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SOLVENT EFFECTS ON THE ELECTRONIC STRUCTURE AND NON-LINEAR OPTICAL PROPERTIES OF PYRENE AND SOME OF ITS DERIVATIVES BASED ON DENSITY FUNCTIONAL THEORY

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ABSTRACT

Pyrene ($C_{16}H_{10}$) is an organic semiconductor which has wide applications in the field of organic electronics suitable for the development of organic light emitting diodes (OLED) and organic photovoltaic cells (OPV). In this work, Density Functional Theory (DFT) using Becke's three and Lee Yang Parr (B3LYP) functional with basis set 6-311++G(d, p) implemented in Gaussian 03 package was used to compute total energy, bond parameters, HOMO-LUMO energy gap, electron affinity, ionization potential, chemical reactivity descriptors, dipole moment, isotropic polarizability (α), anisotropy of polarizability ($\Delta\propto$) total first order hyper-polarizability (β) and second order hyperpolarizability (γ). The molecules used are pyrene, 1-chloropyrene and 4-chloropyrene in gas phase and in five different solvents: benzene, chloroform, acetone, DMSO and water. The results obtained show that solvents and chlorination actually influenced the properties of the molecules. The isolated pyrene in acetone has the largest value of HOMO-LUMO energy gap of 3.814eV and is a bit closer to a previously reported experimental value of 3.850 eV and hence is the most stable. Thus, the pyrene molecule has more kinetic stability and can be described as low reactive molecule. The calculated dipole moments are in the order of 4-chloropyrene (1.7645 D) < 1-chloropyrene (1.9663 D) in gas phase. The anisotropy of polarizability ($\Delta\alpha$) for pyrene and its derivatives were found to increase with increasing polarity of the solvents. In a nutshell, the molecules will be promising for organic optoelectronic devices based on their computed properties as reported by this work.

Keywords: Pyrene, DFT, Guassian 09, solvents and hyperpolarizability.

INTRODUCTION

The study of organic electronics has for a long time been viewed as an essential determinant in the field of display technology, renewable energy and flexible electronics (Shaw, 2001). In the past fifty years, photochemists have been devoting continuous efforts in researching organic semi-conductors (Forrest, 2007), and their integration into high-performance organic electronic devices. Pyrene ($C_{16}H_{10}$) is one of the simplest π-conjugated molecules which has shown electrical conductivity undergoing electrochemical doping (Facchetti, 2011). This feature, together with pyrene's unique radiometric properties and its concentration-dependent excimer (Somerharju, 2002) gives rise to the multiple applications including luminescence-switching chemical sensing and membrane biophysics (Li, 2019). As a result of their outstanding optical and electronic properties, pyrene and mono-chlorinated pyrene derivatives have represented an important building block in optoelectronic devices, such as organic light-emitting diodes (OLEDs) (Kuroda et al., 1963), organic field effect transistors (OFETs) (Abdulaziz et al., 2019), and organic photovoltaics (OPVs). In OLEDs, pyrene's high charge carrier mobility and prominent hole injection ability, together with its high photoluminescence efficiency, is particularly suitable for deep blue OLEDs (Chercka et al., 2014). One of the promising pyrene derivatives are chlorinated pyrene compounds (Abdulaziz et al., 2019). The theoretical study of the electronic structure has proved to be very conducive in predicting the physicochemical properties of a large number of donor-acceptor systems. More so, theoretical computations such as geometry optimizations are very important for understanding the pathways of electron and/or energy transfer processes in photoactive assemblies. The substituent attached to the molecular framework can enhance or diminish the reactivity (Saleh, 2009).

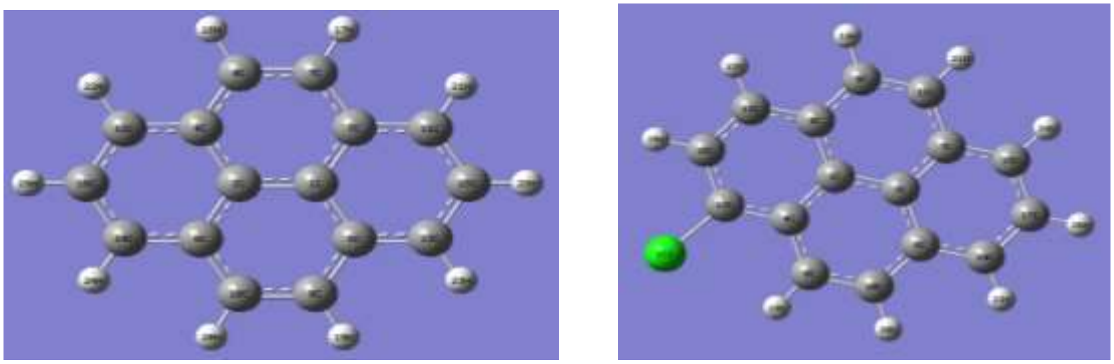
A theoretical study of neutral Pyrene was carried out by (Ehab, 2014) using DFT with B3LYP functional. The results obtained for such work were consistent with the experimental values; particularly the HOMO-LUMO energy of 3.84 eV agreed with the experimental value of 3.85 eV. Similarly in a work carried out by

(Basim et al., 2014) on theoretical study of the electronic structure and spectroscopic properties of Pyrene and its simplest derivatives using DFT/B3LYP functional, the derivatives have been generated by substituting one of the Hydrogen atoms in the molecule with hydroxyl group in different positions. It was found that the presence of this substituent decreased the HOMO-LUMO energy gap. Furthermore, the effects of chlorination and charging pyrene molecule on its molecular and non-linear optical properties have been investigated based on DFT by (Abdulaziz, 2019). The effects covered neutral, ionic and cationic forms of the molecules. The results agreed with previously reported works and showed increasing stability of the molecule (Abdulaziz, 2019).

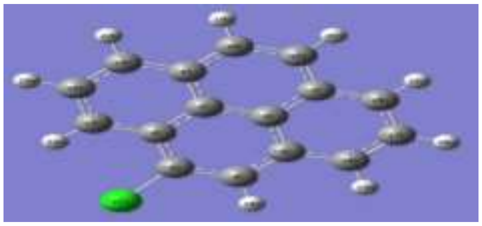
Nonlinear optical (NLO) phenomena have been studied over the last two decades (Basim et al., 2014). Molecules exhibiting large hyperpolarizabilities have a strong NLO potential and could be used, under conditions for optoelectronics and a variety of optical devices (Basim et al., 2014 and Maria et al., 2015). A theoretical study based on DFT of the IR spectra of Polycyclic aromatic hydrocarbons (PAHs) containing (5, 7)-member ring defects with focus on pyrene ($C_{16}H_{10}$) and coronene ($C_{24}H_{12}$) was reported by (Öttl, 2014). It was observed that the addition of (5, 7)-membered ring defects in pyrene and coronene results in a change of the IR spectra by losing their typical spectroscopic signature. The work (Öttl, 2014) also found some shifts in the positions of the band as well as different intensities and an increase in the number of features.

This paper reports a computational study of isolated pyrene, 1-chloropyrene and 4-chloropyrene molecules. The structural, electronic and NLO properties of these molecules in gas phase and in five different solvents : water, DMSO, acetone, chloroform and benzene have been explored theoretically. The effects of these solvents on the molecules under study have not been previously reported.

The structures of the three molecules under study as generated by GaussView 5.0.8 are shown in Fig. 1.0.



(a) pyrene (b) 1-chloropyrene



(c) 4-chloropyrene

Figure 1.0 : Structures of the molecules

Theoretical Background

Density Functional Theory

Density Functional Theory (DFT) is a phenomenally successful approach to finding solutions to the fundamental equation that describes the quantum behavior of atoms and molecules (Sulaiman et al., 2019). Among electronic structure methods, DFT occupies an important place, as it replaces the complexity of multi-dimensional many-electron wavefunction with three-dimensional electron density (Vivekanand, 2016). Quantum-mechanical wavefunction based methods provide an accurate way for predicting ground and excited state properties. These methods rely on the Schrodinger equation which is generally impossible to solve accurately for realistic many-electron systems (Vivekanand, 2016).

DFT is among the most popular and versatile methods available in Condensed-matter Physics, computational Physics, and computational chemistry. Within DFT, the ground state energy can be determine using the density relation given as (Gupta, 2016).

$$\rho(r) = \sum_{i=1}^{n} \left|\psi_{i\,(r)}\right|^2 \qquad (1)$$

where $\psi_i(\mathbf{r})$ is the Kohn-Sham orbitals.

We employ this relation to determine the ground state energy of the molecules.

Local Density Approximation (LDA)

The local density approximation (LDA) is the basis of all approximate exchange-correlation functionals. At the center of this model is the idea of a uniform electron gas. This is a system in which electrons move on a positive background charge distribution such that the total ensemble is neutral. The central idea of LDA is the assumption that we can write E_{XC} in the following form.

$$E_{XC}^{LDA}[\rho] = \int \rho(\overrightarrow{r})\, E_{XC}(\rho(\vec{r}))\, d\vec{r} \qquad (2)$$

Where $E_{XC}(\rho(\vec{r}))$ is the exchange-correlation energy per particle of a uniform electron gas of density $\rho(\vec{r})$. This energy per particle is weighted with the probability $\rho(\vec{r})$ that there is an electron at this position (Gupta, 2016). The quantity $E_{XC}(\rho(\vec{r}))$ can be further split into exchange and correlation contributions as

$$E_{XC}(\rho(\vec{r})) = EX(\rho(\vec{r})) + EC(\rho(\vec{r})) \qquad (3)$$

The exchange part, EX, which represents the exchange energy of an electron in a uniform electron gas of a particular density, was originally derived by Bloch and Dirac in the late 1920's is given by

$$EX = -\frac{3}{4}\left(\frac{3\rho(\vec{r})}{\pi}\right)^{\frac{1}{3}} \qquad (4)$$

Generalized Gradient Approximation (GGA)

Despite its simplicity, the LDA has been found to be inadequate for some problems and for this reasons extensions of LDA have been developed. The logical steps in this regard are the use of not only the information about the density $\rho(\vec{r})$ at a particular point $\vec{r}$, but also information about the gradient of the charge density, $\nabla\rho(\vec{r})$ so as to account for the non-homogeneity of the true electron density distribution in real system. Thus, we may write the exchange-correlation energy in a form known as Generalized Gradient Approximation (GGA) (Gupta, 2016) :

$$E_{XC}^{GGA}[\rho(\vec{r})] = \int f^{GGA}[\rho(\vec{r}), \nabla\rho(\vec{r})]\, d\vec{r} \qquad (5)$$

Where *f* is some function of electron densities and their gradients E_{XC}^{GGA} is usually split into exchange and correlation parts, which are modeled separately $E_{XC}^{GGA} = E_X^{GGA} + E_C^{GGA}$.

Frontier Molecular Orbitals (FMOs)

To explain several types of reaction and for predicting the most reactive position in conjugated systems, molecular orbitals and their properties such as energy are used. The energies of the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) are the most important orbitals in a molecule. HOMO can be through the outermost orbital containing electrons tends to give these electrons such as an electron donor. On the other hand, LUMO can be through the innermost orbital containing free places to accept electron. The Energy of the HOMO is directly related to the ionization potential and LUMO Energy is directly related to the electron affinity . The Energy difference between HOMO and LUMO orbital is called an energy gap which is an important parameter that determines the stability of the structures. The energy gap is also used in determining molecular electrical transport properties (Ismail et al., 2019).

In addition, according to Koopmans' theorem the energy gap, E_{gap}, defined as the difference between HOMO and LUMO energy and is given by (Ismail et al., 2019) :

$$E_{gap} = (E_{LUMO} - E_{HOMO}) \approx IP - EA \qquad (6)$$

The Energies of HOMO and LUMO are used for the determination of global reactivity descriptors. It is important that Ionization potential (I), Electron affinity (A), Electrophilicity (ω), Chemical potential (μ), Electronegativity (χ), Hardness (η) and Softness (S) be put into a Molecular Orbital's framework (Janaki et al., 2016).

The Global Quantities

In DFT, the ground state energy of an atom or a molecule in terms of its electron density ρ(r) is given by (Chandrakumar and Sourav, 2002) :

$$E[\rho] = F[\rho] + \int dr\, v(r)\rho(r) \quad (1) \qquad (7)$$

where $v(r)$ is the external potential that includes the nuclear potential also, and $F[\rho]$ is the universal Hohenberg-Kohn functional composed of the electronic kinetic energy and the electron-electron repulsion energy. The first and second partial derivatives of $E[\rho]$ with respect to the number of electron N under the constant external potential v(r) are defined as the chemical potential μ and the global hardness η of the system respectively (Chandrakumar and Sourav, 2002).

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{v(r)} \quad (8)$$

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{v(r)} \quad (9)$$

The inverse of the hardness is expressed as the global softness as

$$S = \frac{1}{2\eta} \quad (10)$$

The global descriptor of hardness has been an indicator of overall stability of the system. It has been customary to use a finite difference approximation for μ and η. Using the energies of N, $(N+1)$ and $(N-1)$ electron systems, we get the operational definition of μ and η as (Parr and Yang, 1989):

$$\mu \approx \frac{-(IP+EA)}{2} \quad (11)$$

$$\eta \approx \frac{(IP-EA)}{2} \quad (12)$$

Where $IP = -E_{HOMO}$ is the ionization potential of the molecule and $EA = -E_{LUMO}$ is the electron affinity of the molecule.

The electrophilicity (ω) can be calculated using the electronic chemical potential and the chemical hardness using the relation (Parr and Yang, 1989):

$$\omega = \frac{\mu^2}{2\eta} \quad (13)$$

The absolute electronegativity (χ) is given by the relation (Chandrakumar and Sourav, 2002):

$$\chi = \frac{IP+EA}{2} \quad (14)$$

Nonlinear Optical Properties (NLO)

NLO deals with the interaction of materials in the presence of applied electromagnetic field, which changes the wave number, phase and the other physical properties. In the presence of an applied electric field, the energy of a system is a function of the field. In recent years, the NLO phenomena have attracted much attention because of their potential applications in optical communication, optical sensing, data storage, computing etc (Bhawani, 2016).

Molecular materials with nonlinear optical (NLO) properties are attracting considerable attention because of their potential applications in the optoelectronic devices of telecommunications, information storage, optical switching, signal processing (Hamit, 2013 and Clodoaldo et al., 2018).

The dipole moment is defined as

$$\mu_{tot} = \left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)^{\frac{1}{2}} \quad (15)$$

Polarizability is the measure of distortion of a molecule in an electric field. It is a tensor and can be represented in a 3 × 3 real symmetric matrix i.e. the off-diagonal elements are equal. The polarizability $\langle\alpha\rangle$ is calculated using the following equation.

$$\langle\alpha\rangle = \frac{1}{2}\left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right) \quad (16)$$

The quantities $\alpha_{xx} \le \alpha_{yy} \le \alpha_{zz}$ are known as principal values of polarizability tensor. This property measures the strength of molecular interactions (e.g., long-range intermolecular induction, dispersion forces, etc.).

The anisotropy of polarizability could be expressed as (Hamit, 2013 and Clodoaldo et al., 2018):

$$\Delta\alpha = \left[\frac{(\alpha_{xx}-\alpha_{yy})^2+(\alpha_{xx}-\alpha_{zz})^2+(\alpha_{yy}-\alpha_{zz})^2}{2}\right]^{\frac{1}{2}} \qquad (17)$$

The first order hyperpolarizability is a third rank tensor which can be described by a $3 \times 3 \times 3$ matrix. Due to the Kleinman symmetry, the 27 components of the 3-D matrix can be reduced to 10 components. The complete equation for calculating the total static first order hyperpolarizability magnitude of Gaussian output is given as follows (Clodoaldo et al., 2018 and Fuks-Janczarek et al., 2005):

$$\beta_{tot} = \left[(\beta_{xxx}+\beta_{xyy}+\beta_{xzz})^2+(\beta_{yyy}+\beta_{yzz}+\beta_{yxx})^2+(\beta_{zzz}+\beta_{zxx}+\beta_{zyy})^2\right]^{\frac{1}{2}} \qquad (18)$$

The Second order hyperpolarizability is given according to the following equation

$$\gamma = \frac{1}{5}\left[\gamma_{xxxx}+\gamma_{yyyy}+\gamma_{zzzz}+2(\gamma_{xxyy}+\gamma_{xxzz}+\gamma_{yyzz})\right] \qquad (19)$$

where β is the first hyperpolarizability tensor and γ is the second hyperpolarizability tensor; *i, j, k* are *x, y* and *z* components.
Since the value of the polarizabilities α and the hyperpolarizability of Gaussian output are reported in a atomic mass units (a.u.), the calculated values have been converted into electrostatic units (esu) $(\alpha: 1\ a.u = 0.1482 \times 10^{-24} esu\ ;\ \beta: 1\ a.u = 0.0086393 \times 10^{-30} esu\ ;\ \gamma: 1a.u = 5.03717 \times 10^{-40} esu)$ (Fuks-Janczarek et al., 2005).

Computational Method

All the computations were carried out based on density functional theory (DFT) using the standard 6-311G(d, p) basis set (Belghiti et al., 2012) implemented in the Gaussian 03 software package (Frisch et al., 2004). The present calculations were performed in the gas phase and in five different solvents: water $(\varepsilon = 78.39)$, DMSO $(\varepsilon = 46.70)$, acetone $(\varepsilon = 20.70)$, chloroform$(\varepsilon = 4.90)$ and benzene $(\varepsilon = 2.25)$. The Polarizable Continuum Model (PCM) which is default in the Gaussian 03 package was used for all calculations involving solvents. The geometries of the molecules were fully optimized without any constraint with the help of analytical gradient procedure. All the parameters involved were allowed to relax and all the calculations converged to an optimized geometry which corresponds to a true energy minimum as revealed by the lack of imaginary values in the frequency calculations. We have also calculated HOMO and LUMO levels; the energy gap is evaluated as calculated by the difference between the HOMO and LUMO energies. The HOMO and LUMO results obtained were used to calculate Ionization potentials (IPs) , electron affinities (EAs), the chemical potential (μ), global hardness (η), global softness (S), electronegativity (χ) and electrophilicity (ω). Accurate calculation of nonlinear optical properties requires the use of extended basis sets and a high level of theory. In particular, these basis sets need to include *d* and *p* polarization functions together with *s* and *p* diffuse functions (Hamit , 2013). As such the basis set 6-311++G(d, p) used for this work is suitable. Thus, the nonlinear optical properties of the molecules such dipole moment(μ), average polarizability (α_{tol}), First Order Hyperpolarizability (β_{tol}) and Second order hyperpolarizability (γ) were also computed and reported. Gauss Sum 2.2 Program (O'Boyle et al., 2008) has been used to plot the density of the states (DOS) of the molecules in gaseous state.

RESULTS AND DISCUSSION

Ground state Energy

The energies of the molecules in gas phase and in different media by using the PCM model are listed in Table 1. From Table 1, we can see that the calculated energy is dependent on the size of the dielectric constant of the solvents across all the molecules. In the PCM model, the energies *E* decrease with the increasing of dielectric constants of the solvents. The table also shows that chlorine at different positions has effect on the ground state energies of the molecules. The presence of chlorine causes a decrease in energy compared to the isolated pyrene. On the whole, 1-chloropyrene having the least energy of -1075.54918886 a.u is the most stable molecule and found to be in the water solvent.

Table 1: Ground state Energy (a.u)

Phases	Dielectric Constant (ε)	Isolated Pyrene	1-chloropyrene	4-chloropyrene
Gas Phase	------------	-615.916127045	-1075.53777759	-1075.53778450
Water	78.39	-615.928075944	-1075.54918886	-1075.54915359
DMSO	46.70	-615.927824933	-1075.54888862	-1075.54885976

Acetone	20.70	-615.927144088	-1075.54826860	-1075.54823533
Chloroform	4.90	-615.923929579	-1075.54527978	-1075.54526535
Benzene	2.25	-615.920542720	-1075.54206965	-1075.54206745
Gas Phase [10]	-------------	-615.910480870	-1075.53096880	-1075.53084833

Structural parameters

The selected bond distances of the isolated and chlorinated pyrene molecules are collected in Table 2. It is well-known that the solvent polarity influences both the structure and properties of conjugated organic molecules. The structural data for the optimized structures of the molecules in gaseous state and in five different solvents are gathered in Table 2.

Although theoretical results are not exactly close to the experimental values for the titled molecules, this may be due to the fact that the theoretical calculations were aimed at the isolated and chlorinated molecules in gaseous phase and in solvents and the experimental results were aimed at the molecule in the solid state. The calculated geometric parameters also represent good approximation and they can be used as foundation to calculate the other parameters for the molecules. The bond angle is defined as the angle formed between two covalent bonds that originate from the same atom. The strongest bond length has the shortest bond distance and the weakest has the longest bond distance. From the results obtained, for isolated pyrene, the strongest bond length R(11,21) was found to be 1.0843 Å and is in gaseous state and the weakest bond length R(3,7) is 1.4385 Å was found to be in acetone solvent. For 1-chloropyrene, the strongest bond length R(6,12) was found to be 1.0817 Å and is in gas phase and the weakest bond length R(1,2) is 1.7684 Å was found to be also in water. Similarly, for 4-chloropyrene, the strongest bond length R(7,13) was found to be 1.0816 Å and is in gaseous state and the weakest bond length R(1,2) is 1.7686 Å was found to be in water.

Bond angle can be defined as the angle formed between two covalent bonds that originate from the same atom. The stability of a molecule increases as the bond angle increases. Table 4.2 lists some selected values of the bond angles for the three molecules in gaseous state and in different solvents. For isolated pyrene the largest bond angle A(8,4,3) was found to be 122.4470° and in gaseous state ranking it most stable while the smallest A(5,12,22) was found to be 118.2504° and in acetone. For 1-chloropyrene the largest bond angle A(2,3,6) was found to be 124.17180° and in DMSO solvent making it most stable while the smallest A(2,3,5) was found to be 117.1995° and in water. In 4-chloropyrene the largest bond angle A(2,3,7) was found to be 124.1194° and in DMSO solvent also making it the most stable while the smallest A(2,3,5) was found to be 116.7707° and in water. These bond parameters (bond lengths and bond angles) provide insight into the molecular geometry of a compound. On the whole the 4-chloropyrene is the most stable with bond angle A(2,3,7) as 124.1194° being the largest.

Table 2 : Selected bond distances (Å) and bond angles (°) for the isolated and chlorinated pyrene molecules using b3lyp/6-311++G(d,p)

Molecule	Bond Length (Å)	Gas	Water	DMSO	Acetone	Chloroform	Benzene
Pyrene	R(1,2)	1.4252	1.4273	1.4265	1.4261	1.4261	1.4255
	R(1,3)	1.4271	1.4276	1.4277	1.4276	1.4272	1.4274
	R(3,7)	1.4365	1.4378	1.4382	1.4385	1.4378	1.4371
	R(11,21)	1.0843	1.0874	1.0873	1.0872	1.0864	1.0855
1-chloropyrene	R(10,16)	1.4352	1.4371	1.4370	1.4370	1.4366	1.4361
	R(5,9)	1.4268	1.4275	1.4275	1.4274	1.4272	1.4270
	R(6,12)	1.0817	1.0845	1.0840	1.0839	1.0833	1.0826
	R(1,2)	1.7610	1.7684	1.7681	1.7680	1.7667	1.7649
4-chloropyrene	R(10,16)	1.4018	1.4031	1.4031	1.4030	1.4027	1.4023
	R(5,9)	1.4251	1.4259	1.4259	1.4259	1.4256	1.4254
	R(7,13)	1.0816	1.0843	1.0839	1.0838	1.0831	1.0825
	R(1,2)	1.7624	1.7686	1.7684	1.7682	1.7669	1.7652
Pyrene	A(2,1,3)	120.0776	119.9983	120.0342	120.0599	120.0621	120.0734

	A(3,7,12)	121.3908	121.3023	121.3179	121.3273	121.3473	121.3740
	A(5,12,22)	118.3542	118.3173	118.2817	118.2504	118.3067	118.3445
	A(8,4,10)	122.4470	122.312	122.3406	122.3383	122.3554	122.4160
1-chloropyrene	A(1,2,3)	120.3197	120.1168	120.1156	120.1274	120.1822	120.2469
	A(2,3,5)	117.4996	117.1995	117.2076	117.2170	117.2860	117.3657
	A(2,3,6)	123.9187	124.1710	124.1718	124.1614	124.0929	124.0142
	A(15,20,22)	120.8501	120.7974	120.7976	120.8000	120.8134	120.8286
4-chloropyrene	A(1,2,3)	119.0227	118.8080	118.8109	118.8282	118.8770	118.9379
	A(2,3,5)	117.0107	116.7707	116.7730	116.7768	116.8370	116.9027
	A(2,3,7)	123.8636	124.1193	124.1194	124.1121	124.0451	123.9740
	A(15,20,25)	120.3742	120.4798	120.4665	120.4623	120.4258	120.3999

Frontier orbitals energy

In principle, there are several ways to calculate the excitation energies. The simplest one involves the difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of a neutral system, and is a key parameter determining molecular properties. Both HOMO and LUMO are the main orbital taking part in chemical reaction. The HOMO energy characterizes the ability of electron giving, the LUMO characterizes the ability of electron accepting, and the gap between HOMO and LUMO characterizes the molecular chemical stability (Jagannathan and Meenakshi, 2009). The energy gap between the HOMOs and LUMOs is a critical parameter in determining molecular electrical transport properties because it is a measure of electron conductivity (Kosar and Albayrak, 2011). The larger the HOMO-LUMO energy gap, the harder and more stable (but less reactive) the compound will be (Gidado, 2017).

The influence of solvent nature and chlorination is not only observed in the geometric parameters of the molecules, but also in the energies of frontier orbitals. The inclusion of solvation effects leads also to some changes on the molecular orbital energies as shown in Table 4.3. In solutions, the values differ from those in gaseous state due to the effect of polarization. From Table 4.3, it is observed that solvation has only a little effect on the molecules while chlorination effect is more pronounced . On the whole isolated pyrene in acetone appears to have the largest value of 3.814eV and hence is the most stable. Our calculated value ΔE (3.814 eV) for isolated pyrene in acetone is more closer with experimental value of 3.850 eV (Ehab, 2014). The values are in the range of isolated pyrene $>$ 4-chloropyrene $>$ 1-chloropyrene in each of the corresponding gaseous state and solvent. The HOMO-LUMO gaps in solvated media appear to be slightly less than in the corresponding values in gaseous state. The chlorination effect appear to have lower values compare to the isolated state. In the results, the higher frontier orbital gap indicates that the pyrene molecule has more kinetic stability and can be described as low reactive molecule. In addition, the total density of states (DOS), of the molecules in gaseous states are presented in Figure 2(a-c) to observe the varieties of the HOMOs, LUMOs, and energy gaps more easily and vividly. These spectra provide graphical representation of MO compositions and their contributions to chemical bonding showing occupied and virtual orbitals..

4.3 Frontier orbital energies (in a.u), HOMO-LUMO gap (in eV), of the Molecules

Molecule	Gas	Water	DMSO	Acetone	Chloroform	Benzene	Previous Work (Ehab, 2024)
				Isolated Pyrene			
E_{HOMO}(a.u)	-0.20841	-0.20912	-0.20902	-0.20889	-0.20801	-0.20762	3.850
$E_{LUMO}(a.u)$	-0.06839	-0.06904	-0.06900	-0.06871	-0.06792	-0.06757	
E_g (eV)	3.810	3.812	3.810	3.814	3.812	3.811	
				1-chloropyrene			

E_{HOMO}(a.u)	-0.21298	-0.21221	-0.21227	-0.21212	-0.21166	-0.21168	
$E_{LUMO}(a.u)$	-0.07616	-0.07495	-0.07503	-0.07488	-0.07448	-0.07460	
$E_g\ (eV)$	3.723	3.735	3.734	3.734	3.733	3.730	
4-chloropyrene							
E_{HOMO}(a.u)	-0.21495	-0.21391	-0.21398	-0.21384	-0.21342	-0.21350	
$E_{LUMO}\ (a.u)$	-0.07639	-0.07518	-0.07526	-0.07513	-0.07474	-0.07487	
$E_g\ (eV)$	3.770	3.775	3.775	3.774	3.774	3.772	

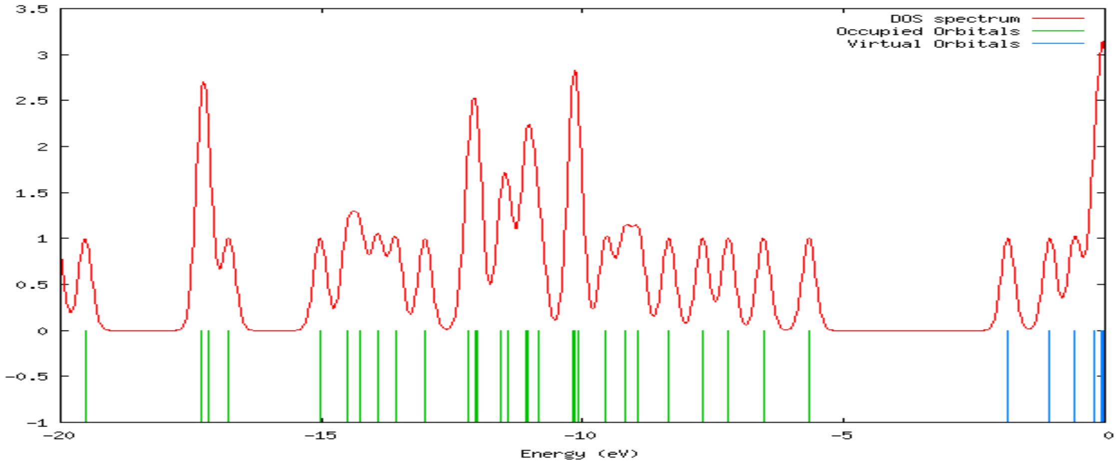


Fig 2 (a) Pyrene Density of energy states in gas phase

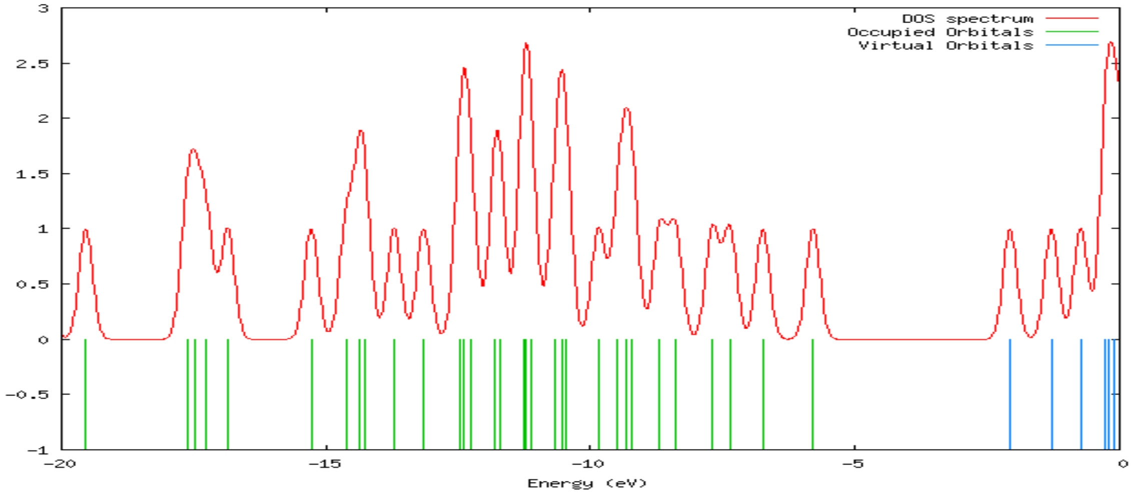


Fig 2 (b) 1-chloropyrene Density of energy states in gas phase

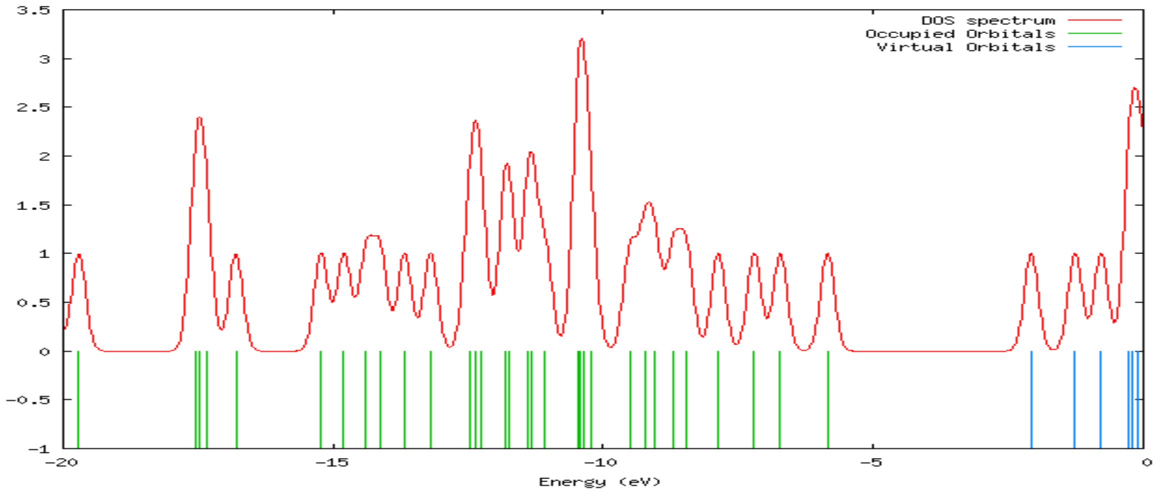


Fig 2 (c) 4-chloropyrene Density of energy states in gas phase

Ionization potentials (IPs), electron affinities (EAs) Global chemical indices

The ionization potential (IP) and electron affinity (EA) are well-defined properties that can be calculated by DFT. These values aim to get in detail rationalization of the relationship between the structure and the electronic behavior of the molecule, in particular the response of the molecule to the formation of a hole, or to the addition of an electron, additional information is derived (Amel, et al., 201). The energies of frontier orbitals HOMO and LUMO are used to determine several chemical reactivity parameters as a measure of relative stability and reactivity. These include chemical hardness (η), global softness (S), absolute electronegativity (χ) , electronic chemical potentials (μ) and electrophilicity (ω). The results are shown in Table 4.4.

The lowest value of the ionization potential (IP=5.6496 eV) is observed in isolated pyrene in benzene solvent, hence that makes it be the best electron donor. The Compound 4-chloropyrene has the largest value of the electron affinity (EA= 2.0787eV) observed in gas phase, so it is the best electron acceptor.

Hardness (η) and softness (S) are a useful concept for understanding the behaviour of chemical systems. A hard molecule has a large energy gap and a soft molecule has a small energy gap [31]. Therefore, soft molecules will be more polarizable than hard molecules. From the results obtained, it was found that isolated pyrene has the highest hardness value (η = 1.9073 eV) in acetone, which indicates that is the hardest molecule. The 1-chloropyrene in gas phase has the highest softness (S = 0.2686 eV), so it is the softest molecule. Electronegativity (χ) represents the ability of molecules to attract electrons, The χ values are displayed in Table 4.4 The Compound 4-chloropyrene in gas phase has highest electronegativity value of $\chi = 3.9639\ \mathrm{eV}$ compared to all the other molecules.

The chemical potential μ (eV) measures the escaping tendency of an electron and it can be associated with the molecular electronegativity. As μ becomes more negative, it is more difficult to lose an electron but easier to gain one. As shown in Table 4.4, isolated pyrene in benzene is the least stable and the most reactive among all the compounds with $\mu = -3.7442\mathrm{eV}$. Electrophilicity (ω), gives an idea of the stabilization energy when the system gets saturated by electrons, which come from the external environment. These reactivity information shows if a molecule is capable of donating charge. A good, more reactive, nucleophile is characterized by a lower value of (ω), while higher values indicate the presence of a good electrophile. Our results show that, isolated pyrene in benzene solvent has lowest value of ($\omega = 2.3365\ \mathrm{eV}$), so that compound is good nucleophile. However 1-chloropyrene in gas phase is a good electrophile having the highest value of $\omega = 2.5794\ \mathrm{eV}$.

Table 4.4: Ionization potentials (IPs), electron affinities (EAs) and Global chemical indices of the optimized Pyrene in the gas phase and in different solvents

Solvents	Molecule	IP(eV)	EA (eV)	η (eV)	S (eV)	χ (eV)	μ (eV)	ω (eV)
Gas Phase	Isolated Pyrene	5.6711	1.8610	1.9051	0.2625	3.7661	-3.7661	2.3639

	1-chloropyrene	5.7955	2.0724	1.8616	0.2686	3.9340	-3.9340	2.5794
	4-chloropyrene	5.8491	2.0787	1.8852	0.2652	3.9639	-3.9639	2.6188
Water	Isolated Pyrene	5.6904	1.8787	1.9059	0.2623	3.7846	-3.7846	2.3872
	1-chloropyrene	5.7745	2.0395	1.8675	0.2677	3.9070	-3.9070	2.5441
	4-chloropyrene	5.8208	2.0457	1.8876	0.2649	3.9333	-3.9333	2.5785
DMSO	Isolated Pyrene	5.6877	1.8776	1.9051	0.2625	3.7827	-3.7827	2.3848
	1-chloropyrene	5.7761	2.0417	1.8672	0.2678	3.9089	-3.9089	2.5466
	4-chloropyrene	5.8227	2.0479	1.8874	0.2649	3.9353	-3.9353	2.5811
Acetone	Isolated Pyrene	5.6842	1.8697	1.9073	0.2622	3.7770	-3.7770	2.3776
	1-chloropyrene	5.7721	2.0376	1.8673	0.2678	3.9049	-3.9049	2.5414
	4-chloropyrene	5.8189	2.0444	1.8873	0.2649	3.9317	-3.9317	2.5764
Chloroform	Isolated Pyrene	5.6602	1.8482	1.9060	0.2623	3.7542	-3.7542	2.3490
	1-chloropyrene	5.7595	2.0267	1.8664	0.2679	3.8931	-3.8931	2.5260
	4-chloropyrene	5.8074	2.0338	1.8868	0.2650	3.9206	-3.9206	2.5619
Benzene	Isolated Pyrene	5.6496	1.8387	1.9055	0.2624	3.7442	-3.7442	2.3365
	1-chloropyrene	5.7601	2.0300	1.8651	0.2681	3.8951	-3.8951	2.5286
	4-chloropyrene	5.8096	2.0373	1.8862	0.2651	3.9235	-3.9235	2.5656

Dipole moment, polarizability, First-order Polarizability and Second-order Polarizability

The dipole moment is a measure of the polarity of the molecule. Dipole moment values of the studied molecules in gas phase and in different media by using the PCM model are listed in Table 4.5. The calculated dipole moments are in the order of 4-chloropyrene (1.7645 D) < 1-chloropyrene (1.9663 D) in gas phase. This predicts that 4-chloropyrene is the more stable compound in organic chlorination reaction media due to its lower dipole moment value followed by 1-chloropyrene. In addition the values of the dipole moment for 1-chloropyrene and 4-chloropyrene are found to increase with the increasing values of the dielectric constants of solvents. For the parent pyrene, it is observed that the dipole moment is zero regardless of whether it is in solvent or gas phase. This is as a result of equal distribution of charges in the entire molecule which made them to cancel themselves, thereby producing no net charge (non-polar).

The anisotropy of polarizability ($\Delta\alpha$) for pyrene was found to increase with increasing polarity of the solvents from $3.0639 \times 10^{-24} esu$ in benzene to $3.5863 \times 10^{-24} esu$ in water. The least value of $\Delta\alpha$ is $2.8838 \times 10^{-24} esu$ was found to be in gas phase. This is similarly observed in 1-chloropyrene with $\Delta\alpha$ in solvent from $2.9882 \times 10^{-24} esu$ in benzene to $3.4958 \times 10^{-24} esu$ in water. The least value of $\Delta\alpha$ is $2.7038 \times 10^{-24} esu$ was found to be in gas phase. For 4-chloropyrene, $\Delta\alpha$ was also found to increase with increasing polarity of the solvents from $2.8441 \times 10^{-24} esu$ in benzene solvent to $3.3412 \times 10^{-24} esu$ in water. The least value of $2.5805 \times 10^{-24} esu$ was also found to be in gas phase. The values of $\Delta\alpha$ are also found to increase in the order of pyrene $>$ 1-chloropyrene $>$ 4-chloropyrene in the gas phase and in all the solvents. This shows that chlorination with change in orientation affects the values of anisotropy of polarization.

The First Order Hyperpolarizability (β_{tol}) of the pyrene molecule all vanish to zero for all the solvents and the gas phase. This is as a result of equal distribution of charges in the entire molecule which made them to cancel themselves, thereby producing no net charge (non-polar). For the 1-chloropyrene, β_{tol} increases with increasing polarity of the solvent from $2.7283 \times 10^{-31} esu$ in benzene solvent to $4.2119 \times 10^{-31} esu$ in water. The smallest value of 1.7257×10^{-31} esu was observed in gas phase. Similarly, for 4-chloropyrene β_{tol} increases with increasing dielectric constant of the solvent from

2.0818×10^{-31} esu in benzene solvent to 3.3752×10^{-31} esu in water. The smallest value of 0.8823×10^{-31} esu was observed in gas phase. The values of β_{tol} are also found to increase in the order of 1-chloropyrene $>$ 4-chloropyrene in the gas phase and in all the solvents. This also shows that chlorination affects the values of first order hyperpolarizability.

The Second-order hyperpolarizability (γ) values in gas phase and in different media by using the PCM model are also shown in Table 4.5. For pyrene molecule the values increase as the dielectric constants of the solvents increase from -6.7253×10^{-37} esu in benzene solvent to -6.5762×10^{-37} esu in water with the least value of -6.8033×10^{-37} esu found in gas phase. Similarly, for 1-chloropyrene, the values of γ increase as the dielectric constants of the solvents increase from -9.1468×10^{-37} esu in benzene solvent to -9.0110×10^{-37} esu in water with the least value of -9.2150×10^{-37} esu found in gas phase. The 4-chloropyrene also follows the same pattern with values of γ also increasing from -8.7709×10^{-37} esu in benzene solvent to -8.6304×10^{-37} esu in water with the least value of -8.8435×10^{-37} esu found in gas phase. The Second-order hyperpolarizability (γ) values are also influenced by chlorination and orientation. Accordingly, the values are found to vary in the order of pyrene $>$ 4-chloropyrene $>$ 1-chloropyrene from water to benzene.

Table 4.5: The anisotropy of Polarizability (α_{tol}), First Order Hyperpolarizability (β_{tol}), Second order hyperpolarizability (γ) and Dipole Moment (μ) for Pyrene

Parameters	Gas	Water	DMSO	Acetone	Chloroform	Benzene
α_{xx}	-99.9168	-100.7048	-100.6956	-100.6417	-100.4282	-100.2026
α_{xy}	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
α_{yy}	-81.0876	-76.6888	-76.8350	-77.1126	-78.3508	-79.5896
α_{xz}	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
α_{yz}	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
α_{zz}	-81.0922	-76.3262	-76.3912	-76.6981	-78.1050	-79.4679
$\langle\alpha\rangle_{tol(esu)} \times (-10^{-23})$	1.29476	1.25338	1.25548	1.25700	1.26901	1.28074
$\Delta\alpha\ (esu) \times 10^{-24}$	2.8838	3.5863	3.5695	3.5411	3.2902	3.0639
$\beta_{tol\,(esu)}$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
γ_{xxxx}	-119.4649	-122.1975	-122.1641	-121.9826	-121.2512	-120.4713
γ_{yyyy}	-1376.0391	-1311.6391	-1313.2195	-1317.2842	-1335.2034	-1353.4477
γ_{zzzz}	-2383.2693	-2271.9462	-2274.5114	-2281.5192	-2313.2608	-2344.6216
γ_{xxyy}	-304.1185	-305.8472	-305.7703	-305.6719	-305.2662	-304.7986
γ_{xxzz}	-513.6823	-516.3825	-516.7251	-516.3865	-515.7948	-514.9430
γ_{yyzz}	-619.3843	-588.7339	-589.9878	-591.5024	-600.0748	-608.8481
γ (esu) $(-) \times 10^{-37}$	6.8033	6.5762	6.5834	6.5966	6.6611	6.7253
μ	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 4.4: The Average Polarizability (α_{tol}), First Order Hyperpolarizability (β_{tol}), Second order hyperpolarizability (γ) and Dipole Moment (μ) for 1-chloropyrene

Parameters	Gas	Water	DMSO	Acetone	Chloroform	Benzene
α_{xx}	-100.1859	-97.8284	-97.8734	-98.0706	-98.8805	-99.5686
α_{xy}	1.7687	2.6304	2.6503	2.6044	2.3823	2.1337
α_{yy}	-90.3927	-84.9140	-85.0107	-85.3397	-86.8623	-88.4185
α_{xz}	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
α_{yz}	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
α_{zz}	-111.4423	-112.1394	-112.1207	-112.0804	-111.8909	-111.6943
$\langle\alpha\rangle_{tol(esu)} \times (-10^{-23})$	1.49198	1.45672	1.45732	1.45972	1.47031	1.48043
$\Delta\alpha(esu) \times 10^{-24}$	2.7038	3.4958	3.4810	3.4333	3.2132	2.9882
β_{xxx}	-35.3941	-59.9925	-59.6217	-58.4011	-52.3127	-45.4081
β_{xxy}	2.2938	3.6483	3.6068	3.5535	3.2601	2.8882
β_{xyy}	3.4232	-0.2305	-0.2214	0.0021	1.0173	2.0702
β_{yyy}	1.6019	3.9590	3.9340	3.8012	3.1711	2.4942
β_{xxz}	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
β_{xyz}	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
β_{yyz}	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
β_{xzz}	12.3028	12.0343	12.0270	12.0362	12.0896	12.1640
β_{yzz}	-0.4053	-0.2106	-0.2153	-0.2255	-0.2781	-0.3341
β_{zzz}	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
$\beta_{tol\,(esu)} \times 10^{-31}$	1.7257	4.2119	4.1792	4.0525	3.4286	2.7283
γ_{xxxx}	-3563.7532	-3501.5197	-3502.3640	-3507.4244	-3528.4166	-3546.6117
γ_{yyyy}	-1643.0256	-1552.4243	-1554.0647	-1559.4073	-1584.2474	-1609.9139
γ_{zzzz}	-131.8948	-134.2620	-134.1997	-134.0647	-133.4276	-132.7607
γ_{xxyy}	-843.4850	-811.9178	-812.4336	-814.3562	-823.1158	-832.0710
γ_{xxzz}	-693.8324	-697.9510	-697.8242	-697.6623	-696.7478	-695.6070
γ_{yyzz}	-366.8290	-368.2005	-368.1502	-368.0858	-367.7391	-367.3426
γ (esu) $(-) \times 10^{-37}$	9.2150	9.0110	9.0140	9.0277	9.0884	9.1468
μ_x	-1.9095	-2.8647	-2.8609	-2.8132	-2.5772	-2.3066
μ_y	0.4694	0.7258	0.7231	0.7095	0.6431	0.5700
μ_z	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

μ (D)	1.9663	2.9552	2.9508	2.9013	2.6562	2.3760
μ (D) (Ehab, 2014)	2.1093					

Table 4.5: The Average Polarizability (α_{tol}), First Order Hyperpolarizability (β_{tol}) Second order hyperpolarizability (γ) and Dipole Moment (μ) for 4-chloropyrene

Parameters	Gas	Water	DMSO	Acetone	Chloroform	Benzene
α_{xx}	-98.1077	-95.0976	-95.1593	-95.3683	-96.2619	-97.0767
α_{xy}	-3.0587	4.9739	4.9641	4.9086	4.6333	4.2988
α_{yy}	-91.5348	-86.5852	-86.6623	-86.9857	-88.4741	-89.9727
α_{xz}	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
α_{yz}	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
α_{zz}	-111.2768	-112.1476	-112.1295	-112.0889	-111.8995	-111.7029
$\langle\alpha\rangle_{tol(esu)}$ $(-)\times 10^{-23}$	1.48654	1.45152	1.45212	1.45455	1.46538	1.47584
$\Delta\alpha\ (esu)$ $\times 10^{-24}$	2.5805	3.3412	3.3283	3.2806	3.0623	2.8441
β_{xxx}	18.1443	-37.4233	-37.2365	-36.2608	-31.4442	-26.1091
β_{xxy}	8.2208	14.0671	13.9525	13.8093	13.0528	12.0817
β_{xyy}	1.6481	-8.4262	-8.3475	-8.1082	-6.9579	-5.6670
β_{yyy}	0.3536	6.0125	5.9806	5.7160	4.4712	3.1178
β_{xxz}	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
β_{xyz}	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
β_{yyz}	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
β_{xzz}	-10.6230	9.8810	9.8780	9.8905	9.9577	10.0431
β_{yzz}	-4.0779	-4.8302	-4.8235	-4.8193	-4.8001	-4.7899
β_{zzz}	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
$\beta_{tol\,(esu)}$ $\times 10^{-31}$	0.8823	3.3752	3.3496	3.2383	2.6921	2.0818
γ_{xxxx}	-2869.3799	-2798.1583	-2799.6484	-2804.4851	-2826.0953	-2846.5313
γ_{yyyy}	-2055.9338	-1955.8579	-1957.5877	-1963.6759	-1991.4148	-2019.9240
γ_{zzzz}	-131.9565	-134.3344	-134.2735	-134.1368	-133.4969	-132.8268
γ_{xxyy}	-833.5121	-806.8742	-807.0444	-808.7767	-816.5691	-824.2515
γ_{xxzz}	-581.7131	-585.0869	-584.9746	-584.8085	-584.0563	-583.1232
γ_{yyzz}	-445.2801	-447.2045	-447.1391	-447.0775	-446.6207	-446.0886
γ (esu)	8.8435	8.6304	8.6335	8.6474	8.7098	8.7709

$(-) \times 10^{-37}$						
μ_x	1.6598	-2.6600	-2.6574	-2.6120	-2.3858	-2.1293
μ_y	0.5986	0.9766	0.9764	0.9675	0.9214	0.8611
μ_z	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
μ (D)	1.7645	2.8336	2.8311	2.7854	2.5575	2.2969
μ (D) [10]	2.0428					

CONCLUSION

The study focuses on the structural, electronic and nonlinear optical properties of pyrene, 1-chloropyrene and 4-chloropyrene molecules based of DFT using b3lyp/6-311++G (d,p) basis set. In the PCM model, the energies E decrease with the increasing of dielectric constants of solvents. The presence of chlorine was found to cause a decrease in energy compared to the isolated chlorine. On the whole, 1-chloropyrene has the least energy of -1075.54918886 a.u and is found in water. The calculated value of HOMO-LUMO energy gap of 3.814 eV for isolated pyrene in gaseous state is a bit closer with experimental value of 3.850 eV [10]. The values are in the range of isolated pyrene > 4-chloropyrene > 1-chloropyrene in each of the corresponding gaseous state and solvent. The HOMO-LUMO gaps in solvated media appear to be slightly less than in the corresponding values in gaseous state. In the results, the higher frontier orbital gap indicates that the pyrene molecule has more kinetic stability and can be described as low reactive molecule. The chemical reactivity parameters which include chemical hardness (η), global softness (S), absolute electronegativity (χ), electronic chemical potentials (μ) and electrophilicity (ω) are also found to be influenced by solvent and chlorination effects. The values of dipole moment, polarizability, first-order polarizability and second-order polarizability were also calculated and reported**.** The values of the dipole moment for 1-chloropyrene and 4-chloropyrene are found to increase with the increasing values of the dielectric constants of the solvents. The parent pyrene is observed to have dipole moment of zero regardless of whether it is in solvent or gas phase. This is as a result of equal distribution of charges in the entire molecule which made them to cancel themselves, thereby producing no net charge (non-polar). The anisotropy of polarizability ($\Delta\alpha$) and the first order hyperpolarizability (β_{tol}) values are also found to be influenced by both the solvents and the chlorination in the order 1-chloropyrene > 4-chloropyrene. The value of second order hyperpolarizabity (γ) are also affected by the chlorination in the order pyrene > 4-chloropyrene > 1-chloropyrene and from lower dielectric constant benzene to a high dielectric constant water. In a nutshell the molecules will be good for organic optoelectronic devices.

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