



## Torsional Energy and Nonlinear Optical Properties of 2-, 3-R-4-Phenylpyridine (R = CH<sub>3</sub>, NH<sub>2</sub> and NO<sub>2</sub>)

HAMIT ALYAR<sup>1,\*</sup> and MEHMET BAHAT<sup>2</sup>

<sup>1</sup>Department of Physics, Faculty of Sciences, Çankiri Karatekin University, 18100 Çankiri, Turkey

<sup>2</sup>Department of Physics, Faculty of Sciences, Gazi University, 06500 Ankara, Turkey

\*Corresponding author: Tel: +90 376 2181123; E-mail: halyar@karatekin.edu.tr

(Received: 3 November 2011;

Accepted: 16 June 2012)

AJC-11626

In this study, the torsional dependence of the electronic energy and nonlinear optical properties of some derivatives of 4-phenylpyridine were calculated by using HF theory and Becke three parameter functional (B3LYP) hybrid approaches within the density functional theory with the 6-31++G(d,p) basis set. We investigated global minimum energy, electric dipole moment ( $\mu$ ), first static polarizability ( $\alpha$ ), polarizability of anisotropy ( $\Delta\alpha$ ), first static hyperpolarizability ( $\beta$ ) and optical band gap ( $E_{\text{HOMO-LUMO}}$ ). The CH<sub>3</sub>, NH<sub>2</sub> and NO<sub>2</sub> 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 CH<sub>3</sub> on the 4-phenylpyridine does not display the dramatic increasing in polarizability and first hyperpolarizability values whereas NH<sub>2</sub> and especially NO<sub>2</sub> generate three times large nonlinearity compared with 4-phenylpyridine.

**Key Words:** 4-Phenylpyridine derivatives, Nonlinear optics, Torsional energy, Hyperpolarizability, HOMO-LUMO energies.

### INTRODUCTION

There is a great interest in the study of linear and non-linear 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<sup>1-3</sup>. As an example azabiphenyls have been subject of many experimental and theoretical studies on conformational behaviour, torsional barrier and non-linear optical (NLO) properties<sup>4-8</sup> due to their potential scientific and technological importance<sup>9</sup>. Phenylpyridines and its derivatives have a much interest as intermediates in synthesis of other compounds<sup>9,10</sup>. 4-Phenylpyridine (4PP) is a very important molecule due to including lone-electron pair on nitrogen atom and p orbital of aromatic rings. Thus, the molecule and its derivatives are used as ligand in coordination complex and also are used in liquid crystal applications<sup>11</sup>.

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

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

where, the  $\mu_i^0$ ,  $\alpha_{ij}$  and  $\beta_{ijk}$  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 behaviour and nonlinear optical properties of phenylpyridines<sup>6</sup>, phenyltriazines<sup>7</sup>, phenyldiazines and phenyltetrazines<sup>8</sup>. In the present study, we report the CH<sub>3</sub>, NH<sub>2</sub> and NO<sub>2</sub> substitution effect on torsional behaviour and non-linear optical properties of title compounds comparing with parent 4-phenylpyridine results. The studied molecules are shown in Fig. 1.

### EXPERIMENTAL

**Computational details:** In the present work, torsional energy calculations were performed with HF and DFT/B3LYP methods using 6-31++G(d,p) basis set<sup>12-14</sup>. The static polarizability, anisotropy of polarizability, first static hyperpolarizability and HOMO-LUMO frontier molecular orbital energy calculations were performed with B3LYP method<sup>15-17</sup> and the 6-31++G(d, p) basis set. The adequacies of HF/6-31++G(d, p) and B3LYP/6-31++G(d, p) level of theories for the calculations of torsional barriers and nonlinear optical properties for similar compounds are discussed in details<sup>6-8</sup>. 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<sup>18</sup>.

TABLE-1  
DIHEDRAL ANGLE ( $\theta$ ) BETWEEN TWO RINGS ( $^\circ$ ), DIPOLE MOMENT ( $\mu$ ), ENERGIES IN  $\text{kJ mol}^{-1}$  RELATIVE TO GLOBAL MINIMUM, GROUND STATE TOTAL ENERGY OF 4-PHENYLPYRIDINE (4PP) AND ALL STUDIED MOLECULES

Molecule	Methods	$\theta$ ( $^\circ$ )	$\mu$ (D)	$E_0$	$E_{90}$	$E(\text{au})$
4-Phenylpyridine	STO-3G		2.34 <sup>b</sup>	11.00 <sup>b</sup>	8.00 <sup>b</sup>	
	HF/6-31++G(d,p)	44.51 <sup>a</sup>	2.85 <sup>a</sup>	14.20 <sup>a</sup>	6.42 <sup>a</sup>	-476.27624 <sup>a</sup>
	B3LYP/6-31++G(d,p)	38.50 <sup>a</sup>	2.91 <sup>a</sup>	8.60 <sup>a</sup>	9.34 <sup>a</sup>	-479.37276 <sup>a</sup>
	CNDO/2		3.04 <sup>c</sup>			
	Exp.		2.57 <sup>d</sup>			
2-Methyl-4-phenylpyridine	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
3-Methyl-4-phenylpyridine	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
2-Amino-4-phenylpyridine	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
3-Amino-4-phenylpyridine	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
2-Nitro-4-phenylpyridine	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
3-Nitro-4-phenylpyridine	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

<sup>a</sup>From Ref.6, <sup>b</sup>From Ref.21, <sup>c</sup>From Ref.22 and <sup>d</sup>Exp. Ref.20

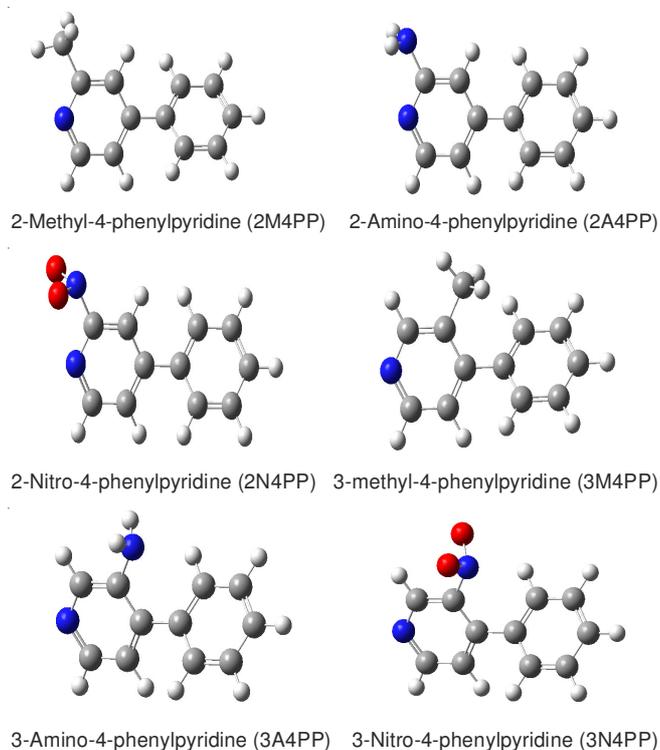


Fig. 1. Molecular structure of studied molecules (on this figure grey ball: C, white ball: H, blue ball: N, red ball: O represents)

The variation of relative energy, static polarizability, anisotropy of polarizability and first static hyperpolarizability against the dihedral angle between  $0^\circ$  and  $90^\circ$  at intervals of  $15^\circ$  due to high symmetry of title compounds. All calculations were performed using Gaussian 03W software package<sup>19</sup>.

## RESULTS AND DISCUSSION

**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 favour a non planar structure. Therefore the conformational analysis has been carried out after geometry optimization. In Fig. 2 the torsion potentials as a function of the torsion angle are presented as relative torsion potential where the optimized global minimum energy structure is taken as a zero level. 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  $38.50^\circ$  and  $44.51^\circ$  between the phenyl and pyridine rings in previous paper, respectively.

The calculated relative energies for  $0^\circ$  and  $90^\circ$ , total energies and dipole moments at ground state are given in Table-1 for 4-phenylpyridine and title compounds. Replacing hydrogen atom with substitution  $\text{CH}_3$  group on 4-phenylpyridine does not change equilibrium dihedral angle of 2-methyl-4-phenylpyridine isomer and increase of equilibrium dihedral angle of 3-methyl-4-phenylpyridine isomer about  $20^\circ$ . Also the  $\text{NH}_2$  and  $\text{NO}_2$  substituted 2-amino-4-phenylpyridine and 2-nitro-4-phenylpyridine molecules do not have significant change in the equilibrium dihedral angle. The  $\text{NH}_2$  and  $\text{NO}_2$  substituted 3-amino-4-phenylpyridine and 3-nitro-4-phenylpyridine molecules have increase in the equilibrium dihedral angle about  $10$ - $14^\circ$ .

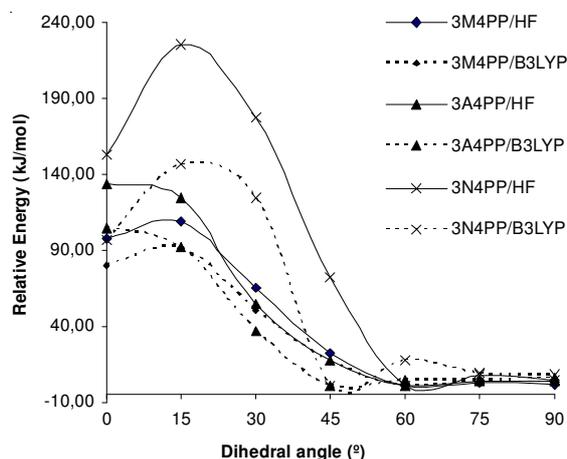


TABLE-2  
GROUND STATE NONLINEAR OPTICAL VALUES AND HOMO-LUMO ENERGY DIFFERENCE OF STUDIED MOLECULES

Molecule	Methods	$\alpha_{ave}$ (a.u)	$\Delta\alpha$ (a.u)	$\beta_{tot}$ (a.u)	$E_{HOMO-LUMO}$ (eV)
4-Phenylpyridine	B3LYP/6-31++G(d,p)	135.90 <sup>a</sup>	74.30 <sup>a</sup>	204.43 <sup>a</sup>	5.42 <sup>a</sup>
2-Methyl-4-phenylpyridine	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
3-Methyl-4-phenylpyridine	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
2-Amino-4-phenylpyridine	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
3-Amino-4-phenylpyridine	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
2-Nitro-4-phenylpyridine	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
3-Nitro-4-phenylpyridine	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

<sup>a</sup>From Ref. 6

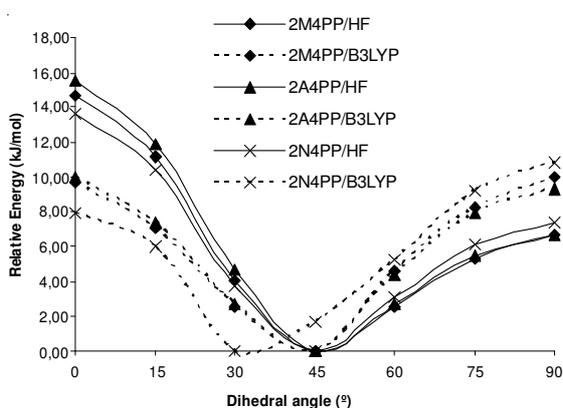
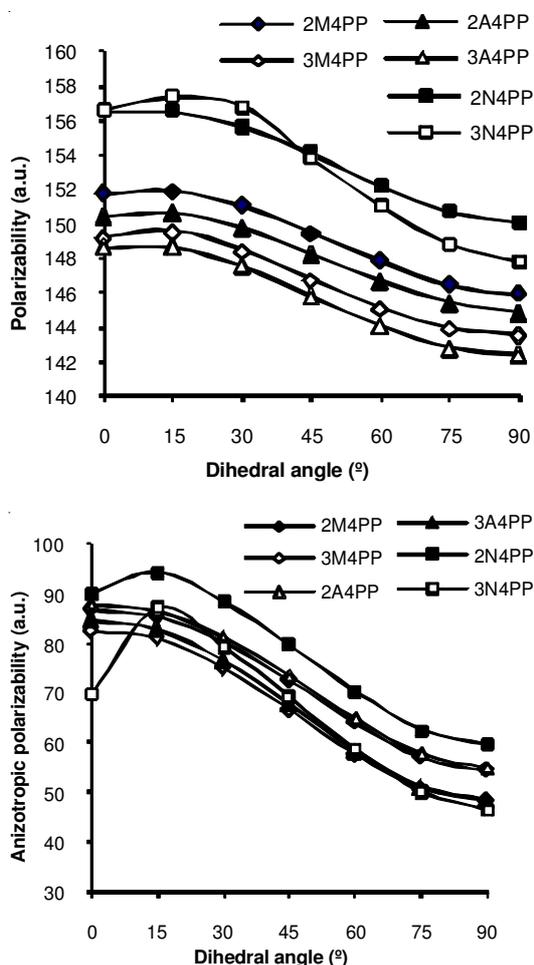


Fig. 2. Relative torsion energies with HF/6-31++G(d,p) and B3LYP/6-31++G(d,p) levels for 2-methyl-4-phenylpyridine (2M4PP), 3-methyl-4-phenylpyridine (3M4PP), 2-amino-4-phenylpyridine (2A4PP), 3-amino-4-phenylpyridine (3A4PP), 2-nitro-4-phenylpyridine (2N4PP) and 3-nitro-4-phenylpyridine (3N4PP) molecules

2-Methyl-4-phenylpyridine has less energy than 3-methyl-4-phenylpyridine 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 3-methyl-4-phenylpyridine, 3-amino-4-phenylpyridine and 3-nitro-4-phenylpyridine is reached at 15°. The dihedral angle at equilibrium geometry becomes smaller at B3LYP level than HF (Table-1) due to the electron delocalization across two rings. Also we can see in this table CH<sub>3</sub>, NH<sub>2</sub> and NO<sub>2</sub> substitution with the H atom at meta position on the 4-phenylpyridine approximately does not change the barrier high at 0° and 90°. Whereas CH<sub>3</sub>, NH<sub>2</sub> and NO<sub>2</sub> substitution with the H atom at ortho position on the 4-phenylpyridine 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 3-methyl-4-phenylpyridine) according to 4-phenylpyridine. 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<sup>20</sup> and previous theoretical results<sup>6,21,22</sup> of 4-phenylpyridine except for 3-amino-4-phenylpyridine, 2-nitro-4-phenylpyridine and 3-nitro-4-phenylpyridine. 2-nitro-4-phenylpyridine molecule has strongest dipole moment that caused large anisotropic polarizability among others.

**Non-linear optical 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<sup>23</sup>. The calculated average polarizability ( $\alpha_{ave}$ ), anisotropy of polarizability ( $\Delta\alpha$ ) and total first hyperpolarizability ( $\beta_{tot}$ ) 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<sub>3</sub>, NH<sub>2</sub> and NO<sub>2</sub> on nonlinear optical properties of 2-, 3- positional substituted methyl, amino, nitro-4-phenylpyridine molecules.



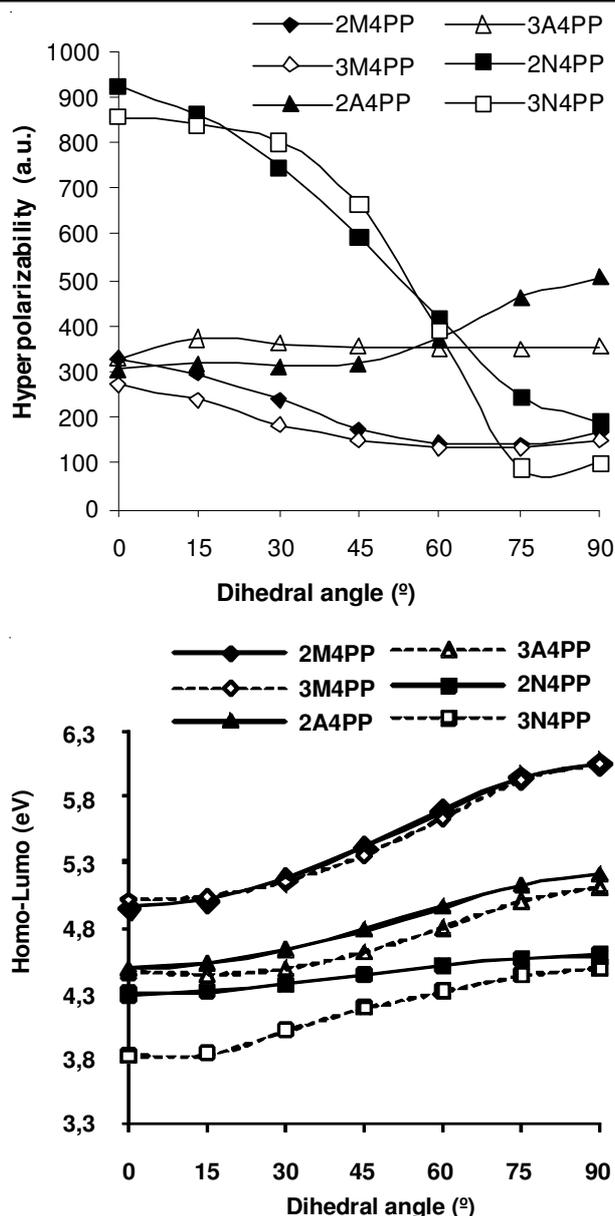


Fig. 3. Variation of static polarizability, anisotropy of polarizability, first static hyperpolarizability and HOMO-LUMO energy gap with the dihedral angle for studied molecules

It is conspicuous that substitution of  $\text{CH}_3$  on the 4-phenylpyridine does not display the dramatic increasing in  $\alpha_{\text{ave}}$  and  $\beta_{\text{tot}}$  values but  $\text{NH}_2$  and especially  $\text{NO}_2$  generate large nonlinearity compared with 4-PP at the equilibrium geometry. 2-, 3- $\text{NH}_2$ -4-phenylpyridine and 2- $\text{NO}_2$ -4-phenylpyridine molecules is larger than about % 50 and % 300  $\beta_{\text{tot}}$  value of the 4-phenylpyridine, respectively. It is expected that  $\beta_{\text{tot}}$  value is lowered when the dihedral angle changed or when deviated from the planarity except for 2-, 3- $\text{NH}_2$ -4-phenylpyridine. The general belief is that the planarity is one of the criterions to satisfy for a molecule to be nonlinear optical active<sup>24</sup>.

We calculated the maximum  $\beta_{\text{tot}}$  at planar structures except for 2-, 3- $\text{NH}_2$ -4-phenylpyridine. The anisotropic polarizability and first static hyperpolarizability values are most sensitive to torsional angle. These molecules shown in Fig. 1 involve a  $\pi$ -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<sup>25</sup>, which can be seen from Fig. 3. As the dihedral angles change from  $0^\circ$  to  $90^\circ$ , the HOMO-LUMO energy differences increase. However static polarizability and anisotropy of polarizability decrease with increasing the interring angles to  $90^\circ$  (Fig. 3).

## Conclusion

We observed that replacing hydrogen atom at meta position with substitution  $\text{CH}_3$ ,  $\text{NH}_2$  and  $\text{NO}_2$  group on 4-phenylpyridine do not change equilibrium dihedral angles of 4-phenylpyridine isomers but replacing hydrogen atom at ortho position with substitution  $\text{CH}_3$ ,  $\text{NH}_2$  and  $\text{NO}_2$  group increases equilibrium dihedral angle of 4-phenylpyridine isomers about between  $14$ - $22^\circ$  on account of steric effect between hydrogen and  $\text{CH}_3$ ,  $\text{NH}_2$  and  $\text{NO}_2$  moieties. The  $\text{CH}_3$  substitution on the 2-methyl-4-phenylpyridine decreased the energy barrier at  $0^\circ$  and at  $90^\circ$ . Whereas  $\text{CH}_3$  substitution on the 3-methyl-4-phenylpyridine increased the energy barrier at  $0^\circ$  (about four fold large barrier) but decreased at  $90^\circ$  (about 1.60 kJ/mol for HF method and 3.87 kJ/mol for B3LYP method) according to 4-PP and 2-methyl-4-phenylpyridine. Substitution of  $\text{CH}_3$  on the 4-phenylpyridine does not display the dramatic increasing in  $\alpha_{\text{ave}}$  and  $\beta_{\text{tot}}$  values whereas  $\text{NH}_2$  and especially  $\text{NO}_2$  generate large nonlinearity compared with 4-PP (at the equilibrium geometry the calculated  $\beta_{\text{tot}}$  value of 2-, 3- $\text{NH}_2$ -4-phenylpyridine and 2- $\text{NO}_2$ -4-phenylpyridine *ca.* 50 % and *ca.* 300 % times larger than 4-phenylpyridine, respectively). The largest hyperpolarizability obtained for 2- $\text{NO}_2$ -4-phenylpyridine as 920.68 a.u. The  $\beta_{\text{tot}}$  value is lowered when the dihedral angle changed or when deviated from the planarity except for 2-, 3- $\text{NH}_2$ -4-phenylpyridine. 2-nitro-4-phenylpyridine 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 non-linear optical activity.

## ACKNOWLEDGEMENTS

This work was funded by Dumlupinar University (BAP: 2007-1) and Gazi University (BAP: 05/2007-15).

## REFERENCES

1. H. Kishida, H. Matsuzaki, H. Okamoto, T. Manabe, M. Yamashita, Y. Taguchi and Y. Tokura, *Nature*, **405**, 929 (2000).
2. S. Kawata and Y. Kawata, *Chem. Rev.*, **100**, 1777 (2000).
3. T. Pons, L. Moreaux, O. Mongin, M. Blanchard-Desce and J. Mertz, *J. Biomed. Opt.*, **8**, 428 (2003).
4. M.A.V.R. da Silva, M.A.R. Matos and C.A. Rio, *J. Phys. Chem. A*, **104**, 1774 (2000).
5. A. Göller and U.W. Grummt, *Chem. Phys. Lett.*, **321**, 399 (2000).
6. H. Alyar, M. Bahat, Z. Kantarci and E. Kasap, *Czech. J. Phys.*, **56**, 349 (2006).
7. H. Alyar, Z. Kantarci, M. Bahat and E. Kasap, *J. Mol. Struct.*, **834-836**, 516 (2007).

8. H. Alyar, Z. Kantarci, M. Bahat and E. Kasap, *Comput. Theor. Chem.*, **977**, 22 (2011).
9. D.V. Gopal and M. Subrahmanyam, *Green Chem.*, **3**, 233 (2001).
10. J. Hu, G. Zhang, H.H. Shih, P. Sun and C.H. Cheng, *Synth. Met.*, **158**, 912 (2008).
11. F.G. Tomas and C. Buess-Herman, *J. Electronal. Chem.*, **318**, 399 (1991).
12. P.C. Hariharan and J.A. Pople, *Mol. Phys.*, **27**, 209 (1974).
13. R. Ditchfield, W.J. Hehre and J.A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).
14. W.J. Hehre, R. Ditchfield and J.A. Pople, *J. Chem. Phys.*, **56**, 2257 (1972).
15. A.D. Becke, *J. Chem. Phys.*, **98**, 5648 (1993).
16. C. Lee, W. Yang and R.G. Parr, *Phys. Rev. B.*, **37**, 785 (1988).
17. B. Miehlich, A. Savin, H. Stoll and H. Preuss, *Chem. Phys. Lett.*, **157**, 200 (1989).
18. J. Hernandez, H.J. Soscun and A. Hinchliffe, *Int. Electron. J. Mol. Des.*, **2**, 589 (2003).
19. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez and J.A. Pople, Gaussian 03W, Revision D.01, Gaussian, Inc: Pittsburgh PA, (2003).
20. C.W. Cumper, R.F.A. Ginman and A.I. Vogel, *J. Chem. Soc.*, 4525 (1962).
21. V. Barone, F. Lelj, C. Cauletti, M.N. Piancastelli and N. Russo, *Mol. Phys.*, **49**, 599 (1983).
22. V. Galasso, G. De Alti and A. Bigotto, *Tetrahedron*, **27**, 991 (1971).
23. H. Soscun, O. Castellano, Y. Bermudez, C.T. Mendoza, A. Marcano and Y. Alvarado, *J. Mol. Struct. (Theochem)*, **592**, 19 (2002).
24. B.A.S. Mendis and K.M.N. de Silva, *Int. Electron. J. Mol. Des.*, **4**, 226 (2003).
25. A. Hinchliffe and H.J. Soscun, *J. Mol. Struct. (Theochem)*, **304**, 109 (1994).