



A Computational Study of Structural, Electronic, and Nonlinear Optical Properties of Phenylpyrroles

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Highlights

- Theoretical physical properties of phenylpyrroles were calculated characterized by DFT.
- Potential energy surface was studied.
- Frontier orbitals and NLO properties were calculated.

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Abstract

In this study, three structural isomers of phenylpyrrole: 1-, 2-, and 3-phenylpyrrole were investigated by using the B3LYP/6-31++G(d,p) level to get the information about their geometry, electronic and nonlinear optical properties. The change in the torsional angle between the pyrrole and phenyl rings was used to investigate the conformational analysis. In addition, we have calculated the electronic properties such as electric dipole moment, frontier orbital energies and energy gap (E_g). Also, we have determined linear, and nonlinear optical (NLO) properties in terms of polarizability and first hyperpolarizability.

1. INTRODUCTION

Phenylpyrroles are composite molecules containing two subsystems as phenyl and pyrrole molecules are connected by a single bond. There are three structural isomers of phenylpyrrole: 1-, 2-, and 3-phenylpyrroles. The three isomers differ only for phenyl ring linked at different site of pyrrole ring. In 1-phenylpyrrole (1PhPyr), the phenyl ring presents on nitrogen atom of pyrrole molecule. In the 2-phenylpyrrole (2PhPyr) and 3-phenylpyrrole (3PhPyr), the phenyl ring presents on carbon atom, 2 or 3 position, of pyrrole molecule. The phenyl and pyrrole rings in phenylpyrroles can freely rotate around inter-ring bond.

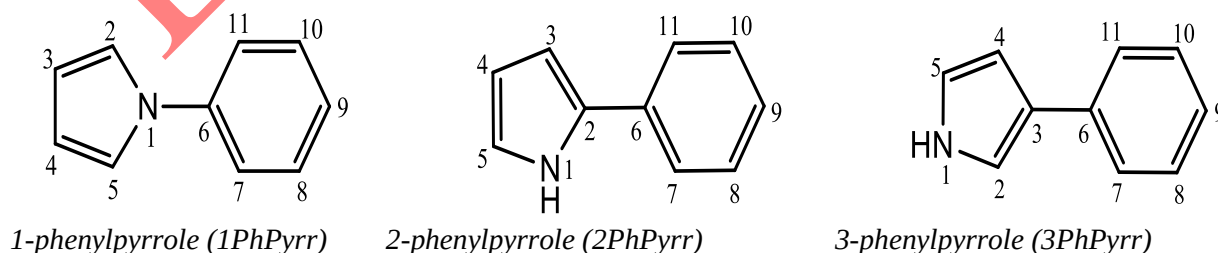


Figure 1. Structure of compounds

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Phenylpyrroles and their derivatives are the important class of molecules used in materials, biological and pharmacological sciences. In 1983, Rettig and Marschner pointed out that 1-phenylpyrrole (also known N-Phenylpyrrole) exhibits an additional red-shifted long wavelength shoulder in its fluorescence spectrum in the polar acetonitrile solvent [1]. Hence, in the literature, increasing number of experimental and theoretical studies were undertaken in order to understand the dual fluorescence and photophysical properties, photoinduced intramolecular charge transfer (ICT), of 1PhPyr and its derivatives [2-13]. They have been reported as a group of twisted intramolecular charge transfer (TICT) molecules [14, 15]. Dual fluorescence spectra from electronic excitation for 1PhPyr compound has been detected in the presence of nonpolar and polar solvent media (for details see references in Ref [13]). In most cases, 1PhPyr is used for the polymerization yields the poly-N-Phenylpyrrole [16-20]. It used in electrochemical capacitors [21], batteries [10], nonlinear optical chromophores [22], brown carbon chromophores [23] and energy storage devices [10]. The compounds of the phenylpyrrole are used in the supramolecular design [24], medical and biological applications [25]. They have interesting pharmacological properties such as antiviral [9], fungicides [26, 27], anti HIV and antioxidant activities [28].

1PhPyr is interesting from structural point of view. Yoshihara [15] and Meindl [29] determined the crystal structure of 1PhPyr by X-ray diffraction [15]. The pyrrole ring of the 1PhPyr is slightly twisted over an angle of 5.7° relative to the plane of the phenyl ring in the solid state. The torsional potential arises from the variation in energy with rotations about inter-ring bond. Okuyama et al. [30] are investigated the electronic spectra of jet-cooled 1-phenylpyrrole [30]. In the ground state, which is the most stable conformation of the structure, is appeared at an angle of 38.7° between the rings in the vapour phase [30]. The torsional potential of twisted compounds has in principle two barriers to internal rotation, one planar at 0° (E_0) and one perpendicular at 90° (E_{90}). Torsional potential including planar and perpendicular conformations has been recognized as an important factor in determining the kinetics for TCIT state formation in ground state and excited state. Only in the case of 1PhPyr, the experimental barriers around the planar and perpendicular conformations were accurately determined by Okuyama et al. [30] under jet cooled conditions and fitting the data with Franck-Condon simulation analysis.

In contrast to 1PhPyr, 2PhPyr and 3PhPyr have been little studied from both experimental and theoretical points of view up to now [25, 31, 32]. On the theoretical side, one can find many studies about relative stabilities and torsional potentials of title compounds in the literature. In 1987, Fabian calculated 3 isomers of phenylpyrrole at the MNDO and AM1 semi empirical levels [33]. In 2012, Rottmannova et al. [34] studied by AM1, MP2/cc-pVDZ, B3LYP/cc-pVDZ and DFTB+ methods the conformation of 2PhPyr [34]. Concerning 3PhPyr no previous calculation was reported at higher level theory. The experimental value for dipole moment of 1PhPyr was measured by Lumbroso et al. [35] in benzene solution. Thomas et al. experimentally obtained dipole moments of 1PhPyr in the ground and excited state from high-resolution fluorescence excitation experiments in the gas phase [36].

2. COMPUTATIONS AND METHODOLOGY

The quantum mechanical calculations are important tools for predicting physicochemical properties of a molecule or molecular system in the gaseous and solution state [18],[32-34] [37, 38]. In this study, we have used B3LYP (Becke gradient corrected exchange functional and Lee-Yang-Parr correlation functional with three parameters) [39, 40] variant of Density Functional Theory (DFT) for the computations with a medium sized basis set of the 6-31++G(d,p) [41, 42] combination implemented in the Gaussian03 program [43]. The B3LYP is one of the most widely used functional of DFT in computational studies. It provides, in generally, an acceptable computational prediction of experimental data, geometry and electronic properties of organic molecules in ground state at low computational cost [18, 44-46]. Firstly, the ground state geometries of three isomers of phenylpyrrole have been determined by the optimization of geometry. Furthermore, harmonic vibrational frequencies were calculated to get the confirmation of the structures in equilibrium, which is related to the minimum energy. Later, the conformational analysis of 1PhPyr, 2PhPyr and 3PhPyr has been carried out by changing the dihedral angle around inter-ring bond from 0° to 90° with a step of 10° . Secondly, we have calculated the electronic properties including electric dipole moment, HOMO-LUMO energies and energy gap of the studied molecules. In addition, linear and

nonlinear optical (NLO) features such as polarizability, anisotropic polarizability, first hyperpolarizability and their change with the torsion angles from 0° to 90° in steps of 10° .

3. RESULTS AND DISCUSSION

3.1. Equilibrium Geometry and Rotational Potentials

The geometry optimization to get global minimum of ground state of the title compounds is the first step of the current study. Subsequently, harmonic vibrational frequency analysis is performed at the optimized geometry. The results confirmed that the existence of global minima of optimized geometries have no imaginary frequency. It is followed by the determination of rotational potential, torsional energy curve, produced by rotating of pyrrole and phenyl rings about the single bond connect them. The molecular structures and atom numbering for studied compounds are shown in Figure 1. The optimal geometry in equilibrium of the molecules results from a balance of the attractive and repulsive forces. One of these effects is conjugation interaction between phenyl and pyrrole rings which raises a tendency to a planar structure (0°). The other one is steric repulsion between non bounded ortho hydrogen atoms which favor a nonplanar structure (90°). Titled compounds prefer a twisted conformation rather than a planar and perpendicular structure. The twisted, planar and perpendicular conformations of phenylpyrroles depicted in Figure 2.

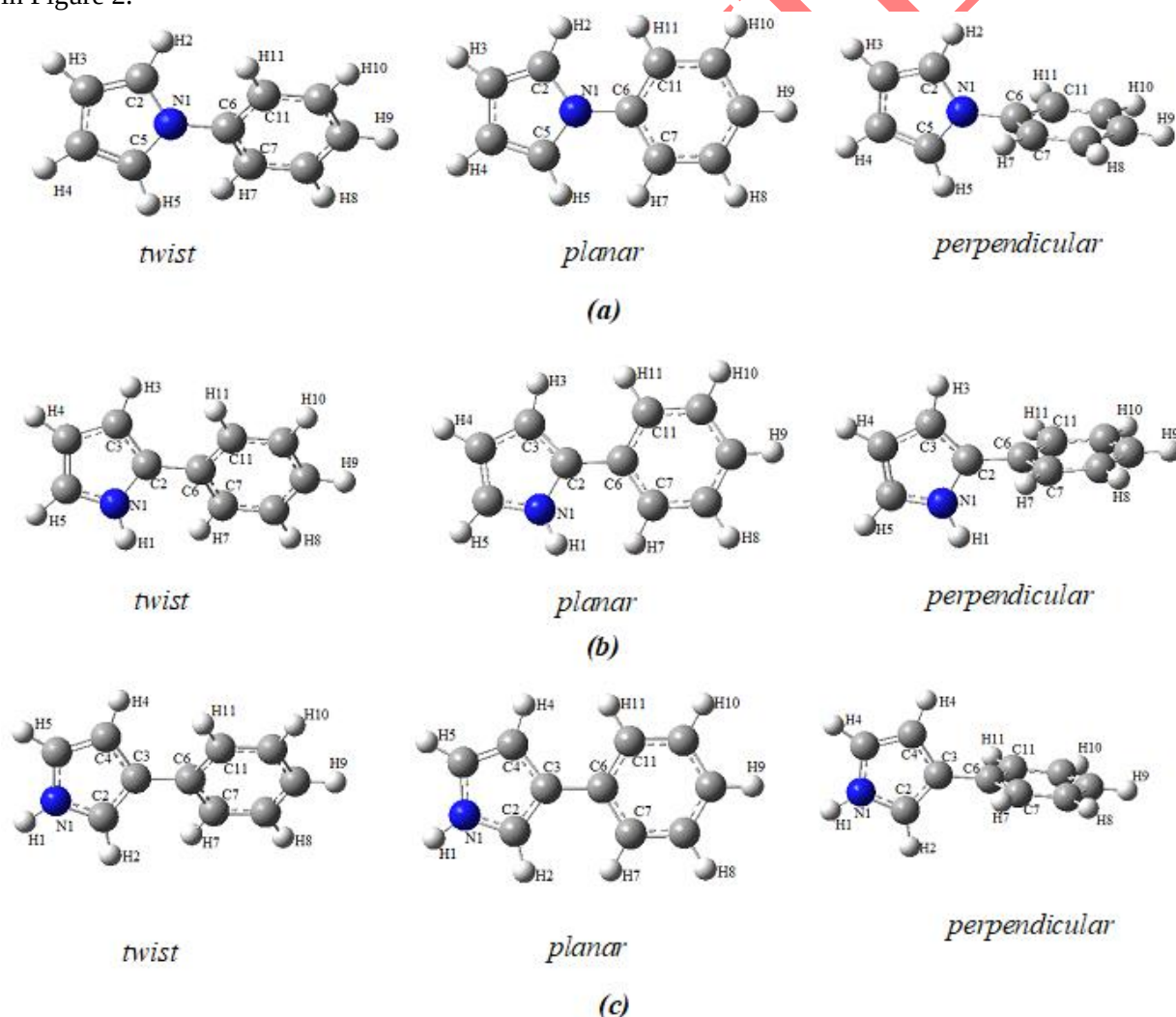


Figure 2. Twisted, planar and perpendicular conformations of phenylpyrroles as a) 1PhPyr, b) 2PhPyr and c) 3PhPyr molecules, respectively

According to the given scheme of numbering the atoms in Figure 1 and Figure 2, dihedral angles that have been determined by atoms are C2-N1-C6-C11, C3-C2-C6-C11 and C4-C3-C6-C11 for 1PhPyr, 2PhPyr and 3PhPyr, respectively. The selected optimized structural parameters: dihedral angle and interring bond length of structural isomers of phenylpyrrole computed at B3LYP/6-31++G(d,p) level are listed in Table 1. For the phenylpyrrole isomers, the equilibrium geometries in ground state have been obtained to be a tilted structure with a dihedral angle between two planes of the phenyl and pyrrole rings. In the case of 1PhPyr, the calculated dihedral angle in the equilibrium structure is 37.28°, which is very close to the experimental value of 38.7° in gas phase obtained by Okuyama et al.[30]. Dihedral angles are calculated as 25.08° for 2PhPyr and 26.90° for 3PhPyr. Rottmannova et al. calculated the optimal dihedral angle of 2PhPyr is 31° for MP2/cc-pVDZ, 24° for B3LYP/cc-pVDZ and PBE/cc-pVDZ, 26° for AM1 and 3° for DFTB+ [34]. The inter-ring bond lengths are the smallest for 1PhPyr with 1.4188 Å (C-N bond) followed by 3PhPyr with 1.4728 Å (C-C) and 2PhPyr with 1.4647 Å (C-C). The C-C bond lengths in phenyl ring are between 1.3951 – 1.4078 Å. The bond lengths N-C and C-C in the pyrrole ring have the values between 1.3737 – 1.3852 Å. and 1.3775 – 1.4344 Å, respectively, for all the three isomers. The bond angles in the phenyl ring have the value between 117.83° – 121.11°. The bond angles in the pyrrole ring have the value between 106.36° – 110.41°.

Table 1 shows the total electronic energy of each compound. The 3PhPyr with smallest electronic energy was found to be more stable isomer. The electronic energy difference order is 3PhPyr (0) < 1PhPyr (24.2 kJ/mol) < 2PhPyr (37.5 kJ/mol). The energy difference between 1PhPyr and 2PhPyr is 13.3 kJ/mol and between 3PhPyr and 2PhPyr is 37.5 kJ/mol.

Table 1. The values of calculated physical quantities from B3LYP/6-31++G(d,p) level at the equilibrium geometry

	Molecule		
Physical quantity	1PhPyr	2PhPyr	3PhPyr
Electronic energy (au)	-441.25141300	-441.26281986	-441.26062487
Dihedral angle (deg, °)	37.28	25.08 (25.99)	26.90 (27.23)
Interring bond length (Å)	1.4188	1.4647	1.4728
Electric dipole moment (D)	1.5688	1.4935	2.4479
E_0 (kJ/mol)	7.74	2.25	1.97
E_{90} (kJ/mol)	8.58	14.48	11.40
The energy of HOMO (E_H , eV)	-5.99	-5.54	-5.67
The energy of LUMO (E_L , eV)	-0.82	-0.88	-0.54
Energy Gap of HOMO-LUMO (E_g , eV)	5.17	4.66	5.13
Polarizability (α , in au)	128	130	127
Anisotropic polarizability ($\Delta\alpha$, in au)	89	106	94
Hyperpolarizability (β , in au)	507	964	651

At the B3LYP/6-31++G(d,p) level, the variation of relative energy, potential energy curve, with the dihedral angle is shown in Figure 3. Where relative energy refers to energy of each rotamer with respect to the lowest energy of optimized geometry. All compounds give one minimum for twisted geometry and two maxima for planar and perpendicular structures. Hence, as noted in the introduction, there are two energy barriers: one corresponding to the maximum at 0° (planarity, E_0) and the other to the maximum at 90° (perpendicularity, E_{90}). The related energies of the located barriers are given in Table 1. The case of 1PhPyr, the barrier heights obtained by B3LYP/6-31++G(d,p) are nearly identical. The planar and perpendicular structures were found to be higher in energy than the twisted structure by 7.74 kJ/mol and 8.58 kJ/mol. The experimental barriers determined for 1PhPyr are $E_0 = 5.47$ kJ/mol and $E_{90} = 8.96$ kJ/mol. The B3LYP and experiment agree for the E_{90} , whereas at 0°, E_0 is about 41% or 2.27 kJ/mol larger than the experimental estimation. As shown in Figure 3, the potential energy curves of 2PhPyr and 3PhPyr exhibit close similarities. The computed barrier arising from planarity is very low and close in height. The values of E_0 are 2.25 kJ/mol and 1.97 kJ/mol for 2PhPyr and 3PhPyr, respectively. In these cases, the

minima are flat and close in energy to the planarity conformation. The 2PhPyrr and 3PhPyrr molecules have higher relative energies for the perpendicular barrier. The values of E_{90} are 14.48 kJ/mol and 11.40 kJ/mol for 2PhPyrr and 3PhPyrr, respectively. Rottmannova et al. calculated the energy barrier of the perpendicular 2PhPyrr is very sensitive to computational level of theory with values from 6 kJ/mol (DFTB+), to 26 kJ/mol (AM1) [34]. They noted that E_{90} value of 2PhPyrr is 11 kJ/mol for MP2/cc-pVDZ, and 16 kJ/mol for B3LYP/cc-pVDZ.

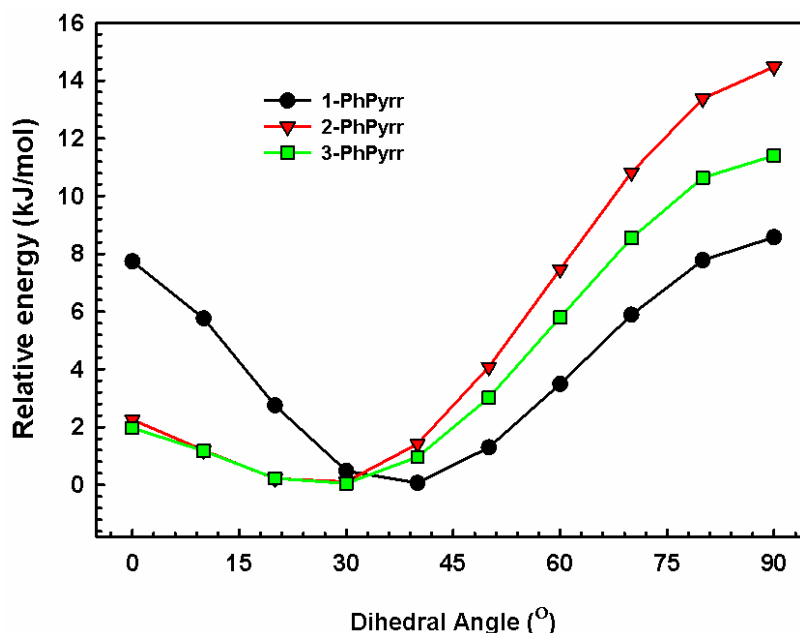


Figure 3. Energy Profile (torsional potential) of the investigated compounds

3.2. Frontier Molecular Orbitals

The optical and electrical features of the structures are generally calculated by using the frontier orbitals of molecules, which are known as the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbitals (LUMO). The HOMO is the highest filled energy level of the molecule and it tends to supply electrons. In contrary, the LUMO holds the lowest unfilled energy level and so, it tends to accept electrons.

The mobility of the electron from HOMO to LUMO depends on the gap between HOMO and LUMO energy levels. While the good thermodynamic stability and low chemical reactivity of the compounds can be attributed to the wide E_g , easy electronic transition can be related to the small values of E_g .

The energy eigenvalues E_H and E_L of HOMOs and LUMOs and the related E_g of compounds under investigation calculated by using B3LYP/6-31++G(d,p) level and given in Table 1. The E_H of 1PhPyrr, 2PhPyrr and 3PhPyrr were estimated to be -5.99, -5.54, and -5.67 eV, respectively. In the meantime, the corresponding E_L of 1PhPyrr, 2PhPyrr and 3PhPyrr changes of about -0.82, -0.88, and -0.54 eV, respectively. The E_g values for 1PhPyrr, 2PhPyrr and 3PhPyrr were 5.17, 4.66, and 5.13 eV, respectively. The compound that has the highest E_H , lowest E_L and lowest E_g values is the 2PhPyrr. So, it to be the softest, best electron donor and electron acceptor molecule than others.

Figure 4 is introduced to show the electron density distribution of the HOMO and LUMO predicted by B3LYP/6-31++G(d,p). It is clear in Figure 4, an electron is disturbed from the HOMO to the LUMO within the first electronic excitation. There are many theoretical studies interested in the HOMO and LUMO pictures of 1PhPyrr. Tuzun et al. [18] showed that all contribution comes from atoms of pyrrole ring to HOMO while no contribution comes from the phenyl ring. In other words, the HOMO is localized on π -molecular orbital of pyrrole ring. However, in LUMO, large and even coefficients are present on π^*

molecular orbitals for the atoms on phenyl ring. This delocalization pattern of the orbitals qualitatively reveals that there is a charge transfer from the pyrrole ring to the phenyl ring in the character of $\pi \rightarrow \pi^*$ electronic transitions.

Previous work on the plots of frontier molecular orbitals of 2PhPyrr has been limited to the B3LYP/cc-pVDZ level. The reported B3LYP/cc-pVDZ [34] and current B3LYP/6-31++G(d,p) calculations show that the HOMO of 2PhPyrr extend over the entire molecule but delocalized mostly over the pyrrole ring, specifically at the carbon-carbon bonds, C2-C3 and C4-C5 and also C6-C7 and C6-C11 bonds of phenyl ring. By contrast, the corresponding LUMO delocalized mostly over the phenyl ring at the C7-C8 and C10-C11 bonds, and C2-C6 bond connecting rings. Similarly, in the case of 3PhPyrr, the HOMO delocalized mostly over the pyrrole ring at the C2-C3 and N1-C5 bonds. The corresponding LUMO delocalized mainly through the C7-C8 and C10-C11 bonds of phenyl ring and C3-C6 bond between rings. In addition, in the case of 2PhPyrr and 3PhPyrr HOMO represent π -type molecular orbitals and LUMO represents π^* -type molecular orbitals [44]. Then, HOMO-LUMO transitions are governed by the $\pi \rightarrow \pi^*$ electronic transitions.

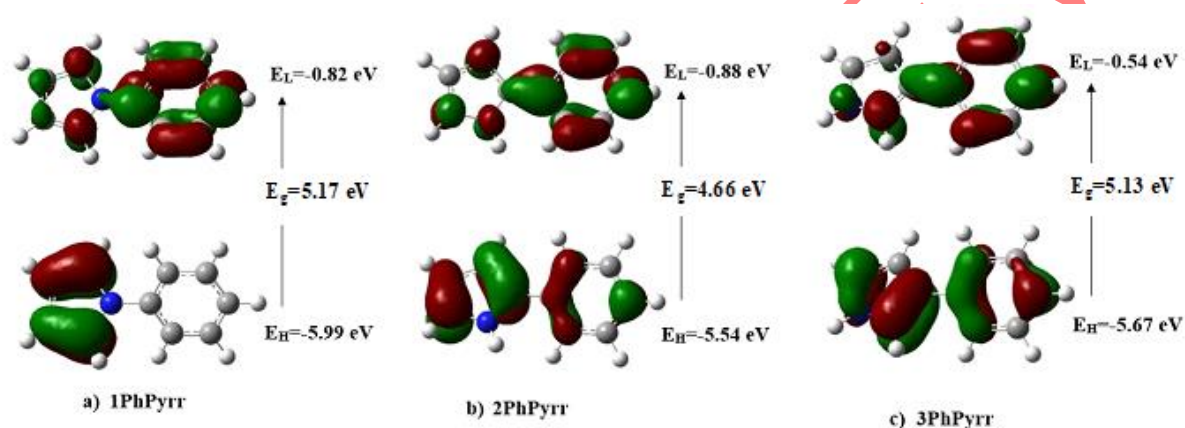


Figure 4. The calculated HOMO and LUMO representation of phenylpyrroles

The torsion dependences of E_g are presented in Figure 5. The E_g increases with the torsion angle that reach maximal values at the perpendicular conformation for 1PhPyrr and 3PhPyrr unlike 2PhPyrr. The monotonically decrease of E_g for 2PhPyrr is negligible.

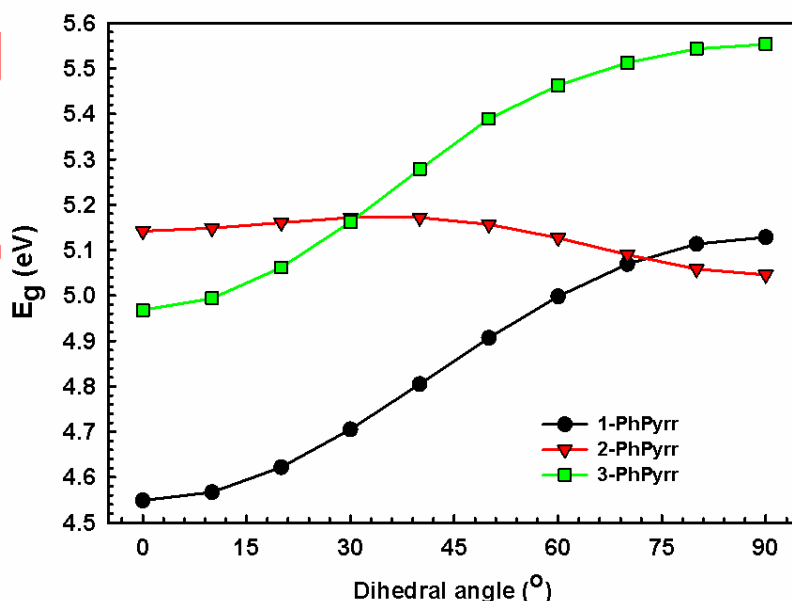


Figure 5. Variation of energy gap versus dihedral angle of phenylpyrroles

3.3. Nonlinear Optical Properties (NLO)

The studies on the nonlinear optical properties (NLO) of organic molecules take great attention because of their potential applications in the electro-optic modulation and data storage technology. The interactions between the electrons within entire molecule and an external electric field responsible from the NLO features of the molecule. The molecular electric dipole moment is dictated from charge distribution and geometry of compounds. When we apply an external electric field to a molecular system with a permanent electric dipole moment μ_0 , a molecule gets an induced electric dipole moment μ_i , that is given with the following equation,

$$\mu_i = \mu_0 + \alpha_{ij}E_{ij} + \beta_{ijk}E_{ijk} + \dots \quad i, j, k = x, y, z \quad (1)$$

where α_{ij} and β_{ijk} are polarizability and first hyperpolarizability parameters, respectively. The averaged polarizability (α), anisotropy of polarizability ($\Delta\alpha$) and first static hyperpolarizability (β) can be expressed in terms of cartesian components that reported as

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})^{1/2} \quad (2)$$

$$\Delta\alpha = \left\{ \frac{1}{2}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{yy} - \alpha_{zz})^2] \right\}^{1/2} \quad (3)$$

$$\beta = \{(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2\}^{1/2} \quad (4)$$

Here, cartesian components of α and β are acquired from output of Gaussian program. The NLO related properties as electric dipole moment, total polarizability, anisotropic polarizability and first hyperpolarizability of the phenylpyrroles determined by B3LYP/6-31++G(d,p) calculations are given in Table 1. The B3LYP/6-31++G(d,p) calculated dipole moment is 1.5688 D to be compared with 1.39 D from experiment in benzene solution [35] and 1.56 D in gas phase [36]. The polarizabilities are nearly identical for all compounds with 128 ± 2 au. Anisotropic polarizability results show that 2PhPyr has the biggest value with 106 au while 1PhPyr has the smallest with 90 au and 3PhPyr with 94 au. The hyperpolarizability values are found to be 507, 964 and 651 au for the 1PhPyr, 2PhPyr and 3PhPyr, respectively. These results reveal that 2PhPyr molecule is up to 2 times more polarizable than 1PhPyr under influence of external electric field. Urea is one of the prototypical molecules for the NLO properties of the organic molecules for the comparative purposes [47, 48], so NLO properties of urea were calculated at the same level. The calculated α and β values for urea are 33 au and 90 au. The results show that the phenylpyrroles would be good candidates for NLO materials.

Variation of average polarizability, anisotropic polarizability and hyperpolarizability as a function of torsion angle are plotted in Figure 6. The average polarizabilities of titled molecules are little affected by the torsion, varying within 5-6%. However, the anisotropic polarizabilities are more affected than average polarizabilities by the conformation. On the other hand, electronic first order hyperpolarizabilities are usually heavily influenced by torsion than electronic polarizabilities. All these quantities (in Figure 6) exhibit a similar shape of torsional dependence with minima at perpendicular and maxima at planar or nearly planar conformation.

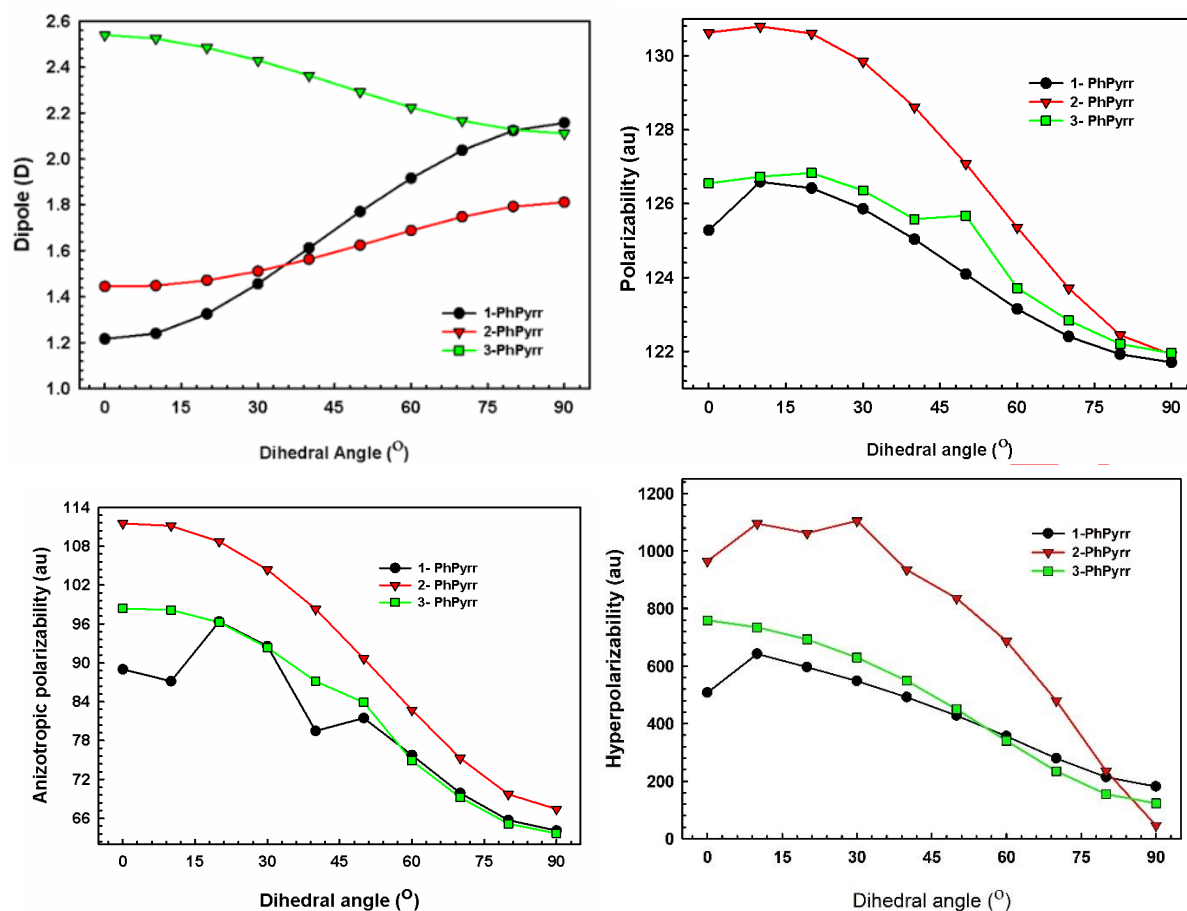


Figure 6. Variations of NLO related properties versus dihedral angle of phenylpyrroles

As noted within introduction section, researchers were inspired to develop phenylpyrrole derivatives with potential for new materials design in a broad range of applications and pharmaceuticals in life sciences [17-22]. In this study, we presented theoretical data on the structural, electronic and NLO properties of the three isomers of phenylpyrroles. The findings to be drawn within text will be useful for next researches in new material design.

4. CONCLUSION

In this work, the molecular structures and structural parameters of the three isomers of phenylpyrrole have been obtained at the B3LYP/6-31++G(d,p) level. The structural analysis clearly showed 1PhPyrr, 2PhPyrr and 3PhPyrr adopt a tilted geometry between the phenyl and pyrrole rings. We have calculated numerous molecular properties of studied compounds providing information into the structural, electronic and (non)linear optical characteristics and their dependence of torsion angle. B3LYP/6-31++G(d,p) shows a small deviation from planar geometry and low twist barriers at 0° and a higher barrier at 90° in the gas phase. Also, we produced well experimentally obtained energy barriers of 1PhPyrr. The calculated dihedral angle, dipole moment and perpendicular energy barrier of 1PhPyrr agree very well with the experimental values. Frontier molecular orbital calculations show that 2PhPyrr is softest, best electron donor and electron acceptor among three compounds. Also, it possesses higher NLO property including polarizability, anisotropic polarizability, and hyperpolarizability values than all compounds. Phenylpyrroles have much higher polarizability and first hyperpolarizability values than urea. This suggest that phenylpyrroles would be good NLO substances. The hyperpolarizability increases with the decrease of the energy gap value. Our theoretical findings provide a better understanding into the structural, electronic and NLO properties of Phenylpyrroles to be used in many applications.

CONFLICTS OF INTEREST

No conflict of interest was declared by the authors.

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