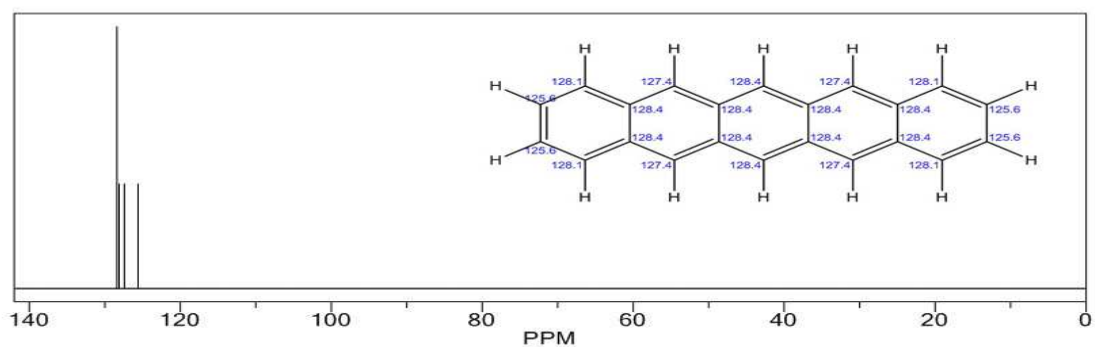


Figure (4): Calculated ^{13}C NMR of 1- pentacene molecule by using ChemBioDraw program

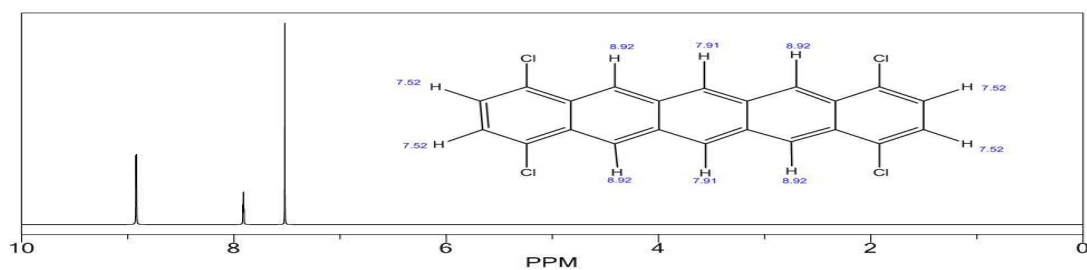


Figure (5): Calculated ^1H NMR of 2- tetrachloropentacene molecule by using ChemBioDraw program.

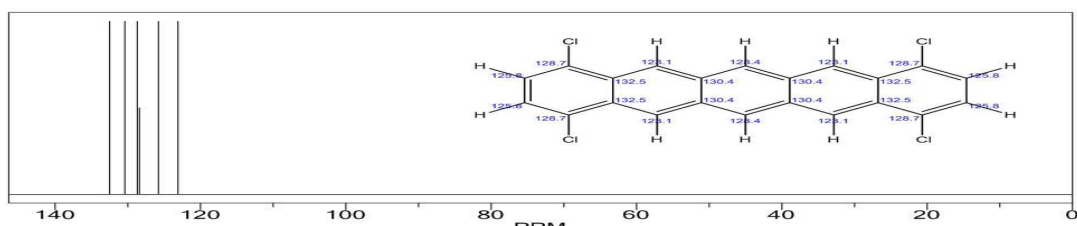


Figure (6): Calculated ^{13}C NMR of 2- tetrachloropentacene molecule by using ChemBioDraw program

Figure (7): Calculated H^1 NMR of 3- tetrachloropentacene molecule by using ChemBioDraw program

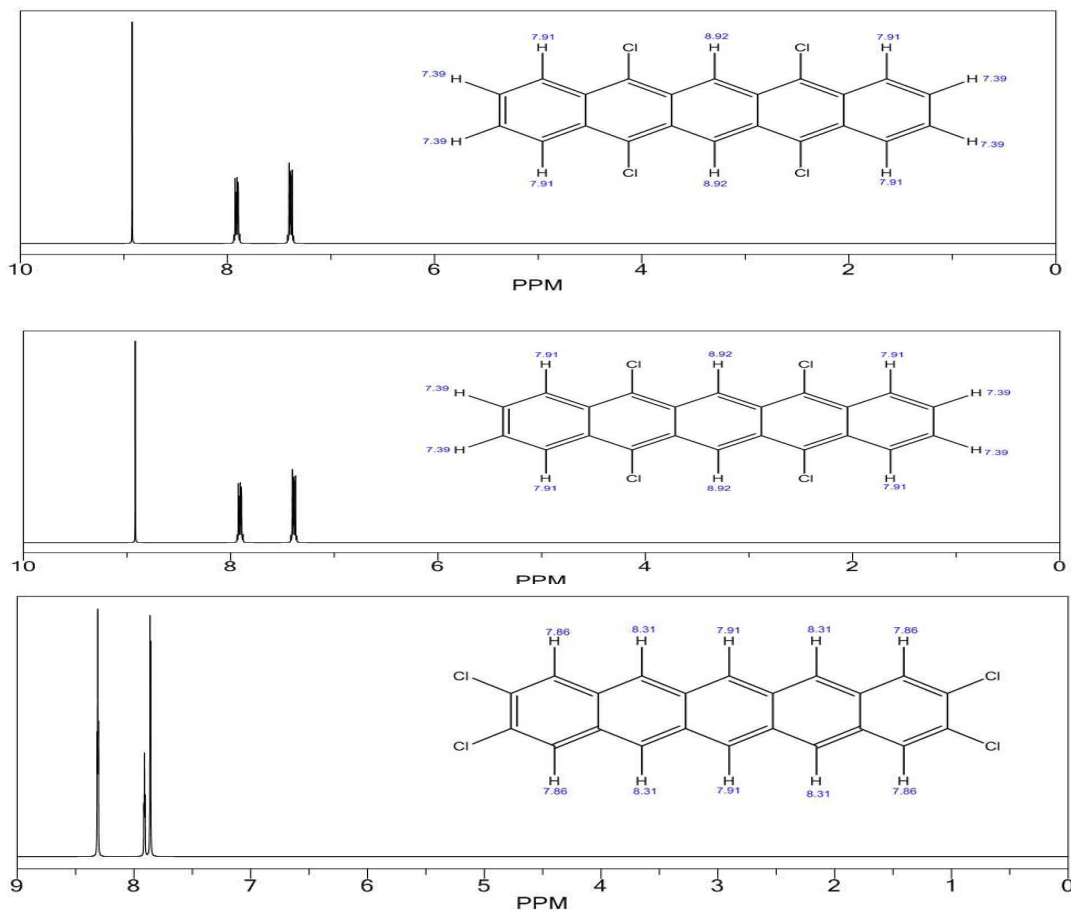


Figure (9): Calculated H^1 NMR of 4- tetrachloropentacene molecule by using ChemBioDraw program

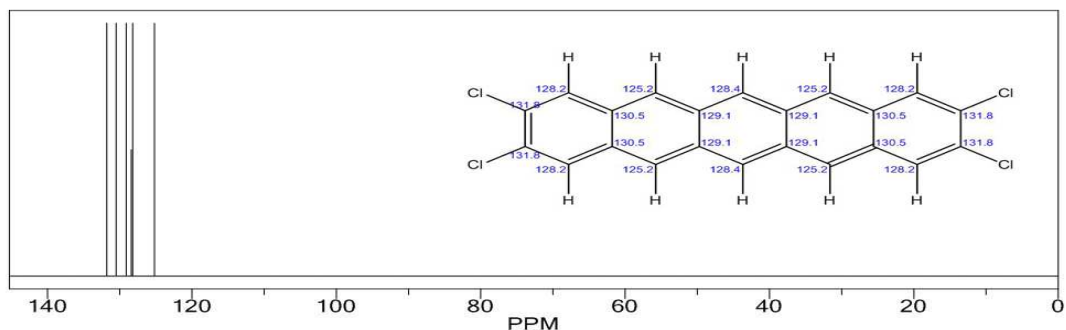


Figure (10): Calculated C^{13} NMR of 4- tetrachloropentacene molecule by using ChemBioDraw program

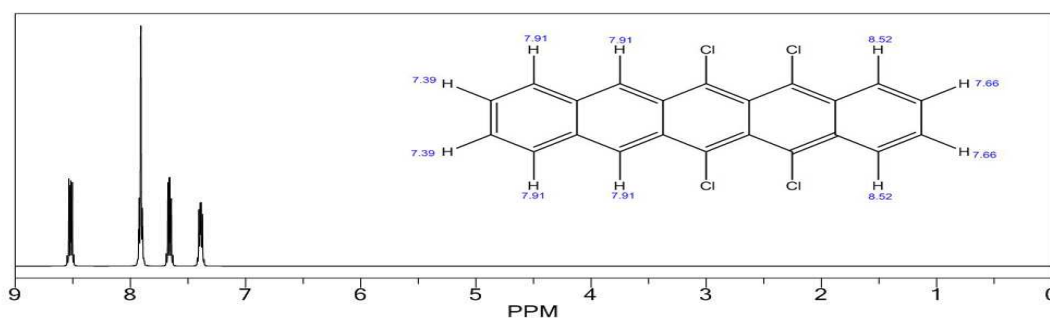


Figure (11): Calculated C^{13} NMR of 5-tetrachloropentacene molecule by using ChemBioDraw program

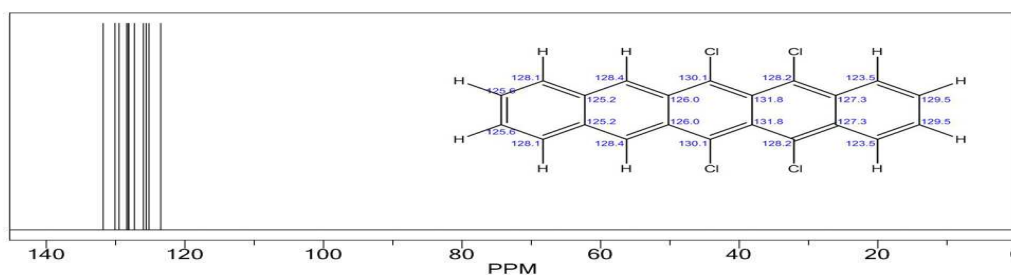


Figure (12): Calculated C^{13} NMR of 5-tetrachloropentacene molecule by using ChemBioDraw program

vibrational modes. While the stretching vibrational for (2-5) pentacene molecules is slight difference than the 1-pentacene molecule.

5- It was found the substitution hydrogen for chloride atoms in NMR spectrum causes to increase the H^1 NMR and C^{13} NMR spectrum for (2-5) tetrachloropentacene molecules. The 4- molecule has low chemical shift compared with the others pentacene molecules of hydrogen and carbon atoms, while the H^1 NMR of (2-5) tetrachloropentacene molecules are smaller than that the 1-pentacene molecule and C^{13} NMR spectrum of pentacene molecules are higher than that the 1-pentacene molecule, because the diamagnetic shielding and ring current effect.

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1- The geometric optimization (bond length) for 1-pentacene molecule in a good agreement with theoretical previous study. While for (2-5) tetrachloropentacene molecules are slight increasing with substitution hydrogen for chloride atoms.

2- The values of HOMO are slight increasing, while LUMO are decreasing with substitution hydrogen for chloride atoms.

3- Electronic properties (increasing IP, while decreasing EA) with substitution hydrogen for chloride atoms, the values of IP and EA for 1-pentacene molecules is a good agreement with experimental values. Whereas of χ , S, and W increasing and η decreasing with substitution hydrogen for chloride atoms.

4- It was found that for IR spectra that the substitution hydrogen for chloride atoms leads to increasing the

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