

Electronic Structure and Non-Linear Optical Properties of Neutral and Ionic Pyrene and its Derivatives based on Density Functional Theory

Abstract

Pyrene ($C_{16}H_{10}$) is an organic semiconductor suitable for the development of organic light emitting diodes (OLED), organic photovoltaic cells (OPV) and many other electronic components. Ionic and chlorination effects on electronic and non-linear optical properties of pyrene molecule have been investigated based on Density Functional Theory (DFT) using Becke's three and Lee Yang Parr (B3LYP) functional with basis sets 6-311G and 6-311+G (d). Parameters such as minimum energy, bond lengths and angles, HOMO-LUMO energy gap, chemical reactivity descriptors, isotropic polarizability (α), anisotropy of polarizability ($\Delta\alpha$), and total first hyper-polarizability (β_{tot}) for neutral and ionic forms were computed to determine the relative stability and reactivity of the molecules. All computations have been performed using Gaussian 03. The results showed that charging the molecule and the introduction of chlorine in the ring have changed the electronic and non-linear-optical properties of the molecule. It is revealed that cationic and anionic forms of 2-chloropyrene have smaller values of energy gap as 3.641eV and 0.078eV respectively compared to the neutral form which has 3.822eV showing a significant change in the energy gap. Addition of chlorine atom to the neutral molecule is less significant in changing the energy gap. Cationic form of 2-chloropyrene has hyperpolarizability value of 128.881a.u compared to 75.508a.u of the neutral form while anionic molecule has 27.515a.u which is below that of the neutral molecule. The computed results agreed with reported works. To this effect, charged Pyrene is considered to be a potential candidate over the neutral molecule for practical applications.

Keywords: Pyrene, organic semiconductor, DFT, Gaussian 03, HOMO-LUMO energy and hyperpolarizability

Introduction

The rise of organic electronics and Photovoltaics stands as one of the possible answers to appease the demand for a sustainable and risk-free future of electronics and solar energy industries. However, the implications of the development of organic electronics and Photovoltaics do not stop at answering environmental concerns but also open up the possibility of new technological advancements. These could not be achieved without the keen study of the properties of organic materials that could serve as active components in organic devices. Pyrene ($C_{16}H_{10}$) is one of the organic materials possessing an extended π -conjugation that received immense attention in recent years. This is due to their unique photo-physical and charge transport properties, which make them potential materials for applications in electronic

devices [1]. Pyrene is a polycyclic aromatic hydrocarbon (PAH) consisting of four fused benzene rings. Pyrene is a flat aromatic compound and forms during incomplete combustion of organic compounds [2]. Pyrene and its derivatives are very important industrial materials. They are used commercially to make dyes and dye precursors. Mono-chlorinated pyrene derivatives have been synthesized by organic chemistry and find applications as organic light emitting diodes (OLEDs) [3]. Pyrene ring is of special interest because its hydrogen atoms can easily be substituted using a wide range of chemical groups of interest. The derivatives then become potential candidate for electronic materials (AlShamaileh, 2014). One of the promising pyrene derivatives are chlorinated pyrene compounds.

Theoretical calculations such as geometry optimizations are very important for understanding the pathways of electron and/or energy transfer processes in photoactive assemblies [4].

A theoretical study of neutral Pyrene **has been** carried out by [2] using DFT with B3LYP functionals. The results obtained were in agreement with the experimental values; particularly the HOMO-LUMO energy of 3.84 eV was consistent with the experimental value of 3.85 eV. However, the work did not report theoretical study on anionic and cationic forms of Pyrene molecule. Similarly, the work did not report the NLO properties of the molecules.

Similarly in a work carried out 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 and the effects on positional variation of hydroxyl group **has been** analyzed [5]. It **has been** found that the presence of this substituent decrease the HOMO-LUMO energy gap. Benzene is an aromatic compound when fused together to form pyrene aromatic ring. Work has been conducted by [6] and study benzene aromatic ring and its derivatives using DFT/B3LYP functional. The study tried to identify the effect of addition of nitrogen to the ring. The work explained that, introducing nitrogen to the ring caused a reduction in the HOMO-LUMO energy gap and improved their average polarizability from 69.181a.u of benzene up to 112.316 a.u of one of the its derivative (Pyrizine) apart from having good electronic values which were in conformity with the experimental values. In all the literatures above, adding substituent to the original Pyrene molecule showed improvement in the electronic and NLO properties of the molecule.

In this work, the effects of chlorination and charging pyrene molecule on its molecular and non-linear optical properties **have been** investigated based on DFT using two different basis sets (6-311G and 6-311+G (d)). The effects covered neutral, ionic and cationic forms of the molecules. The results agreed with reported works and show increasing stability of the molecule.

Theoretical Background

Density Functional Theory

The quantum mechanical wave function contains, in principle, all the information about a given system, including the case of a simple 2-D square potential or even a hydrogen atom. One can solve the Schrödinger equation exactly in order to get the wave function of the system and the allowed energy states of the system can be determined. Unfortunately, it is impossible to solve the Schrödinger equation for N-body system. Evidently, some approximations are involved to render the problem solvable. Kohn *et al* (1996) defined Density Functional Theory (DFT) as a theory of electronic structure based on the electron density distribution $n(r)$, instead of the many-electron wave function $\Psi(r_1, r_2, r_3, \dots)$. Having been widely used for over 30 years by Scientists working on the electronic structure of solids, surfaces, defects, molecules e.t.c., it has also become popular with theoretical and computational chemists. Hohenberg and Kohn (1964) in their DFT formulation described the Hamiltonian as [7]:

$$H = T + V_{ext}(r) + V_{int}(r) \quad (1)$$

where T is the kinetic energy of the system given by;

$$T = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 \quad (2)$$

and $V_{int}(r)$ is coulomb potential, which is defined by;

$$V_{int}(r) = \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} \quad (3)$$

In the spin-unrestricted form, the Kohn-Sham equation becomes [8]:

$$\left[-\frac{\hbar^2}{2m_e} \nabla^2 + V_H(r) + V_{XC}^\sigma(r) \right] \Psi_i^\sigma = \varepsilon_i^\sigma \Psi_i^\sigma \quad (4)$$

where $-\frac{\hbar^2}{2m_e} \nabla^2$ is the kinetic energy of the system,

$V_H(r) = \frac{\delta E_H}{\delta n(r)}$ as the Hartree potential,

$V_{XC}(r) = \frac{\delta E_{XC}}{\delta n(r)}$ as the exchange correlation potential and

ε_i^σ and Ψ_i^σ are the energy and wave function of the unrestricted state.

Global Quantities

In this study, electron affinity (EA) and ionization potential (IP) are calculated from the energies of frontier orbitals : Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) values as identified by the Koopmans's theorem: $IP = -\varepsilon_{HOMO}$ and $EA = -\varepsilon_{LUMO}$, likewise the Energy Gap is also found from the difference between HOMO and LUMO using the equation given by [9]:

$$E_{gap} = \varepsilon_{LUMO} - \varepsilon_{HOMO} \approx IP - EA \quad (5)$$

Chemical potential (μ), hardness (η), softness (S), electrophilic index (ω) and the electric dipole polarizability (α) are determined from the obtained values of the frontier orbital energies. Within the framework of the density functional theory (DFT), one of the global quantities is chemical potential (μ), which measures the escaping tendency of an electronic cloud, and equals the slope of the energy versus the number of electrons (N) curve at external potential $v(r)$ is given by the expression [10]:

$$\mu = \left[\frac{\partial E}{\partial N} \right]_{v(r)} \quad (6)$$

The approximated form of chemical potential could be expressed as [6]:

$$\mu = -\chi = (\varepsilon_{LUMO} + \varepsilon_{HOMO})/2 \approx -(IP + EA)/2 \quad (7)$$

where χ is the electro- negativity parameter given by;

$$\chi = (IP + EA)/2 \quad (8)$$

The chemical hardness (η) could be expressed in terms of IP and EA as [11]:

$$\eta = (\varepsilon_{LUMO} - \varepsilon_{HOMO})/2 \approx (IP - EA)/2 \quad (9)$$

and the chemical softness is given by

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

Electrophilic index (ω) is defined as[10]:

$$\omega = \frac{\mu^2}{2\eta} \quad (11)$$

For ionic molecules, the HOMO is replaced by SOMO (Singly occupied molecular orbital) for ionic molecules. Also properties like; total dipole moment (μ_{tot}), molecular mean polarizability ($\langle\alpha\rangle$), anisotropy of polarizability ($\Delta\alpha$) and the total first order hyperpolarizability (β_{tot}) are some of the NLO properties. The calculated result of these properties are paramount in determining the NLO properties of a material which remain like a litmus test and qualifies the material for many electronic and photonic applications. A material should have large value of these calculated properties for it to be a good NLO material.

The molecule's dipole moment represents a generalized measure of bond properties and charge densities in a molecule [12]. The total dipole moment of the studied molecule could be calculated from;

$$M_{tot} = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{\frac{1}{2}} \quad (12)$$

Electric dipole polarizability is another vital global property in determining polarizability of a molecule or compound; it is a measure of the linear response of the electron density in the presence of an infinitesimal electric field (F) and represents a second-order variation in energy [10]:

$$\alpha = -\left(\frac{\partial^2 E}{\partial F_a \partial F_b}\right) \quad (13)$$

where a and b are coordinates of x, y and z

The mean polarizability $\langle\alpha\rangle$ is calculated using the equation [13]:

$$\langle\alpha\rangle = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (14)$$

where $\alpha_{xx} \leq \alpha_{yy} \leq \alpha_{zz}$ are termed as the polarizability tensor eigenvalues.

The anisotropy of polarizability could be expressed as;

$$\Delta\alpha = \left[\frac{(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6(\alpha_{xz}^2 + \alpha_{xy}^2 + \alpha_{yz}^2)}{2} \right]^{\frac{1}{2}} \quad (15)$$

First hyperpolarizability (β_{tot}) is a third rank tensor that can be described by a $3 \times 3 \times 3$ matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry [14]. The components of the first hyperpolarizability can be calculated using the following equation.

$$\beta_{tot} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{\frac{1}{2}} \quad (16)$$

where $\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$,

$$\beta_y = \beta_{yyx} + \beta_{yxx} + \beta_{yzz} \text{ and}$$

$$\beta_z = \beta_{zzz} + \beta_{zxx} + \beta_{zyy}$$

Theoretical Methodology

The geometries of the neutral pyrene and its derivatives were fully optimized without any constraint based on the analytical gradient procedure implemented within Gaussian 03W program [15- 18]. All the parameters were fully allowed to relax and each of the calculations converged to an optimized geometry which corresponds to a true energy minimum. Prior to geometry optimization, stability check was performed on the molecule to confirm its stability status. The molecular properties of Pyrene and its derivatives both in neutral and ionic forms (anionic and cationic) were computed with three different standard basis sets; 6-311G, 6-311+G(d) and 6-311++G(d,p). The Lee, Yang and Parr correlation functional with Becke's three parameters (B3LYP) has been adopted in the calculations as exchange correlation functional. All the computations have been carried out using the density functional theory (DFT) implemented in the Gaussian 03 suite program. The molecular properties of Pyrene and its derivatives in neutral form were computed with three different basis sets: 6-311G, 6-311+G(d) and 6-311++G(d,p). The Lee, Yang and Parr correlation functional with Becke's three parameters (B3LYP) was adopted in the calculations as exchange correlation functional. Single point energy calculations for the molecules were performed using the optimized geometry to obtain parameters such as HOMO, SOMO, LUMO, total energy and ionization potential. Chemical hardness, chemical softness, electronegativity and electrophilic index were obtained from values of HOMO, LUMO and SOMO. Similarly, computations of ionic form (anionic and cationic) of the molecules were performed using the same procedure but changing the charge status from neutral molecule 0 to -1 for anionic and +1 for cationic molecule. The nonlinear optical properties of the molecules such as dipole moment, isotropic isotropic polarizability, anisotropic polarizability and total first order polarizability were also computed by using similar procedure.

Results and Discussion

Optimized Parameters

Tables 1 and 2 show some structural parameters such as bond length and bond angle calculated at DFT/B3LYP level of theory with the three basis sets under study. The distance between the nuclei of two atoms bonded together is termed as bond length while bond angle is the angle between two adjacent bonds at an atom in a molecule. A molecule with a short bond distances and small bond angles that exist between its substituent atoms is expected to be stronger than the one with long bond distance and a large

bond angle. Considering the values of bond lengths and angles in neutral and ionic forms, it can be observed that the three forms of molecules displayed almost the same character across the studied basis sets except a little change in behavior that exist at carbon-chlorine bond in the derivatives of both neutral and ionic forms. Robert *et al* [16] opined that the C-H and C-C bond length is between 106-112 pm and 120-154 pm respectively, while the C-Cl bond length is 176 pm (1.7600 Å). This increase in bond length makes Pyrene derivatives less strong than the parent molecule. Moreover, basis set specification and charging the molecule has no significant influence in changing the structural parameters. The calculated results of the optimized parameters were reasonable and in conformity with the available experimental value obtained by X-ray crystal diffraction [17] and previous literatures.

Table 1: Selected Bond Length of Pyrene and its derivatives for neutral and charged molecules

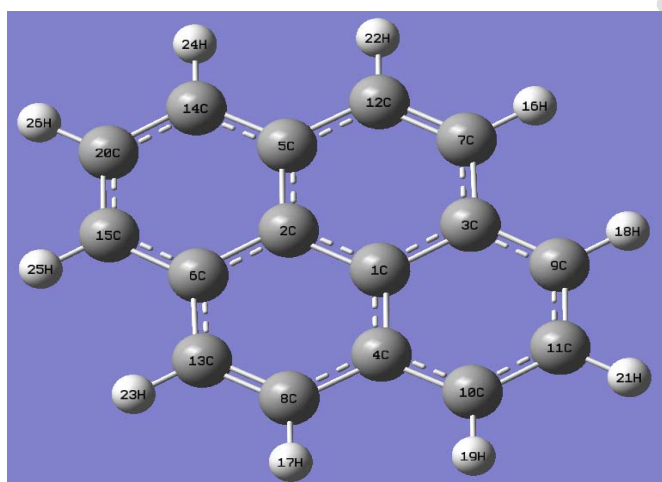
NEUTRAL			
Bond Length (Å)	B3LYP		Experimental Value
	6-311G	6-311+G(d)	
Pyrene			
R(3,7)	1.4395	1.4363	-
R(1,2)	1.4284	1.4254	1.3950 [17]
R(20,26)	1.0820	1.0854	-
1-chloropyrene			
R(10,16)	1.4390	1.4351	-
R(5,9)	1.4298	1.4269	-
R(C-Cl)	1.8370	1.7611	1.7600 [16]
2-chloropyrene			
R(5,10)	1.4400	1.4368	-
R(2,3)	1.3869	1.3891	-
R(C-Cl)	1.8335	1.7602	1.7600 [16]
ANIONIC			
Bond Length (Å)	B3LYP		Experimental Value
	6-311G	6-311+G(d)	
Pyrene			
R(1,3)	1.4411	1.4372	NA
R(1,2)	1.4356	1.4331	NA
R(12,16)	1.3941	1.3912	NA
1-chloropyrene			
R(2,4)	1.4476	1.4423	NA
R(2,3)	1.4360	1.4337	NA
R(C-Cl)	1.8730	1.7854	NA
2-chloropyrene			
R(3,6)	1.4405	1.4368	NA
R(2,3)	1.4342	1.4315	NA

R(C-Cl)	1.8770	1.7914	NA
CATIONIC			
Bond Length (Å)	B3LYP		Experimental Value
	6-311G	6-311+G(d)	
Pyrene			
R(1,3)	1.4273	1.4231	NA
R(1,2)	1.4187	1.4150	NA
R(12,16)	1.3937	1.3905	NA
1-chloropyrene			
R(2,4)	1.4317	1.4269	NA
R(2,3)	1.4208	1.4172	NA
R(C-Cl)	1.7939	1.7241	NA
2-chloropyrene			
R(3,6)	1.4271	1.4229	NA
R(2,3)	1.4176	1.4138	NA
R(C-Cl)	1.8041	1.7374	NA

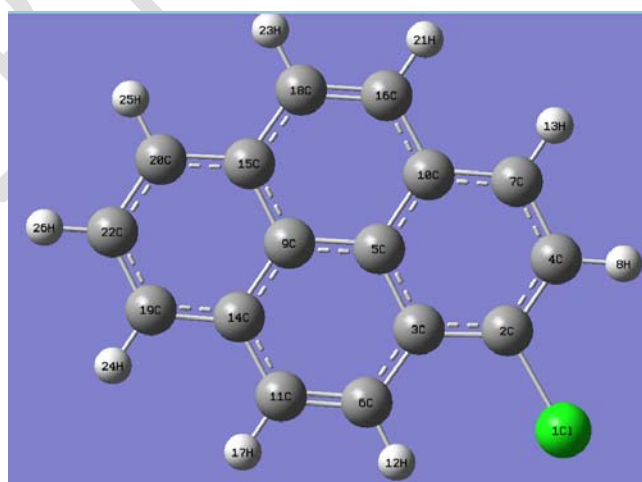
Table 2: Selected Bond Angles of Pyrene and its derivatives for neutral and charged molecules

NEUTRAL		
Bond Angle (°)	B3LYP	
	6-311G	6-311+G(d)
Pyrene		
A(2,1,3)	120.0856	120.0810
A(3,7,12)	121.4253	121.4041
A(7,3,9)	122.5086	122.4666
1-chloropyrene		
A(3,2,4)	123.0838	122.0177
A(2,3,6)	124.4071	123.9425
A(Cl,2,3)	119.9512	120.3988
2-chloropyrene		
A(3,5,10)	122.0358	122.0602
A(3,2,4)	123.0726	121.9989
A(Cl,2,3)	118.4637	119.0005
ANIONIC		
Bond Angle (°)	B3LYP	
	6-311G	6-311+G(d)
Pyrene		
A(7,3,11)	122.9308	122.9127
A(3,7,8)	121.6907	121.7158
A(2,1,3)	120.0392	120.0502
1-chloropyrene		
A(8,4,12)	125.3014	124.6887
A(4,12,16)	123.9334	122.6101
A(Cl,12,4)	119.1473	119.6331

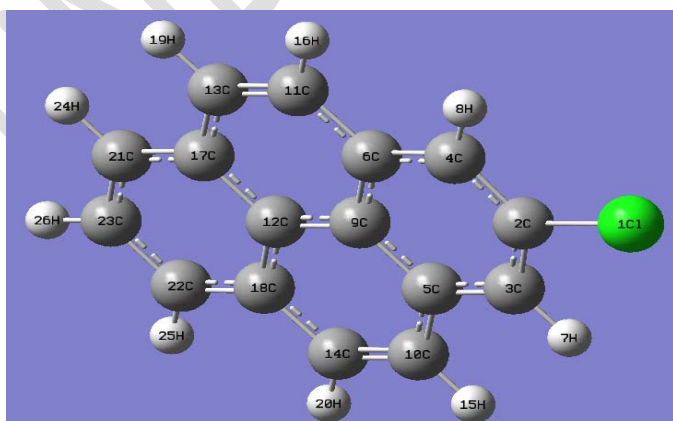
2-chloropyrene		
A(12,16,13)	125.4150	124.0790
A(10,6,14)	122.9066	122.9220
A(Cl,16,12)	117.2925	117.9605
CATIONIC		
Bond Angle (°)	B3LYP	
	6-311G	6-311+G(d)
Pyrene		
A(7,3,11)	122.0918	122.0491
A(3,7,8)	120.9716	120.9367
A(2,1,3)	120.0133	120.0176
1-chloropyrene		
A(8,4,12)	123.7202	123.3664
A(4,12,16)	122.3444	121.5860
A(Cl,12,4)	120.1186	120.4736
2-chloropyrene		
A(10,6,14)	122.1040	122.0833
A(9,5,13)	121.7765	121.7261
A(Cl,16,12)	119.2040	119.6887



(a) Pyrene



(b) 1-chloropyrene



(c) 2-chloropyrene

Fig 1: Optimized Molecular Structure of Pyrene and it Derivatives

Frontier Orbitals Energies

In Table 3, the energies of frontier orbitals : the Highest Occupied Molecular Orbital/Singly occupied molecular orbital (HOMO/SOMO) which correspond to neutral/ionic molecules, the Lowest Unoccupied Molecular Orbital (LUMO) and the energy gap (HOMO-LUMO) are presented. From Table 3, the E_{HOMO} increases in the order of Pyrene > 1-chloropyrene > 2-chloropyrene. Likewise, the E_{LUMO} manifest the same behavior. Charging molecules were observed to decrease the $SUMO-LUMO$ energy gaps of the molecules especially the case of anionic 2-chloropyrene with a basis set of 6-311+G(d) which possesses the lowest energy gap of 0.0775eV. This value is comparatively very small when compared with the $HOMO-LUMO$ energy gap of the neutral 2-chloropyrene. This property will enhance the conductivity of the molecule, making them to become more reactive and good for designing electronic component and other photonic applications. In all the cases, neutral 2-chloropyrene at 6-311G basis set was considered to be the most stable compound due to its largest energy gap of 3.8732eV. It can also be seen that addition of chlorine atom into the neutral molecule is less significant in changing the energy gap.

Positioning of the chlorine atom in the parent molecule and the type of basis set used were seen to be significant in changing the energy gap.

Table 3: HOMO/LUMO for neutral and SOMO/LUMO for charged molecules and the Energy Gap in Pyrene and its Derivatives

NEUTRAL				
Molecules	Basis Set	E_{HOMO} (eV)	E_{LUMO} (eV)	Gap(eV)
Pyrene	6-311G	-5.5968	-1.7276	3.8691
	6-311+G(d)	-5.6501	-1.8318	3.8183
1-chloropyrene	6-311G	-5.8305	-2.0163	3.8142
	6-311+G(d)	-5.7788	-2.0487	3.7301
2-chloropyrene	6-311G	-5.9236	-2.0504	3.8732
	6-311+G(d)	-5.8958	-2.0743	3.8215
ANIONIC				
Molecules	Basis Set	E_{SOMO} (eV)	E_{LUMO} (eV)	Gap(eV)
Pyrene	6-311G	1.1649	3.3804	2.2155
	6-311+G(d)	0.9429	2.8455	1.9026
1-chloropyrene	6-311G	0.7894	2.9712	2.1818
	6-311+G(d)	0.6631	2.7426	2.0795
2-chloropyrene	6-311G	0.7380	2.9968	2.2588
	6-311+G(d)	0.6253	2.7328	0.0775
CATIONIC				
Molecules	Basis Set	E_{SOMO} (eV)	E_{LUMO} (eV)	Gap(eV)
	6-311G	-10.0999	-6.4539	3.6460

Pyrene	6-311+G(d)	-10.1026	-6.4708	3.6319
1-chloropyrene	6-311G	-10.1366	-6.5962	3.5404
	6-311+G(d)	-10.0387	-6.5437	3.4950
2-chloropyrene	6-311G	-10.3380	-6.6819	3.6561
	6-311+G(d)	-10.2703	-6.6291	3.6411

Total Ground State Energy

Table 4 presents the total energy of the parent molecule and its derivatives in both neutral and ionic forms. It is clearly shown that the neutral and charged parent molecule have nearly the same total energy across the basis sets. The same behavior is observed in Pyrene derivatives (1-chloropyrene and 2-chloropyrene). So, basis set specification and charging the molecule play insignificant role in determining total energy, but addition of chlorine in place of hydrogen atom to the molecule is most significant. 6-311+G(d,p) basis set always produces slightly lower values than the others. Therefore, Pyrene derivatives are expected to be more stable with 6-311+G(d,p) due to their lower energy compared to the parent molecule. Cationic molecule of Pyrene has the highest energy of -615.494594251a.u at 6-311G, anionic molecule of 2-Chloropyrene happened to have the lowest energy with -1075.54945482a.u at 6-311+G(d). Addition of chlorine to the molecule makes it to be more stable by reducing the total energy of the molecule. Total energy values of 1-chloropyrene and 2-chloropyrene in neutral and ionic form shows uniformity, hence total energy is independent of placing chlorine at the first or second position of the pyrene ring.

Table 4: Total Ground State Energy (a.u) of Pyrene and its derivatives

PYRENE		
Molecule	6-311G	6-311+G(d)
Neutral	-615.755504142	-615.898788925
Anionic	-615.765691368	-615.914673975
Cationic	-615.494594251	-615.636958804
1-CHLOROPYRENE		
Molecule	6-311G	6-311+G(d)
Neutral	-1075.35957037	-1075.52200972
Anionic	-1075.38203813	-1075.54717915
Cationic	-1075.09247901	-1075.25773134
2-CHLOROPYRENE		
Molecule	6-311G	6-311+G(d)
Neutral	-1075.36056205	-1075.52303595

Anionic	-1075.38458979	-1075.54945482
Cationic	-1075.08940159	-1075.25381262

Ionization Potentials and Electron Affinities

The EA and IP for the ionic molecules are determined respectively from $EA = E_{(\text{optimized neutral})} - E_{(\text{optimized anion})}$ and $IP = E_{(\text{optimized cation})} - E_{(\text{optimized neutral})}$ where E_s are values of total energy [18]. In this case the total energy are shown in Table 4. Ionization Potentials (IP), Electron Affinities (EA) of Pyrene and its derivatives in two forms (neutral and ionic) are presented in Table 5. The higher the IP, the more difficult it is to remove an electron to form an ion. Consequently, the lower the electron affinity, the less easy it is to add electron. It is clear that ionic form of 2-Chloropyrene molecule has the largest value of ionization potential of 7.401 eV with 6-311G basis set, so the molecule requires high energy before it can donate an electron. However for electron affinity which is the strength of the acceptor molecule to accept electron, the neutral molecule of 2-Chloropyrene has 5.92 eV. as the highest value with the same basis set. Large value of EA compared to the IP in anionic molecule implies the molecule's greater chance and ability to be easily ionized or accommodate more electrons. High reactivity in anionic makes it least stable, and the stability of the molecules is in the order of Neutral > ionic. Addition of chlorine and basis set specification has little role to play in changing the ionization potential and electron affinity of Pyrene and its derivatives. The results revealed that ionic molecules have taken the major noticeable changes in IP and EA that occur among the molecules studied.

Table 5: Ionization Potential (IP) and Electron Affinity (EA) of Pyrene and its derivatives for neutral and charged molecules

Molecules	Basis sets	NEUTRAL		IONIC	
		IP(eV)	EA(eV)	IP(eV)	EA(eV)
Pyrene	6-311G	5.60	1.73	7.102	0.272
	6-311+G(d)	5.65	1.83	7.129	0.435
1-Chloropyrene	6-311G	5.83	2.02	7.293	0.599
	6-311+G(d)	5.78	2.05	7.184	0.680
2-Chloropyrene	6-311G	5.92	2.05	7.401	0.653
	6-311+G(d)	5.90	2.07	7.320	0.707

Global Chemical Indices

Chemical reactivity indices of Pyrene and its derivatives in neutral and ionic forms are presented in Table 6. The HOMO-LUMO for neutral and SOMO-LUMO in the case of ionic compounds are used to determine several chemical reactivity parameters as a measure of relative stability and reactivity. These include chemical hardness (η), electronic chemical potentials (μ) and electrophilicity (ω). Chemical hardness is linked to the stability and reactivity of a chemical system. According to the frontier molecular

orbital approach, chemical hardness is directly proportional to the energy gap between the HOMO and the LUMO. The larger the HOMO-LUMO energy gap, the harder and more stable (less reactive) the compound [19]. Considering Table 6, neutral form of 2-Chloropyrene is the most stable with the highest chemical hardness of 1.94eV followed by its cationic form (1.83eV), and then its anionic form (1.13eV). The negative of electro-negativity is termed as electrochemical potential, lower value of this global quantity indicates the stability of a compound or molecule. Table 6 shows that the anionic molecules have lower electrochemical potential than others with cationic molecules having the highest. The neutral and cationic molecules display some similarities in electronic softness while anionic has shown slightly higher values which characterized the molecule as the softest (electronically) and reactive due to small energy gap. Electrophilicity (ω) measures the capacity of a species to accept electrons and therefore measures the stabilization in energy after a system accepts additional electronic charge [2]. The parent pyrene has stronger nucleophiles due to its lower ω while 2-Chloropyrene has the strongest electrophiles due to its higher ω . Generally, addition of chlorine and basis set specification has little impact in describing the chemical reactivity of the molecules.

Table 6: Global quantities of Pyrene and its derivatives for neutral and charged molecules

NEUTRAL				
Property	Basis sets	Pyrene	1-Chloropyrene	2-Chloropyrene
μ (eV)	6-311G	3.66	3.92	3.99
	6-311+G(d)	3.74	3.91	3.99
η (eV)	6-311G	1.93	1.91	1.94
	6-311+G(d)	1.91	1.87	1.91
S (eV)	6-311G	0.52	0.52	0.52
	6-311+G(d)	0.52	0.54	0.52
ω (eV)	6-311G	3.47	4.03	4.10
	6-311+G(d)	3.67	4.11	4.16
ANIONIC				
Property	Basis sets	Pyrene	1-Chloropyrene	2-Chloropyrene
μ (eV)	6-311G	-2.27	-1.88	-1.87
	6-311+G(d)	-1.89	-1.70	-1.68
η (eV)	6-311G	1.11	1.09	1.13
	6-311+G(d)	0.95	1.04	1.05

S (eV)	6-311G	0.90	0.92	0.89
	6-311+G(d)	1.05	0.96	0.95
CATIONIC				
Property	Basis sets	Pyrene	1-Chloropyrene	2-Chloropyrene
μ (eV)	6-311G	8.28	8.37	8.51
	6-311+G(d)	8.29	8.29	8.45
η (eV)	6-311G	1.82	1.77	1.83
	6-311+G(d)	1.82	1.75	1.82
S (eV)	6-311G	0.55	0.56	0.55
	6-311+G(d)	0.55	0.57	0.55

Electrodonating Power(ω^-) , Electroaccepting Power (ω^+) and Net electrophilicity ($\Delta\omega^\pm$)

The Electrodonating Power(ω^-) , Electroaccepting Power (ω^+) and Net electrophilicity ($\Delta\omega^\pm$) have been calculated from the equations [20] and presented in Table 8.

$$\omega^- = \frac{(3I+A)^2}{16(I-A)}, \quad \omega^+ = \frac{(I+3A)^2}{16(I-A)} \quad \text{and} \quad \Delta\omega^\pm = \omega^+ + \omega^-$$

It follows that a larger ω^+ value corresponds to a better capability of accepting charge, whereas a smaller value of ω^- value of a system makes it a better electron donor. From Table 7, it can be seen that 2-Chloropyrene has a better capability of accepting when compare with other molecules particularly with basis set 6-311+G(d) with the highest value of ω^+ as 0.842eV. However the parent pyrene proved to be a better electron donor with ω^- value as 3.935 eV on the basis set 6-311+G(d).

Table 7: Electrodonating Power(ω^-) , Electroaccepting Power (ω^+) and Net electrophilicity ($\Delta\omega^\pm$)

Molecule	Basis set	ω^- (eV)	ω^+ (eV)	$\Delta\omega^\pm$ (eV)
Pyrene	6-311G	4.261	0.574	4.835
	6-311+G(d)	3.935	0.664	4.599
1-Chloropyrene	6-311G	4.717	0.771	5.488
	6-311+G(d)	4.750	0.818	5.568
2-Chloropyrene	6-311G	4.838	0.811	5.649
	6-311+G(d)	4.856	0.842	5.698

Non-Linear Optical Properties

The Non-linear Optical (NLO) Properties such as dipole moment, polarizability (isotropic and anisotropy) and first hyperpolarizability for the studied molecules in neutral and ionic forms are shown in Table 7. These properties of a material are important in determining its potentials in electronic and photonic applications. Organic materials that exhibit large NLO properties have emerged as an important class of electronic materials with interesting characteristics. Experimentally, NLO of materials could be improved through the appropriate addition of some chemical substituent that is, chlorine as in the case of this study. From Table 8, it can be seen from the neutral and charged molecules, the dipole moment and the first order hyperpolarizability of the parent molecule **have been** completely diminished (equals to zero). This is as a result of equal distribution of charges in the entire molecule that made them to cancel themselves, thereby producing no net charge (non-polar). It can also be observed from Table 7 that, basis set specification has not shown prominent impact on the NLO properties. Significant variations of NLO properties among the studied molecules exist as a result of charge status, addition and placing of chlorine at the first or second positions in the pyrene ring. Such remarkable variations in NLO properties have even multiply others several times as in the case of dipole moment of cationic 2- Chloropyrene at 6-311G which has the highest dipole moment of 5.5369 (D). This value is 43% greater than 3.1670 (D) which was the highest in neutral molecule and 5 times that of the anionic molecule. For isotropic polarizability; anionic 2-chloropyrene has the largest value (128.097a.u). This amount was 20% more than the highest value in neutral molecule and 61% greater, when compared with the highest value in cationic molecule. Looking at the anisotropic polarizability; the cationic value is 57% and 18% greater than the neutral and anionic counterparts. The highest difference was realized in hyperpolarizability values when the largest hyperpolarizability of a cationic molecule was 75% more than the largest value in anionic molecule. 6-311G basis set lifted and yielded good values of NLO properties than the other studied basis set. Moreover, placing chlorine in the second position is seen to favour and improve the NLO behavior of a chlorinated pyrene than in the first position apart from incorporation of the substituent into the ring.

Table 8: Calculated Total Dipole Moment, μ_{tot} , (D), Average Isotropic Polarizability, $\langle\alpha\rangle$, (a. u), Anisotropic Polarizability, $\Delta\alpha$, (a. u) and total first order hyperpolarizability (β_{tot}) (a.u) values for neutral and charged molecules.

NEUTRAL					
Molecule	Basis Sets	μ_{tot}	$\langle\alpha\rangle$	$\langle\Delta\alpha\rangle$	β_{tot}

Pyrene	6-311G	0.0000	87.1276	19.3797	0.0000
	6-311+G(d)	0.0000	87.2545	19.4415	0.0000
1-chloropyrene	6-311G	2.7386	101.4918	20.2184	44.7076
	6-311+G(d)	1.9932	100.5794	19.0132	21.0574
2-chloropyrene	6-311G	3.1670	103.0233	19.7841	75.5078
	6-311+G(d)	2.3533	101.7501	18.2499	42.9313
ANIONIC					
Molecule	Basis Sets	μ_{tot}	$\langle\alpha\rangle$	$\langle\Delta\alpha\rangle$	β_{tot}
Pyrene	6-311G	0.0000	109.5370	13.4657	0.0000
	6-311+G(d)	0.0000	111.0865	14.4335	0.0000
1-chloropyrene	6-311G	1.0830	125.8812	27.3322	14.4933
	6-311+G(d)	0.5761	126.2267	24.6387	32.1218
2-chloropyrene	6-311G	1.1296	128.097	38.4421	27.5152
	6-311+G(d)	0.1641	127.9144	34.4025	15.0463
CATIONIC					
Molecule	Basis Sets	μ_{tot}	$\langle\alpha\rangle$	$\langle\Delta\alpha\rangle$	β_{tot}
Pyrene	6-311G	0.0000	65.6506	46.1558	0.0000
	6-311+G(d)	0.0000	65.1303	46.1609	0.0000
1-chloropyrene	6-311G	4.0551	65.1303	46.1353	76.8279
	6-311+G(d)	3.2323	76.1880	46.8593	53.9581
2-chloropyrene	6-311G	5.5369	78.9441	42.9993	128.8808
	6-311+G(d)	4.7514	77.1770	44.6762	99.7249

Conclusion

The DFT/B3LYP level of theory **has been** used to study the effects of chlorination and charging pyrene molecule on its molecular and non-linear optical properties using different basis sets. The effects covered neutral, ionic and cationic forms of the molecules. The results agreed with reported works and show increasing stability of the molecule. It **has been** found that, charging and basis set specification has insignificant impact on the optimized parameters. Little change in behavior exists at carbon- chlorine bond in the derivatives of both neutral and ionic forms due to the addition of chlorine to the molecule, the result agreed with the experimental values. Making the molecules ionic improve the conductivity of the

molecules by reducing its SOMO-LUMO energy gap and make them to possess good values of chemical reactivity descriptors. Addition of chlorine to the molecule makes it more stable by lowering the total energy of the molecule especially for anionic form of 2-chloropyrene at 6-311+G (d) having -1075.54945482 a.u which is the lowest energy. Cationic of 2-chloropyrene has the largest NLO property. The relative stability and reactivity is in the order of 2-chloropyrene > 1-chloropyrene > pyrene. To be more precise, addition of chlorine and making the molecules ionic greatly improved its chance of becoming a potential candidate for organic electronics.

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