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Solvent Effects on the Structural, 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 among all authors. Author NMS performed all calculations on the electronic properties and part of the calculations on the structural properties of the molecule. Author LST managed the literature searches and guided the team. Authors AL and AM carried out the calculations of the non-linear optical properties and thermo dynamic properties respectively. Author ASG initiated the work and performed calculations with author NMS on structural properties of the molecule. All authors read and approved the final manuscript.

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ABSTRACT

Perylene ($C_{20}H_{12}$) is an important member of the polycyclic aromatic hydrocarbons (PAHs) that has a wide applications such as organic photovoltaic cells, field effect transistors and biosensors. Optimized bond lengths and bond angles, HOMO-LUMO energy gap, global chemical indices, total energy, nonlinear optical and thermodynamic properties of Perylene in the gas phase and in solvents (water, chloroform, benzene and acetone) were obtained based on Density Functional Theory with B3LYP/6-311++G(d,p) basis set. All the computations were carried out using Gaussian 03 package and revealed that the solvents have an effect on the optimized parameters. It was observed that the bond lengths increase with an increase in the polarity of the solvents, while the bond angles were found to increase as the polarity of the solvents decreases. Perylene molecule was found to have a higher stability in the gas phase with HOMO-LUMO energy gap of 2.9935eV.

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The HOMO and HOMO-LUMO energy gap were found to increase with an increase in polarity of the solvents. The molecule was found to be harder and less reactive in the gas phase with chemical hardness of 1.4968eV. The maximum value of ionization potential 5.3227eV and minimum value of electron affinity 2.2757eV were obtained in water and gas phase respectively, as such it is difficult to remove an electron from the molecule in water to form an ion and it is also difficult to add an electron to the molecule in gas phase. The ground state total energy of the molecule was found to increase with an increase in polarity of the solvents. Similarly, the chemical hardness, chemical softness, electronegativity, chemical potential and electrophilicity index were found to increase with an increase in the dielectric constant of the solvents. In the non-linear optical (NLO) properties calculations, it was observed that Perylene is a neutral molecule. It was found that the specific heat capacity of perylene increases with an increase in the polarity of the solvent while the entropy and the zero-point vibrational energy of the molecule decreases as the polarity of the solvent increases. In the non-linear optical properties calculations, it was found that the polarizability (⟨α⟩) of Perylene increases with decrease in the polarity of the solvents and the anisotropic polarizability (Δα) of Perylene increase with an increase in the polarity of the solvents. In the Natural Bond Orbital (NBO) analysis, high intensive interaction between donor and acceptor electrons of Perylene was observed in chloroform due to to large stabilization energy of 4.49Kcal/mol. The result shows that careful selection of the solvents and basis sets can tune the frontier molecular molecular orbital energy gap.

Keywords: Density functional theory; Gaussian 03; HOMO-LUMO; non-linear optical properties and perylene.

1. INTRODUCTION

With rising demand for sustainably risk free energy, there is no better alternative than organic electronic materials which have proved to be a promising candidates for advanced optoelectronic applications such as in light emitting diodes, photovoltaic cells [1], organic field effect transistors, organic solar cells and transparent white displays [2,3]. To fully understand and use these materials, their basic fundamental physical properties must be sufficiently explored. To acquire such vital information, their structural, electronic, optical, non-linear optical and thermodynamic properties are required.

Rylene are series of polycyclic aromatic hydrocarbons (PAHs) with general chemical formula C10nH4n+4 among which are the most widely investigated perylene ($C_{20}H_{12}$) and its derivatives such as pyrelenebisimides, perylene tetracarboxylic acid (PTDCA) and perylene-3,4,9,10-tetracarboxylic anhydride (PDA) which, due to their promising electronic, optical and charge-transport properties, are widely used in high-tech applications such as organic photovoltaic, organic field effect transistors, biolabels, sensors, single molecular spectroscopy, super molecular assemblies and opto-electronic devices [4].

Interestingly, wide ranges of experimental and theoretical studies have explored the synthesis and applications of perylene and its derivatives including Density Functional Theory. For instance, [5] presented within the framework of Density Functional Theory (DFT) as well as a comparative study of the electronic, optical, and transport properties of some selected polycyclic aromatic hydrocarbons (Perylene included). Similarly, the structural, and optoelectronic properties of different classes of perylene: insolated perylene, diindo [1,2,3-cd:1ˈ,2ˈ,3ˈ-Im]perylene (DIP) molecule and DIP molecular crystal were investigated [6]. The effect of aggregation on the excited-state electronic structure of Perylene through transient absorption measurements of isolated molecules, excimers in solution, monomeric crystal forms (β-perylene), and dimeric crystal forms (α-perylene) were studied [7]. The aggregation of water soluble, dicationic Perylene bisimide derivatives using absorption and emission spectroscopies, X-ray and neutron scattering techniques as well as electron microscopy, provides evidence for the existence of higher order molecular aggregates in solution [2]. The structure and electronic properties of pyrelene and coronene under pressure were also theoretically investigated using DFT [8] and Van der Waals interaction which were also used in obtaining the electronic structure of crystalline perylene [9]. However, to the best of our knowledge, the effects of solvents on this promising organic material have never been studied before. In the present investigation, computational studies have been carried out to investigate the effects of solvents on the structural, electronic, thermodynamic and non-linear optical properties of Perylene based on density functional theory.

Choice of a suitable solvent is of paramount scientific interest to obtain desired efficiency, selectivity and kinetics of chemical reaction [10]. The solvents used in this work include Water, Chloroform, Benzene and Acetone with the following dielectric constants; Water ($\varepsilon = 80.37$), Chloroform ($\varepsilon = 4.806$), Benzene ($\varepsilon = 2.284$) and Acetone ($\varepsilon = 37.50$).

2. THEORETICAL BACKGROUND

2.1 Density Functional Theory

Density Functional Theory is a phenomenally successful approach to finding solutions to the fundamental equation that describes the quantum behavior of atoms and molecules [11]. DFT has proved to be highly successful in describing structural and electronic properties in a vast class of materials, ranging from atoms and molecules to simple crystals to complex systems [12]. Density functional theory (DFT) was proposed by Hohenberg and Khon 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 [13,14]. In 1965, Khon and Sham (KS) reformulated the problem in a more familiar form and opened the way to practical application of DFT [12]. For a system of non- interacting electrons, the ground state charge density is representable as a sum over one-electron orbitals (KS orbitals) n(r) [12]. That is;

$$n(r) = 2\sum_i |\Psi_i(r)|^2 \qquad (1)$$

If we assume double occupancy of all states, and the Khon-Sham orbitals are the solution to the Schrodinger equation.

$$\Big[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(r)]\Psi_i(r) = \epsilon_i\ \Psi_i(r) \qquad (2)$$

where,

$$V_{KS} = V_{ext} + \int \frac{e^2 n(r) n(r')}{|r-r'|} dr dr' + V_{XC}[n(r \qquad (3)$$

is a unique potential having $n(r)$ as its charge density. Thus we have;

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_H(r) + V_{XC}[n(r)] + V(r)\right)\Psi_i(r) = \epsilon_i\ \Psi_i(r) \qquad (4)$$

where, $V_H(r)$ is the Hartree potential and $V_{XC}[n(r)]$ is the exchange correlation potential.

A wide variety of different approximations have been developed to take care of the effects of electron-electron interactions such as the generalized gradient approximation (GGA), local density approximation (LDA) and Hybrid Approximations.

In the LDA, the exchange correlation energy at a point in space is taken to be that of the homogeneous electron gas with local-density $\epsilon_{XC}\ (n)$. Thus the total exchange correlation energy functional is approximated as [15];

$$E_{XC}^{LD} = \int n(r)\ \epsilon_{XC}\ (n(r))dr \qquad (5)$$

From which the potential is obtained as;

$$V_{XC} = \frac{\delta E_{XC}}{\delta n} \qquad (6)$$

where, δE_{XC} and δn are the derivatives of the exchange energy and the electron density respectively.

Whereas, the generalized gradient approximation (GGA) depends on both local density and it's gradient, it can be expressed as;

$$E_{XC}^{GGA} = \int n(r)\ \epsilon_{XC}\ (n|\nabla n|\nabla^2 n)dr \qquad (7)$$

where, $n(r)$ is the electron density.

Unlike LDA and GGA, the hybrid function is a linear combination of Hartree-Fock exchanges expressed as [15]:

$$E_{XC}^{hybrid} = \alpha E_{XC}^{HF} + E_C \qquad (8)$$

Where, $E_{XC}^{HF}$is the Hartree-Fock exchange energy and α can be chosen to satisfy particular criteria.

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 potentials (IP) and electron affinities (EA) of the molecule in the gas phase and in solvents are computed using Koopman's Hypothesis, through the HOMO and LUMO energy orbitals respectively using the following expressions;

$$IP = -E_{HOMO} \qquad (9)$$

$$EA = -E_{LUMO} \qquad (10)$$

The difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) known as energy gap can be obtained from the relation;

$$E_{gap} = E_{LUMO} - E_{HOMO} \approx IP - EA \tag{11}$$

Chemical hardness is given by half of the energy band gap [16];

$$η = \frac{IP-EA}{2} \tag{12}$$

The softness of a molecule can be obtained by taking the inverse of its chemical hardness [17];

$$S = \frac{1}{η} \tag{13}$$

The chemical potential is given by [17];

$$\mu = -(\frac{IP+EA}{2}) \tag{14}$$

The electronegativity is given by [17];

$$χ = \frac{IP+EA}{2} \tag{15}$$

The electrophilic index is expressed as [17,18];

$$\omega = \frac{\mu^2}{2η} \tag{16}$$

2.3 Non-Linear Optical Properties

In order to gain an insight on the effects of solvent on the non-linear optical properties (NLO) of perylene; the dipole moment, polarizability, anisotropic polarizability and hyperpolarizability were calculated.

Dipole moment is a property used in describing the polarity of a system. For molecular systems, this property can be obtained from [19];

$$\mu_{tot} = \left[\mu_x^2 + \mu_y^2 + \mu_z^2\right]^{1/2} \tag{17}$$

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

Electric dipole polarizability is an important property used in determining the polarizability of a molecule or compound. It is a measure of the linear response of an infinitesimal electric field (F) and represents second-order variation energy [20];

$$\alpha = -\frac{\partial^2 E}{\partial F_a \partial F_b} \tag{18}$$

where a, and b are coordinates of x, y and z. The mean polarizability is calculated using [16];

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{19}$$

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

The anisotropic polarizability is given by [17]:

$$\Delta\alpha = \left[\frac{(\alpha_{xx}-\alpha_{yy})^2+(\alpha_{yy}-\alpha_{zz})^2+(\alpha_{zz}-\alpha_{xx})^2+6(\alpha_{xz}^2+\alpha_{xy}^2+\alpha_{yz}^2)}{2}\right]^{1/2} \tag{20}$$

The mean first hyperpolarizability is defined as [17, 21]:

$$\beta_{tot} = \left(\beta_x^2 + \beta_y^2 + \beta_z^2\right)^{1/2} \tag{21}$$

where *βx, βy* and *βz* are defined as:

$$\begin{aligned} \beta_x &= \beta_{xxx} + \beta_{xyy} + \beta_{xzz} \\ \beta_y &= \beta_{yyy} + \beta_{xxy} + \beta_{yzz} \\ \beta_z &= \beta_{zzz} + \beta_{xxz} + \beta_{yyz} \end{aligned} \tag{22}$$

The β_x, β_y and β_z refer to the components of hyperpolarizability along *x, y* and *z* components of molecular dipole moment.

2.4 Natural Bond Orbital (NBO)

NBO analysis provides an efficient method for studying intra and intermolecular bonding interactions among bonds, and also provides a convenient basis for investigation of charge transfer or conjugative interactions in molecular systems [22]. The second-order Fock matrix is used to evaluate the donor-acceptor interactions in the NBO basis. For each donor and acceptor, the stabilization energy $E^{(2)}$ associated with the electron delocalization between donor and acceptor is estimated as [23];

$$E^{(2)} = -n_\sigma \frac{\langle\sigma|F|\sigma\rangle^2}{\varepsilon_{\sigma*}-\varepsilon_\sigma} = -n_\sigma \frac{{F_{ij}}^2}{\Delta E} \tag{23}$$

where $\langle\sigma|F|\sigma\rangle^2$, or ${F_{ij}}^2$ is the Fock matrix element between i and j NBO orbitals, $\varepsilon_{\sigma*}$ and ε_σ are the energies of $\sigma*$ and σ NBO's and n_σ is the population of the donor orbital.

3. COMPUTATIONAL METHOD

Geometry of perylene was optimized with no symmetry constraint using Becke's threeparameter hybrid exchange [24] combined with Lee-Yang-Parr's gradient-corrected correlation [25] functional (B3LYP) method with 6-311++G(d,p) basis set. 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.

For the study of solvation effects, a Self-Consistent Reaction Field (SCRF) approach based on Polarizable Continuum Model (PCM) were employed. The effects of four solvents (water, chloroform, benzene and acetone) were investigated by means of the SCRF method based on PCM as implemented in the Gaussian 03 [26]. The optimized geometries were then used to obtain the HOMO-LUMO energy gap, chemical hardness, chemical softness, chemical potential, electronegativity, electrophilcity index, dipole moment, polarizability, anisotropic polarizability, hyperpolarizability, entropy and the specific heat capacity of the investigated molecule at the same level of theory (B3LYP/6-311++G(d,p)). Finally, the NBO calculations [27] were performed using NBO 3.1 program as implemented in the Gaussian 03 package at same level of theory in order to understand the various second-order interactions between the filled orbitals of one subsystem and the vacant orbitals of another subsystem. All calculations were performed within the framework of Density Functional Theory (DFT) as coded in Gaussian 03 package [26].

4. RESULTS AND DISCUSSION

4.1 Optimized Parameters

The optimized values of bond lengths and bond angles of the studied molecule were calculated at DFT/B3LYP level using 6-311++G(d,p) basis set in the gas phase and in different solvents (water, chloroform, benzene and acetone). The results are shown in Tables 1 and 2. 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 of an atom in a molecule [20].

From Table 1, there are little changes in the bond lengths of Perylene when optimized with water, chloroform, benzene and acetone compared with the gas phase. The result shows that the lowest value obtained was 1.0825Å in benzene. However, when compared with results of an isolated perylene molecule [6], the bond lengths here tend to be a little smaller. It is worth noting that, the smaller the bond length, the higher the bond energy and stronger the bond [28]. Consequently, this has affirmed that the bond lengths of perylene in the gas phase and in solvents are a little stronger than that of an isolated perylene molecule. Hence, an enormous amount of energy is required to break these bonds. It was also observed that the bond length increases with an increase in the polarity of the solvents.

Table 1. Selected bond lengths (Å) of the optimized structure of perylene in the gas phase and in different solvents

Bond Lengths (Å)	Gas Phase	Water	Chloroform	Benzene	Acetone	Previous work
R(2,5)	1.4762	1.4773	1.4769	1.4765	1.4772	1.4700[a]
R(1,4)	1.4339	1.4346	1.4342	1.434	1.4345	1.4360[a]
R(1,2)	1.4315	1.4324	1.4319	1.4316	1.4323	1.4310[a]
R(28,32)	1.0858	1.0877	1.0866	1.0858	1.0875	1.0900[a]
R(14,25)	1.0853	1.0872	1.0862	1.0854	1.087	1.0900[a]
R(13,24)	1.0827	1.0846	1.0833	1.0825	1.0841	1.0900[a]

[a] *[6]*

Table 2. Selected bond angles (˚) of the optimized structure of perylene in the gas phase and in different solvents

Bond Angles (˚)	Gas Phase	Water	Chloroform	Benzene	Acetone
A(6,3,8)	122.184	122.106	122.130	122.143	122.119
A(3,8,15)	122.001	121.870	121.918	121.944	121.890
A(14,9,18)	120.748	120.919	120.866	120.838	120.900
A(11,20,27)	119.592	119.640	119.626	119.612	119.639
A(20,28,32)	118.965	118.859	118.894	118.905	118.876
A(14,7,16)	117.706	117.733	117.717	117.759	117.679

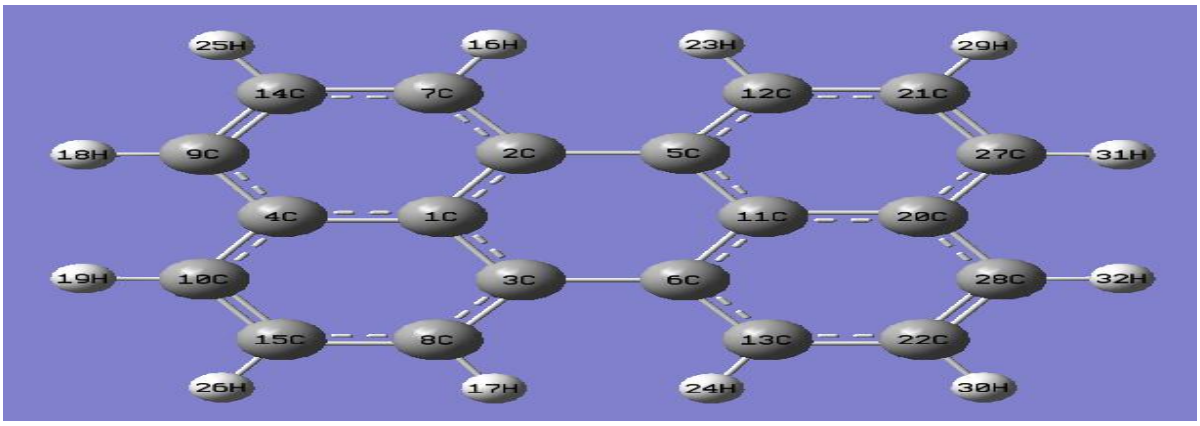

Fig. 1. Optimized structure of perylene

However, the longest bond length is 1.477Å, which is almost the same in both gas phase and solvents. The structural geometry of the studied molecule that consists of bond lengths and bond angles are found to be in good agreement with those from previous work [6]. But in [6] the molecule is in the form of an insolated perylene, diindo[1,2,3-cd:1',2',3'- lm]perylene (DIP) molecule and DIP molecular crystal.

4.2 Frontier Molecular Orbital Energies (FMOEs)

Table 3 presents the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) and HOMO and LUMO energy gaps of perylene in the gas phase and in solvents calculated at the DFT/B3LYP level in the 6-311++G(d,p) basis set. The values of HOMO, LUMO and their energy gaps reflect the chemical activity of the molecule. The energy gap between HOMO and LUMO determines the kinetic stability, chemical reactivity, optical polarizability and chemical hardness-softness of a molecule [21]. Compounds with large HOMO-LUMO gap value tend to have higher stability [18]. In this work, the order of stability of the molecule is more in the gas phase> water> acetone> chloroform> benzene. Interestingly, the order of stability increases with an increase in polarity of the solvents.

HOMO as an electron donor represents the ability to donate an electron, while LUMO as an electron acceptor represents the ability to accept an electron. The smaller the LUMO and HOMO gaps, the easier it is for the HOMO electron to be excited; the higher the HOMO energies, the easier it is for HOMO to denote electrons; the lower the LUMO energies, the easier it is for the LUMO to accepts electrons [29].

It can be observed from Table 3, that the LUMO energy of perylene in benzene (-2.2829 eV) is smaller than that in the gas phase and in the rest of the solvents. Hence, the electron transfer from HOMO to LUMO of the molecule in benzene is relatively easier than that in the gas phase and in the rest of the solvents. It can also be observed that the HOMO and energy gap of perylene increases with increase in polarity of the solvents.

The HOMO-LUMO gap of 2.976 eV obtained in the gas phase is found to be very close to 2.972 eV of an isolated Perylene reported by [6].

4.3 Total Ground State Energy

Table 4 presents the dielectric constants of the solvents and total energy in atomic mass unit (a.u) of Perylene molecule in the gas phase and in different solvents calculated at the DFT/B3LYP

Table 3. Calculated HOMO, LUMO and energy gap in (eV) of the optimized structure of perylene in the gas phase and different solvents using B3LYP methods with 6-311++G(d,p) basis set

Solvents	E_{HOMO} (eV)	E_{LUMO}(eV)	Gap (eV)	Previous Work
Gas Phase	-5.2693	-2.2757	2.9935	2.9740[a] 2.98[b]
Water	-5.3227	-2.3332	2.9895	
Chloroform	-5.2878	-2.3005	2.9873	
Benzene	-5.2729	-2.2829	2.9860	
Acetone	-5.3167	-2.3274	2.9893	

[a][6] [b][5]

Table 4. Ground state total energies in atomic mass unit (a.u) of the optimized structure of perylene in the gas phase and different solvents

Solvents	B3LYP/6-311++G(d,p)	ε
Gas Phase	-769.5611634	-
Water	-769.5983746	80.37
Chloroform	-769.5914965	4.806
Benzene	-769.5874674	2.284
Acetone	-769.5954100	37.50

4.4 Ionization Potentials and Electron Affinity

The ionization potential (IP) and electron affinity (EA) measure the tendency of compounds to lose or gain an electron [30]. The IPs and EAs are presented in Table 5. The higher the ionization potential (IP), the more difficult it is to remove an electron to form an ion. The lower the electron affinity (EA), the less easy it is to add an electron.

Table 5. Ionization potentials and electron affinities of the optimized structure of a perylene molecule in the gas phase and different solvents

Solvents	IP (eV)	EA (eV)
Gas Phase	5.2693	2.2757
Water	5.3227	2.3332
Chloroform	5.2878	2.3005
Benzene	5.2729	2.2829
Acetone	5.3167	2.3274

In Table 5, it can be observed that it is more difficult to remove an electron from water> acetone> chloroform> benzene> gas phase to form an ion. Similarly, it is more difficult to add an electron in terms of their EAs to the molecule in gas phase> benzene>chloroform> acetone >water. It was observed that the ionization potential increases with an increase in the polarity of the solvents while the electron affinity decreases as the polarity of the solvents decreases. Non-polar hydrocarbon molecules such as perylene are hydrophobic (water fearing) in nature. Water and some other polar solvents are unable to form significant attractive interactions with non polar molecules in which the carbon and hydrogen atoms are well bonded together through non polar vander waals interactions. In other words the energy derived from the interactions of polar solvents and non polar organic molecule is not enough to breakup the ion-ion interaction within the molecule.

4.5 Global Chemical Indices

The global chemical indices such as chemical hardness, chemical softness, chemical potential, electronegativity and electropilicity index of the molecule in the gas phase and in different solvents were computed and reported in Table 5 using the frontier molecular orbital energy.

Chemical hardness is proportional to the HOMO-LUMO energy gap. An Increase in the chemical hardness makes the molecule more stable and less reactive. As seen in Table 6, Perylene molecule in the gas phase with slightly higher value of chemical hardness of 1.4968eV is considered to be harder and more stable than in the rest of the solvents, followed by benzene, water and acetone with chemical hardness of 1.4950eV, 1.4948eV and 1.4947eV respectively. This indicates that Perylene in chloroform is more stable than in the rest of the solvents.

4.6 Thermodynamic Properties

Table 7 presents the components and total contribution of the electronic, translational, rotational and vibrational energies to the entropy (S) and heat capacity (Cv) as well as the rotational constants and zero-point vibrational energies (ZPVE) of Perylene in the gas phase and in different solvents.

It can be observed in Table 7 that specific heat capacity of perylene is found to increase with an increase in the polarity of the solvents, while

Table 6. Global chemical indices of the optimized Perylene in the gas phase and in different solvents

Solvents	η (eV)	S (eV)	χ (eV)	μ (eV)	ω (eV)
Gas Phase	1.4968	0.6680	3.7725	-3.7725	4.7540
Water	1.4948	0.6690	3.8279	-3.8279	4.9013
Chloroform	1.4937	0.6695	3.7942	-3.7942	4.8188
Benzene	1.4950	0.6689	3.7772	-3.7772	4.7734
Acetone	1.4947	0.6690	3.8221	-3.8221	4.8867

Table 7. Thermodynamic properties of the optimized structure of perylene in the gas phase and different solvents

	Gas Phase		**Water**		**Chloroform**		**Benzene**		**Acetone**	
Positions	**Cv (Kcal/Mol)**	**S (Kcal/Mol)**	**Cv (Kcal/Mol)**	**S (Kcal/Mol)**	**Cv (Kcal/Mol)**	**S (Kcal/Mol)**	**Cv (Kcal/Mol)**	**S (Kcal/Mol)**	**Cv (Kcal/Mol)**	**S (Kcal/Mol)**
Electronic	0	0	0	0	0	0	0	0	0	0
Translational	2.981	42.474	2.981	42.474	2.981	42.474	2.981	42.474	2.981	42.474
Rotational	2.981	33.242	2.981	33.246	2.981	33.244	2.981	33.243	2.981	33.246
Vibrational	50.951	37.398	50.961	36.331	50.939	36.745	50.913	37.045	50.964	36.454
Total	56.913	113.114	56.922	112.051	56.901	112.463	56.875	112.762	56.925	112.174
Rotational Constants (GHz)		0.62504	0.62372		0.62427		0.62464		0.62388	
		0.3306	0.33026		0.33042		0.33056		0.33027	
		0.21623	0.21593		0.21606		0.21616		0.21595	
ZPVE (Kcal/Mol)		158.55182	157.37117		157.80191		158.12372		157.48719	

Table 8. Non-linear optical properties (in Debye) of the optimized perylene molecule in the gas phase and different solvents

Solvents	$\boldsymbol{\mu_{tot}}$	$\langle\boldsymbol{\alpha}\rangle$	$\langle\Delta\boldsymbol{\alpha}\rangle$	$\boldsymbol{\beta_{tot}}$
Gas Phase	0.0000	108.2104	24.4360	1.00 E-4
Water	0.0000	104.3552	31.0839	4.36 E-4
Chloroform	0.0000	105.9012	28.2349	3.00 E-4
Benzene	0.0000	107.0436	26.1246	1.41 E-4
Acetone	0.0000	104.6985	30.4309	2.83 E-4

Table 9. Natural Bond Orbital (NBO) of optimized perylene molecule in the gas phase and in different solvents

Donor NBO (i)	Acceptor NBO (j)	$E^{(2)}$ Kcal/mol	E(j)-E(i) a.u	Fji a.u	Donor NBO (i)	Acceptor NBO (j)	$E^{(2)}$ Kcal/mol	E(j)-E(i) a.u	Fji a.u
Water					**Chloroform**				
σC2-C5	σ*C1-C2	1.40	1.18	0.036	σC2-C5	σ*C1-C3	4.29	1.16	0.052
σC2-C5	σ*C1-C4	4.03	1.18	0.062	σC2-C5	σ*C1-C4	3.88	1.16	0.060
σC2-C5	σ*C2-C7	2.81	1.22	0.052	σC2-C5	σ*C2-C5	3.27	1.10	0.054
σC2-C5	σ*C5-C11	2.33	1.16	0.046	σC2-C5	σ*C2-C7	4.49	1.21	0.066
σC2-C5	σ*C5-C12	3.74	1.20	0.057	σC2-C5	σ*C3-C8	2.27	1.23	0.047
σC2-C5	σ*C7-C14	1.95	1.21	0.044	σC2-C5	σ*C4-C10	2.41	1.18	0.048
σC2-C5	σ*C11-C20	2.66	1.22	0.049	σC2-C5	σ*C5-C12	2.30	1.23	0.048
σC2-C5	σ*C12-C21	1.87	1.20	0.042	σC2-C5	σ*C7-H16	2.37	1.11	0.046
σC11-C20	σ*C2-C5	2.61	1.13	0.049	σC11-C20	σ*C2-C5	3.10	1.09	0.052
σC11-C20	σ*C3-C6	2.58	1.11	0.048	σC11-C20	σ*C3-C6	2.91	1.09	0.050
σC11-C20	σ*C5-C11	4.04	1.17	0.062	σC11-C20	σ*C5-C11	3.07	1.16	0.053
σC11-C20	σ*C6-C11	3.89	1.17	0.060	σC11-C20	σ*C6-C11	3.36	1.15	0.056
σC11-C20	σ*C20-C27	2.69	1.20	0.051	σC11-C20	σ*C20-C27	3.73	1.18	0.060
σC11-C20	σ*C20-28	2.71	1.20	0.051	σC11-C20	σ*C20-C28	3.72	1.18	0.060
σC11-C20	σ*C27-H31	2.35	1.11	0.046	σC11-C20	σ*C27-H31	1.81	1.10	0.040
σC11-C20	σ*C28-H32	2.36	1.11	0.046	σC11-C20	σ*C28-H32	1.85	1.10	0.041
Benzene					**Gas Phase**				
σC1-C2	σ*C1-C3	4.31	1.16	0.063	σC1-C2	σ*C1-C3	4.30	1.16	0.063
σC1-C2	σ*C1-C4	4.31	1.17	0.063	σC1-C2	σ*C1-C4	4.31	1.17	0.063
σC1-C2	σ*C2-C5	2.49	1.12	0.047	σC1-C2	σ*C2-C5	2.49	1.12	0.047
σC1-C2	σ*C2-C7	3.75	1.25	0.061	σC1-C2	σ*C2-C7	3.75	1.25	0.061
σC1-C2	σ*C3-C8	2.29	1.21	0.047	σC1-C2	σ*C3-C8	2.29	1.21	0.047
σC1-C2	σ*C4-C10	2.67	1.20	0.051	σC1-C2	σ*C4-C10	2.67	1.20	0.051
σC1-C2	σ*C5-C12	2.23	1.21	0.047	σC1-C2	σ*C5-C12	2.23	1.21	0.047
σC1-C2	σ*C7-H16	2.42	1.12	0.047	σC1-C2	σ*C7-H16	2.45	1.11	0.047
σC11-C20	σ*C2-C5	3.07	1.12	0.052	σC11-C20	σ*C2-C5	3.06	1.12	0.052
σC11-C20	σ*C3-C6	2.24	1.11	0.045	σC11-C20	σ*C3-C6	2.24	1.11	0.045
σC11-C20	σ*C5-C11	4.25	1.16	0.063	σC11-C20	σ*C5-C11	4.24	1.16	0.063
σC11-C20	σ*C6-C11	3.95	1.16	0.061	σC11-C20	σ*C6-C11	3.94	1.16	0.061
σC11-C20	σ*C20-C27	3.83	1.18	0.060	σC11-C20	σ*C20-C27	3.86	1.18	0.060

σC11-C20	σ*C20-C28	4.03	1.19	0.062	σC11-C20	σ*C20-C28	4.06	1.19	0.062
σC11-C20	σ*C27-H31	1.92	1.10	0.041	σC11-C20	σ*C27-H31	1.95	1.10	0.042
σC11-C20	σ*C28-H32	1.80	1.10	0.040	σC11-C20	σ*C28-H32	1.83	1.10	0.040
Acetone									
σC1-C2	σ*C1-C3	4.30	1.16	0.063					
σC1-C2	σ*C1-C4	3.89	1.16	0.060					
σC1-C2	σ*C2-C5	3.27	1.10	0.054					
σC1-C2	σ*C2-C7	4.48	1.21	0.066					
σC1-C2	σ*C3-C8	2.27	1.23	0.047					
σC1-C2	σ*C4-C10	2.24	1.18	0.048					
σC1-C2	σ*C5-C12	2.31	1.23	0.048					
σC1-C2	σ*C7-H16	2.34	1.12	0.046					
σC11-C20	σ*C2-C5	3.11	1.09	0.052					
σC11-C20	σ*C3-C6	2.92	1.09	0.051					
σC11-C20	σ*C5-C11	3.07	1.16	0.053					
σC11-C20	σ*C6-C11	3.37	1.15	0.056					
σC11-C20	σ*C20-C27	3.71	1.18	0.060					
σC11-C20	σ*C20-C28	3.70	1.18	0.059					
σC11-C20	σ*C27-H31	1.78	1.10	0.040					
σC11-C20	σ*C28-H32	1.38	1.10	0.040					

the entropy decreases as the dielectric constant increases. The zero-point vibrational energy (ZPVE) decreases with an increase in the polarity of the solvents.

4.7 Non-Linear Optical Properties

Our investigation also highlighted the effects of solvents on the nonlinear optical properties of the molecule. This is necessary for sufficient understanding of the nonlinear optical response of the molecule. Nonlinear optical (NLO) effect arises from the interactions of electromagnetic fields in various media to produce new fields altered in phase, frequency, amplitude and other propagation characteristics from the incident fields [31].

Table 8 presents the non-linear optical properties in atomic mass unit (a.u) of perylene molecule in the gas phase and in solvents. The properties computed and reported are dipole moment (μ_{tot}), polarizability ($\langle\alpha\rangle$), anisotropic polarizability ($\Delta\alpha$) and hyperpolarizability (β_{tot}).

The dipole moment in a molecule is an important electronic property which results from non-uniform distribution of charges on the various atoms in the molecule [21]. It can be observed in Table 8 that perylene is a neutral molecule with a dipole moment of 0.000eV both in the gas phase and in the solvents. It can also be observed that the polarizability of Perylene increases as the polarity of the solvents decreases whereas the anisotropic polarizability increases with an increase in the polarity of the solvents. Consequently, increasing or decreasing the polarity of the solvents plays a significant role in determining the values of the non-linear optical properties of perylene.

4.8 Natural Bond Orbital (NBO) Analysis

Natural Bond Orbital (NBO) analysis provides an efficient method for studying intra-and inter-molecular interaction among bonds and also provides a convenient basis for investigating charge transfer or conjugative interactions in molecular systems. Table 9 presents the results of Natural Bond Orbital analysis of the optimized structure of perylene molecule in the gas phase and in different solvents.

The larger $E^{(2)}$ value, the more intensive is the interaction between electron donors and acceptors. The more donation tendency from electron donors to electron acceptors, the greater is the extent of conjugation of the whole system [23]. It can be seen from Table 9 that the largest value of stabilization (4.49 Kcal/mol) energy $E^{(2)}$ of perylene was obtained in chloroform. Hence, there is high intensive interactions between σC1-C2 and σ*C2-C7 and has greater conjugation in the molecule. The order of this interaction is more in Chloroform>Acetone>Benzene>Gas Phase>Water. This phenomenon occurs as the polarity decreases between chloroform and benzene.

5. CONCLUSION

To understand the effects of solvents on structural, electronic, thermodynamic and non-linear optical properties of Perylene molecule, we have carried out an extensive computational study of the HOMO, LUMU, HOMO-LUMO energy gap, ionization potential, electron affinity, chemical hardness, chemical softness, chemical potential, electronegativity, electrophilicity index, dipole moment, polarizability, anisotropic polarizability, hyperpolarizability, entropy, heat capacity, rotational constants and zero-point vibrational energy using the B3LYP methods under 6-311++G(d,p) basis set.

In the structural properties calculations, Our findings revealed that the bonds of perylene tend to be stronger in the gas phase and in solvents compared to that of an isolated perylene as reported in the literature. It was observed that the bond lengths increases with an increase in the polarity of the solvents, while the bond angles were found to increase as the polarity of the solvents decreases. In the global quantities calculations, it was found that the electron transfer from HOMO to LUMO was found to be relatively easier in chloroform than in the gas phase an in the rest of the solvents. The global quantities, HOMO and HOMO-LUMO energy gaps were found to increase as the polarity of the solvents increases. The ground state energy of perylene increases with decrease in polarity of the solvents.

In the Thermodynamic part of our work the specific heat capacity of Perylene increases with an increase in the polarity of the solvents while the entropy and the zero-point vibrational energy decreases as the polarity of the molecule increases. In the non-linear optical properties calculations, the polarizability increases with decrease in the dielectric constant of the solvents while the anisotropic polarizability increases as the polarity of the solvents increases. In the NBO analysis, high intensive interaction between donor and acceptor electrons was observed in chloroform due to large value of stabilization energy. The results also show that careful selection of basis set and solvents can be utilized to tune the optoelectronic properties of Perylene. The same investigation should be carried out in future for neutral and charged perylene molecule.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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