



Density Functional Theory Investigation of the Doping Effects of Bromine and Fluorine on the Electronic and Optical Properties of Neutral and Ionic Perylene

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/PSIJ/2021/v25i830273

Editor(s):

(1) Dr. Lei Zhang, Salem State University, USA.

(2) Dr. Roberto Oscar Aquilano, School of Exact Science, National University of Rosario (UNR), Rosario Physics Institute (IFIR) (CONICET-UNR), Argentina.

Reviewers:

(1) Venkatesh, Periyar University, India.

(2) Eugene O. Onori, Lagos State University, Nigeria.

Complete Peer review History: <https://www.sdiarticle4.com/review-history/5853>

Original Research Article

Received 11 August 2021
Accepted 22 October 2021
Published 20 November 2021

ABSTRACT

Perylene and its derivatives are some of the promising organic semiconductors. They have found vast applications in many areas such as photovoltaic systems, organic light-emitting diodes, and so on. The instability of organic molecules under ambient conditions is one factor deterring the commercialization of organic semiconductor devices. Currently, most of the investigation of Perylene and its derivatives concentrated on its diimide and bisimide derivatives. In this work, an investigation of the effects of doping Bromine and Fluorine on the electronic and non-linear optical properties was carried out based on Density Functional Theory (DFT) as implemented in the Gaussian 09 software package. We computed the Molecular geometries of the molecules, HOMO-LUMO energy gap, global chemical indices and non-linear optical properties using the same method. The bond lengths and angles of the mono-halogenated molecules at different charge states were found to be less than that of the isolated Perylene. 1-fluoroperylene was found to be the most stable amongst the studied molecule for having the least bond angles and bond lengths. In the calculation of the energy bandgap neutral 1-fluoroperylene was observed to have the highest

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energy gap 3.0414 eV and 3.0507 eV for 6-31++G(d,p) and 6-311++G(d,p) basis sets respectively. These results were found to agree with the existing literature. This reconfirmed 1-fluoroperylene as the most stable molecule. The computations of the ionic molecules reported small values of the energy gap. The molecule with the most chemical hardness was obtained to be the neutral 1-fluoroperylene with a chemical hardness of 1.5253eV. All the ionic molecules results were found to be more reactive than their neutral form for having lower values of chemical hardness. For NLO calculations, the results showed an increment in their values with the ionic hybrid molecules having the largest values. In the case of first-order hyper-polarizability, 1-bromoperylene (neutral), 1-fluoroperylene (neutral), 1-bromoperylene (anionic), 1-fluoroperylene (anionic), 1-bromoperylene (cationic) and 1-fluoroperylene (cationic) were found to be 73.93%, 1.71%, 83.9%, 39.2%, 38.7% and 41.7% larger than that of Urea respectively. These calculated results make these hybrid molecules suitable for a wide range of optoelectronic applications.

Keywords: Perylene; organic semiconductor; density functional theory; gaussian 09; homo-lumo energy and non-linear optical properties.

1. INTRODUCTION

Organic semiconductor materials have found vast application in light-emitting diodes; photovoltaic cells [1] electro-fluidic display [2] and nanolasers [3]. This development is because of the strong optical absorption, mechanical flexibility, low cost and solubility these materials exhibit [4]. Perylene ($C_{20}H_{12}$) and its derivatives such as Perylene bisimide, Perylene tetracarboxylic acid (PTDCA) and Perylene 3,4,9,10-tetracarboxylic acid (PDA) have found vast application in organic photovoltaics, organic field-effect transistors (OFET), sensors and molecular spectroscopy because of their promising electronic, optical and charge transport properties [5].

Halogenation has become an effective way of improving the stability of many organic semiconducting materials by increasing the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) energies of the molecule [6]. Many works have been carried out to investigate the properties of different molecules. A high-performance air-stable OTFT transistors base on halogenated Perylene bisimide was reported by [7], where they analysed seven Perylene Bisimides (PBI) derivatives and found out that the substituents reduce the LUMO of the PBIs. Naphthalene diimide derivatives (N_1 , N_2 , N_3) with various electron-withdrawing substituents were also studied. The result shows that the N_3 derivative has excellent air stability when exposed to air for forty-two days [8]. Furthermore, [9] studied experimentally the effect of halogenation of Aza-octacene, the result showed that Chlorination, Fluorination and Bromination of Aza-octacenes at the end-phenyl ring increases both its Electron Affinity (EA) and Ionization Energy (IA). They

also showed that terminal halogenation influences the polarity of the charge transport behaviours of the Organic semiconductor. A Perylene-Bromine complex was also studied by [10] and the complex was found to have good electrical conductivity and is fairly stable. The study of the effect of mono halogenation on the electron properties of Perylene diimides X-PDI (X= F, H, Br and Cl) showed an increase in the electron mobilities of the hybrids in order of F-PDI > H-PDI > Cl-PDI = Br-PD [11]. The solvent effects on structural, electronic and non-linear optical were investigated by [5]. They showed that the bond lengths, energy gap, anisotropic hyper-polarizability increase as the polarity increases while the bond angle and polarizability decrease as the polarity increases. A study on semicarbazide derivative was also reported by [12] and the result showed that the molecule have good NLO properties.

Although a lot of progress has been made in realizing n-type semiconductors with ambient stability, there is still room for more exploration. The effect of the halogenation of the Perylene molecule is one of the unexploited areas. Of recent, [13] investigated the effect of mono-halogenation substitution on the properties of Perylene. However, the work did not report the theoretical study of the effects of halogens on the anionic and cationic forms of the Perylene molecule.

In this study, the electronic, non-linear optical properties, and global chemical reactivity of isolated Perylene and mono-halogenated Perylene at different charge states will be analysed using density functional theory embedded in Gaussian 09 software at two different basis sets b3lyp6-31++(d,p) and b3lyp6-311++ (d,p).

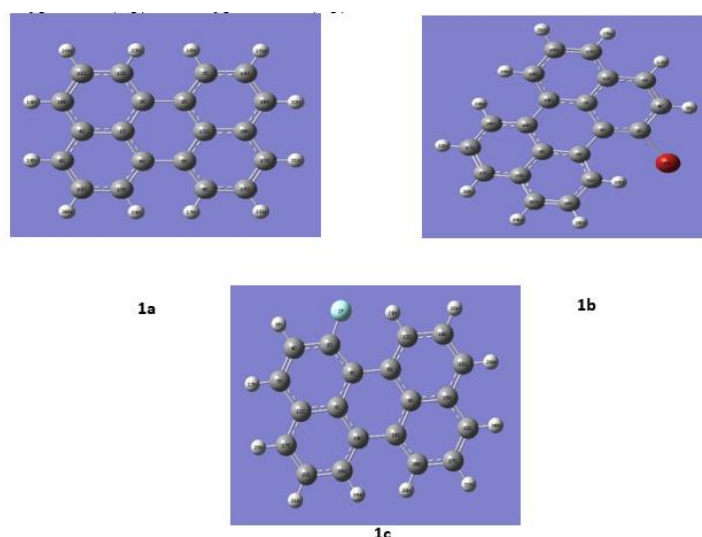


Fig. 1. Molecular structure of Perylene and its mono-halogenated derivatives

2. THEORETICAL BACKGROUND

2.1 Density Functional Theory

The properties of materials are ultimately determined by the interactions of electrons and nuclei, and fundamental descriptions of those interactions require quantum mechanics. One of the successful quantum mechanical theories to calculate the physical and other non-physical quantities of molecules with many atoms by considering the many-electron wave function is density functional theory. Density functional theory is the theory of electronic structure based on the electron density distribution $n(r)$ instead of the many-electron wave function equation [14].

2.2 Global Quantities

Global reactivity descriptors such as chemical potential, chemical hardness-softness, electronegativity and electrophilicity index are useful quantities in predicting and understanding global chemical reactivity trends. The ionization potential (IP) and electron affinity (EA) are expressed in terms of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) according to Koopmans approximation [15] as:

$$IP = -E_{HOMO} \quad (1)$$

$$EA = -E_{LUMO} \quad (2)$$

The difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) known as the energy band-gap can be obtained from the relation [15]:

$$E_{gap} = E_{LUMO} - E_{HOMO} = IP - EA \quad (3)$$

The chemical hardness (η), a quantum parameter introduced by Pearson to account the stability of the compound, can be expressed in terms of HOMO and LUMO as,

$$\eta = \frac{IP - EA}{2} \quad (4)$$

The chemical softness of a molecule can be obtained by fetching the inverse of its chemical hardness

$$S = \frac{1}{\eta} \quad (5)$$

The chemical potential is given by (Hasan, 2013):

$$\mu = -\left(\frac{IP + EA}{2}\right) \quad (6)$$

The electronegativity is given by (Hasan, 2013):

$$\chi = \frac{IP + EA}{2} \quad (7)$$

The electrophilicity index is a measure of energy lowering because of maximal electron flow between donor and acceptor. Electrophilicity index (ω) is expressed as [15]:

$$\omega = \frac{\mu^2}{2\eta} \quad (8)$$

2.3 Non-Linear Optical (NLO) Properties

To gain an insight into the study of non-linear optical properties (NLO) of Perylene and its derivatives in an anionic and neutral state; the dipole moment, polarizability, anisotropic polarizability and hyper-polarizability will be computed.

For molecular systems, dipole moment can be obtained from [16].

$$\mu_{tot} = [\mu_z^2 + \mu_y^2 + \mu_x^2]^2 \quad (9)$$

Where μ_x , μ_y and μ_z are the components of the dipole moment in x, y and z coordinates.

Electric dipole polarizability is a measure of linear response of an infinitesimal electric field (F) and represents second-order variation energy (Gidado, 2019) given by:

$$\alpha = - \frac{\partial^2 E}{\partial F_a \partial F_b} \quad (10)$$

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

The mean polarizability is calculated using (Gidado, 2019):

$$\langle \alpha \rangle = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (11)$$

where α_{xx} , α_{yy} and α_{zz} are known as the principal values of the polarizability tensor.

The anisotropic polarizability is given by (Hasan, 2013):

$$\Delta \alpha = \left[\frac{(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6(\alpha_{xz} + \alpha_{xy} + \alpha_{yz})}{2} \right]^{\frac{1}{2}} \quad (12)$$

The first order hyper-polarizability is defined as (Hasan, 2013):

$$\beta_{tot} = \left[\frac{(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2}{2} \right]^{\frac{1}{2}} \quad (13)$$

3. COMPUTATIONAL METHOD

In this research, the Gaussian 09W package was used to study the effects of mono-halogenation substitution on Perylene at different charge states. Geometry optimization parameters for the ground electronic states of Perylene and its derivatives were fully optimized without any constraints. All of the parameters were allowed to relax completely, and each calculation converged to an optimized geometry that correspond to a true energy minimum. Using the optimized geometry, single-point energy calculations of the molecules were performed to obtain parameters such as HOMO (highest occupied molecular orbital), SOMO (singly occupied molecular orbital), LUMO (lowest unoccupied molecular orbital), total energy and ionization potential were calculated using density functional theory (DFT) method with the three-parameter hybrid exchange functional of Becke and Lee-Yang-Parr correlation functional (B3LYP) [16],[17] with two basis sets 6-311++(d,p) and the 6-31++g(d,p). The chemical hardness, chemical softness, electronegativity and electrophilic index were also computed from the HOMO and LUMO energy gap. The same procedure was also adopted for the computation of the ionic (anionic and cationic) molecules by changing the charge state from 0 to -1 and +1 respectively. The non-linear optical properties such as dipole moment, mean polarizability, anisotropic polarizability and hyper-polarizability of the molecules were also computed using the Gaussian 09 package and basis set specification.

4. RESULTS AND DISCUSSION

4.1 Optimized Parameters

Tables 1a, 1b and 1c show some selected values of bond lengths and bond angles calculated at DFT/b3lyp level using 6-31++(d,p) and 6-311++(d,p) basis sets for the studied molecules. The bond length is the measurement of the distance between two covalently bonded atoms [18]. The bond energy of the molecules with small bond angles and bond length is higher than that of the one with large bond length and bond angles.

In Tables 1a, 1b and 1c the bond lengths and angles of the halogen-substituted molecules were found to be less than that of the isolated Perylene. With 1-fluoroethylene having the lowest bond lengths and angles. This implies that 1-fluoroperylene has higher energy and is stronger when compared with the other molecules for both basis sets. It also implies that halogenation of Perylene decreases its bond lengths and bond angles which increases its bond energy. We also observed a similar result for the ionic molecules. The computed bond lengths and bond angles of the neutral isolated Perylene are similar to those in the existing literature [19],[20]. Basis set specification was seen to have little effect on the bond length and angles of the studied molecules.

4.2 Frontier Molecular Orbitals

The HOMO and LUMO energy gap values of the neutral and ionic forms of the isolated and mono-

halogenated Perylene are presented in Table 2 for the two basis sets under study. Compounds with large HOMO-LUMO energy gap values are found to have low reactivity and high kinetic stability [5]. The lower the energy gap, of a molecule the easier it is for an electron to be emitted from the ground state [15]. It is clear from the results that in the neutral form 1-bromoperylene has the highest E_{homo} and E_{lumo} , followed by 1-fluoroperylene and finally the isolated Perylene. It was also observed that 1-fluoroperylene has the highest energy gap, 3.0414 eV and 3.0507 eV for 6-31++G(d,p) and 6-311++G(d,p) basis sets respectively. Therefore, 1-fluoroperylene is more stable and has a high tendency to donate electrons compared with the isolated Perylene and 1-bromoperylene molecules. The result for the neutral perylene was found to agree with existing literature [19].

Table 1a. Selected bond lengths and bond angles of neutral and ionic Perylene

| | 6-31++G(d,p) | | | 6-311++G(d,p) | | | Previous work: (Markiewicz & Wudl, 2015) |
|------------------|------------------|------------------|-------------------|------------------|------------------|-------------------|--|
| Bond Lengths (Å) | Neutral Perylene | Anionic perylene | Cationic perylene | Neutral Perylene | Anionic perylene | Cationic perylene | |
| R(1,3) | 1.4338 | 1.4365 | 1.4293 | 1.4313 | 1.4293 | 1.4266 | 1.4210 |
| R(6,12) | 1.3927 | 1.4165 | 1.4131 | 1.3893 | 1.4168 | 1.4101 | 1.4310 |
| R(16,20) | 1.3771 | 1.3903 | 1.3893 | 1.3734 | 1.3868 | 1.3859 | |
| | 6-31++G(d,p) | | | 6-311++G(d,p) | | | |
| Bond Angles (°) | Neutral Perylene | Anionic perylene | Cationic perylene | Neutral Perylene | Anionic perylene | Cationic Perylene | |
| A(3,1,4) | 121.4048 | 121.3418 | 121.2828 | 121.4036 | 121.0587 | 121.2770 | |
| A(1,3,5) | 119.2976 | 119.4729 | 119.3587 | 119.2980 | 119.4708 | 119.3615 | |
| A(18,10,22) | 117.8040 | 118.4421 | 117.9418 | 117.8168 | 118.4570 | 117.9669 | |

Table 1b. Selected bond length and bond angles of neutral and ionic 1-bromoperylene

| | 6-31++G(d,p) | | | 6-311++G(d,p) | | |
|------------------|-------------------------|-------------------------|--------------------------|-----------------------|-------------------------|--------------------------|
| Bond Lengths (Å) | Neutral 1-bromoperylene | Anionic 1-bromoperylene | Cationic 1-bromoperylene | Neutral bromoperylene | Anionic 1-bromoperylene | Cationic 1-bromoperylene |
| R(1,10) | 1.9290 | 1.9527 | 1.9055 | 1.9332 | 1.9415 | 1.9070 |
| R(3,7) | 1.4923 | 1.4145 | 1.4098 | 1.4792 | 1.4285 | 1.4117 |
| R(16,20) | 1.3713 | 1.3856 | 1.3836 | 1.3722 | 1.3863 | 1.3839 |
| | 6-31++G(d,p) | | | 6-311++G(d,p) | | |
| Bond Angles (°) | Neutral 1-bromoperylene | Anionic 1-bromoperylene | Cationic 1-bromoperylene | Neutral bromoperylene | Anionic 1-bromoperylene | Cationic 1-bromoperylene |
| A(4,2,5) | 121.7617 | 121.3418 | 121.7721 | 120.8790 | 120.7310 | 121.1101 |
| A(3,7,5) | 118.2501 | 119.0682 | 118.9746 | 119.0414 | 119.5184 | 118.7070 |
| A(18,14,25) | 119.5707 | 119.7183 | 118.9835 | 120.2784 | 120.6834 | 120.3406 |

Table 1c. Selected bond length and bond angles of neutral and ionic 1-fluoroperylene

| Bond Lengths (Å) | 6-31++G(d,p) | | | 6-311++G(d,p) | | |
|------------------|-------------------------|-------------------------|--------------------------|-----------------------|-------------------------|--------------------------|
| | Neutral 1-bromoperylene | Anionic 1-bromoperylene | Cationic 1-bromoperylene | Neutral bromoperylene | Anionic 1-bromoperylene | Cationic 1-bromoperylene |
| R(1,10) | 1.3643 | 1.3852 | 1.3445 | 1.3602 | 1.3798 | 1.3396 |
| R(3,7) | 1.4324 | 1.4344 | 1.4167 | 1.4298 | 1.4317 | 1.4138 |
| R(16,20) | 1.3742 | 1.3882 | 1.3868 | 1.3703 | 1.3847 | 1.3883 |

| Bond Angles (°) | 6-31++G(d,p) | | | 6-311++G(d,p) | | |
|-----------------|-------------------------|-------------------------|--------------------------|-----------------------|-------------------------|--------------------------|
| | Neutral 1-bromoperylene | Anionic 1-bromoperylene | Cationic 1-bromoperylene | Neutral bromoperylene | Anionic 1-bromoperylene | Cationic 1-bromoperylene |
| A(4,2,5) | 120.9836 | 121.3418 | 120.9342 | 121.0035 | 120.7310 | 119.5369 |
| A(3,7,5) | 118.6047 | 119.5120 | 119.4037 | 119.3124 | 119.5184 | 119.4166 |
| A(18,14,25) | 119.2712 | 120.5531 | 120.6324 | 120.5871 | 120.5486 | 120.1517 |

Table 2. HOMO/LUMO for neutral, SOMO/LUMO for Charged and Energy gap for Perylene and its derivatives

| Neutral | | | | | |
|------------------|---------------|------------------------|------------------------|---------|---|
| Molecules | Basis Set | E _{HOMO} (eV) | E _{LUMO} (eV) | Gap(eV) | Previous work (Markiewicz and Wudl, 2015) |
| Perylene | 6-31++G(d,p) | -5.2352 | -2.2591 | 2.9761 | 2.9935 |
| | 6-311++G(d,p) | -5.2895 | -2.3045 | 2.9850 | 2.9740 |
| 1-bromoperylene | 6-31++G(d,p) | -5.3889 | -2.3589 | 3.0300 | |
| 1-fluoroperylene | 6-311++G(d,p) | -5.4648 | -2.4204 | 3.0414 | |
| | 6-31++G(d,p) | 1-5.3309 | -2.2895 | 3.0414 | |
| | 6-311++G(d,p) | -5.3870 | -2.3363 | 3.0507 | |

| Anionic | | | | | |
|------------------|---------------|------------------------|------------------------|---------|--|
| Molecules | Basis Set | E _{SOMO} (eV) | E _{LUMO} (eV) | Gap(eV) | |
| Perylene | 6-31++G(d,p) | 0.2985 | 2.2313 | 1.9328 | |
| | 6-311++G(d,p) | 0.2644 | 2.3788 | 2.1143 | |
| 1-bromoperylene | 6-31++G(d,p) | 0.1317 | 2.1676 | 2.0359 | |
| 1-fluoroperylene | 6-311++G(d,p) | 0.0386 | 2.1668 | 2.1282 | |
| | 6-31++G(d,p) | 0.2655 | 2.1199 | 1.9544 | |
| | 6-311++G(d,p) | 0.2280 | 2.2008 | 1.9728 | |

| Cationic | | | | | |
|------------------|---------------|------------------------|------------------------|---------|--|
| Molecules | Basis Set | E _{SOMO} (eV) | E _{LUMO} (eV) | Gap(eV) | |
| Perylene | 6-31++G(d,p) | -9.2467 | -6.4546 | 2.8121 | |
| | 6-311++G(d,p) | -9.3003 | -6.4867 | 2.8134 | |
| 1-bromoperylene | 6-31++G(d,p) | -9.2771 | -6.4565 | 2.8405 | |
| 1-fluoroperylene | 6-311++G(d,p) | -9.3166 | -6.5051 | 2.8115 | |
| | 6-31++G(d,p) | -9.3721 | -6.5046 | 2.8675 | |
| | 6-311++G(d,p) | -9.3177 | -6.4520 | 2.8657 | |

It was also observed from Table 2 that the ionic molecules yield a lower energy gap when compared with their neutral forms, especially with the anionic Perylene with a bandgap of 1.9328 eV and anionic 1-fluoro Perylene with a bandgap of 1.9544eV. This implies that the ionic forms of the molecules are less stable than the neutral form of the molecules. The basis set

specification was seen to have effects on the energy gap of the molecules with 6-311++G(d,p) giving bigger values.

4.3 Total Ground State Energy

The total energy of the isolated Perylene and the mono-halogenated Perylene in both neutral and

ionic forms are shown in Table 3. The total ground state energy of the isolated Perylene in the neutral and ionic state was found to be almost identical with a slightly higher value in the cationic form. In all the molecules, the molecule with the lowest ground state energy was found to be the anionic form of 1-bromoperylene with a value -3343.15539311 au at B3LYP6-311++G(d,p).

4.4 Ionization Potential and Electron Affinity

The ability of a molecule to accept or released an electron is determined by its ionization potential (IP) and the electron affinity (EA) [21]. The lower the electron affinity the less easy it is to add an electron and the higher the ionization potential (IP) the less easy it is to remove an electron. The IPs and EAs of the neutral and ionic forms of the molecules are presented in Table 4. The EA and IP of the ionic molecules were obtained using $EA = E_{\text{optimized neutral}} - E_{\text{optimized anion}}$ and $IP = E_{\text{optimized cation}} - E_{\text{optimized neutral}}$ [22]. It was observed that 1-bromoperylene has the highest ionization potential

of 6.7545eV at B3lyp6-311++G(d,p). Thus, high energy will be required to remove an electron from it. The molecule with the largest electron affinity is found to be 1-bromoperylene with a value of 2.4204eV at B3lyp6-311++G(d,p). The ionic molecules were observed to have more IP and less EA when compared with their neutral forms. This makes the ionic molecules more electron donors than electron receptors. It was also observed that charging the molecules and basis set specification has an impact on the ionization potential and electron affinity of the molecules.

4.5 Global Chemical Reactivity Descriptors

The global chemical reactivity descriptors of the studied molecule such as the chemical hardness (η), chemical softness (S), chemical potential (μ), electronegativity (χ) and electrophilic index (ω) of the molecules in the neutral and ionic form are presented in Table 5. These properties were calculated based on the difference between the HOMO and LUMO energies of the molecules using the Koopmans theorem.

Table 3. Total Ground State Energy (a.u) of the Neutral and Ionic Molecules

| Perylene | | |
|------------------|----------------|----------------|
| Molecule | 6-31++G(d,p) | 6-311++G(d,p) |
| Neutral | -769.44777616 | -769.58234425 |
| Anionic | -769.48363152 | -769.61963826 |
| Cationic | -769.20597167 | -769.33849607 |
| 1-bromoperylene | | |
| Molecule | 6-31++G(d,p) | 6-311++G(d,p) |
| Neutral | -3340.56267644 | -3343.11194224 |
| Anionic | -3340.60340129 | -3343.15539311 |
| Cationic | -3340.31685960 | -3342.86371556 |
| 1-fluoroperylene | | |
| Molecule | 6-31++G(d,p) | 6-311++G(d,p) |
| Neutral | -868.68505404 | -868.84789876 |
| Anionic | -868.72206095 | -868.88647702 |
| Cationic | -868.43997815 | -868.60073911 |

Table 4. Ionization Potential (eV) and Electron Affinities of the neutral and ionic molecules

| Molecules | Basis sets | Neutral | | Ionic | |
|------------------|---------------|---------|---------|---------|---------|
| | | IP (eV) | EA (eV) | IP (eV) | EA (eV) |
| Perylene | 6-31++G(d,p) | 5.2352 | 2.2590 | 6.5798 | 0.9721 |
| | 6-311++G(d,p) | 5.2895 | 2.3045 | 6.6381 | 1.1823 |
| 1-bromoperylene | 6-31++G(d,p) | 5.3889 | 2.3589 | 6.6890 | 1.1081 |
| | 6-311++G(d,p) | 5.4648 | 2.4204 | 6.7545 | 1.1823 |
| 1-fluoroperylene | 6-31++G(d,p) | 5.3309 | 2.2895 | 6.6688 | 1.0008 |
| | 6-311++G(d,p) | 5.3870 | 2.3363 | 6.7255 | 1.0497 |

The chemical hardness of a molecule is directly proportional to the energy gap of the molecule. The larger the energy gap the harder and less reactive the molecule [17], which determine the stability of the molecule. The results presented in Table 5 show that the neutral form of 1-fluoroperylene has the highest value of the chemical hardness of 1.5253eV followed by neutral 1-bromoperylene, isolated Perylene with a chemical hardness of 1.5220eV and 1.4925eV respectively. All the ionic forms of the molecules resulted in a lower value of the chemical hardness when compared with their neutral form. Cationic 1-fluoroperylene has the lowest chemical hardness of 0.7560eV. The result obtained implies that neutral 1-fluoroperylene is considered to be harder, less reactive and more stable, while the ionic forms of the molecule are found to be softer and highly reactive.

The electrochemical potential is the negative of the electronegativity [23], lower values of this global quantity show the stability of the molecule. The electronegativity, electrochemical potential, softness and electrophilic index of the cationic molecules were found to be larger than those of the neutral and anionic molecules. This implies that positively charging the molecules increases their softness and reduces their stability. Basis set specification was observed to not affect the values of the global quantities.

4.6 Electro-donating power (ω^-), Electro-accepting power (ω^+) and Net electrophilicity (ω^\pm)

The electro-donating power, electro-accepting power were proposed to complement the definition of electrophilicity. They have been used for the classification of molecules as either electron-donors or electron-receptors. Molecules with larger values ω^+ are categorized as better electron acceptors and those with smaller values of ω^- considered as better electron-donors [24]. The values of these properties were calculated using the equations below and presented in Table 6.

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

$$\square \omega^\pm = \omega^+ + \omega^- \quad [23].$$

Where I is the ionization energy and A is the electron affinity.

From Table 6, neutral molecules were found to have higher values ω^+ when compared with their ionic forms. This makes the neutral molecules more electro-donors than their corresponding ionic form, with 1-bromoperylene having the highest value of 3.2052eV and 3.3247eV at 6-31++G(d,p) and 6-311++G(d,p) respectively. In the case of ω^- , the ionic molecules were found to be having small values compared to their neutral form. Thus, the ionic form of the molecules is more ready to accept electrons. The basis set 6-311++G(d,p) was observed to give better results than the 6-31++G(d,p) basis set.

4.7 Non-linear Optical (NLO) Properties

The computed results of the NLO properties such as the dipole moment, mean polarizabilities, anisotropic polarizabilities, and the first-order hyper-polarizabilities of the isolated and the mono-halogenated Perylene are shown in Table 6. These properties of materials are important in determining their potentials in electronic and photonic applications. Molecules with a large value of NLO are classified as important materials for photonic applications [18]. Dipole moment is the property that describes the polarity of a molecule [25]. The larger its value, the larger the polarity of the molecule [18]. The ease of the distortion of the electron cloud of a molecule in an external electric field is known as polarizability [25]. From Table 6, it can be seen that the dipole moment of the isolated Perylene in all the charge states is zero. An increase in the dipole moment was observed in the mono-halogenated molecules with cationic 1-bromoperylene having the highest values of 4.7811 Debye and 4.5108 Debye at 6-31++G(d,p) and 6-311++G(d,p) respectively. This shows that the isolated Perylene is a non-polar molecule and the mono-halogenated molecules are polar with cationic 1-bromoperylene being more polar.

The hyper-polarizability property of Urea ($0.1947 \times 10^{-30} esu$) is regarded as a threshold for comparison with the hyper-polarizability of other molecules. The hyper-polarizability of the molecules under study are presented in Table 7. It was found that; isolated Perylene has zero polarizability. This is due to the equal distribution of charges in the molecules. However, for the first-order hyper-polarizability of other molecules, 1-bromoperylene (neutral), 1-fluoroperylene (neutral), 1-bromoperylene (anionic), 1-

Table 5. Global quantities of Perylene and its derivatives for neutral and charged molecules

| Neutral | | | | | | |
|---------------|--------------|-----------------|------------------|---------------|-----------------|------------------|
| Property | 6-31++G(d,p) | | | 6-311++G(d,p) | | |
| | Perylene | 1-bromoperylene | 1-fluoroperylene | Perylene | 1-bromoperylene | 1-fluoroperylene |
| μ (eV) | -3.7421 | -3.8739 | -38102 | -3.7970 | -3.9426 | -3.8616 |
| η (eV) | 1.4880 | 1.5150 | 1.5207 | 1.4925 | 1.5220 | 1.5253 |
| \int (eV) | 0.6720 | 0.6600 | 0.6575 | 0.6700 | 0.6560 | 0.6555 |
| ω (eV) | 4.7170 | 4.9520 | 5.1040 | 4.8298 | 5.1000 | 4.8830 |
| Anionic | | | | | | |
| Property | 6-31++G(d,p) | | | 6-311++G(d,p) | | |
| | Perylene | 1-bromoperylene | 1-fluoroperylene | Perylene | 1-bromoperylene | 1-fluoroperylene |
| μ (eV) | -1.2649 | -1.1496 | -1.2427 | -1.3216 | -1.1027 | -1.2144 |
| η (eV) | 0.9664 | 0.9521 | 0.9772 | 1.0571 | 1.0641 | 0.7580 |
| \int (eV) | 1.0347 | 0.6940 | 1.0233 | 0.8262 | 0.6469 | 1.0137 |
| ω (eV) | 0.8262 | 0.6940 | 0.7901 | 0.8262 | 0.6469 | 0.7550 |
| Cationic | | | | | | |
| Property | 6-31++G(d,p) | | | 6-311++G(d,p) | | |
| | Perylene | 1-bromoperylene | 1-fluoroperylene | Perylene | 1-bromoperylene | 1-fluoroperylene |
| μ (eV) | -7.8906 | -7.8568 | -7.8845 | -7.8936 | -7.9108 | -7.9383 |
| η (eV) | 1.4660 | 1.4202 | 1.4328 | 1.4067 | 1.4057 | 1.4337 |
| \int (eV) | 0.7112 | 0.7040 | 0.6974 | 0.7108 | 0.7113 | 0.6979 |

Table 6. Electro-donating Power (ω^-), Electro-accepting Power (ω^+) and Net electrophilicity ($\chi\omega^\pm$) of the neutral and ionic molecules

| Property | Basis set | Neutral | | | Ionic | | |
|-----------------------|---------------|----------|-----------------|------------------|----------|-----------------|------------------|
| | | Perylene | 1-bromoperylene | 1-fluoroperylene | Perylene | 1-bromoperylene | 1-fluoroperylene |
| ω^+ (eV) | 6-31++G(d,p) | 3.0301 | 3.2052 | 3.0583 | 1.0050 | 1.1228 | 1.0313 |
| | 6-311++G(d,p) | 3.1496 | 3.3247 | 3.1480 | 1.1674 | 1.1884 | 1.0737 |
| ω^- (eV) | 6-31++G(d,p) | 6.7772 | 7.0791 | 6.8685 | 4.7809 | 5.1558 | 4.8861 |
| | 6-311++G(d,p) | 6.9149 | 7.2673 | 7.0096 | 5.0985 | 4.8861 | 4.9613 |
| $\chi\omega^\pm$ (eV) | 6-31++G(d,p) | 9.8073 | 10.2843 | 9.9268 | 5.7859 | 6.3442 | 5.0184 |
| | 6-311++G(d,p) | 10.0645 | 10.5920 | 10.1596 | 5.0985 | 5.0184 | 6.0350 |

Table 7. Calculated total dipole moment (Debye), mean polarizability (esu), anisotropic-polarizability (esu) and hyper-polarizability (esu)

| Property | Neutral | | | | | |
|--|--------------|-----------------|------------------|---------------|-----------------|------------------|
| | 6-31++G(d,p) | | | 6-311++G(d,p) | | |
| | Perylene | 1-bromoperylene | 1-fluoroperylene | Perylene | 1-bromoperylene | 1-fluoroperylene |
| μ_{total} | 0.0000 | 1.6228 | 1.4220 | 0.0000 | 1.6558 | 1.4309 |
| $\langle\alpha\rangle \times 10^{-24}$ | 16.0910 | 18.6971 | 16.8062 | 16.0603 | 18.6842 | 16.7832 |
| $\langle\chi\alpha\rangle \times 10^{-24}$ | 3.4500 | 3.5903 | 3.3816 | 3.5010 | 3.4568 | 3.1299 |
| $\beta_{total} \times 10^{-30}$ | 0.0000 | 1.2990 | 0.2015 | 0.0000 | 1.2747 | 0.1920 |
| Anionic | | | | | | |
| Property | 6-31++G(d,p) | | | 6-311++G(d,p) | | |
| | Perylene | 1-bromoperylene | 1-fluoroperylene | Perylene | 1-bromoperylene | 1-fluoroperylene |
| μ_{total} | 0.0000 | 1.7931 | 0.6774 | 0.0000 | 1.3142 | 0.6867 |
| $\langle\alpha\rangle \times 10^{-24}$ | 20.4348 | 23.3786 | 21.1746 | 20.3452 | 23.2543 | 21.0971 |
| $\langle\chi\alpha\rangle \times 10^{-24}$ | 2.6717 | 2.1142 | 2.1043 | 2.6628 | 2.1053 | 2.0524 |
| $\beta_{total} \times 10^{-30}$ | 0.0000 | 2.2301 | 0.4461 | 0.0000 | 1.9516 | 0.4269 |

| Neutral | | | | | | |
|--|---------------------|------------------------|-------------------------|----------------------|------------------------|-------------------------|
| Property | 6-31++G(d,p) | | | 6-311++G(d,p) | | |
| | Perylene | 1-bromoperylene | 1-fluoroperylene | Perylene | 1-bromoperylene | 1-fluoroperylene |
| μ_{total} | 0.0000 | 4.7811 | 2.1412 | 0.0000 | 4.5108 | 2.1491 |
| $\langle \alpha \rangle \times 10^{-24}$ | 12.0158 | 14.2639 | 12.7081 | 12.0163 | 14.3228 | 12.7163 |
| $\langle \square \alpha \rangle \times 10^{-24}$ | 8.6851 | 9.7010 | 8.8263 | 8.7125 | 8.6734 | 8.8525 |
| $\beta_{total} \times 10^{-30}$ | 0.0000 | 0.4411 | 0.0920 | 0.0000 | 0.4742 | 0.1073 |

fluoroperylene (anionic), 1-bromoperylene (cationic) and 1-fluoroperylene (cationic) were found to be 73.93%, 1.71%, 83.9%, 39.2%, 38.7% and 41.7% larger than that of Urea respectively. These results show that mono-halogenation substitution and charging of the molecules have increased the NLO properties of the molecules, thereby making them suitable candidates for electronic and photonic applications. It was also observed that the choice of basis does not affect the NLO properties, only the charge does.

5. CONCLUSION

In this work, we investigated the effects of mono-halogenation of Perylene at different charge states. The molecular geometry, the HOMO and LUMO, energy bandgap, Global chemical reactivity parameters and non-linear optical properties of Perylene and its mono-halogenated derivatives at different charge states using density functional theory as implemented in Gaussian 09 software, with two different basis sets were calculated. Our findings show that neutral 1-fluoroperylene having the largest band-gap is the most stable molecule. We also reported low values of band-gap of ionic forms of the molecules, which makes them less stable than their neutral forms. The results obtained for the Global Chemical Reactivity Parameters show that the neutral form of the molecules resulted in high values of the Global parameters when compared with their ionic forms, this implies that charging the molecules increases their reactivity and decreases their stability. For the NLO computations, our result shows that isolated Perylene is a non-polar molecule, but the mono-halogenated derivatives were found to be polar with 1-bromoperylene being more polar. The hyper-polarizability of the mono-halogenated molecules were found to be greater than Urea. The result showed that mono-halogenation of the Perylene molecules improves its NLO properties by providing larger values of the dipole moment, anisotropic polarizability and hyper-polarizability.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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