Study The Spectral and Thermal Properties of The Molecule Tetracene (C\textsubscript{18}H\textsubscript{12}) by Using Semi Empirical Quantum programs

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ABSTRACT. The aim of this study is to determine the spectral properties of the Tetracene molecule (C\textsubscript{18}H\textsubscript{12}) using the Semi-empirical quantum programs (HyperChem8.0, WinMopac7.21) by (MNDO-PM3) method (Modified Neglect of Differential Overlap-Parameterization Model3) The study envelope computation of the space geometry of the Tetracene molecule was calculated using the initial and final matrices, including the length, the angle between the bonds, the angle of the dipole, and the charge of each atom in the Tetracene molecule, The total energy, binding energy, electronic energy, core-core repulsion, ionization potential, molecular weight, moment of inertia, and dipole moment of the molecule were also calculated The curved potential energy of each molecule has been plotted as it is adopted to vary the length of the bonds, (C\textsubscript{1}-H\textsubscript{19}) and (C\textsubscript{1}-H\textsubscript{15}) in the Tetracene molecule compared to the result of the total energy values of Tetracene in equilibrium. In addition to the potential energy curve, the dissociation energy of spectroscopy was calculated for molecule and the molecular orbit including ELUMO equal to (-1.353), EHOMO equal to (-7.87eV), Egap equal to (6.517 eV) of Tetracene. Likewise, the vibration frequencies of the Tetracene molecule were obtained in the infrared region and electron transmission in the UV region. Some thermal properties (thermodynamics) of Tetracene were also calculated, including heat of formation, entropy, heat capacity, enthalpy and, gibbs free energy, at a temperature (298K), the value of the Tetracene molecule was equal to (84.445)kcal.mol\textsuperscript{-1}, (114.6487)Cal.mol\textsuperscript{-1}.K\textsuperscript{-1}, (54.8085)Cal.mol\textsuperscript{-1}.K\textsuperscript{-1}, (8484.7728)Cal.mol\textsuperscript{-1} (-25716.70)Cal.mol\textsuperscript{-1} respectively. The results of the theoretical study agreed with the experimental results and almost with the previous research.

Keywords : Tetracene (C\textsubscript{18}H\textsubscript{12}) , MNDO-PM3 , potential Energy , UV , ELUMO , EHOMO , Egap , Semi-empirical

1. Introduction

The tetracene molecule consists of four linked rings of benzene and its molecular formula is C\textsubscript{18}H\textsubscript{12} and has the appearance of a pale orange powder, which is a polycyclic aromatic hydrocarbon. Tetracene is an organic semiconductor that refers to substances that are composed mostly of carbon and hydrogen atoms, and tetracene is ethylnylacene which is a conductive
polymer used as a donor material. It has a high photoluminescence and quantum yield that makes it a promising candidate in the development of single crystal electronic material \[1\][2]. In May 2007, researchers from two Japanese Universities, Tohoku University in Sendai and Osaka University, reported an ambipolar light-emitting transistor made of a single tetracene crystal \[3\]. Ambipolar means that the electric charge is transported by both positively charged holes and negatively charged electrons. Tetracene can be also used as a gain medium in dye lasers as a sensitizer in chemoluminescence Jan Hendrik Schon during his time at Bell Labs (1997-2002) claimed to have developed an electrically pumped laser based on tetracene. However, his results could not be reproduced, and this is considered to be a scientific farad [4]. Tetracene used in wide of organic electronic based devices, which include organic light emitting diodes (OLED),[5] solar cells, organic photovoltaics (OPVs), thin films transistors (TFTs), and other single crystal based organic semiconductors. [6,7] One of the most important molecular modeling software (WinMopac 7.21 and HyperChem8.0) to define MOPAC: MOPAC are semi-experimental, generally targeted, molecular orbital programs that have facilities for studying chemical reaction related to molecules. Linear polymers and ions applied to the quasi-experimental MNDO, AM1, MNDO/PM3 and MNDO / 3 Hamiltonians. This program provides the computation of vibrational spectra, isotopic substitution effects, thermodynamic quantities, and force constants in an integrated program. [8,9]. HyperChem8.0 is a multifaceted molecular modeling program that provides a set of powerful and large computations and many types of molecular calculations based on quantum mechanics calculations. As the program contains graphical axes and shapes, we can obtain the correct structure of the molecule by drawing and studying its properties as it supports building and mapping for the implementation of the molecule easily and the programs represent the functions of orbitals by means of quasi-experimental calculations [10]. Quasi-experimental methodologies are based on the electronic Schrödinger equation obtained after separating the nuclear and electronic motion, (Born - Oppenheimer – approximation)

$$\hat{H}(r,R)\Psi(r,R) = E(r,R)\Psi(r,R)$$ ................................(1)

Here \(r\) and \(R\) refer to the coordinates of the electrons and the nucleus respectively [11].

This project aims to study the spectral properties of the tetracene molecule (C\(_{18}\)H\(_{12}\)) in the infrared (IR) region and electron transport in the ultraviolet region, using quasi-experimental calculations via (MNDO-PM3) methods. This study also aimed to punish the low energy steady state of the molecule via potential energy curves.

2. THEOREY

The quantitative number of energy levels for any molecule is very large. Thus, the energy is divided into different energies according to the following equation:

$$E_{total} = E_T + E_N + E_R + E_V + E_e \cdots \cdots \cdots$$ .................(2)

Where \(E_T\): represents transition energy, \(E_N\): nuclear energy, \(E_R\): rotational energy, \(E_V\): vibrational energy and \(E_e\): electronic energy. In this paper, the focus is on the vibrational energy, which represents the energy and kinetic energy that particles possess as a result of their vibrational movement. Here this energy is measured. The vibration of the molecule is subject to the effect of the beam in terms of expansion and contraction, which is very similar to the behavior of the spring subject to the law of hooks, hence it is called the simple harmonic oscillation model. The harmonic oscillator model is an approximate model in which
the relationship between the potential energy of vibration and the interlayer distance can be plotted as follows [12].

\[ V(r) = \frac{1}{2} k(r - r_e)^2 \]  .......... ....... (3)

Where \( V(r) \) represents the potential energy, \( k \): the force constant, \( r \): the displacement, \( r_e \): the equilibrium distance between the two atoms. Both groups can move together as one effective block denoted by (\( \mu \)).

\[ I. \quad \mu = (m_1 + m_2)/(m_2 + m_2) \]  .......... ....... (4)

Or it is constantly vibrating with respect to its center of mass at a frequency given by the equation [13]:

\[ \nu = 1/2\pi \sqrt{k/\mu} \] ...............................(5)

Where (\( \nu_{\text{vb}} \)) is the vibration frequencies.

According to quantum mechanics, the Schrödinger equation can be representing as follows [14]:

\[ \left[ -\frac{\hbar^2}{2\mu} \nabla^2 + \frac{1}{2} k(r - r_e)^2 \right] \Psi = E\Psi \]  .......... ....... (6)

\[ E_v = \hbar \nu_{\text{vb}} \left( \nu + \frac{1}{2} \right) \] ..............................(7)

\( V=0,1,2,\ldots\)

Where \( \nu_{\text{vb}} \) is the total vibration frequency and \( (V) \) is the vibration quantum number, \((1/2 h\nu_{\text{vb}})\) when \( \nu = 0 \), it is called the zero point energy. This value represents the difference between classical mechanics and the amount of molecular vibration. The energy in classical mechanics can be zero, which means that a molecule has no vibrational energy under normal conditions, while quantum mechanics asserts that the molecule must suffer a certain vibration. From the Schrödinger equation, we find that the energy of the vibrational plane is in terms of the wave form, as is customary in the study of spectra as in the equation.

\[ G(\nu) = \omega(\nu + \frac{1}{2}) \] .................(8)

Several potential Morse function functions have been proposed with respect to the proposed scientist, as in the following equation [15]

\[ V_m = D_e [1 - e^{-\beta(r-r_e)}]^2 \] ................. (9)

Where is a constant for the electronic energy levels of the molecule, \( V_m \) represents the potential energy of the current, it is clear from the equation that the value of \( V_m \) approaches De when the value of \( r \) approaches infinity and this corresponds to the true behavior of the
diatomic particles. When compensating for the potential energy of the potential Morse code function in the Schrödinger equation, the levels of vibrational energy are equal:

\[ G(v) = \left( v + \frac{1}{2} \right) \omega_v - (v + \frac{1}{2})^2 x_v \omega_v \quad \ldots \ldots (10) \]

Where \( \omega_v \) is the vibrational frequency in the asymmetric \( x_v \) non-harmonic motion of the Constant. The zero point energy becomes zero point \( (\text{when } v=0) \) \[14\]

\[ G(0) = \frac{1}{2} \omega_v \left( 1 - \frac{1}{2} x_v \right) cm^{-1} \quad \ldots \ldots (11) \]

\[ \sum L_i (F_{ij} - \lambda M_{ij}) = 0 \quad \ldots \ldots (12) \]

Calculations of vibration frequency and normal coordinates can also be made from the molecular force constant, which is the most popular method, since we can solve the abstract Wilson equation:

Where \( L_i \): values of Eigen vector modulus values, \( F_{ij} \) is a matrix component of the force constant, \( \lambda \): Eigen \( M_{ij} \) value: the mass Matrix of atoms. From solving the abstraction equation, we will obtain the fundamental vibration frequencies of the molecule \((3N-6)\) Substitute the values of into the equation

\[ \lambda = 4\pi\nu^2 c^2 \quad \ldots \ldots (13) \]

The dipolar moment is the electrostatic force that acts between two equal and different charges by indicating the amount of charge \( q \) and the distance between them. The equation can be written as follows:

\[ \mu = q.d \quad \ldots \ldots (14) \]

3. Results & Discussion

3.1 Molecular Structure

Tetracene \( C_{18}H_{12} \) is represented as shown in Fig1, which was plotted by Hyperchem8.0 software. The calculation of the program is based on the internal coordinates \((r, \Theta, \Phi)\) and the geometric figure in equilibrium.

Figure(1). molecular structure of tetracene molecule depicted by Hyperchem8.0 software.

These properties were found after initialization matrix was obtained and incorporated into the array using WinMopac7.21. These properties include formation temperature, total energy, binding energy, electronic energy, fundamental repulsion, ionization potential, electronic momentum, zero point, number of filled plane, and molecular weight. For Table
It demonstrates some of the spectral properties that give complete descriptions of the molecular properties.

**Table (1)** The result of the spectral properties of the tetracene molecule computed by (WinMopac7.21, HyperChem8.0).

| Quantity                  | Calculated Value      | Unit     |
|---------------------------|-----------------------|----------|
|                           | WinMopac              | HyperChem|
| Heat of Formation         | 84.335653             | 83.9091283 | Kcal/mol |
| Total Energy              | -2315.85928           | -2313.66819 | eV       |
| Electronic Energy         | -15540.42858          | -15436.01881 | eV       |
| Core-Core Repulsion       | 13134.56970           | 13122.35062 | eV       |
| Dipole Moment             | 0.000                 | 0.000     | Debyes   |
| Zero Point Energy         | 151.344               | 151.28864 | Kcal/mol |
| No. of Filled Level       | 42                    | 42        |
| Molecular Weight          | 228.293               | C         | amu      |

**3.2 Calculation of Tetracene potential energy**

Several bond distances were determined for (C1–H19), (C2–H20) for the tetracene molecule. On the other hand, the total energy value of the molecule was calculated for each distance. The bond length and total power values were calculated by WinMopac 7.21. The inconsistent potential energy curve and the equilibrium distance at which we obtain the lowest total value of energy as in Fig. (2), (3), the molecule is closer to stable than, and the values of the total energy at the equilibrium position of the bonds (C1–H19), (C2–H20) were: at distance \( r_{eq} = (1.09 \text{Å}) \), \( -3617.333 \text{eV} \) on distance \( r_{eq} = (1.095 \text{Å}) \) and \( -3617.3339 \text{eV} \) respectively.

**Table (2)** Total Energy change by distance(C1–H19) for tetracene molecule from the Tetracene molecule
Figure (2). Total energy change by distance (C1-H19)

Table (3) Total energy change by distance (C2-H20) for tetracene molecule

| R (A) | Total Energy (eV) |
|-------|-------------------|
| 0.596 | -3411.1306        |
| 0.695 | -3502.3913        |
| 0.795 | -3627.7304        |
| 0.895 | -3566.6667        |
| 0.995 | -3611.3011        |
| 1.095 | -3617.3339        |
| 1.195 | -3614.2241        |
| 1.295 | -3608.7905        |
| 1.395 | -3596.9811        |
| 1.495 | -3587.3049        |
| 1.595 | -3572.3139        |
| 1.695 | -3566.2917        |
| 1.795 | -3547.7614        |
| 1.895 | -3529.6232        |
| 1.995 | -3516.4284        |
| 2.095 | -3504.1484        |
| 2.194 | -3493.5627        |
| 2.295 | -3487.6969        |
| 2.395 | -3474.6374        |
| 2.494 | -3464.1877        |
| 2.595 | -3453.6494        |

Figure (3). Total energy change by distance (C2-H20) from the tetracene molecule.

When the atom is rounded together, a lower equilibrium is created after the equilibrium distance is very high and accompanied by a large potential energy that increases rapidly. Either when the atoms are removed from each other more than after the equilibrium, weak gravity will appear accompanying it. Weak potential energy that increases at a slower speed. Then start the effect of bond expansion (C-H) and the potential curve moves from harmonic behavior to non-harmonic behavior, so increasing the distance (C-H) will increase energy until the molecule starts to separate until the bond is broken, The energy takes the form of a half straight line called the dissociation energy, so for (C1-H19) and (C2-H20) bonds, the values of the dissociation energies were as follows: (C1-H19) (De =4.02 eV) as shown in Figure (3), (C2-H20) (De =4.019 eV) as shown in Figure (3) When comparing the values of the dissociation energies of each of the bonds in the tetracene molecule, the difference is due to the difference in the length of the bonds due to the difference in inertia determined by the difference in mass according to equation (4) and (5). The difference in the moment of inertia
(I) leads to a difference in the continuous rotation (B) of the molecule and the relationship between B and I is inverse.

3.3 Calculate the frequencies and patterns of vibrations

Table (4) shows the basic vibrational frequencies in the infrared (IR) region of the tetracene molecule with a density and symmetry where their number was (88) according to the relationship (3N-6) as it represents the number of a compound atom. The table also showed that the frequencies (wave number) of the molecule are close to the result of the programs HyperChem 8.0 and WinMopac 7.21.

Table (4) Tetracycline vibrational frequencies calculated by (Hyperchem8.0) and (WinMopac) Programs, and comparison with the practical values of other works

| Vibrational mode | Intensity Km/mol | Wave number 1/cm Cal. by [HyperChem] | SYMMETRY Cal by [HyperChem] | Wave number 1/cm Cal. by [WinMopac] | Wave number |
|------------------|------------------|--------------------------------------|-----------------------------|-------------------------------------|-------------|
| 1                | 0.18668          | 51.71                                | B3                          | 52.12                               | 52.71       |
| 2                | 0                | 74.95                                | AU                          | 75.75                               |             |
| 3                | 0                | 136.64                               | B1                          | 136.99                              |             |
| 4                | 0                | 162.89                               | B2                          | 163.35                              |             |
| 5                | 0.14193          | 175.27                               | B1                          | 175.48                              | 175.44      |
| 6                | 0.16514          | 234.13                               | B3                          | 234.51                              | 234.89      |
| 7                | 0                | 277.71                               | AU                          | 277.83                              |             |
| 8                | 0                | 316.35                               | B1                          | 316.6                               |             |
| 9                | 0                | 326.93                               | B3                          | 327.17                              | 327.28      |
| 10               | 0                | 332.71                               | AG                          | 332.76                              | 332.76      |
| 11               | 14.27131         | 443.72                               | B3                          | 443.76                              |             |
| 12               | 0                | 446.84                               | B1                          | 447.04                              |             |
| 13               | 0.12573          | 451.65                               | B3                          | 451.82                              |             |
| 14               | 0                | 464.92                               | B2                          | 465.04                              | 465.44      |
| 15               | 0.00037          | 481.71                               | B1                          | 482.08                              | 482.03      |
| 16               | 0                | 490.83                               | AU                          | 490.87                              |             |
| 17               | 0                | 509.5                                | B3                          | 509.6                               | 509.66      |
| 18               | 0.56311          | 561.19                               | B2                          | 561.26                              | 567.29      |
| 19               | 0.63643          | 626.06                               | B1                          | 626.21                              | 626.18      |
| 20               | 0                | 628.49                               | AG                          | 628.59                              | 628.60      |
| 21               | 0.10092          | 643.44                               | B2                          | 643.61                              | 643.61      |
| 22               | 0                | 713.48                               | B2                          | 713.59                              |             |
| 23               | 0                | 732.15                               | AU                          | 732.38                              | 732.52      |
| 24               | 0                | 736.64                               | B2                          | 736.6                               | 736.59      |
| 25               | 0                | 760.7                                | B1                          | 760.46                              |             |
| 26               | 41.16274         | 767.71                               | B3                          | 767.5                               |             |
| 27               | 0                | 790.69                               | B3                          | 790.81                              | 790.84      |
| 28               | 0                | 851.47                               | AU                          | 851.57                              |             |
|   |   |   |   |
|---|---|---|---|
| 29 | 0 | 864.73 | B2 | 864.88 |
| 30 | 0 | 876.34 | AG | 876.47 | 876.61 |
| 31 | 0 | 885.25 | B3 | 885.34 | 885.39 |
| 32 | 0.71103 | 886.08 | B2 | 886.78 | 886.91 |
| 33 | 0 | 889.34 | B1 | 889.27 | 889.49 |
| 34 | 0.18359 | 908.86 | B1 | 908.98 | 908.98 |
| 35 | 0.00001 | 926.49 | AU | 926.46 | 926.67 |
| 36 | 22.18395 | 938.78 | B3 | 938.85 | 938.85 |
| 37 | 0 | 972.87 | B1 | 973.03 | 973.03 |
| 38 | 0 | 973.85 | B2 | 973.93 | 973.93 |
| 39 | 17.78074 | 978.66 | B3 | 978.84 | 978.84 |
| 40 | 0 | 1009.49 | AU | 1009.61 | 1009.61 |
| 41 | 0 | 1012.87 | B2 | 1012.98 | 1012.98 |
| 42 | 0 | 1019.03 | AG | 1019.25 | 1019.25 |
| 43 | 0.09243 | 1089.95 | B2 | 1089.84 | 1089.90 |
| 44 | 0.00842 | 1091.33 | B2 | 1092.44 | 1092.55 |
| 45 | 0 | 1093.1 | AG | 1093.16 | 1093.16 |
| 46 | 0.46562 | 1126.93 | B1 | 1127.04 | 1127.04 |
| 47 | 0 | 1127.53 | B3 | 1127.68 | 1127.68 |
| 48 | 0 | 1150.18 | B3 | 1150.34 | 1150.04 |
| 49 | 0 | 1157.18 | AG | 1157.53 | 1157.61 |
| 50 | 0.0419 | 1159.3 | B2 | 1159.61 | 1159.71 |
| 51 | 0.09061 | 1188.5 | B1 | 1188.62 | 1188.65 |
| 52 | 0 | 1228.47 | B3 | 1228.56 | 1228.62 |
| 53 | 9.30558 | 1235.39 | B2 | 1236.84 | 1236.84 |
| 54 | 0.00273 | 1254.08 | B1 | 1254.14 | 1254.14 |
| 55 | 0 | 1255.49 | AG | 1225.63 | 1225.63 |
| 56 | 0 | 1389.93 | B3 | 1390.16 | 1390.16 |
| 57 | 9.80918 | 1400.07 | B1 | 1400.4 | 1400.4 |
| 58 | 2.52452 | 1411.97 | B2 | 1412.17 | 1412.17 |
| 59 | 0.22577 | 1435.57 | B1 | 1435.81 | 1435.81 |
| 60 | 0 | 1449.52 | AG | 1449.77 | 1449.77 |
| 61 | 0 | 1560.88 | AG | 1561.64 | 1561.81 |
| 62 | 0.88598 | 1605.5 | B2 | 1605.71 | 1605.75 |
| 63 | 0 | 1612.28 | AG | 1612.49 | 1612.73 |
| 64 | 0 | 1630.84 | B3 | 1631.14 | 1631.19 |
| 65 | 0.14693 | 1661.44 | B2 | 1661.69 | 1661.69 |
| 66 | 0 | 1734.83 | AG | 1735.2 | 1735.2 |
| 67 | 0.4005 | 1742.24 | B2 | 1742.58 | 1742.58 |
| 68 | 0 | 1784.99 | AG | 1749.36 | 1749.56 |
| 69 | 0.10697 | 1785.42 | B1 | 1785.75 | 1785.97 |
| 70 | 0 | 1815.5 | B3 | 1815.9 | 1815.9 |
| 71 | 0 | 1833.69 | B3 | 1834.06 | 1843.10 |
| 72 | 1.98911 | 1843.45 | B1 | 1843.82 | 1843.84 |
| 73 | 39.15844 | 3043.34 | B1 | 3043.34 | 3043.34 |
| 74 | 0.00073 | 3044.54 | AG | 3045.06 | 3045.06 |
| 75 | 0 | 3044.97 | B3 | 3045.47 | 3045.47 |
It was concluded from Table (4) that the frequencies of the two oscillations of the atom (C-H) were at agreement with previous studies [17]. Figure (4) shows some of the vibrational patterns of the tetracene molecule and shows the atoms and the directions of movement represented by the arrows. The shape also determines the intensity, symmetry, and frequency for each position.
Figure (4) The main tetracene vibrational modes, frequency, intensity and symmetry of TMIn for each mode drowned by HyperChem8.0 software

3.4 Molecular Orbital Eigen Values

Tetracene therap with HyperChem8.0. Figure (6) shows 42 occupied and 42 unmanned orbits. The energy of the higher occupied molecular orbital ($E_{\text{HOMO}} = -7.87$) and the energy of the lower unoccupied molecular orbital ($E_{\text{LUMO}} = -1.353$) were calculated by measurement according to the relationship ($E_{\text{gap}} = E_{\text{LUMO}} - E_{\text{HOMO}}$), and ($E_{\text{gap}} = 6.517 \text{ eV}$), and close to the previous studies (6.519 eV) [17]. Ionizing energy (I.P) was calculated from the absolute value of the highest occupied orbit and was equal to ($-7.870 \text{ eV}$) and close to the previous studies ($-7.871 \text{ eV}$) [17].
3.5 UV Spectroscopy of Tetracene

The electron transition of the tetracene molecule was obtained after plotting the molecular structure in the best geometrically balanced shape by the program (HyperChem8.0), and the highest transmission was at the wavelength \( \lambda = 266.8 \text{ nm} \). This value was consistent with previous studies (\( \lambda = 266.7 \text{ nm} \)) [17], and Table (5) represents the value between (wavelength, strength of the oscillator) As shown in Figure (7).
Table (5) shows the electron transport of tetracene in UV region.

| Wave Length nm | Oscillator strength |
|----------------|--------------------|
| 705.3          | 0                  |
| 406.7          | 0.2463             |
| 399.4          | 0                  |
| 386.3          | 0.0564             |
| 375.3          | 0                  |
| 318.5          | 0                  |
| 302.6          | 0                  |
| 286.5          | 2.9642             |
| 287.8          | 0                  |
| 287.2          | 0                  |
| 287.1          | 0                  |
| 286.3          | 0                  |
| 286.3          | 0.3574             |
| 287.8          | 0                  |
| 287.2          | 0                  |

Figure (6) Tetracycline UV-vis spectrosc computed by HyperChem8.0 programs

3.6 The Thermal Properties of Tetracene

A number of thermal properties of the tetracene molecule were studied after obtaining the stable shape of the tetracene molecule through the HyperChem8.0 program and obtaining the final matrix as in Table (6) that contains the atom charge of the molecule through WinMopac 7.21, the reaction properties and the effect of temperature were calculated and studied. On the tetracene molecule on three stages and for different values of temperature, which include melting, boiling, and standard degree. Tetracene molecule matrix shows that can be obtained after the molecule is withdrawn upon reaching the optimization state for optimum geometry placement. The table shows the atoms of the molecule, the distance between this atom (r), the best position of this atom (Opt), the values of the angles ($\Theta^0$), and the angles of the diagonal ($\Phi^0$).

Table (6). The primary matrix of a tetracene molecule shows the internal coordinates (r, $\Theta^0$, $\Phi^0$) in the equilibrium condition computed by Hyperchem8.0

| ATOM | r (Å) | OPT | $\Theta^0$ | OPT | $\Phi^0$ | OPT | charge |
|------|-------|-----|------------|-----|----------|-----|--------|
| C    | 00000.0000 | 0   | 00000.0000 | 0   | 00000.0000 | 0   | -0.0888 |
| C    | 00001.3559  | 1   | 00000.0000 | 0   | 00000.0000 | 0   | -0.0995 |
| C    | 00001.4390  | 1   | 00120.6745 | 1   | 00000.0000 | 0   | -0.0334 |
| C    | 00001.4303  | 1   | 00118.6963 | 1   | 00000.0000 | 1   | -0.0333 |
| C    | 00001.4306  | 1   | 00120.6290 | 1   | 00000.0000 | 1   | -0.0995 |
| C    | 00001.3559  | 1   | 00120.6290 | 1   | 00000.0000 | 1   | -0.0888 |
| C    | 00001.3844  | 1   | 00121.3844 | 1   | 00179.9999 | 1   | -0.0776 |
| C    | 00001.4118  | 1   | 00120.6501 | 1   | 00000.0000 | 1   | -0.0318 |
| C    | 00001.4238  | 1   | 00119.4305 | 1   | 00000.0000 | 1   | -0.0317 |
| C    | 00001.3844  | 1   | 00119.9192 | 1   | 00000.0000 | 1   | -0.0776 |
| C    | 00001.4118  | 1   | 00121.1389 | 1   | 00179.9999 | 1   | -0.0776 |
| C    | 00001.3844  | 1   | 00120.6501 | 1   | 00179.9999 | 1   | -0.0334 |
| C    | 00001.4303  | 1   | 00119.9192 | 1   | 00000.0000 | 1   | -0.0333 |
| C    | 00001.3844  | 1   | 00119.9192 | 1   | 00000.0000 | 1   | -0.0776 |
| C    | 00001.4390  | 1   | 00121.3843 | 1   | 00179.9999 | 1   | -0.0888 |
3.6.1 Heat of formation $\Delta H_f^0$

For a tetracene molecule, the formation temperature calculated per unit (kcal.mol$^{-1}$) is a function of temperature in unit (K) and for different temperatures of formation values (100$^\circ$K-600$^\circ$K) as shown in Table (7). Figure (7) shows that Heat of formation depends on the temperature, which increases with increasing temperature. The formation temperature at standard temperature (298$^\circ$K) and standard pressure (1 bar) was equal to (84.445) kCal.mol$^{-1}$, and the experimental value obtained from the previous studies (84.345) kCal.mol$^{-1}$[17].
Table(7). Tetracene temperature to the formation value and the corresponding temperature.

| T (K) | H.O.F.(KCAL/MOL) |
|-------|------------------|
| 100   | 77.232           |
| 110   | 77.431           |
| 120   | 77.644           |
| 130   | 77.873           |
| 140   | 78.117           |
| 150   | 78.377           |
| 160   | 78.644           |
| 170   | 78.924           |
| 180   | 80.238           |
| 190   | 80.640           |
| 200   | 81.085           |
| 210   | 81.567           |
| 220   | 82.068           |
| 230   | 82.588           |
| 240   | 83.138           |
| 250   | 83.697           |
| 260   | 84.246           |
| 270   | 84.820           |
| 280   | 85.403           |
| 290   | 85.980           |
| 300   | 86.566           |
| 310   | 87.161           |
| 320   | 87.760           |
| 330   | 88.370           |
| 340   | 88.996           |
| 350   | 89.624           |
| 360   | 89.252           |
| 370   | 89.890           |
| 380   | 89.424           |
| 390   | 89.062           |
| 400   | 89.700           |
| 410   | 89.348           |
| 420   | 88.996           |
| 430   | 88.644           |
| 440   | 88.292           |
| 450   | 87.940           |
| 460   | 87.588           |
| 470   | 87.236           |
| 480   | 86.884           |
| 490   | 86.532           |
| 500   | 86.180           |
| 510   | 85.828           |
| 520   | 85.476           |
| 530   | 85.124           |
| 540   | 84.772           |
| 550   | 84.420           |
| 560   | 84.068           |
| 570   | 83.716           |
| 580   | 83.364           |
| 590   | 83.012           |
| 600   | 82.660           |
| 610   | 82.308           |
| 620   | 81.956           |
| 630   | 81.604           |
| 640   | 81.252           |
| 650   | 80.900           |
| 660   | 80.548           |
| 670   | 80.196           |
| 680   | 79.844           |
| 690   | 79.492           |
| 700   | 79.140           |

Figure(7): The relationship between the Heat of formation and the temperature of the tetracene.

3.6.2 Entropy

At different temperatures extending from (100 °K-630 °K) which includes the standard temperature, as shown in Table(8), the entropy values of the tetracene molecule were calculated and we observed that the entropy changes according to the temperature. Figure(7) shows the values obtained for entropy in the MNDO-PM3 method from the diagram, and it shows that the entropy increases greatly by increasing the temperature and the values of the entropy at a temperature of 298 °K is equal to (114.684) Cal.K⁻¹.mol⁻¹, and the experimental value obtained from the previous studies (114.209) Cal.K⁻¹.mol⁻¹[17].
3.6.3 Heat Capacity

Another properties that is no less important the other properties, is the heat capacity, for the tetracene molecule and for different temperature of (100 K-600 K), as shown in Table(9). The heat capacity of tetracene was calculated at room a temperature (298 K), (54.806) Cal.mol⁻¹.K⁻¹, and the experimental value obtained from the previous studies (54.398) Cal.mol⁻¹.K⁻¹[17]. The Figure (8) shows the thermal relationship between the heat capacity function of temperature and depends on a large temperature and directly proportional to it. As the temperature increases, the number of the molecule increases from different levels of a higher vibrational energy, the heat capacity increases of each vibrational level.

**Table(8):** Tetracene entropy and corresponding temperature.

| T (K) | ENTROPY(CAL/K/MOL) |
|-------|---------------------|
| 100   | 78.5857             |
| 110   | 80.477              |
| 120   | 82.3318             |
| 130   | 84.1595             |
| 140   | 86.8914             |
| 150   | 89.7713             |
| 160   | 92.6747             |
| 170   | 95.5465             |
| 180   | 98.435              |
| 190   | 101.3199            |
| 200   | 104.206             |
| 210   | 107.102             |
| 220   | 109.9255            |
| 230   | 112.708             |
| 240   | 115.447             |
| 250   | 118.145             |
| 260   | 120.772             |
| 270   | 123.352             |
| 280   | 125.891             |
| 290   | 128.391             |
| 300   | 130.848             |
| 310   | 133.258             |
| 320   | 135.607             |
| 330   | 137.903             |
| 340   | 139.143             |
| 350   | 141.329             |
| 360   | 143.461             |
| 370   | 145.544             |
| 380   | 147.584             |
| 390   | 149.584             |
| 400   | 151.548             |
| 410   | 153.469             |
| 420   | 155.351             |
| 430   | 157.203             |
| 440   | 159.009             |
| 450   | 160.772             |
| 460   | 162.507             |
| 470   | 164.212             |
| 480   | 165.883             |
| 490   | 167.537             |
| 500   | 169.165             |
| 510   | 170.767             |
| 520   | 172.334             |
| 530   | 173.868             |
| 540   | 175.383             |
| 550   | 176.868             |
| 560   | 178.325             |
| 570   | 179.769             |
| 580   | 181.181             |
| 590   | 182.565             |
| 600   | 183.919             |
| 610   | 185.244             |
| 620   | 186.530             |
| 630   | 187.792             |

**Figure(8):** The relationship between the entropy and tetracene temperature.
Table(9 ). Tetracene heat capacity values and corresponding temperatures.

| T (K) | HEAT CAPACITY |
|-------|---------------|
| 100   | 18.1374       |
| 110   | 19.6567       |
| 120   | 21.2668       |
| 130   | 22.9510       |
| 140   | 24.6977       |
| 150   | 26.4894       |
| 160   | 28.3461       |
| 170   | 30.2390       |
| 180   | 32.1627       |
| 190   | 34.1215       |
| 200   | 36.1159       |
| 210   | 38.1445       |
| 220   | 40.1975       |
| 230   | 42.2741       |
| 240   | 44.3746       |
| 250   | 46.5004       |
| 260   | 48.6489       |
| 270   | 50.8218       |
| 280   | 53.0199       |
| 290   | 55.2311       |
| 298   | 54.8066       |
| 300   | 55.6588       |
| 310   | 56.7316       |
| 320   | 57.9245       |
| 330   | 59.2271       |
| 340   | 60.6393       |
| 350   | 62.1657       |
| 360   | 63.8052       |
| 370   | 65.5582       |
| 380   | 67.4208       |
| 390   | 69.3833       |
| 400   | 71.4437       |
| 410   | 73.5991       |
| 420   | 75.8466       |
| 430   | 78.1823       |
| 440   | 80.6064       |
| 450   | 83.1167       |
| 460   | 85.7188       |
| 470   | 88.3962       |
| 480   | 91.1449       |
| 490   | 93.9613       |
| 500   | 96.8454       |
| 510   | 99.7966       |
| 520   | 102.8143      |
| 530   | 105.8962      |
| 540   | 108.9597      |
| 550   | 110.9941      |
| 560   | 112.9097      |
| 570   | 114.8074      |
| 580   | 116.6875      |
| 590   | 118.5481      |
| 600   | 119.3939      |
| 610   | 120.2132      |
| 620   | 120.9063      |
| 630   | 121.5741      |
| 640   | 122.2155      |
| 650   | 122.8318      |
| 660   | 123.4224      |
| 670   | 123.9870      |
| 680   | 124.5260      |
| 690   | 125.0391      |
| 700   | 125.5362      |

Figure(9 ). The relationship between the heat capacity and tetracene temperature.

3.6.4 Enthalpy

The an atomical value of the molecule was calculated with different temperatures ranging from (1000K-6300K) as in Table( 10), at (2980K), and (1bar) the enthalpy value was equal to (8484.7128)Cal.mol⁻¹, and the experimental value obtained close from the previous studies (8367.315) Cal.mol⁻¹[17]. Figure(9 ) shows the relationship between the temperature and enthalpy, where the image shows that the higher temperature, the higher the enthalpy, meaning that the enthalpy is a function of temperature.
Table(10). Tetracene enthalpy and corresponding temperature.

| T (K) | ENTHALPY (CAL/MOL) |
|-------|---------------------|
| 100   | 1271.9128           |
| 110   | 1470.4960           |
| 120   | 1683.7959           |
| 130   | 1912.2607           |
| 140   | 2156.3351           |
| 150   | 2416.4607           |
| 160   | 2693.0739           |
| 170   | 2986.6524           |
| 180   | 3297.4592           |
| 190   | 3626.0357           |
| 200   | 3972.6948           |
| 210   | 4337.7650           |
| 220   | 4721.5249           |
| 230   | 5124.2509           |
| 240   | 5546.1106           |
| 250   | 5987.2701           |
| 260   | 6447.6361           |
| 270   | 6927.9700           |
| 280   | 7427.9330           |
| 290   | 7946.3664           |
| 300   | 8484.7728           |
| 310   | 9042.4742           |
| 320   | 9619.3566           |
| 330   | 10215.2630          |
| 340   | 10830.0103          |
| 350   | 11463.9252          |
| 360   | 12115.1835          |
| 370   | 12785.1492          |
| 380   | 13473.9946          |
| 390   | 14178.9968          |
| 400   | 14901.3656          |
| 410   | 15641.2946          |
| 420   | 16397.9984          |
| 430   | 17171.1786          |
| 440   | 17960.5337          |
| 450   | 18765.7608          |
| 460   | 19566.5564          |
| 470   | 20422.6178          |
| 480   | 21272.9440          |
| 490   | 22139.5303          |
| 500   | 23019.3991          |
| 510   | 23913.5407          |
| 520   | 24821.4732          |
| 530   | 25745.9136          |
| 540   | 26677.5837          |
| 550   | 27625.2104          |
| 560   | 28585.5299          |
| 570   | 29558.2681          |
| 580   | 30543.1823          |
| 590   | 31540.0116          |
| 600   | 32546.5168          |
| 610   | 33566.4584          |
| 620   | 34599.0283          |

Figure(10): relationship between enthalpy and tetracene temperature

3.6.5 Gibbs Free Energy

After calculating the enthalpy and entropy at different temperatures ranging from (100°K-630°K) as in Table(11), a they were linked to an important function. We know whether the reaction occurs automatically or not automatically, which is a Gibbs free energy denoted by G, as calculated by relationship \( \Delta G = \Delta E - T \Delta S \), at (298°K), the Gibbs Free Energy value was equal to (-25716.70) Cal.mol\(^{-1}\), and the experimental value obtained close from the previous studies (-25667.1) Cal.mol\(^{-1}\)[17], and the relationship between the Gibbs free energy and the temperature shown in Figure(10), noting that the negative sign means that the reaction is automatic.
Table (11). Values of the Gibbs free energy values of Tetracene and the corresponding temperature

| T(K) | G(Cal/mol) |
|------|------------|
| 100  | -6529.86   |
| 110  | -7330.41   |
| 120  | -8157.44   |
| 130  | -9008.22   |
| 140  | -9744.80   |
| 150  | -10634.10  |
| 160  | -11547.31  |
| 170  | -12484.60  |
| 180  | -13443.60  |
| 190  | -14234.90  |
| 200  | -15228.20  |
| 210  | -16243.20  |
| 220  | -17279.33  |
| 230  | -18336.12  |
| 240  | -19174.19  |
| 250  | -20063.16  |
| 260  | -20921.13  |
| 270  | -21778.48  |
| 280  | -22716.70  |
| 290  | -23653.60  |
| 300  | -24580.49  |
| 310  | -25517.31  |
| 320  | -26454.20  |
| 330  | -27401.11  |
| 340  | -28348.00  |
| 350  | -29294.91  |
| 360  | -30240.82  |
| 370  | -31186.73  |
| 380  | -32132.64  |
| 390  | -33078.55  |
| 400  | -34024.46  |
| 410  | -34970.37  |
| 420  | -35916.28  |
| 430  | -36862.19  |
| 440  | -37807.99  |
| 450  | -38753.79  |
| 460  | -39699.59  |
| 470  | -40645.39  |
| 480  | -41591.19  |
| 490  | -42536.99  |
| 500  | -43482.79  |
| 510  | -44428.59  |
| 520  | -45374.39  |
| 530  | -46320.19  |
| 540  | -47265.99  |
| 550  | -48211.79  |
| 560  | -49157.59  |
| 570  | -50103.39  |
| 580  | -51049.19  |
| 590  | -52004.99  |
| 600  | -52960.79  |
| 610  | -53916.59  |
| 620  | -54872.39  |
| 630  | -55828.19  |
| 640  | -56783.99  |
| 650  | -57739.79  |

Figure (11): The relationship between the Gibbs Free Energy of Tetracene and temperature

CONCLUSION

From the study of the molecular properties of the molecule, it has been concluded that:

1-The study was found that the equilibrium distance (bond length) of Tetracene was approximately of the bonds (C1-H1), (C2-H2), equal to (1.09Å), and the total energy is (-3617.3339eV) whereas the dissociation energy is ((4.02eV), (4.019eV), respectively. These results confirmed that as the bond length increases , the molecule begin to separate when the bond length reaches the point where the bond breaks. 

2-Molecule (84) showed a vibrational mode in the infrared region due to the base (3N-6).
3-The UV-vis spectra of molecule using semi-empirical theory in the gas phase the wave length was (266.8nm) and a good agreement with the result experimental (266.75nm).

4-The molecule has (42) orbitals occupied by electrons and (42) orbitals unoccupied by electrons, the energy gap was (6.577eV) and the ionization energy was (7.87eV).

5- By noting the value of the formation temperature of the molecule (C_{18}H_{12}) that is under study and in the standard degree of (83.907 kcal/mol), as the formation temperature indicates that the molecule is endothermic. The relationship between the temperature of the formation and the temperature is positive, that is, the temperature of the formation increases with the increase in temperature.

6- The more complex the molecule, the greater the value of heat capacity, especially if the temperature effect is greater. Heat capacity of molecule was (54806 Cal K^{-1} mol^{-1}).

7-The Gibbs free energy of the molecule was (-25716.70 cal./mol) as the less negative molecules are more stable. The Gibbs energy is inversely proportional to the temperature.

8- Controlling the band gap of the organic semiconductors is an important issue, for application such as light emitting diode, organic photovoltaic devices and the photodynamic therapy as a photosensitizer.

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