

# Electronic and Nonlinear Optical (NLO) Properties of Fluorophenylpyridines

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**Abstract** In this paper, we present a theoretical investigation of the electronic and NLO properties such as global minimum energy, electric dipole moment ( $\mu$ ), first static polarizability ( $\alpha$ ), polarizability of anisotropy ( $\Delta\alpha$ ), first static hyperpolarizability ( $\beta$ ) and optical band gap ( $E_{HOMO-LUMO}$ ) of a series of 39 fluorophenylpyridine derivatives. All calculations were carried out by using two different density functional approach (B3LYP and B3PW91) with 6-31++G(d,p) as basis set. The results show that fluorinations of phenylpyridines have not effected on the mean polarizability ( $\langle\alpha\rangle$ ), and both phenylpyridines and fluorophenylpyridines present low nonlinear optical activity.

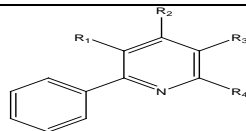
**Keywords:** Fluorophenylpyridines, hyperpolarizability, optical band gap, B3LYP

## 1 Introduction

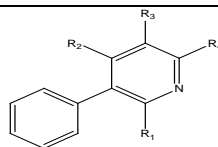
In recent years, nonlinear optical molecular materials are attracting considerable attention because of their potential applications in optoelectronic devices of telecommunications, information storage, optical switching, signal processing [Chemla (1987); Shen (1984); Parasad and Williams (1991); Nalwa and Miyata (1997); Marder *et al.* (1997); Shi *et al.* (2000)] and terahertz (THz) wave generation [Krishnakumar and Nagalakshmi (2008)]. Numerous experimental [Kanis *et al.* (1994); Wong, Jen *et al.* (1994); Clays and Coe (2003); Das (2006)] as well as theoretical [Lee *et al.* (1999); Calaminici *et al.* (2000); Thanthiriwatte and de Silva (2002); Mendis and de Silva (2004); Kamiya *et al.* (2005); Champagne *et al.* Kirtman (2000); Sergeyev *et al.* Champagne (2010) ] investigations have been performed for the NLO properties of organic molecules.

The design of efficient organic materials for the applications in nonlinear optical effect is based on asymmetric polarization induced by electron donor and electron acceptor groups on either sides of the molecule at appropriate positions in the molecular systems. The position of the substitutions is vital important as substitution in a context NLO activity. The ability of many compounds containing pyridine moiety to exhibit antitumor activity has been documented in numerous publications and reviews [Olsen *et al.* (2004); Frost *et al.* (2002); French *et al.* (1974); Amr *et al.* (2006)]. Phenylpyridines are important intermediates in synthesis of drugs, agrochemicals, herbicides, insecticides, desiccants, surfactant agents and anti-inflammatory agents [Gopal and Subrahmanyam (2001)]. 2-phenylpyridine and its derivatives are widely used as ligand in the preparation of coordination complexes [Gopal and Subrahmanyam (2001)]. Phenylpyridines are usually used in liquid crystal and dye laser technology [Barone *et al.* (1983)].

Density functional theory (DFT) calculations with various functional are the excellent methods in the design of NLO molecules and it helps to predict properties of the new materials, such as molecular dipole moments, polarizabilities, and hyperpolarizabilities [Wu *et al.* (2007); Kolev *et al.* (2008); Kenawi *et al.* (2008); Fantin *et al.* (2007); Drozd and Marchewka (2006)]. Nonlinear optical properties of 2-, 3-, 4-phenylpyridine were reported previously by Alyar *et al.* [Alyar *et al.* (2006)]. In this research, electronic and nonlinear optical properties of 39 fluorophenylpyridine derivatives were calculated with two different DFT functional. The studied molecules are presented in **Table 1-3**.

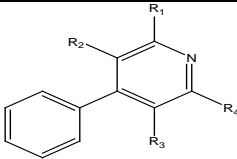
**Table 1.** Structures and IUPAC names of 2-phenylpyridine derivatives


Mol.	R1	R2	R3	R4	IUPAC NAMES
1	F	H	H	H	3-fluoro-2-phenylpyridine( <b>3F-2PP</b> )
2	H	F	H	H	4-fluoro-2-phenylpyridine( <b>4F-2PP</b> )
3	H	H	F	H	5-fluoro-2-phenylpyridine( <b>5F-2PP</b> )
4	H	H	H	F	6-fluoro-2-phenylpyridine( <b>6F-2PP</b> )
5	F	F	H	H	3,4-difluoro-2-phenylpyridine( <b>34DF-2PP</b> )
6	F	H	F	H	3,5-difluoro-2-phenylpyridine( <b>35DF-2PP</b> )
7	F	H	H	F	3,6-difluoro-2-phenylpyridine( <b>36DF-2PP</b> )
8	H	F	F	H	4,5-difluoro-2-phenylpyridine( <b>45DF-2PP</b> )
9	H	F	H	F	4,6-difluoro-2-phenylpyridine( <b>46DF-2PP</b> )
10	H	H	F	F	5,6-difluoro-2-phenylpyridine( <b>56DF-2PP</b> )
11	F	F	F	H	3,4,5-trifluoro-2-phenylpyridine( <b>345TF-2PP</b> )
12	F	F	H	F	3,4,6-trifluoro-2-phenylpyridine( <b>346TF-2PP</b> )
13	F	H	F	F	3,5,6-trifluoro-2-phenylpyridine( <b>356TF-2PP</b> )
14	H	F	F	F	4,5,6-trifluoro-2-phenylpyridine( <b>456TF-2PP</b> )
15	F	F	F	F	3,4,5,6-tetrafluoro-2-phenylpyridine( <b>3456TTF-2PP</b> )

**Table 2.** Structures and IUPAC names of 3-phenylpyridine derivatives


Mol.	R1	R2	R3	R4	IUPAC NAMES
16	F	H	H	H	2-fluoro-3-phenylpyridine( <b>2F-3PP</b> )
17	H	F	H	H	4-fluoro-3-phenylpyridine( <b>4F-3PP</b> )
18	H	H	F	H	5-fluoro-3-phenylpyridine( <b>5F-3PP</b> )
19	H	H	H	F	6-fluoro-3-phenylpyridine( <b>6F-3PP</b> )
20	F	F	H	H	2,4-difluoro-3-phenylpyridine( <b>24DF-3PP</b> )
21	F	H	F	H	2,5-difluoro-3-phenylpyridine( <b>25DF-3PP</b> )
22	F	H	H	F	2,6-difluoro-3-phenylpyridine( <b>26DF-3PP</b> )
23	H	F	F	H	4,5-difluoro-3-phenylpyridine( <b>45DF-3PP</b> )
24	H	F	H	F	4,6-difluoro-3-phenylpyridine( <b>46DF-3PP</b> )
25	H	H	F	F	5,6-difluoro-3-phenylpyridine( <b>56DF-3PP</b> )
26	F	F	F	H	2,4,5-trifluoro-3-phenylpyridine( <b>245TF-3PP</b> )
27	F	F	H	F	2,4,6-trifluoro-3-phenylpyridine( <b>246TF-3PP</b> )
28	F	H	F	F	2,5,6-trifluoro-3-phenylpyridine( <b>256TF-3PP</b> )
29	H	F	F	F	4,5,6-trifluoro-3-phenylpyridine( <b>456TF-3PP</b> )
30	F	F	F	F	2,4,5,6-tetrafluoro-3-phenylpyridine( <b>2456TTF-3PP</b> )

**Table 3.** Structures and IUPAC names of 4-phenylpyridine derivatives



Mol.	R1	R2	R3	R4	IUPAC NAMES
<b>31</b>	F	H	H	H	2-fluoro-4-phenylpyridine( <b>2F-4PP</b> )
<b>32</b>	H	F	H	H	3-fluoro-4-phenylpyridine( <b>3F-4PP</b> )
<b>33</b>	F	F	H	H	2,3-difluoro-4-phenylpyridine( <b>23DF-4PP</b> )
<b>34</b>	H	F	F	H	3,5-difluoro-4-phenylpyridine( <b>35DF-4PP</b> )
<b>35</b>	F	H	H	F	2,6-difluoro-4-phenylpyridine( <b>26DF-4PP</b> )
<b>36</b>	H	F	H	F	3,6-difluoro-4-phenylpyridine( <b>36DF-4PP</b> )
<b>37</b>	F	F	F	H	2,3,5-trifluoro-4-phenylpyridine( <b>235TF-4PP</b> )
<b>38</b>	F	F	H	F	2,3,6-trifluoro-4-phenylpyridine( <b>236TF-4PP</b> )
<b>39</b>	F	F	F	F	2,3,5,6-tetrafluoro-4-phenylpyridine( <b>2356TTF-4PP</b> )

## 2 Computational method

Quantum mechanical calculations related to global minimum energy, dipole moment, HOMO-LUMO band gap and NLO were performed with Gaussian 03W program [Frisch et al. (2003)]. Input data were prepared for Gaussian 98/03W using Gauss View 04 graphical program.

As the first step of our DFT calculations, the geometries of these 39 molecules were optimized and then, all the geometries were characterized by the frequency analysis and they are proved to be the most stable point on the potential energy surface.

The performance of various DFT functional and of basis sets in hyperpolarizability calculations have been extensively studied for organic NLO materials [Calaminici *et al.* (2000); Champagne *et al.* (2000); Sergeyev *et al.* (2010)]. In this study, electronic and nonlinear optical properties of fluorophenylpyridines were computed with two different approximations because the quality of approximation might have an important effect in DFT for such hydrogen-bonded systems [Haman (1997)]. The Becke's three-parameter exchange functional and the gradient corrected functional of Lee, Yang, and Parr (B3LYP) [Becke (1993); Lee, Yang and Parr (1988)] and Becke's three-parameter functional with Perdew–Wang correlation functional (B3PW91) [Becke (1993); Lee, Yang and Parr (1988); Perdew *et al.* (1992)] were used in this study. Accurate calculation of nonlinear optical properties requires the use of extended basis sets and high level of theory. In particular, these basis sets have to include d and p polarization functions together with s and p diffuse functions. In the present work, considering the number of molecules taking into account the 6-31++G(d, p) [Hariharan and Pople (1974); Ditchfield, Hehre and Pople (1971); Hehre, Ditchfield and Pople (1972)] basis set was chosen for the calculations.

## 3 Results and Discussion

The nonlinear response of an isolated molecule in an electric field  $E_i(\omega)$  can be represented as a Taylor expansion of the total dipole moment ( $\mu_{tot}$ ) induced by the field:

$$\mu_{tot} = \mu_0 + \alpha_{ij}E_j + \beta_{ijk}E_jE_k + \dots$$

Where  $\alpha$  is the linear polarizability,  $\mu_0$  the permanent dipole moment and  $\beta$  is the first hyperpolarizability tensor components. The isotropic (or average) linear polarizability and anisotropy of polarizability is defined as [Soscun *et al.* (2002)]:

$$\langle \alpha \rangle = 1/3 (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

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

The complete equation for calculating the total static first hyperpolarizability magnitude of from Gaussian output is given as follows [Thanthiriwatte and de Silva (2002); Mendis and de Silva (2004); Kamiya *et al.* (2005)],

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

Nonlinear optical properties of 2-,3-,4-phenylpyridine molecules were studied previously by Alyar *et al.* [Alyar *et al.* (2006)]. The mean polarizabilities of 2-,3-,4-phenylpyridines were found as 139, 136.4 and 135.9 a.u. by B3LYP/6-31++G(d,p) method, respectively. In this study, mean polarizabilities were calculated as;

138.77-141.94 a.u. and 136.53-139.67 a.u. for fluoro-2-phenylpyridines

134.99-136.86 a.u. and 132.92-134.95 a.u. for fluoro-3-phenylpyridines

135.22-136.74 a.u. and 132.82-134.46 a.u. for fluoro-4-phenylpyridines

by B3LYP and B3PW91 methods, respectively. One other nonlinear optical properties for 2-,3-,4-phenylpyridines, anisotropy of polarizability were found as 81.14, 80.68 and 74.30 a.u. by B3LYP/6-31++G(d,p) method, respectively [Alyar *et al.* (2006)]. In this study, anisotropic polarizabilities were calculated as;

81.25-86.50 a.u. and 79.77-85.37 a.u. for fluoro-2-phenylpyridines

68.57-74.22 a.u. and 65.73-75.64 a.u. for fluoro-3-phenylpyridines

65.97-71.86 a.u. and 63.98-70.84 a.u. for fluoro-4-phenylpyridines

by B3LYP and B3PW91 methods, respectively. Maximum total hyperpolarizability for 2-, 3-, 4-phenylpyridines were obtained, as 456.7, 199.9 and 303.8 a.u. using B3LYP method, respectively [Alyar *et al.* (2006)]. In this study nonlinear optical properties of all fluorophenylpyridines are presented in **Table 4**.

The equilibrium geometry of the molecules results from a balance between two effects. One of these effects is conjugation interaction between phenyl and fluoropyridine rings which raises a tendency to a planar structure. The other one is steric repulsion between atoms in ortho positions which favors a non planar structure. The global minimum energies, twist angles between two ring, electric dipole moments and molecular orbital energy band gaps ( $E_{HOMO-LUMO}$ ) obtained by the DFT structures optimization were presented in **Table 5**.

The notable futures arising from **Table 4** and **Table 5** are as follows:

1. Fluorination of phenylpyridines have not effected on the mean polarizability ( $\langle\alpha\rangle$ ). Also, the difference between B3LYP and B3PW91 methods is only c.a 2 a.u. for mean polarizability of fluorophenylpyridines.
2. The effect of fluorination on anisotropy of polarizability ( $\Delta\alpha$ ) for phenylpyridines; the number of fluorine atoms on the ring increases, anisotropy of polarizability increases. Also the difference between B3LYP and B3PW91 methods is only c.a 1-2 a.u. for anisotropy of polarizability.
3. In previous study, the largest first static hyperpolarizability obtained for the 2PP as 456.7 a.u. In this study, largest first static hyperpolarizability obtained for the compound (**5**) as 650.02 a.u.
4. As can be seen from **Table 4** and **Table 5**, fluoro-2-phenylpyridines has lover band gaps ( $E_{HOMO-LUMO}$ ) than other fluorophenylpyridines. However, fluoro-2-phenylpyridines has largest first static

hyperpolarizabilities among the other fluorophenylpyridine molecules. Therefore previous and present calculations show the inverse relationship between the polarizability and HOMO-LUMO energy gaps [Hincliffe and Sosun (1994)].

5. Previous and new calculations reveal that phenylpyridines and fluorophenylpyridines present low nonlinear optical properties.
6. It can be seen from **Table 5**, the steric effect of fluoro atoms on the ortho position is larger than meta and para position (see dihedral angles of **1**, **2**, **3** and **4** molecules).
7. The same local environments around the central C-C bond (i.e. the same ortho groups or atoms) have very similar equilibrium conformations. As an example, dihedral angle of molecule **20**, **26** and **27** is approximately 50°.

**Table 4.** Nonlinearoptical properties of fluorophenylpyridines in a.u. units

No	Mol. Name	$\alpha_{ave}$		$\Delta\alpha$		$\beta_{tot}$	
		B3LYP	B3PW91	B3LYP	B3PW91	B3LYP	B3PW91
1	3F-2PP	139.53	137.04	81.32	80.47	647.59	606.95
2	4F-2PP	139.14	136.67	81.99	81.06	423.72	396.00
3	5F-2PP	138.77	136.53	82.93	82.34	167.33	160.71
4	6F-2PP	139.73	137.33	83.20	82.36	479.13	452.27
5	34DF-2PP	139.80	137.32	81.25	79.77	650.02	601.74
6	35DF-2PP	139.43	137.14	82.72	81.69	100.08	93.06
7	36DF-2PP	140.62	138.17	84.16	83.08	638.03	594.20
8	45DF-2PP	139.24	137.05	83.45	82.69	218.54	211.91
9	46DF-2PP	140.02	137.65	84.33	83.32	414.92	385.57
10	56DF-2PP	140.23	138.01	85.32	84.61	266.01	256.17
11	345TF-2PP	140.01	137.74	82.62	81.37	247.63	236.61
12	346TF-2PP	140.97	138.55	84.59	83.05	603.98	554.17
13	356TF-2PP	141.24	138.93	86.31	85.02	111.54	93.43
14	456TF-2PP	140.82	138.64	86.22	85.37	186.21	180.27
15	3456TTF-2PP	141.94	139.67	86.50	85.14	81.50	67.72
16	2F-3PP	135.89	134.06	71.37	71.31	351.33	337.70
17	4F-3PP	135.87	133.46	71.43	70.33	209.24	190.19
18	5F-3PP	136.08	134.34	73.95	73.89	99.54	93.79
19	6F-3PP	135.65	133.93	74.22	74.32	414.86	393.60
20	24DF-3PP	135.48	132.92	67.74	65.73	367.06	317.50
21	25DF-3PP	136.86	134.51	73.66	72.47	199.66	176.15
22	26DF-3PP	136.45	134.13	73.83	72.77	333.32	324.35
23	45DF-3PP	136.20	133.87	71.18	69.98	282.93	265.33
24	46DF-3PP	134.99	133.48	72.22	71.22	251.32	249.16
25	56DF-3PP	137.04	134.95	76.35	75.64	456.22	441.13
26	245TF-3PP	136.14	133.68	68.57	66.60	290.76	245.50
27	246TF-3PP	135.57	133.13	68.62	66.70	147.61	146.34
28	256TF-3PP	136.75	135.17	75.33	74.17	281.05	279.85
29	456TF-3PP	136.68	134.48	71.78	71.80	399.77	377.15
30	2456TTF-3PP	136.75	134.41	70.20	68.35	168.39	179.92
31	2F-4PP	135.56	133.80	70.39	70.35	236.81	235.60
32	3F-4PP	135.22	133.45	68.68	68.63	399.69	399.67
33	23DF-4PP	136.26	133.87	68.84	67.50	455.97	432.55
34	35DF-4PP	134.51	132.82	66.21	64.18	496.01	433.15

35	26DF-4PP	136.25	133.98	71.86	70.84	135.81	131.39
36	36DF-4PP	135.99	133.68	69.54	68.27	321.37	305.10
37	235TF-4PP	135.95	133.53	65.97	63.98	425.54	398.06
38	236TF-4PP	136.74	134.46	70.26	68.45	297.33	275.26
39	2356TTF-4PP	136.65	134.41	66.66	64.59	332.51	293.08

**Table 5.** Ground state electronic energies (E), dihedral angles ( $\theta$ ), molecular dipole moments ( $\mu$ ) and optical band gap ( $E_{\text{HOMO-LUMO}}$ ) of fluorophenylpyridines

No	Mol. Name	E/a.u.	$\theta/^\circ$	$\mu/D$	$E_{\text{HOMO-LUMO}}/eV$
1	3F-2PP	-578.58839979	-27.42	1.52	4.96
2	4F-2PP	-578.59192967	-21.44	0.33	5.11
3	5F-2PP	-578.61459247	-23.52	1.94	4.97
4	6F-2PP	-578.62555589	-20.34	3.16	4.84
5	34DF-2PP	-677.84729203	-26.80	1.45	4.97
6	35DF-2PP	-677.84977285	-28.47	0.85	4.87
7	36DF-2PP	-677.85877645	-44.75	2.28	4.97
8	45DF-2PP	-677.84868983	-22.55	2.12	5.02
9	46DF-2PP	-677.86482775	-19.15	1.97	4.89
10	56DF-2PP	-677.85574536	-21.11	3.46	4.83
11	345TF-2PP	-777.07591293	-28.63	1.53	4.99
12	346TF-2PP	-777.09204246	-24.24	0.83	4.81
13	356TF-2PP	-777.09087506	-24.22	2.60	4.71
14	456TF-2PP	-777.09047933	-19.80	3.71	4.89
15	3456TTF-2PP	-876.31648454	-24.68	2.62	4.82
16	2F-3PP	-578.61925783	-41.56	3.18	5.20
17	4F-3PP	-578.61324578	-44.86	1.40	5.40
18	5F-3PP	-578.61245214	-39.54	2.65	5.22
19	6F-3PP	-578.62215478	-40.72	4.10	5.37
20	24DF-3PP	-677.85865985	-49.24	2.37	5.39
21	25DF-3PP	-677.85532658	-40.78	2.61	5.07
22	26DF-3PP	-677.86545784	-41.91	4.10	5.12
23	45DF-3PP	-677.84332546	-45.01	2.26	5.37
24	46DF-3PP	-677.85912457	-45.67	3.02	5.46
25	56DF-3PP	-677.85424578	-39.81	4.53	5.26
26	245TF-3PP	-777.07727389	-48.50	1.70	5.17
27	246TF-3PP	-777.10308079	-50.18	3.21	5.44
28	256TF-3PP	-777.09528639	-41.21	4.09	5.06
29	456TF-3PP	-777.08425484	-45.86	3.93	5.46
30	2456TTF-3PP	-876.32536410	-49.16	3.26	5.76
31	2F-4PP	-578.62365121	-37.92	4.41	5.35
32	3F-4PP	-578.61098654	-40.44	2.71	5.31
33	23DF-4PP	-677.85442157	-42.79	4.61	5.35
34	35DF-4PP	-677.84532549	-46.56	1.51	5.37
35	26DF-4PP	-677.86712478	-38.08	4.66	5.26
36	36DF-4PP	-677.85632564	-42.12	3.62	5.23
37	235TF-4PP	-777.08636020	-46.46	3.47	5.24
38	236TF-4PP	-777.09759730	-41.54	4.88	5.21
39	2356TTF-4PP	-876.32454771	-46.55	4.09	5.23



## 4 Conclusions

In the present study, we report electronic and nonlinear optical properties of 39 derivatives of fluorophenylpyridine at two different density functional approach (B3LYP and B3PW91) with 6-31++G(d,p) as basis set. Fluorination of phenylpyridines did not bring on a very large change in the mean polarizability. However, the number of fluorine atoms on the pyridine ring increases, anisotropy of polarizability increases. Fluoro-2-phenylpyridines roughly have largest hyperpolarizability and lower band gap ( $E_{\text{HOMO-LUMO}}$ ) than other fluorophenylpyridines. Largest first static hyperpolarizability was obtained for 2-phenylpyridine molecule, but now obtained for the compound (**5**) as 650.02 a.u. However, previous and present study reveal that phenylpyridines and fluorophenylpyridines present low nonlinear optical properties.

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