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Investigating the Effects of Mono-Halogen-Substitutions on the Electronic, Non-Linear Optical and Thermodynamic Properties of Perylene Based on Density Functional Theory

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Authors' contributions

This work was carried out in collaboration between both authors. Author RNM initiated the work, performed all calculations on the electronic and structural properties of the molecule. Author ASG carried out the calculations of the non-linear optical properties and IR spectra, managed the literature searches and guided the team. Both authors read and approved the final manuscript.

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ABSTRACT

Perylene ($C_{20}H_{12}$) is polycyclic aromatic hydrocarbons (PAHs) used in the production of organic field- effect transistors, organic photovoltaic cells, and biosensors. In this work, the molecular geometry, HOMO-LUMO energy gap, global indices, thermodynamic properties, non-linear optical properties, IR frequencies, and intensities of isolated perylene and its substituted molecules were calculated and reported. DFT/B3LYP using 6-311+G(d) basis sets was used for the work. All the computations were performed by using Gaussian 03 package and revealed that the substitutions affect the optimized parameters of the titled molecule. The results obtained for the bond lengths indicate that the strongest bond is C19-H12 with a value of 1.0757Å found in 1-fluoroperylene while the bond angles were found to be so close to 120^0, revealing that the molecules are planar benzene in which the carbon atoms are sp^2 hybridized. The calculated value of the energy gap of 3.0572 eV shows that perylene has higher stability in a chemical reaction by substitution of fluorine. The value of the energy gap is closer to the reported value in the literature (2.9740 and 2.9935) eV.

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The molecule was found to be harder and less reactive in a chemical reaction by substitution of fluoride atom with a chemical hardness of 1.5286 eV. It was found that the specific heat capacity and entropy of the molecule increased while zero-point vibrational energy decreased due to the effect of the substitutions. From the results obtained for non-linear optical properties, it was found that substitution of bromine gives a higher value of the first-order hyperpolarizability with a value of 1.2748 $\mathrm{x}10^{-30}$esu, which is at least 3 fold than that of prototype urea (0.3728 $\mathrm{x}10^{-30}$esu) molecule. This suggests that 1-bromoperylene can be the best candidate for non-linear optical applications among the substituted molecules. The calculated frequencies and intensities results show that 1-bromoperylene with a value of 826.37cm^{-1} at 96.9614 km/mol has the most intense frequency among the substituted molecules. The results of this work indicate that choosing a better halogen atom and basis sets can improve the electronic and nonlinear optical properties of the titled molecule for better applications.

Keywords: Perylene; DFT; HOMO-LUMO gaps; polarizability; and IR spectrum.

1. INTRODUCTION

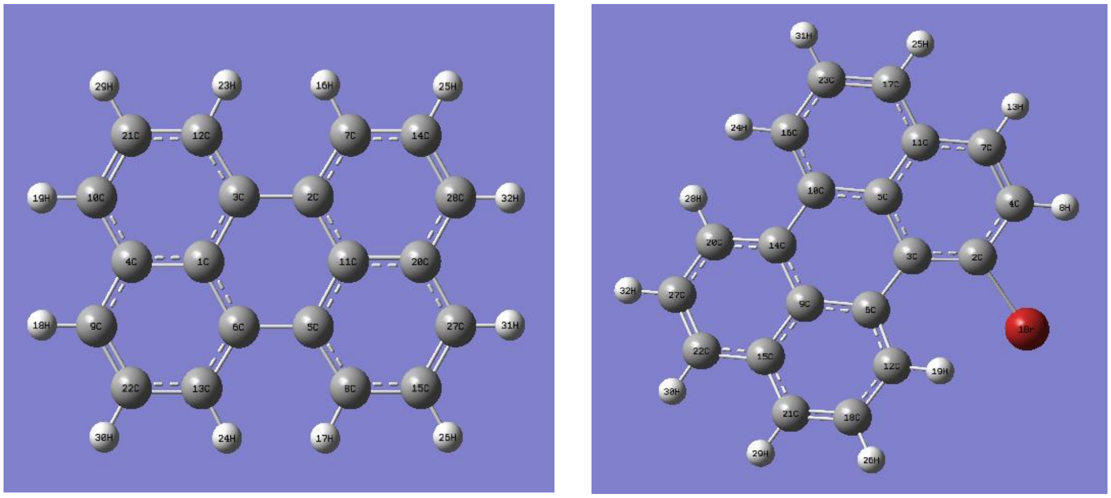
Partly in response to predictions that silicon technology is nearly reaching the limits of its evolution, there is rising interest in controlling charge transport across nanometer-scale metal-molecule-metal junctions [1,2] and exploiting the properties of single-molecular materials. Many years ago, significant research efforts were redirected from inorganic to organic electronic materials due to their interesting properties and promising applications in multi-functional organic semiconductor devices such as solar cells (Raj et al*.,* 2013), sensors [3], nanolasers [4], organic field-effect transistors (OFETs) [5,6] and organic light-emitting diode (OLEDs) [7,8]. However, these materials have shown with evidence strong stability, high carrier mobility, and better efficiency in terms of lifetime, manufacturing cost as well as the outcome performance of organic electronic materials.

Although inorganic semiconductors such as silicon, germanium, and gallium arsenide have been the keystone of the semiconductor industry. For the past decade, demands for extensive computing have led to a dramatic improvement in the performance of organic semiconductors [9]. Perylene ($C_{20}H_{12}$) and its derivatives such as perylene bisimides, perylene tetracarboxylic acid (PTDCA), and perylene-3,4,9,10-tetracarboxylic anhydride (PDA) are the most commonly investigated polycyclic aromatic hydrocarbons (PAHs) due to their promising electronic, optical, and charge-transport properties, which are commonly used in high-tech applications such as organic photovoltaics, organic field-effect transistors, bio-labels, sensors, single molecular spectroscopy, supermolecular assemblies and optoelectronic devices [10]. The potential application using perylene and its derivatives is the identification of the practical use of perylene, which was found better comparable to inorganic compounds [11,12].

Interestingly, many experimental and theoretical studies have been carried out in the synthesis and applications of perylene and its derivatives including Density Functional Theory. For example, [13,14] carried out the study of electronic structure of Perylene through transient absorption measurements of isolated molecules, monomeric crystal forms (β-perylene), and dimeric crystal forms (α-perylene). Similarly, the structures and electronic properties of perylene and coronene under pressure were theoretically investigated using DFT [15]. Moreover, Mohamad et al*,* [16], reported the studies on the structure-dependent optoelectronic properties of perylene, diindenoperylene (DIP) isolated molecule, and DIP molecular crystal. Furthermore, it was reported that the bond lengths and the bond angles of the isolated perylene molecule are in agreement with the previous experimental work [17] and the theoretical work of [18]. In the foregoing report, it was observed that the obtained bond lengths of DIP and the attached indeno DIP molecule are slightly different as compared to the perylene molecule. The HOMO-LUMO energy of isolated perylene by using B3LYP was obtained as 2.9740eV [16].

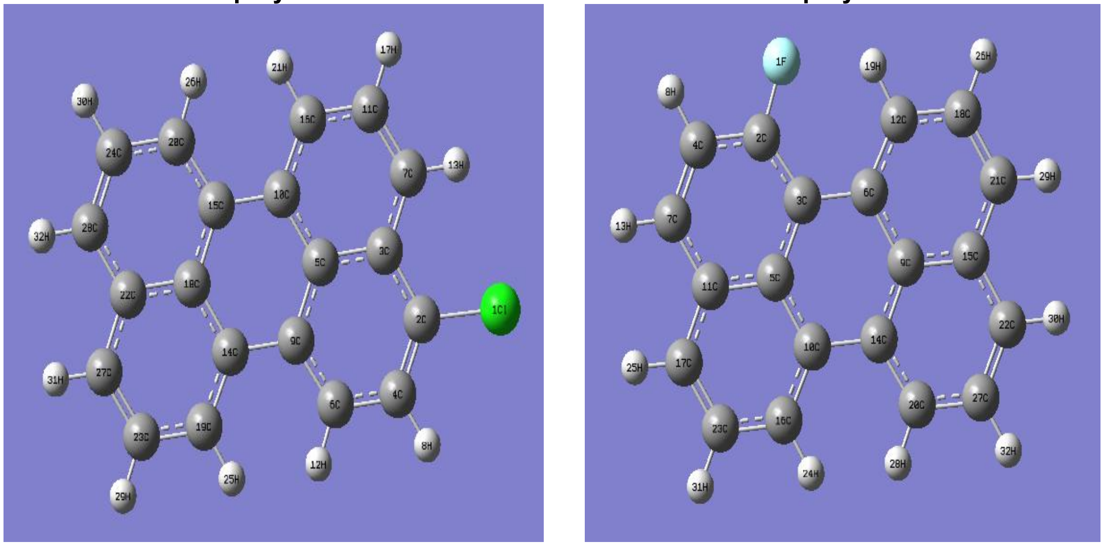
Very recently, in 2019, Suleiman et al. investigated the solvent effects on the structural, electronic, non-linear optical, and thermodynamic properties of perylene based on Density Functional Theory. It was reported that the bond lengths, energy gap, specific heat capacity and anisotropic polarizability ($\Delta\alpha$) of the perylene molecule increased as the polarity of the solvent increased while the bond angles and polarizability (α) of the molecule decreased as the polarity of the solvents increased. Perylene was found to have higher stability in the gas phase with a HOMO-LUMO gap of about 2.9935eV [19]. In the same work, global chemical index parameters were found to increases due to the increase in the dielectric constant of the solvents, while the zero-point vibrational constant energy decreased as the polarity of the solvent increases. Similarly, the NBO analysis confirmed that high intensive interaction between donor and acceptor electrons of Perylene was obtained in chloroform due to large stabilization energy of 4.49cal/mol [19]. In the investigated results of Suleiman et al,. IR spectra calculation was not reported.

To the best of our knowledge, work on halogen effects on the global chemical index, non-linear optical properties, thermodynamics properties, and IR spectra of isolated perylene have not been reported. Thus, the purpose of the present work is to investigate the effect of mono-halogen (bromide, chloride and fluoride) substitution on the electronic, non-linear optical, thermodynamic properties and IR frequencies of the Perylene using the theoretical framework of density functional theory.



1a: Isolated perylene molecule

1b: 1-bromoperylene molecule



1c: 1-chloroperylene molecule

1d: 1-fluoroperylene molecule

Fig. 1. Optimized structure of isolated and substituted perylene molecules

2. THEORETICAL BACKGROUND

2.1 Density Functional Theory

Density functional theory (DFT) is a computational quantum mechanical modeling method successfully applied for finding solutions to the fundamental equation that describes the behavior of atoms and molecules [20]. Density functional theory (DFT) was proposed by Hohenberg and Kohn as a method to determine the electronic structure of a system at ground-state with a theory stating that all ground-state properties for many-particle systems are functional of the electron density. In 1965, Kohn and Sham (KS) reformulated the problem in a more familiar form and opened the way to the practical application of DFT.

2.2 Global Chemical Reactivity Parameters (GCRP)

Global reactivity parameters such as chemical potential, chemical hardness-softness, electronegativity and electrophilicity index are useful parameters in estimating and understanding global chemical reactivity of molecules. The ionization potential (IP) and electron affinities (EA) of the studied molecules are computed by using Koopmans's equation as;

$$\mathrm{IP} = -\mathrm{E}_{\mathrm{HOMO}} \qquad (1)$$

$$\mathrm{EA} = -\mathrm{E}_{\mathrm{LUMO}} \qquad (2)$$

The energy gap E_g can be obtained from the relation;

$$\mathrm{E_g} = \mathrm{E_{LUMO}} - \mathrm{E_{HOMO}} \approx \mathrm{IP} - \mathrm{EA} \qquad (3)$$

The chemical hardness (η) could be expressed in terms of IP and EA as [21];

$$\eta == (\,\mathrm{E_{LUMO}} - \mathrm{E_{HOMO}}) \,/\, 2 \;\approx (\mathrm{IP} \;- \mathrm{EA}\,)/2 \qquad (4)$$

and the chemical softness is given by [21];

$$\mathrm{s} = \frac{1}{\eta} \qquad (5)$$

The chemical potential is given by [22];

$$\mu = -(\frac{\mathrm{IP+EA}}{2}) \qquad (6)$$

The electronegativity is given by [22];

$$\mathrm{X} = \frac{\mathrm{IP+EA}}{2} \qquad (7)$$

The electrophilicity index is a measure of energy lowering due to maximal electron flow between donor and acceptor. Electrophilicity index ($\boldsymbol{\omega}$) is expressed as [22,23];

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

2.3 Non-Linear Optical Properties

To study the non-linear optical properties (NLO) of perylene and its substituted molecules; the dipole moment (μ), polarizability (α), anisotropic polarizability (Δα), and hyperpolarizability (β and γ) were computed at DFT/B3LYP with two basis sets.

For molecular systems, dipole moment can be obtained from [22];

$$\mu_{\mathrm{tot}} = [\mu_x^2 + \mu_y^2 + \mu_z^2]^{1/2} \qquad (9)$$

Where $\mu_x, \mu_y\ and\ \mu_z$ are the components of dipole moment in x, y and z coordinates.

Electric dipole polarizability is given by [24];

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

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

The mean polarizability is calculated using [25];

$$< \alpha >= \frac{1}{3}\,(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \qquad (11)$$

where α_{xx}, $\alpha_{yy}\ and\ \alpha_{zz}$ quantities are known as principal values of polarizability tensor.

The anisotropic polarizability is given by [22];

$$\Delta\alpha = 2^{-1/2}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 +$$
$$(\alpha zz{-}\alpha xx)2{+}6\alpha xx2]1/2$$
(12)

The first hyperpolarizability is defined as [26];

$$\beta = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} +$$
$$\beta yxx)2{+}(\beta zzz{+}\beta zxx{+}\beta zyy)2]1/2$$
(13)

The second order hyperpolarizability is given by [24];

$$\gamma = \frac{1}{5}[\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\big(\gamma_{xxyy} + \gamma_{xxzz} +$$
$$\gamma yyzz] \qquad (14)$$

3. COMPUTATIONAL METHODS

The molecular geometries of perylene and mono-halogen substituted perylene were completely optimized using Ab-initio quantum mechanical technique at the level of Density Functional Theory (DFT). To investigate the effects of mono-halogen atoms substitutions on the structure of perylene molecule, we carried out Density Functional Theory (DFT) calculations using Gaussian 03 package [27] with B3LYP functional and 6-311+G(d) and 6-311++G(d,p) basis sets. All the parameters were fully allowed to relax and each of the calculations converged to an optimized geometry that corresponded to a true energy minimum. Geometry optimization was performed by locating both the minima and transition states on the potential surface of the molecular orbital and this was repeated until the lowest energy geometry was obtained. The optimized geometries were then used to compute the HOMO-LUMO energy gap (E_g) values and global chemical index parameters. At the same level of the theory, dipole moment (μ_{tot}), Electric dipole polarizability (α), mean polarizability (<α>), anisotropic polarizability ($\Delta\alpha$), hyperpolarizability (β and γ), entropy (S) and the specific heat capacity (C_v) of the investigated molecules were also computed using the same optimized geometries. From the optimized geometry obtained, frequency calculations were also carried out. The IR frequencies were calculated by obtaining the Hessian matrix and the force constants for all the normal modes of the molecule. The optimized molecule obtained from geometry optimization was used at the starting point of geometry for IR spectra calculations, and then the frequency job proceeded by computing the energy of the input structure, it then finally went on to compute the frequencies for the structure of the molecules. Gaussian predicted the frequencies and intensities of each spectral line. Analysis of the spectra was done using IRPal 2.0 version software. All calculations employed Density Functional Theory (DFT) as contained in Gaussian 03 software [28].

4. RESULTS AND DISCUSSION

4.1 Optimized Parameters

Some selected values of bond lengths and bond angles of the studied molecules calculated at DFT/B3LYP level using 6-311+G (d) and 6-311++G (d, p) basis sets are listed in Tables 1a, 1b, and 1c. The bond length is the quantifiable distance between two atoms covalently bonded together. It is worth noting that, if the bond length is shorter, then the bond energy is higher [29]. The bond angle is the mean angle between the orbitals of the central atom containing the bonding electron pairs in the molecule, measured in degrees [30].

From Table 1b, the substitution of mono-halogen atoms to the isolated perylene molecule shows little changes in the bond lengths. The result shows that the smallest value obtained was 1.0757Å in 1-fluoroperylene using a 6-311++G (d, p) basis set. However, comparing the results obtained with that of an isolated perylene molecule, the bond length in 1-fluoroperylene molecule tends to be a little smaller which implies 1-fluoroperylene has the strongest bond energy than the other substituted molecules. It is found that the bonds C19-H12 between carbon and hydrogen atoms at the indicated positions possess the lowest values of the bond lengths ranging between 1.0765Å and 1.0757Å for both basis sets. These are the strongest bonds and have the largest bond energy in the substituted perylene molecules which cannot be easily broken. A large amount of energy is needed to break them. This shows that the presence of mono-halogen atoms increases the bond energy of the titled molecule. Table 1b also shows that the basis set 6-311++G(d,p) gives the smallest values of bond lengths than the 6-311+G(d) basis set.

Similarly from Table1c, there is a slight increase in the bond angles of the studied molecules. From the results, the values obtained in 1-bromoperylene are a bit bigger than the ones obtained in the other substituted molecules. The bond angles are found to be closer to 120^0 for all basis sets used demonstrating that the molecules are sp^2 hybridized like planar benzene..The bond lengths and bond angles are found to be in good agreement with those from previous work.

4.2 Molecular Orbital Energies (MOEs)

Table 2 presents the HOMO, LUMO, and HOMO-LUMO energy gaps of the isolated and substituted perylene molecules calculated at the DFT/B3LYP level with two basis sets. The higher HOMO-LUMO energy gap indicates a high kinetic energy and chemical reactivity, thus compounds with large HOMO-LUMO energy gap values show a tendency to have higher stability [23].

Table 1a. Selected bond lengths (*Å*) and bond angles of the optimized structure of isolated perylene molecule by using B3LYP with 6-311+G(d) and 6-311++G (d, p) basis sets

	Basis sets			**Basis sets**	
Bond Lengths (Å)	**6-311+G(d)**	**6-311++G(d,p)**	**Bond Angle (˚)**	**6-311+G(d)**	**6-311++G(d,p)**
R(1,6)	1.4314	1.4313	A(1,3,4)	119.3076	119.2982
R(3,12)	1.3895	1.3893	A(1,3,6)	121.3847	121.4036
R(7,16)	1.0827	1.0817	A(2,7,16)	120.2937	120.2125
R(9,18)	1.0858	1.0846	A(4,10,19)	118.9655	118.9655
R(10,19)	1.0858	1.0846	A(7,14,25)	119.3444	119.4375

Table 1b. Selected bond Lengths (*Å*) of the optimized structure of substituted perylene molecules by using B3LYP with 6-311+G (d) and 6-311++G (d, p) basis sets

	6-311+G(d)			**6-311++G(d,p)**			
Bond lengths (Å)	**1-bromo perylene**	**1-chloro perylene**	**1-fluoro perylene**	**1-bromo perylene**	**1-chloro Perylene**	**1-fluoro Perylene**	**Previous work [16]**
R(2,4)	1.4113	1.3715	1.3999	1.4111	1.3715	1.3999	1.4150
R(4,8)	1.0827	1.0835	1.0839	1.0818	1.0824	1.0829	
R(7,13)	1.0854	1.0819	1.0850	1.0843	1.0812	1.0840	
R(9,14)	1.4260	1.4749	1.4301	1.4259	1.4750	1.4298	1.4310
R(19,12)	1.0783	---------	1.0765	1.0774	---------	1.0757	

Table 1c. Selected bond angles (˚) of the optimized structure of substituted perylene molecules by using B3LYP with 6-311+G (d) and 6-311++G (d, p) basis sets

Basis sets	**6-311+G(d)**			**6-311++G(d,p)**		
Bond Angles(˚)	**1-bromo Perylene**	**1-chloro perylene**	**1-fluoro perylene**	**1-bromo perylene**	**1-chloro perylene**	**1-fluoro Perylene**
A(1,2,3)	124.9529	120.3558	121.2534	124.9834	120.2646	121.2217
A(2,3,5)	116.1973	118.0238	115.6120	116.1558	188.0103	115.5913
A(3,5,10)	120.8353	119.0889	120.9891	120.8781	119.0643	121.0036
A(6,9,14)	121.2001	121.9130	121.7751	121.2488	121.8917	121.7953
A(7,11,17)	120.8776	119.9893	120.1432	120.8052	199.9841	120.1660

Table 2. Calculated HOMO, LUMO, and Energy gap in (e V) of the Optimized Structure of Substituted Perylene Molecules by using B3LYP with 6-311+G (d) and B3LYP/6-311++G (d, p) Basis Sets

Basis Sets	**6-311+G(d)**			**6-311++G(d,p)**			
Molecules	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{gap} (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{gap} (eV)	**Previous work [16]**
Isolated perylene	-5.2692	-2.2757	2.9935	-5.2894	-2.3045	2.9848	2.9740 2.9935
1-bromo Perylene	-5.4491	-2.3979	3.0512	-5.4641	-2.4205	3.0444	
1-chloro Perylene	-5.4083	-2.4654	2.9429	-5.4251	-2.4904	2.9347	
1-fluoro Perylene	-5.3685	-2.3113	3.0572	-5.3870	-2.3364	3.0506	

The results obtained in Table 2 show that the presence of the substituted mono-halogen atoms causes a slight increase in the HOMO-LUMO energy gap of the isolated perylene molecule for both basis sets. Thus, 1-fluoroperylene has the highest values of the energy gap of about (3.0572 and 3.0506) eV for both basis sets; follow by 1-bromoperylene with (3.5012 and 3.0444eV) eV and then 1-chloropeylene with (2.9429 and 2.9347) eV. This shows that the 1-fluoroperylene molecule has the highest HOMO-LUMO gap which implies kinetic energy is higher in 1-fluoroperylene. Therefore, 1-fluoroperylene will have high chemical reactivity than the other substituted perylene molecules. However, smaller basis set (6-311+G(d)) gives a slight difference in HOMO-LUMO gap of about 0.0066eV than 6-311++G(d,p) basis set. The result obtained for isolated perylene for both basis sets was found to agree with theoretical and experimental results [16,19].

4.3 Ionization Potential and Electron Affinity

The Ionization potential (IP) and electron affinity (EA) are parameters that measure the tendency of compounds to lose or gain an electron [31]. The IPs and EAs are presented in Table 3. From the results obtained, it was observed that 1-bromoperylene has the highest ionization potential than the other substituted perylene molecules. On the other hand, 1-fluoroperylene has the lowest values of electron affinities for both basis sets used. This makes it more difficult to remove an electron from 1-bromoperylene to form an ion than in 1-chloroperylene and 1-fluoroperylene. Similarly, it will be easier to add an electron in 1-fluoroperylene than in the other substituted perylene molecules. From the results of the basis sets used, we can conclude that the bigger basis set (6-311++G(d,p)) gives slightly higher values of IP's and EA's than the smaller basis set (6-311+G(d)). Therefore, the effect of the substituted mono-halogen atoms increases the IPs and EA's of the isolated perylene.

4.4 Global Chemical Reactivity Parameters (GCRP)

GCR parameters of molecules such as hardness (η), softness (ʃ), chemical potential (μ), electronegativity (χ) and electrophilicity index (ω) of the isolated perylene and its substituted molecules are reported in Tables 4a and 4b using molecular orbital energy. Chemical hardness is said to increase with the increase in the HOMO-LUMO energy gap. A molecule with higher chemical hardness is said to be more stable and less reactive. As seen in Tables 4a and 4b, 1-fluoroperylene with a slightly higher value of chemical hardness of (1.5286 and 1.5256) eV is considered to be harder and more stable than the rest of the substituted molecules, follow by 1-bromoperylene and 1-chloroperylene with chemical hardness of (1.5256 and 1.5218) eV and (1.4715 and 1.4674) eV respectively. This shows that the substitution of fluorine in the perylene molecule makes it more stable than the rest of the mono-halogen atoms. This indicates that the presence of the substituted mono-halogen atoms increases the stability and chemical reactivity of the studied molecule. By comparing the result of Tables 4a and 4b, it is revealed that the 6-311+G (d) basis set gives more stable and harder compounds than the 6-311++G (d,p) basis set.

Table 3. Ionization Potentials and Electron Affinities of the Optimized Structure of Substituted Perylene Molecules by using B3LYP with 6-311+G (d) and 6-311++G (d,p) Basis Sets

Basis Set	6-311+G(d)		6-311++G(d,p)	
Molecules	**IP (e V)**	**EA (eV)**	**IP (eV)**	**EA (e V)**
Isolated perylene	5.2692	2.2757	5.2894	2.3045
1-bromoperylene	5.4491	2.3979	5.4641	2.4205
1-chloroperylene	5.4083	2.4654	5.4251	2.4905
1-fluoroperylene	5.3685	2.3113	5.3870	2.3364

Table 4a. Global chemical indices of the optimized structure of the substituted perylene molecules by using B3LYP/6-311+G (d) basis set

Molecules	$\eta\ (eV)$	$\int(eV)$	$X(eV)$	$\mu(eV)$	$\omega(eV)$
Isolated perylene	1.4968	0.6681	3.7725	-3.7725	4.7541
1-bromoperylene	1.5256	0.6555	3.9235	-3.9235	5.0452
1-chloroperylene	1.4715	0.6796	3.9369	-3.9369	5.2665
1-fluoroperylene	1.5286	0.6542	3.8399	-3.8399	4.8229

Table 4b Global Chemical Indices of the Optimized Structure of the Substituted Perylene Molecules by using B3LYP/6-311++G (d, p) Basis Set

Molecules	$\eta\ (eV)$	$\int(eV)$	$X(eV)$	$\mu(eV)$	$\omega(eV)$
Isolated perylene	1.4925	0.6700	3.7970	-3.7970	4.8299
1-bromoPerylene	1.5218	0.6571	3.9423	-3.9423	5.1064
1-chloroPerylene	1.4674	0.6815	3.9578	-3.9578	5.2078
1-fluoroPerylene	1.5253	0.6556	3.8617	-3.8617	4.8885

Table 5a. Thermodynamic properties of the optimized structure of isolated and substituted perylene molecules using B3LYP/6-311+G (d) basis set

Molecules	Isolated perylene		1-bromoperylene		1-chloroperylene		1-flouroperylene	
Position	**Cv**	**S**	**Cv**	**S**	**Cv**	**S**	**Cv**	**S**
Electronic	0	0	0	0	0	0	0	0
Translational	2.981	42.474	2.981	43.277	2.981	42.851	2.981	42.680
Rotational	2.981	33.241	2.981	34.479	2.981	34.047	2.981	33.598
Vibrational	50.951	37.351	55.100	42.785	52.888	37.272	51.887	34.939
Total	56.913	113.114	61.062	120.541	58.850	114.170	57.849	111.217
Rotational constants (GHz)	0.62504,0.33060, 0.21623		0.33790, 0.25439, 0.14964		0.60675, 0.20992, 0.15596		0.49301, 0.32390, 0.19548	
ZPVE(Kcal/Mol)	158.55182		152.12308		152.41086		153.30718	

Table 5b. Thermodynamic properties of the optimized structure of isolated and substituted perylene molecules using B3LYP/6-311++G (d,p) basis set

Molecules	Isolated perylene		1-bromoperylene		1-chloroperylene		1-flouroperylene	
Position	**Cv**	**S**	**Cv**	**S**	**Cv**	**S**	**Cv**	**S**
Electronic	0	0	0	0	0	0	0	0
Translational	2.981	42.474	2.981	43.277	2.981	42.851	2.981	42.680
Rotational	2.981	33.241	2.981	34.480	2.981	34.046	2.981	33.598
Vibrational	50.875	37.351	55.044	42.811	52.817	37.221	51.887	34.939
Total	56.837	113.067	61.006	120.568	58.779	114.118	57.849	111.217
Rotational constants (GHz)	0.62508, 0.33072, 0.21629		0.33829, 0.25416, 0.14945		0.60685, 0.21001, 0.15602		0.49307, 0.32398, 0.19561	
ZPVE(Kcal/Mol)	158.53383		152.08698		152.37585		153.29263	

4.5 Thermodynamic Properties

The thermodynamic parameters presented in Tables 5a and 5b such as predicted total energy (E), electronic, translational, rotational, vibrational, zero-point vibrational energy (ZPVE), entropy (S), molar heat capacity (C_v), and rotational constant for both isolated and substituted perylene molecules were calculated at constant temperature and pressure of about 298.1K and 1atm respectively. The analysis of thermodynamic parameters is important to estimate the outcome of a chemical reaction [32]. Our findings show that substitution of bromine to the structure of the perylene molecule improves the molar heat capacity (C_v) and entropy of the molecule while substitution of fluorine increases the zero-point vibrational energy (ZPVE). By analyzing the results obtained in Tables 5a and 5b, the variation of thermodynamic properties changes slightly due to the effect of the substitutions. Therefore, we conclude that the substitutions influence on the thermodynamic properties of the molecules. The results affirm that these substituted molecules have high chemical reactivity and thermal resistivity than isolated perylene due to the increase in their kinetic energy. By comparing the results of the two basis sets, we can conclude that the smaller basis set (6-311+G(d)) gives higher values of specific heat capacity and ZPVE than the larger basis set (6-311++G(d,p)) and more so the larger basis set gives larger values of entropy for the studied molecules.

4.6 Non-Linear Optical Properties

Nonlinear optics plays a key role in the current demand in global research, as NLO active materials find applications in data processing and storage, telecommunications, and potential applications in modern technologies, [33]. To understand the relationships between molecular structure and nonlinear optical properties, the mean and anisotropic polarizabilities, first and second-order hyperpolarizabilities of perylene and its substituted molecules were calculated at DFT / B3LYP level using 6-311+G(d) and 6-311++G(d,p) basis sets. It is a well- known fact that higher values of first-order dipole moment,polarizability, and hyperpolarizability are important for more active NLO materials.

The calculated values for nonlinear optical properties parameters are presented in Tables 6a and 6b. It was observed from Tables 6a and 6b that there is an increase in values of total dipole moments, (μ_{tot}), the total polarizability (α_{tot}) , anisotropy of polarizability ($\Delta\alpha$), first-order hyperpolarizability (β_{tot}) , and second-order hyperpolarizability (γ_{tot}), due to the effects of the substitutions. The significant increase in the dipole moments of the new materials leads to our belief that the substituted molecules are polar materials. Our finding reveals that the isolated perylene molecule is neutral and does not exhibit non-linear optical behavior. However, when substituted with halogen atoms (chlorine and bromine) we realized that its first-order hyperpolarizability (β_{tot}) values turn out to be larger than that of the prototype urea (0.3728 x10^{-30}esu) molecule, which is commonly used for the comparison of NLO properties with other materials, makes them good NLO materials. Given the foregoing, we conclude that substitution of perylene with halogen placed it in another field of application in the linear and nonlinear optics. This implies that the presence of the substitutions improved the NLO properties of the studied molecule. Also, it is observed that the larger basis sets (6-311++G(d,p)) give better results than the smaller basis set (6-311+G(d)).

4.7 IR Intensities

The main idea of frequency analysis is to get vibrational modes connected with precise molecular structures of the measured compound [34]. Fig. 2 a-d show the graphical representations of the calculated vibrational frequencies and intensities of the isolated and substituted molecules. The graphs show that there is a slight increase in the peak values of frequencies for the titled molecule due to the presence of the halogens. From the graphs, the most intense frequencies for 1-bromoperylene and 1-fluoroperylene molecules for both basis sets have values ranging between (825.65cm^{-1} and 832.73 cm^{-1}) with corresponding intensities of 107.2699 *km/mol* and 72.9463

Table 6a. Non-Linear Optical Properties of Isolated and Substituted Perylene Molecules using B3LYP/6-311+G(d) Basis Set

Parameters	Isolated Perylene	1-bromo perylene	1-chloro perylene	1-fluoro perylene
μ_{tot}(DEBYE)	0.0000	1.6827	2.0800	1.4467
$\langle\alpha_{tot}\rangle$ (esu) x 10^{-24}	16.0368	18.6636	18.1662	16.7605
$\langle\alpha_{tot}\rangle$ (esu) x 10^{-24}	26.0254	31.3298	31.6738	26.1008
β_{tot} (esu) x10^{-30}	0.0000	1.2618	0.3826	0.1872
γ_{tot}(esu)x(-10^{-36})	1.0928	1.3847	1.4466	1.1567

Table 6b. Non-linear optical properties of isolated and substituted perylene molecules by using B3LYP/6-311++G(d,p) basis set

Parameters	Isolated perylene	1-bromo perylene	1-chloro perylene	1-fluoro perylene
μ_{tot} (DEBYE)	0.0000	1.6539	2.0515	1.4309
$\langle\alpha_{tot}\rangle$ (esu) x 10^{-24}	16.0603	18.6843	18.1861	16.7832
$\langle\Delta\alpha\rangle$ (esu) x 10^{-24}	26.1206	31.3919	31.7466	26.1992
β_{tot} (esu) x 10^{-30}	0.0000	1.2748	0.3692	0.1921
γ_{tot}(esu)x(-10^{-36})	1.0940	1.3866	1.4474	1.1579

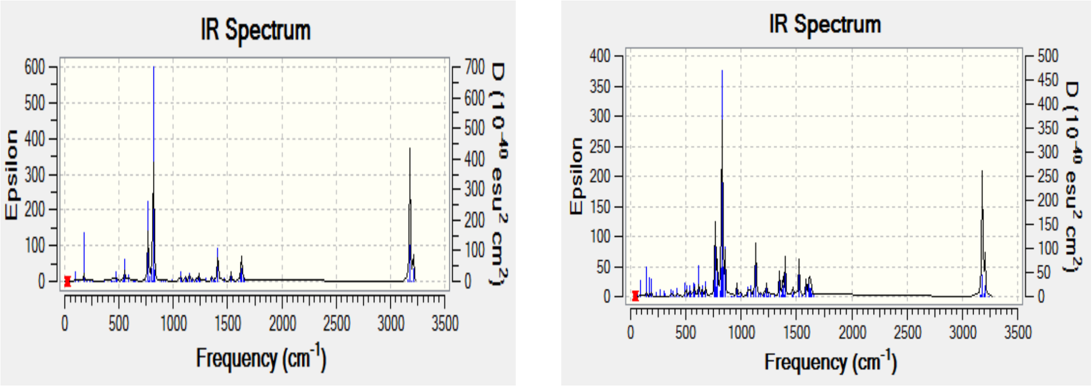


Fig. 2a. Isolated perylene molecule

Fig. 2b. 1-bromoperylene

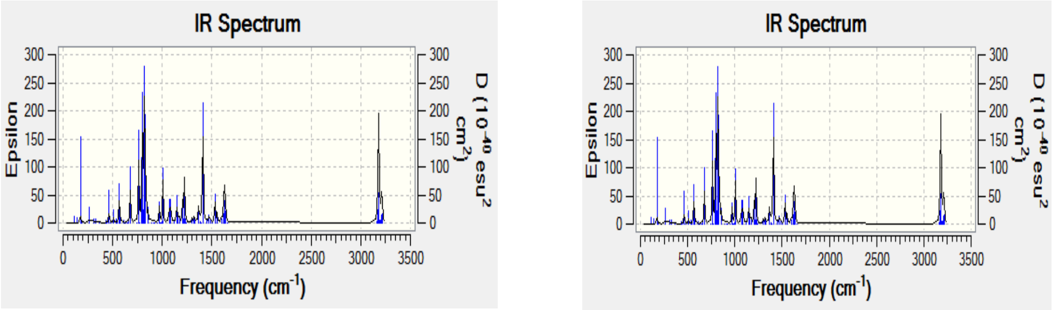


Fig. 2c. 1chloroperylene molecule

Fig. 2d. 1-fluoroperylene molecule

Fig. 2. IR spectra of isolated and substituted perylene molecules.

km/mol. At these frequencies, strong =CH out-of-plane, C-Cl stretch, medium C-H out-of-plane, strong S-OR esters, and strong (broad) N-H wag amines were observed. While in 1-chloroperylene, the highest intense frequency was observed at 1407.01cm^{-1} which occurred at intensities 75.8172 km/mol. At this frequency, strong S=O sulfate ester and medium Ar C-C stretch were observed. IRPAL was used to interpret these frequencies. Comparing the graphs presented, 1-bromoperylene has slightly higher peak values of frequencies with corresponding intensities to the rest of the molecules. Also, the frequencies of the calculated values revealed that 1-bromoperylene does not have imaginary frequencies which affirm its stability than the rest of the mono-halogen molecules.

5. CONCLUSION

In summary, the optimized parameters, electronic properties, thermodynamic parameters, non-linear optical properties, and vibrational frequencies of isolated perylene and its substituted molecules have been investigated. Our main aim was to study the effect of mono-halogen atom substitution (bromine, chlorine, and fluorine) on the structure of perylene. The results obtained show that substitution of fluorine to the titled molecule improves the strength of its bond energy. The calculated values for the bond angles reveal that the molecules under study are planar benzene in which the carbon atoms are sp^2 hybridized. The HOMO-LUMO energy gap calculations demonstrate that perylene has higher stability by substitution of fluorine atom. Our finding further reveals that the band gaps increase with a smaller basis set for the investigated molecule. On the other hand, the thermodynamic properties calculation shows that the effect of the substitution improved the chemical reactivity and thermal resistivity of the molecule. In the frequencies and intensities computations, it was found that the most intense frequency was 826.37cm^{-1} and 96.9614KM/mol in 1-bromopeylene molecule. The vibrational frequencies and intensities results show that the titled molecule will be more stable by substitution of bromide atom than the rest of the mono-halogen atoms as a result of the fact that no imaginary frequencies were observed in 1-

bromoperylene. Moreover, the results obtained for NLO analysis show that isolated perylene is a neutral molecule and has a weak nonlinear optical (NLO) behavior. However the substitution of hydrogen by mono-halogen atoms (chlorine, fluorine, and bromine) shows more interesting properties such as high dipole moments and first-order hyperpolarizability (β). On the whole, we conclude that the substituted molecules are good candidates for applications in NLO materials, renewable energy, and emerging technologies. Investigation on the ionic form of perylene molecule may be the field of interest for future researchers.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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