

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 were investigated based on Density Functional Theory (DFT) using Becke's three and Lee Yang Parr (B3LYP) functional with basis sets 6-311G, 6-311+G (d) and 6-311++G (d,p). 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 were 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 3.64110eV and 0.07745eV respectively compared to the neutral form which has 3.82151eV 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 128.8808a.u compared to 75.5078a.u of the neutral form while anionic molecule has 27.5152a.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. Monochlorinated 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 was 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 were 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 was analyzed [5]. It was 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. Also in a work conducted by [6] a study on 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 69.181 a.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 were investigated based on DFT using different basis sets. The effects covered

66 neutral, ionic and cationic forms of the molecules. The results agreed with reported works and show
67 increasing stability of the molecule.
68

69 **Theoretical Background**

70 **Density Functional Theory**

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

$$81 \quad H = T + V_{ext}(r) + V_{int}(r) \quad (1)$$

82
83 where T is the kinetic energy of the system given by;
84

$$85 \quad T = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 \quad (2)$$

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

$$87 \quad V_{int}(r) = \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} \quad (3)$$

88 In the spin-unrestricted form, the Kohn-Sham equation becomes [8]:
89

$$90 \quad \left[-\frac{\hbar^2}{2m_e} \nabla^2 + V_H(r) + V_{XC}^\sigma(r) \right] \Psi_i^\sigma = \epsilon_i^\sigma \Psi_i^\sigma \quad (4)$$

91 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: $IP = \epsilon_{HOMO}$ and $EA = -\epsilon_{LUMO}$, likewise the Energy Gap is also found from the difference between HOMO and LUMO using the equation given by [9]:

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

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]:

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

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]:

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

and the chemical softness is given by

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

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

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

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 3×3×3 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 $\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$,
 $\beta_y = \beta_{yyy} + \beta_{yxx} + \beta_{yzz}$ 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]. 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) was adopted in the calculations as exchange correlation functional. All the computations were 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, LUMO, total energy and ionization potential. 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 were also computed for using the same method above.

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. Addition of chlorine has insignificant impact on the bond angles but shows approximately uniform increase in bond lengths at C-Cl bonds of the chlorinated Pyrene molecules across the 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 (1.76 Å). This increase in bond length makes Pyrene derivatives less stronger 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 in neutral and charged state

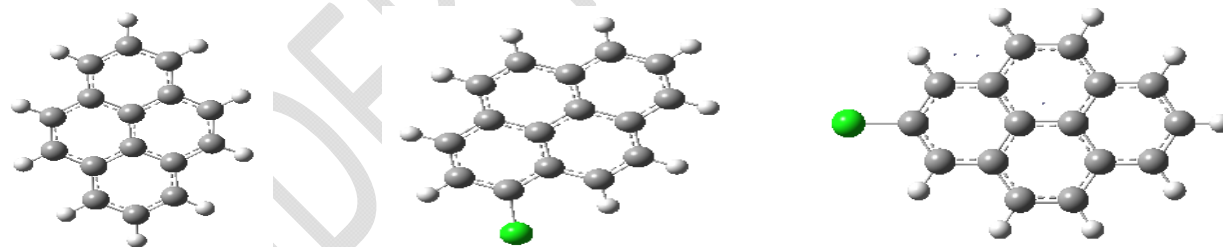
NEUTRAL				
Bond Length (Å)	B3LYP			Experimental Value [17]
	6-311G	6-311+G(d)	6-311++G(d,p)	
Pyrene				
R(3,7)	1.4395	1.4363	1.4365	-
R(1,2)	1.4284	1.4254	1.4252	1.3950
R(20,26)	1.0820	1.0854	1.0843	-
1-chloropyrene				
R(10,16)	1.4390	1.4351	1.4352	-
R(5,9)	1.4298	1.4269	1.4268	-
R(C-Cl)	1.8370	1.7611	1.7610	1.7600
2-chloropyrene				
R(5,10)	1.4400	1.4368	1.4369	-
R(2,3)	1.3869	1.3891	1.3890	-
R(C-Cl)	1.8335	1.7602	1.7604	1.7600
ANIONIC				
Bond Length	B3LYP			Experimental Value [17]
	6-311G	6-311+G(d)	6-311++G(d,p)	
Pyrene				
R(1,3)	1.4411	1.4372	-	-
R(1,2)	1.4356	1.4331	-	-
R(12,16)	1.3941	1.3912	-	-
1-chloropyrene-				
R(2,4)	1.4476	1.4423	-	-
R(2,3)	1.4360	1.4337	-	-
R(C-Cl)	1.8730	1.7854	-	1.7600

2-chloropyrene-				
R(3,6)	1.4405	1.4368	-	-
R(2,3)	1.4342	1.4315	-	-
R(C-Cl)	1.8770	1.7914	-	1.7600
CATIONIC				
Bond Length (Å)	B3LYP			Experimental Value [17]
	6-311G	6-311+G(d)	6-311++G(d,p)	
Pyrene				
R(1,3)	1.4273	1.4231	-	-
R(1,2)	1.4187	1.4150	-	-
R(12,16)	1.3937	1.3905	-	-
1-chloropyrene				
R(2,4)	1.4317	1.4269	-	-
R(2,3)	1.4208	1.4172	-	-
R(C-Cl)	1.7939	1.7241	-	1.7600
2-chloropyrene				
R(3,6)	1.4271	1.4229	-	-
R(2,3)	1.4176	1.4138	-	-
R(C-Cl)	1.8041	1.7374	-	1.7600

189 **Table 2:** Selected Bond Angles of Pyrene and its derivatives in neutral and charged state

NEUTRAL			
Bond Angle (°)	B3LYP		
	6-311G	6-311+G(d)	6-311++G(d,p)
Pyrene			
A(2,1,3)	120.0856	120.081	120.0776
A(3,7,12)	121.4253	121.4041	121.3908
A(7,3,9)	122.5086	122.4666	122.447
1-chloropyrene			
A(3,2,4)	123.0838	122.0177	122.038
A(2,3,6)	124.4071	123.9425	123.9187
A(Cl,2,3)	119.9512	120.3988	120.3197
2-chloropyrene			
A(3,5,10)	122.0358	122.0602	122.0345
A(3,2,4)	123.0726	121.9989	122.0539
A(Cl,2,3)	118.4637	119.0005	118.973
ANIONIC			
Bond Angle (°)	B3LYP		
	6-311G	6-311+G(d)	6-311++G(d,p)
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)	125.415	124.079	-
A(10,6,14)	122.9066	122.922	-
A(Cl,16,12)	117.2925	117.9605	-
CATIONIC			
Bond Angle (°)	B3LYP		
	6-311G	6-311+G(d)	6-311++G(d,p)
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	121.586	-
A(Cl,12,4)	120.1186	120.4736	-
2-chloropyrene			
A(10,6,14)	122.104	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 2: Optimized Molecular Structure of Pyrene and it Derivatives

Frontier Orbitals Energies

In Table 3, the energies of frontier orbitals: the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) and the energy gap (HOMO-LUMO) are reported. From Table 3, the E_{HOMO} increases in the order of Pyrene > 1-chloropyrene > 2-chloropyrene. Likewise, the

198 E_{LUMO} manifest the same behavior. Charging molecules were observed to decrease the HOMO-LUMO
 199 energy gaps of the molecules especially the case of anionic 2-chloropyrene with a basis set of 6-311+G(d)
 200 which possesses the lowest energy gap of 0.07745eV. This value is comparatively very small when
 201 compared with that of the neutral 2-chloropyrene. This property will enhance the conductivity of the
 202 molecule, making them to become more reactive and good for designing electronic component and other
 203 photonic applications. In all the cases, neutral 2-chloropyrene at 6-311G basis set was considered to be the
 204 most stable compound due to its largest energy gap of 3.87321eV. It can also be seen that addition of
 205 chlorine atom into the neutral molecule is less significant in changing the energy gap.
 206 Positioning of the chlorine atom in the parent molecule and the type of basis set used were seen to be
 207 significant in changing the energy gap.

208 **Table 3:** HOMO/LUMO and the Energy Gap in Pyrene and its Derivative for neutral, anionic and
 209 cationic forms

NEUTRAL				
Molecules	Basis Set	E_{HOMO} (eV)	E_{LUMO} (eV)	Gap(eV)
Pyrene	6-311G	-5.59676	-1.72763	3.86913
	6-311+G(d)	-5.65009	-1.83184	3.81825
	6-311++G(d, p)	-5.67104	-1.86096	3.81008
1-chloropyrene	6-311G	-5.83050	-2.01634	3.81417
	6-311+G(d)	-5.77880	-2.04872	3.73008
	6-311++G(d, p)	-5.79540	-2.07239	3.72301
2-chloropyrene	6-311G	-5.92356	-2.05035	3.87321
	6-311+G(d)	-5.89581	-2.07429	3.82151
	6-311++G(d, p)	-5.91486	-2.10069	3.81417
ANIONIC				
Molecules	Basis Set	E_{HOMO} (eV)	E_{LUMO} (eV)	Gap(eV)
Pyrene	6-311G	1.16490	3.38042	2.21552
	6-311+G(d)	0.94286	2.84545	1.90259
	6-311++G(d, p)	-	-	-
1-chloropyrene	6-311G	0.78939	2.97117	2.18178
	6-311+G(d)	0.66313	2.74260	2.07946
	6-311++G(d, p)	-	-	-
2-chloropyrene	6-311G	0.73796	2.99675	2.25879
	6-311+G(d)	0.62531	2.73280	0.07745
	6-311++G(d, p)	-	-	-
CATIONIC				
Molecules	Basis Set	E_{HOMO} (eV)	E_{LUMO} (eV)	Gap(eV)
Pyrene	6-311G	-10.09991	-6.45390	3.64600
	6-311+G(d)	-10.10263	-6.47078	3.63185
	6-311++G(d, p)	-	-	-
1-chloropyrene	6-311G	-10.13664	-6.59622	3.54042
	6-311+G(d)	-10.03868	-6.54370	3.49498
	6-311++G(d, p)	-	-	-

2-chloropyrene	6-311G	-10.33800	-6.68193	3.65607
	6-311+G(d)	-10.27025	-6.62914	3.64110
	6-311++G(d, p)	-	-	-

210

211 Molecular Total Ground State Energies

212 Table 4 presents the total energy of the parent molecule and its derivatives in both neutral and ionic
 213 forms. It is clearly shown that the neutral and charged parent molecule have nearly the same total energy
 214 across the basis sets. The same behavior is observed in Pyrene derivatives (1-chloropyrene and 2-
 215 chloropyrene). So, basis set specification and charging the molecule play insignificant role in determining
 216 total energy, but addition of chlorine in place of hydrogen atom to the molecule is most significant. 6-
 217 311++G(d,p) basis set always produces slightly lower values than the others. Therefore, Pyrene
 218 derivatives are expected to be more stable with 6-311++G(d,p) due to their lower energy compared to the
 219 parent molecule. Cationic molecule of Pyrene has the highest energy of -615.490496746a.u at 6-311G,
 220 anionic molecule of 2-Chloropyrene happened to have the lowest energy with -1075.5495482a.u at 6-
 221 311+G(d). Addition of chlorine to the molecule makes it to be more stable by reducing the total energy of
 222 the molecule. Total energy values of 1-chloropyrene and 2-chloropyrene in neutral and ionic form shows
 223 uniformity, hence total energy is independent of placing chlorine at the first or second position of the
 224 pyrene ring.

225

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

PYRENE			
Neutral Molecule	Energy (a.u) at different Basis sets		
	6-311G	6-311+G(d)	6-311++G(d,p)
1	-615.747941570	-615.892329341	-615.909683787
2	-615.755031580	-615.898329236	-615.915653268
3	-615.755481334	-615.898769137	-615.916107205
4	-615.755504142	-615.898788925	-615.916127046
Anionic Molecule			
1	-615.758106894	-615.908812476	-
2	-615.765488063	-615.914490773	-
3	-615.765684900	-615.914669559	-
4	-615.765691368	-615.914673975	-
5	-615.765691368	-615.914673975	-
Cationic Molecule			
1	-615.490496746	-615.634115674	-

2	-615.494479526	-615.636856831	-
3	-615.494589072	-615.636955049	-
4	-615.494594251	-615.636958804	-
5	-615.494594251	-615.636958804	-
1-CHLOROPYRENE			
Neutral Molecule	Basis sets		
	6-311G	6-311+G(d)	6-311++G(d,p)
1	-1075.34775935	-1075.51468966	-1075.53037946
2	-1075.35837796	-1075.52144327	-1075.53719069
3	-1075.35948905	-1075.52198503	-1075.53775137
4	-1075.35957037	-1075.52200972	-1075.53777759
5	-1075.35957880	-	-
Anionic Molecule			
1	-1075.36775253	-1075.53953198	-
2	-1075.38055038	-1075.54671893	-
3	-1075.38182248	-1075.54713930	-
4	-1075.38201317	-1075.54717340	-
5	-1075.38203671	-1075.54717915	-
6	-1075.38203813	-1075.54717915	-
7	-1075.38203813	-	-
Cationic Molecule			
1	-1075.08603092	-1075.25368449	-
2	-1075.09212972	-1075.25755428	-
3	-1075.09245198	-1075.25772626	-
4	-1075.09247679	-1075.25773134	-
5	-1075.09247901	-1075.25773134	-
6	-1075.09247901	-	-
7	-	-	-
2-CHLOROPYRENE			
Neutral Molecule	Basis sets		
	6-311G	6-311+G(d)	6-311++G(d,p)
1	-1075.34872067	-1075.51620228	-1075.53189281
2	-1075.35929003	-1075.52244516	-1075.53820736
3	-1075.36048999	-1075.52301245	-1075.53879152
4	-1075.36056205	-1075.52303595	-1075.53881701
5	-1075.36056924	-	-
Anionic Molecule			
1	-1075.36981320	-1075.54200997	-
2	-1075.38248554	-1075.54876411	-
3	-1075.38430251	-1075.54936888	-
4	-1075.38456872	-1075.54944818	-
5	-1075.38458979	-1075.54945482	-
6	-1075.38458979	-1075.54945482	-
Cationic Molecule			

1	-1075.08288709	-1075.25108148	-
2	-1075.08891659	-1075.25373924	-
3	-1075.08935673	-1075.25380533	-
4	-1075.08940159	-1075.25381262	-
5	-1075.08940159	-1075.25381262	-

227

228 Ionization Potentials and Electron Affinities

229 Ionization Potentials (IP), Electron Affinities (EA) of Pyrene and its derivatives in two forms (neutral and
 230 ionic) were presented in Table 5. The higher the IP, the more difficult it is to remove an electron to form
 231 cation. Consequently, the lower the electron affinity, the less easy it is to add electron. It is clear that
 232 cationic 2-Chloropyrene molecule has the largest value of ionization potential of 10.34eV with 6-311G
 233 basis set, so the molecule requires high energy before it can donate an electron. The same behavior is
 234 observed with electron affinity which is the strength of the acceptor molecule to accept electron. It has
 235 6.68eV as the highest value with the same basis set. Large value of EA compared to the IP in anionic
 236 molecule implies the molecule's greater chance and ability to be easily ionized or accommodate more
 237 electrons. High reactivity in anionic makes it least stable, and the stability of the molecules is in the order
 238 of Neutral > Cationic > Anionic. Addition of chlorine and basis set specification has little role to play in
 239 changing the ionization potential and electron affinity of Pyrene and its derivatives. The results revealed
 240 that ionic molecules have taken the major noticeable changes in IP and EA that occur among the
 241 molecules studied.

242

243 **Table 5:** Ionization Potential (IP) and Electron Affinity (EA) of Pyrene and its derivatives

Molecules	Basis sets	NEUTRAL		ANIONIC		CATIONIC	
		IP(eV)	EA(eV)	IP(eV)	EA(eV)	IP(eV)	EA(eV)
Pyrene	6-311G	5.60	1.73	1.16	3.38	10.10	6.45
	6-311+G(d)	5.65	1.83	0.94	2.85	10.10	6.47
	6-311++G(d,p)	5.67	1.86	-	-	-	-
1-Chloropyrene	6-311G	5.83	2.02	0.79	2.97	10.04	6.60
	6-311+G(d)	5.78	2.05	0.66	2.74	10.04	6.54
	6-311++G(d,p)	5.80	2.07	-	-	-	-
2-Chloropyrene	6-311G	5.92	2.05	0.74	3.00	10.34	6.68
	6-311+G(d)	5.90	2.07	0.63	2.73	10.27	6.63
	6-311++G(d,p)	5.91	2.10	-	-	-	-

244

245 **Global Chemical Indices**

246 Chemical reactivity indices of Pyrene and its derivatives in neutral and ionic forms are presented in Table
 247 6. The HOMO-LUMO is used to determine several chemical reactivity parameters as a measure of
 248 relative stability and reactivity. These include total energy (E_0), chemical hardness (η), electronic
 249 chemical potentials (μ) and electrophilicity (ω). Chemical hardness is linked to the stability and reactivity
 250 of a chemical system. According to the frontier molecular orbital approach, chemical hardness is directly
 251 proportional to the energy gap between the HOMO and the LUMO. The larger the HOMO-LUMO energy
 252 gap, the harder and more stable (less reactive) the compound [18]. Considering Table 6, neutral form of 2-
 253 Chloropyrene is the most stable with the highest chemical hardness of 1.94eV followed by its cationic
 254 form (1.83eV), and then its anionic form (1.13eV). The negative of electro-negativity is termed as
 255 electrochemical potential, lower value of this global quantity indicates the stability of a compound or
 256 molecule. Table 6 shows that the anionic molecules have lower electrochemical potential than others with
 257 cationic molecules having the highest. The neutral and cationic molecules display some similarities in
 258 electronic softness while anionic has shown slightly higher values which characterized the molecule as the
 259 softest (electronically) and reactive due to small energy gap. Electrophilicity (ω) measures the capacity of
 260 a species to accept electrons and therefore measures the stabilization in energy after a system accepts
 261 additional electronic charge [2]. Anionic molecules were the stronger nucleophiles due to their lower ω
 262 while cationic molecules were the strongest electrophiles due to their higher ω followed by the neutral
 263 molecules. Generally, addition of chlorine and basis set specification has little impact in describing the
 264 chemical reactivity than charging the molecules.

265

266 **Table 6:** Global quantities of pyrene and its derivatives for neutral, anionic and cationic forms

267

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
	6-311++G(d,p)	3.77	3.93	4.01
η (eV)	6-311G	1.93	1.91	1.94
	6-311+G(d)	1.91	1.87	1.91
	6-311++G(d,p)	1.91	1.86	1.91
S (eV)	6-311G	0.52	0.52	0.52

	6-311+G(d)	0.52	0.54	0.52
	6-311++G(d,p)	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
	6-311++G(d,p)	3.72	4.16	4.21
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
	6-311++G(d,p)	-	-	-
η (eV)	6-311G	1.11	1.09	1.13
	6-311+G(d)	0.95	1.04	1.05
	6-311++G(d,p)	-	-	-
S (eV)	6-311G	0.90	0.92	0.89
	6-311+G(d)	1.05	0.96	0.95
	6-311++G(d,p)	-	-	-
ω (eV)	6-311G	2.86	1.62	1.54
	6-311+G(d)	1.89	1.39	1.34
	6-311++G(d,p)	-	-	-
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
	6-311++G(d,p)	-	-	-
η (eV)	6-311G	1.82	1.77	1.83
	6-311+G(d)	1.82	1.75	1.82
	6-311++G(d,p)	-	-	-
S (eV)	6-311G	0.55	0.56	0.55
	6-311+G(d)	0.55	0.57	0.55
	6-311++G(d,p)	-	-	-
ω (eV)	6-311G	18.79	19.77	19.81

	6-311+G(d)	18.91	19.67	19.61
	6-311++G(d,p)	-	-	-

268

269 Non-Linear Optical Properties

270 The Non-linear Optical (NLO) Properties such as dipole moment, polarizability (isotropic and anisotropy)
 271 and first hyperpolarizability for the studied molecules in neutral and ionic forms are shown in Table 7.
 272 These properties of a material are important in determining its potentials in electronic and photonic
 273 applications. Organic materials that exhibit large NLO properties have emerged as an important class of
 274 electronic materials with interesting characteristics. Experimentally, NLO of materials could be improved
 275 through the appropriate addition of some chemical substituent that is, chlorine as in the case of this study.

276 From Table 7, it can be seen from the neutral and charged molecules, the dipole moment and the first
 277 order hyperpolarizability of the parent molecule were completely diminished (equals to zero). This is as a
 278 result of equal distribution of charges in the entire molecule that made them to cancel themselves, thereby
 279 producing no net charge (non-polar). It can also be observed from Table 7 that, basis set specification has
 280 not shown prominent impact on the NLO properties. Significant variations of NLO properties among the
 281 studied molecules exist as a result of charge status, addition and placing of chlorine at the first or second
 282 positions in the pyrene ring. Such remarkable variations in NLO properties have even multiply others
 283 several times as in the case of dipole moment of cationic 2- Chloropyrene at 6-311G which has the
 284 highest dipole moment of 5.5369 (D). This value is 43% greater than 3.1670 (D) which was the highest in
 285 neutral molecule and 5 times that of the anionic molecule. For isotropic polarizability; anionic 2-
 286 chloropyrene has the largest value (128.097a.u). This amount was 20% more than the highest value in
 287 neutral molecule and 61% greater, when compared with the highest value in cationic molecule. Looking
 288 at the anisotropic polarizability; the cationic value is 57% and 18% greater than the neutral and anionic
 289 counterparts. The highest difference was realized in hyperpolarizability values when the largest
 290 hyperpolarizability of a cationic molecule was 75% more than the largest value in anionic molecule. 6-
 291 311G basis set lifted and yielded good values of NLO properties than other studied basis sets. Moreover,
 292 placing chlorine in the second position is seen to favour and improve the NLO behavior of a chlorinated
 293 pyrene than in the first position apart from incorporation of the substituent into the ring.

294 **Table 7:** Calculated Total Dipole Moment, μ_{tot} , (D), Average Isotropic Polarizability, $\langle\alpha\rangle$, (a. u),
 295 Anisotropic Polarizability, $\Delta\alpha$, (a. u) and total first order hyperpolarizability (β_{tot}) (a.u) values for neutral
 296 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
	6-311++G(d,p)	0.0000	-87.3655	18.8269	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
	6-311++G(d,p)	1.9663	-100.6736	18.4996	19.9754
2-chloropyrene	6-311G	3.1670	-103.0233	19.7841	75.5078
	6-311+G(d)	2.3533	-101.7501	18.2499	42.9313
	6-311++G(d,p)	2.3324	-101.8446	17.8243	41.8019
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
	6-311++G(d,p)	-	-	-	-
1-chloropyrene	6-311G	1.0830	-125.8812	27.3322	14.4933
	6-311+G(d)	0.5761	-126.2267	24.6387	32.1218
	6-311++G(d,p)	-	-	-	-
2-chloropyrene	6-311G	1.1296	-128.097	38.4421	27.5152
	6-311+G(d)	0.1641	-127.9144	34.4025	15.0463
	6-311++G(d,p)	-	-	-	-
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
	6-311++G(d,p)	-	-	-	-
1-chloropyrene	6-311G	4.0551	-65.1303	46.1353	76.8279
	6-311+G(d)	3.2323	-76.1880	46.8593	53.9581
	6-311++G(d,p)	-	-	-	-
2-chloropyrene	6-311G	5.5369	-78.9441	42.9993	128.8808
	6-311+G(d)	4.7514	-77.1770	44.6762	99.7249
	6-311++G(d,p)	-	-	-	-

Conclusion

The DFT/B3LYP level of theory was 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 was 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 HOMO-LUMO energy gap and make them to possessed 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. IR spectra of the molecules have agreed very well with the previous literature and experimental results. Vibrational mode increases with the addition of chlorine, which is due to its electro-negativity.

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