

Quantum Chemical Study on the Torsional Energy and Nonlinear Optical Properties of 2-, 3-R-4-Phenylpyridine (R=CH₃, NH₂ and NO₂) Compounds

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Abstract: In this study, the torsional dependence of the electronic energy and nonlinear optical properties of some derivatives of 4-phenylpyridine molecule has been investigated by quantum mechanical methods. We investigated electronic energy, HOMO-LUMO energy gap, static dipole moment, static polarizability, anisotropy of polarizability, and first static hyperpolarizability. The CH₃, NH₂ and NO₂ substitution effect on the physical properties of title compounds compared with 4-phenylpyridine results. Torsional energy calculations were performed with HF/6-31++G(d,p) and B3LYP/6-31++G(d, p) levels of theory. The nonlinear optical properties performed with only at the B3LYP/6-31++G(d, p) and B3LYP/6-311++G(2d, 2p) levels of theory. In our calculations we have found that substitution of CH₃ on the 4-phenylpyridine does not display the dramatic increasing in polarizability and first hyperpolarizability values whereas NH₂ and especially NO₂ generate three times large nonlinearity compared with 4-phenylpyridine.

Keywords: 4-phenylpyridine, B3LYP, torsional energy, nonlinear optics, orbital energies

1. INTRODUCTION

There is a great interest in the study of linear and nonlinear optical properties of polymeric organic materials due to their potential application in technologies such as frequency conversion, optical communications, optical computing, optical switching, wave-guiding, high optical 3D data storage, chemical and biological sensing (Kishida et.al., 2002; Kawata et.al., 2000; Pons et.al., 2003). As an example azabiphenyls have been subject of many experimental and theoretical studies on conformational behavior, torsional barrier and nonlinear optical (NLO) properties (Silva et.al.,2000; Goller and Grummt, 2000; Alyar et.al., 2006; Alyar et.al., 2007) due to their potential scientific and technological importance (Gopal and Subrahmanyam, 2001). Phenylpyridines and its derivatives have a much interest as intermediates in synthesis of other compounds (Gopal and Subrahmanyam, 2001; Hu et.al., 2008). 4-phenylpyridine (4PP) is a very important molecule due to including lone-electron pair on nitrogen atom and π orbitals of aromatic rings. Thus, the molecule and its derivatives are used as ligand in coordination complex and also are used in liquid crystal applications (Tomas, 1991).

At the molecular level, the response of a molecule to a homogenous static electric field (E) can be written as dipole expansion Eq. (1)

$$\mu_i = \mu_i^0 + (1/2)\alpha_{ij}E_j + (1/6)\beta_{ijk}E_jE_k + \dots \quad (1)$$

Where the μ_i^0 , α_{ij} , and β_{ijk} coefficients are the components of the dipole moment of the unperturbed system, dipole polarizability, and first static hyperpolarizability, respectively.

In our earlier studies we reported the calculations of torsional behavior and nonlinear optical properties of phenylpyridines (Alyar et.al., 2006), phenyltriazines (Alyar et.al., 2007). In the present study we report the CH₃, NH₂ and NO₂ substitution effect on torsional behavior and NLO properties of title compounds comparing with parent 4-phenylpyridine results. The studied molecules are shown in Fig. 1.

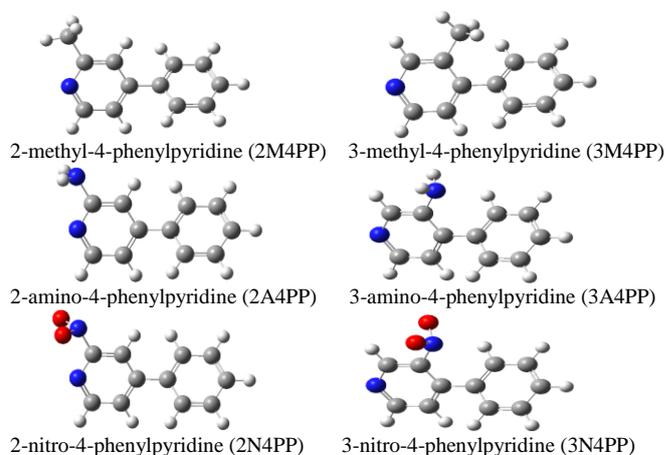
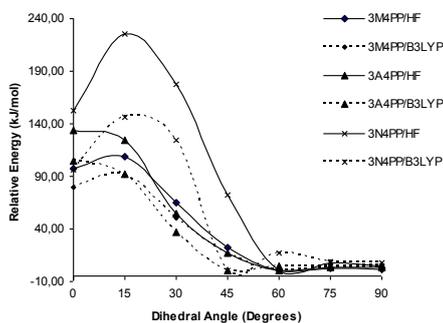


Fig.1. Molecular structure of studied molecules (on this figure grey ball: C, white ball: H, blue ball: N, red ball: O represents)

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2. METHODS

In the present work, torsional energy calculations were performed with HF and DFT/B3LYP methods using 6-31++G(d,p) basis set (Hariharan and People, 1974; Ditchfield et.al.,1971; Hehre et.al., 1972). The static polarizability, anisotropy of polarizability, first static hyperpolarizability and HOMO-LUMO frontier molecular orbital energy calculations are performed with B3LYP method (Becke, 1993; Lee et.al., 1988, Miehlich et.al., 1989) and the 6-31++G(d, p) basis set. Adequacies of methods and basis sets for NLO calculations discussed in details for similar compounds (Hernandez et.al., 2003). In our previous paper we showed the adequacies of HF/6-31++G(d,p) and B3LYP/6-31++G(d,p) schemes for the calculations of torsional barriers and NLO properties of phenylpyridines that, in order to comparing 4-phenylpyridine results, these methods have also been used in this work again. It's common knowledge that polarizabilities can only be calculated accurately from calculations employing extended basis sets. In particular, these basis sets have to include diffuse and polarization functions. For this reason we used 6-311++G(2d,2p) basis set for calculations of polarizabilities at the equilibrium geometries.



The variation of relative energy, static polarizability, anisotropy of polarizability and first static hyperpolarizability against the dihedral angle between 0° and 90° at intervals of 15° due to high symmetry of title compounds. All calculations were performed using Gaussian 03W software package (Frisch et.al., 2003).

3. RESULTS and DISCUSSION

3.1. Torsion energy profile

The equilibrium geometry of the molecules results from a balance between two effects. One of them is the conjugation interaction between phenyl and methyl, amino and nitro-pyridine rings tend to a planar structure. The other is the steric repulsion between ortho ring hydrogen and methyl, amino and nitro groups favor a non planar structure. Therefore the conformational analysis has been carried out after geometry optimization. Fig.2 shows the torsional behavior of title compounds with the dihedral angles. As seen at the Table 1, the potential energy minimum was predicted with B3LYP/6-31++G(d, p) and HF/6-31++G(d, p) levels of theory at twist angle of 38.50° and 44.51° between the phenyl and pyridine rings in previous paper, respectively.

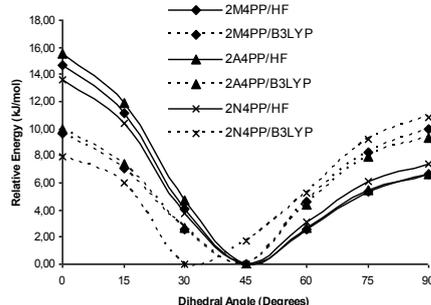


Fig. 2. Torsional behavior for 2M4PP, 3M4PP, 2A4PP, 3A4PP, 2N4PP and 3N4PP molecules. Energies are relative to minimum.

The calculated relative energies for 0° and 90°, total energies and dipole moments at ground state are given in Table 1 for 4PP and title compounds. Replacing hydrogen atom with substitution CH₃ group on 4PP does not change equilibrium dihedral angle of 2M4PP isomer and increase of equilibrium dihedral angle of 3M4PP isomer about 20 degrees. Also the NH₂ and NO₂ substituted 2A4PP and 2N4PP molecules do not have significant change in the equilibrium dihedral angle. The NH₂ and NO₂ substituted 3A4PP and 3N4PP molecules have increase in the equilibrium dihedral angle about 10-14 degrees.

2-methyl-4PP has less energy than 3-methyl-4PP isomer by 18.93 kJ/mol and 16.90 kJ/mol at the HF and B3LYP levels respectively. As seen from Fig.2, the maximum value of the relative energy for 3M4PP, 3A4PP and 3N4PP is reached at 15°. The dihedral angle at equilibrium geometry becomes smaller at B3LYP level than HF (seen from Table 1) due to

the electron delocalization across two rings. Also we can see in this table CH₃, NH₂ and NO₂ substitution with the H atom at meta position on the 4PP approximately does not change the barrier high at 0° and 90°. Whereas CH₃, NH₂ and NO₂ substitution with the H atom at ortho position on the 4PP increased the barrier at 0° but decreased at 90° (about 1.60 kJ/mol for HF method and 3.87 kJ/mol for B3LYP method for 3M4PP) according to 4PP. We are unaware of any experimental determination of dipole moment of title compounds. It can be seen from Table 1, all dipole moment results are very similar with available experimental (Cumper et.al., 1962) and previous theoretical results (Barone et.al., 1983; Alyar et.al.,2006; Galasso et.al.,1971) of 4PP except for 3A4PP, 2N4PP and 3N4PP. 2N4PP molecule has strongest dipole moment that caused large anisotropic polarizability among others.

Table 1. Dihedral angle (θ) between two rings (in degree), dipole moment (μ), energies in kJ mol^{-1} relative to global minimum, ground state total energy of 4PP and all studied molecules.

Molecule	Methods	θ (Deg.)	μ (D)	E_0	E_{90}	E(au)
4PP	HF/6-31++G(d,p)	44.51 ^a	2.85 ^a	14.20 ^a	6.42 ^a	-476.27624 ^a
	B3LYP/6-31++G(d,p)	38.50 ^a	2.91 ^a	8.60 ^a	9.34 ^a	-479.37276 ^a
	Exp.		2.57 ^b			
2M4PP	HF/6-31++G(d,p)	44.78	2.40	14.66	6.63	-515.32084
	B3LYP/6-31++G(d,p)	38.66	2.41	9.68	9.99	-518.69944
3M4PP	HF/6-31++G(d,p)	66.87	2.96	96.84	1.60	-515.31348
	B3LYP/6-31++G(d,p)	57.48	3.14	79.65	3.87	-518.69287
2A4PP	HF/6-31++G(d,p)	45.18	2.34	15.54	6.62	-531.32520
	B3LYP/6-31++G(d,p)	39.26	2.25	9.96	9.36	-534.74816
3A4PP	HF/6-31++G(d,p)	58.99	3.36	133.73	3.16	-531.30986
	B3LYP/6-31++G(d,p)	52.61	3.57	104.44	5.16	-534.73627
2N4PP	HF/6-31++G(d,p)	43.16	7.21	13.61	7.42	-679.74730
	B3LYP/6-31++G(d,p)	36.49	7.17	7.88	10.81	-683.88142
3N4PP	HF/6-31++G(d,p)	58.10	4.57	152.46	4.71	-679.73854
	B3LYP/6-31++G(d,p)	48.95	4.41	95.74	7.23	-683.87162

^a From Ref.(Alyar, 2006), ^b From Ref.(Cumper, 1962)

3.2. Nonlinear Optical (NLO) Properties

In this section we present nonlinear optical properties of title compounds. The calculation of static polarizability, anisotropic polarizability and first static hyperpolarizability from the Gaussian 98W/03W output were explained previously (Galasso et.al., 1971). The calculated average

polarizability (α_{ave}), anisotropy of polarizability ($\Delta\alpha$) and total first hyperpolarizability (β_{tot}) values are shown in Table 2 (along with 4-PP) and torsional dependence of these properties are graphically shown in Fig.3. In this paper we report the influence of rotation and substitution of CH_3 , NH_2 and NO_2 on NLO properties of 2-,3- positional substituted methyl, amino, nitro-4-phenylpyridine molecules.

Table 2. Ground state nonlinear optical values and HOMO-LUMO energy difference of all studied molecules.

Molecule	Methods	α_{ave} (a.u)	$\Delta\alpha$ (a.u)	β_{tot} (a.u)	H-L(eV)
4PP	B3LYP/6-31++G(d,p)	135.90 ^a	74.30 ^a	204.43 ^a	5.42 ^a
2M4PP	B3LYP/6-31++G(d,p)	150.32	68.33	204.30	5.30
	B3LYP/6-311++G(2d,2p)	151.88	75.96	211.45	5.32
3M4PP	B3LYP/6-31++G(d,p)	145.81	60.63	126.60	5.57
	B3LYP/6-311++G(2d,2p)	146.99	59.30	130.55	5.60
2A4PP	B3LYP/6-31++G(d,p)	148.95	76.37	299.81	4.72
	B3LYP/6-311++G(2d,2p)	150.92	76.52	299.37	4.74
3A4PP	B3LYP/6-31++G(d,p)	145.48	64.25	332.06	4.68
	B3LYP/6-311++G(2d,2p)	146.51	63.06	297.39	4.71
2N4PP	B3LYP/6-31++G(d,p)	155.11	85.17	687.08	4.41
	B3LYP/6-311++G(2d,2p)	156.46	84.64	661.71	4.48
3N4PP	B3LYP/6-31++G(d,p)	151.32	62.77	341.82	4.43
	B3LYP/6-311++G(2d,2p)	152.24	61.35	325.94	4.52

It is conspicuous that substitution of CH_3 on the 4PP does not display the dramatic increasing in α_{ave} and β_{tot} values but NH_2 and especially NO_2 generate large nonlinearity compared with 4-PP at the equilibrium geometry. The calculated β_{tot} value of 2-, 3- NH_2 -4PP and 2- NO_2 -4PP ca. 50% and ca. 300% larger than 4PP, respectively. It is

expected that β_{tot} value is lowered when the dihedral angle changed or when deviated from the planarity except for 2-,3- NH_2 -4PP. The general belief is that the planarity is one of the criterions to satisfy for a molecule to be NLO active (Mendis and de Silva, 2003).

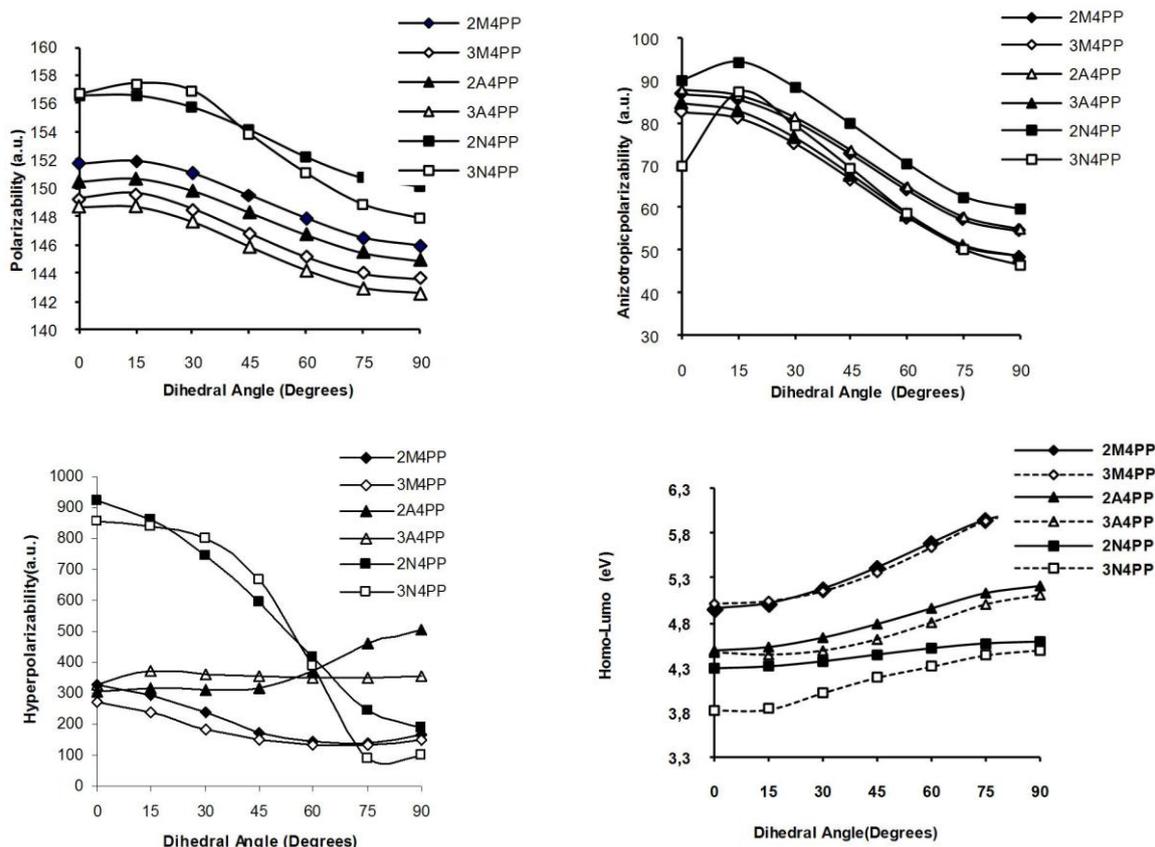


Fig. 3. The variation of static polarizability, anisotropic polarizability, first static hyperpolarizability and HOMO-LUMO energy gap with the dihedral angle for studied molecules.

We calculated the maximum β_{tot} at planar structures except for 2-, 3-NH₂-4PP. The anisotropic polarizability and first static hyperpolarizability values are most sensitive to torsional angle. These molecules shown in Fig.1 involve a π -coupling between phenyl and substituted pyridine rings that minimizes nonlinearity. The investigation of dihedral angle and first static hyperpolarizability correlation is explained by the calculation of frontier molecular orbital energies which helps to use intra molecular charge transfer to explain the hyperpolarizability. The variations of HOMO-LUMO energy gap with the dihedral angle for all compounds are given in Fig.3. Therefore previous and present calculations show the inverse relationship between the polarizability and HOMO-LUMO energy gaps (Hinchliffe and Soscun, 1994), which can be seen from Fig.3. As the dihedral angles change from 0° to 90°, the HOMO-LUMO energy differences increase. However static polarizability and anisotropy of polarizability decrease with increasing the interring angles to 90° (Fig.3).

4. CONCLUSION

We observed that replacing hydrogen atom at meta position with substitution CH₃, NH₂ and NO₂ group on 4PP do not change equilibrium dihedral angles of 4PP isomers but replacing hydrogen atom at ortho position with substitution CH₃, NH₂ and NO₂ group increases equilibrium dihedral

angle of 4PP isomers about between 14-22 degrees on account of steric effect between hydrogen and CH₃, NH₂ and NO₂ moieties. The CH₃ substitution on the 2-methyl-4PP decreased the energy barrier at 0° and at 90°. Whereas CH₃ substitution on the 3-methyl-4PP increased the energy barrier at 0° (about four fold large barrier) but decreased at 90° (about 1.60 kJ/mol for HF method and 3.87 kJ/mol for B3LYP method) according to 4-PP and 2-methyl-4PP. Substitution of CH₃ on the 4PP does not display the dramatic increasing in α_{ave} and β_{tot} values whereas NH₂ and especially NO₂ generate large nonlinearity compared with 4-PP (at the equilibrium geometry the calculated β_{tot} value of 2-,3-NH₂-4PP and 2-NO₂-4PP ca. 50% and ca. 300% times larger than 4PP, respectively). The largest hyperpolarizability obtained for 2-NO₂-4PP as 920.68 a.u. The β_{tot} value is lowered when the dihedral angle changed or when deviated from the planarity except for 2-, 3-NH₂-4PP. 2N4PP molecule has strongest dipole moment that caused large anisotropic polarizability among others. Also previous and new calculations reveal that such 4-phenylpyridine derivatives may be the candidate systems for use in the areas related to the nonlinear optical activity.

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