LINEAR AND NON LINEAR OPTICAL PROPERTIES OF ELECTRON DONOR AND ACCEPTOR PYRIDINE MOIETY: A STUDY BY AB INITIO AND DFT METHODS

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ABSTRACT

The Donor-Acceptor type conjugated molecular structures containing pyridine as a bridge have been explored for Non linear optical properties. The ab- initio Hartee Fock calculations and Density Functional Theory with B3LYP method have been carried out employing 6-31G basis set. The dipole moments (μ), polarizability (α), first hyperpolarizability (β), and HOMO-LUMO energy gap are calculated using the same level of theory. The dependence of the hyperpolarizability of different molecular structure on the nature of donor and acceptor on the pyridine is discussed on the basis of molecular orbital picture. Of all the molecular systems studied, the molecular system containing nitro as an acceptor and dimethylaniline as a donor is found to have largest value of hyperpolarizability; 49.92 X 10^{-30} esu and 164.61x10^{-30} esu with ab-initio/HF and DFT/B3LYP respectively. The large value of β for the Donor-Acceptor pyridine derivative suggests the potential applications of these molecular systems in the development of non linear materials.

Keywords: DFT, non linear optics, polarizability, first hyperpolarizability, frontier molecular orbital's, Ab initio.

INTRODUCTION

Organic compounds with delocalized π-electrons showing large values of non linear optical parameters are gaining interest among researcher because of their potential applications in field of optoelectronics such as optical communication, optical computing, optical switching and image processing (Chemla and Zyss, 1987; Prasad and Williams, 1990; Zyss, 1994; Venkatram et al., 2005). Organic molecules are good candidates for nonlinear devices as they are chemically flexible, and they show large and fast non linear optical response (Gunter, 2000) as a result of which, their optical and electronic properties can be tuned. Variety of organic and organometallic molecular systems has been studied for predicting nonlinearity (Kanis et al., 1994). Organic compounds with electron donating group on one side of the molecule and electron accepting group on other side have been studied by experimental and theoretical scientists for NLO properties (Poornesh et al., 2009). Designs of these organic NLO active materials are based on the approach of charge transfer (CT) due to π- electron cloud movement from donor (D) to acceptor (A) groups on either side of these π-conjugated systems which in turn affects the value of hyperpolarizability (Prasad and William, 1990). It has been known from the recent studies that molecular systems, based on electron donor (D) and electron acceptor (A) units connected through pi electron moieties show many interesting non linear optical characteristics and have higher value of second order NLO properties (Cheng et al., 1991; Thanthiriwatte et al.,

2002; Liyanage et al., 2003; Tillekaratne et al., 2003). The types of pi-bridges studied so far for developing efficient NLO materials and molecules include D-A acetylenes (Atalay et al., 2008), azo complexes (Moylan et al., 1993) aromatic ring (Cheng et al., 1991) and heteroaromatic rings (Rao et al., 1994). A good deal of work has been done for investigating nonlinear optical behavior of conjugated polymers consisting of six-member and five-member aromatic units such as benzene, pyridine, Thiophene and pyrrole etc (Rao et al., 1994; Jen et al., 1993). Their derivatives are also considered to be promising candidates for electronic and nonlinear optical technology. Pyridine, pyridine-oxide (POM1, POM2) and nitro pyridine oxide (Berthier et al., 1992; Hammoutenea et al., 1993; Soscun et al., 2002) have large optical nonlinearities, which were associated with intramolecular charge transfer between the NO donor and the aromatic (pyridine) ring and the NO_2 acceptor. So far many studies have also been carried out to investigate the nonlinear behavior of two π-conjugated rings attached with a single bond such as biphenyls (Rumi et al., 1999) and phenylpyridine (Alyar et al., 2006). However, pyridine moiety can further be investigated as a bridge for the search of better NLO material and for understanding the mechanism at the atomic level.

Theoretical calculations are quite useful both in understanding the relationship between the molecular structures and nonlinear optical properties as well as they also provide guidelines to experimentalists for the design and synthesis of new organic NLO materials. A large

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number of semi-empirical and ab initio calculations have been reported on molecular hyperpolarizability (β), which is one of the key parameter in investigating second order NLO materials (Soscun *et al.*, 2002; Li *et al.*, 2006; Champagne *et al.*, 2009). The aim of the present work is to design and predict NLO properties of molecular systems with better NLO behavior. The idea is to study the charge transfer effect from donor to acceptor through pyridine moiety. For calculating non linear behavior for the designed molecular systems, ab-initio and DFT calculations have been carried out with 6-31G basis set. Though there is a effect of basis set of the calculation used on the estimated value of β, but the effect is not very profound and the β value has been reported to be slightly increased on taking up higher basis sets like 631G (d), 6-31G (d) (Atalay *et al.*, 2008), and this is the reason for not carry out the computation of β values with higher basis set at this stage.

Computational Methodology

All calculations of polarizability and first static hyperpolarizability of pyridine derivatives were performed using Gaussian 03W (Frisch *et al.*, 2003). Geometries of all molecules were optimized with 6-31G basis set by employing ab initio Hartee Fock and Becke three-parameter mixing of exchange and Lee–Yang–Parr correlation functional (B3LYP) method. All NLO calculations were performed at same level of theory, which provides reliable results for β (Atalay *et al.*, 2008).

The values of mean polarizability (α) of molecular systems, reported in the present work can be calculated by the following equations:

$$\alpha = 1/3(\alpha_{XX}+\alpha_{YY}+\alpha_{ZZ}) \tag{1}$$

The total hyperpolarizability is defined as

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

The magnitude of β_{tot} is calculated from the computed components β using following equation:

$$\beta_{tot} = [(\beta_{xxx}+\beta_{xyy}+\beta_{xzz})^2+(\beta_{yyy}+\beta_{yzz}+\beta_{yxx})^2+ (\beta_{zzz}+\beta_{zxx}+\beta_{zyy})^2]^{1/2} \tag{3}$$

Since the values of β components of GAUSSIAN 03W output are reported in atomic units, thus, the calculated values have been converted into electrostatic units.

RESULTS AND DISCUSSION

The molecular structures of the donor-acceptor pyridine based seven molecular systems viz N,N-dimethyl-5-nitropyridin-2-amine (DMNP), N,N-diethyl-5-nitropyridin-2-amine (DENP), 5-nitro-2-phenylpyridine (NPP), N,N-dimethyl-5-(1,3,4-oxadiazol-2-yl)pyridin-2-amine (DMOP), N,N-diethyl-5-(1,3,4-oxadiazol-2-yl) pyridin-2-amine (DEOP), 5-(1,3,4-oxadiazol-2-yl)-2-phenylpyridine (OPP) and N,N-dimethyl-4-(5-nitropyridin-2-yl) aniline (DMNPA) are shown in Table 1. Ab initio and DFT Calculations for optimized geometry show that all the molecular structures have C1 point group symmetry. The ground state dipole moments (μ), polarizability (α), hyperpolarizability (β) and Homo-Lumo energy gap of all molecular structures computed using ab initio Hartee Fock method and DFT/B3LYP method with 6-31G basis set are presented in table 2. The fact that the magnitude of polarizability depends on the strength of donor and acceptor unit substituted across conjugated bridge (Atalay *et al.*, 2008), led us to investigate pyridine as a conjugated bridge and the effect of the substitution of donors and acceptors on its nonlinear behavior. To begin with, we started the study by adding nitro group as an acceptor with different donors viz dimethylamine (N(Me)$_2$), diethylamine (N(Et)$_2$) and phenyl on the pyridine. The choice of nitro as an acceptor has been obvious due to the large values of β for molecules containing nitro as an acceptor (Latajka *et al.*, 2007).

For DMNP the value of β obtained using ab initio/HF method is ~12x10^{-30} esu. In order to improve the electronic conjugation between donor and acceptor group the conjugated length is increased in the next molecular structure (DENP), which has diethylamine as donor. The value of β for DENP as computed by using HF method is found to increase ~13.58x10^{-30} esu. The value of β for 5-nitro-2-phenylpyridine (NPP) computed with ab initio/RHF and that with DFT/B3LYP are found to be 13.58x10^{-30} esu 42.95x10^{-30} esu and respectively. The substitution of the nitro group as an acceptor has resulted in large enhancement of β value, as compared with computed values of β as 1.90 x10^{-30}, 0.74x10^{-30}, 1.21x10^{-30} esu respectively for 2-,3-,4- phenylpyridines using HF method as reported by Alyar et al (Latajka *et al.*, 2007). They also reported the β values of 3.94x10^{-30}, 1.72x10^{-30} and 2.62x10^{-30} esu respectively for the same molecules using DFT/B3LYP method (Rumi *et al.*, 1999). By employing DFT/B3LYP method on DMNP and DENP, the value of β is found to be 24.56x10^{-30} esu for DMNP which is slightly larger than that of DENP (~23.62x10^{-30} esu). The value of α and β obtained with HF method is observed to follow the increasing order as DMNP<DENP<NPP and with DFT/B3LYP the value of hyperpolarizability for these molecular structures is found to be in the order of DENP<DMNP<NPP. Phenyl is found to be conjugating well with pyridine to give larger value of polarizability and hyperpolarizability as predicted by two theoretical methods. The next three molecular structures viz DMOP, DEOP, OPP in the series are studied to examine the behavior of pyridine with some other acceptor keeping the donor at the same position. For this we have chosen 1, 3, 4- oxadiazole as an acceptor. The magnitude of hyperpolarizability for DEOP using HF/6-31G method is found to be more than that of DMOP as expected but it is found to decrease as the donor is

changed to phenyl in OPP. Whereas the polarizability (α) is found to increase in the same manner when the nitro group is used as an acceptor on the pyridine. The values of hyperpolarizability as estimated using HF/6-31G method for the molecules with oxadiazole acceptor is found to increase as OPP<DMOP<DEOP. By employing DFT/B3LYP method the trend has been found to be, DMOP<DEOP<OPP. A close examination of table 2 tells that nitro as an acceptor across pyridine is continuing to give good value of hyperpolarizability as compared to 1,3,4- oxadiazole as estimated using HF as well as DFT method. The last molecular structure reported in the present study is DMNPA designed with strong acceptor NO_2 and a strong donor dimethylaniline (Atalay *et al*., 2008). The good electronic communication through pyridine from donor to acceptor in this molecule (DMNPA) is inferred from the enhanced value of hyperpolarizability. Using the HF method, the calculated value of β for the DMNPA is found to be 49.92×10^{-30} esu and larger value of β ($\sim 164.61 \times 10^{-30}$ esu) is obtained with DFT/B3LYP method. The values of hyperpolarizability estimated for the molecular systems in present work are quite high as compared with that of para nitro aniline (PNA) (Yang *et al*., 2006; Isborn *et al*., 2007). The enhancement in β value for the pyridine based D-A systems is significant as compared to the β value of 0.168×10^{-30} esu, 0.305×10^{-30} esu and 2.3×10^{-30}, 1.65×10^{-30} esu for pyridine and pyridine N-oxide respectively as computed with HF and B3LYP methods respectively (Soscun *et al*., 2002). The magnitude of hyperpolarizability as predicted in the present work is two order higher than the magnitude reported in the literature.

In order to evaluate the effect of polarizability, which is associated with the electronic distribution of charges, intermolecular charge transfer is analyzed. The Mulliken Population Analysis (MPA) using HF/6-31G and B3LYP/6-31G methods have been carried out to understand the charge transfer (CT) in the molecular systems, as shown in Table 3. The molecular systems were regarded as three fragments NO_2 or 1,3,4-oxadiazole groups an acceptor, pyridine (PY) and substituents (R). The charge distribution over atoms for the seven molecular structures obtained using the ab-initio/HF and DFT/B3LYP with 6-31G basis set optimizations, evidences the charge transfer from donors (($N(Me)_2$, $N(Et)_2$, phenyl, dimethylaniline) to acceptors (NO_2 and 1,3,4-oxadiazole) are displayed in figures 1 and 2. The donor and acceptor moieties affect the electron withdrawing or releasing ability of pyridine and thus influencing CT in molecular systems. The acceptor property of nitro and oxadiazole group is analyzed by the delocalization of negative charge over the fragments. The dipole moment is an important factor as it is mainly used to study the intermolecular charge transfer. The introduction of $N(Me)_2$ and $N(Et)_2$ in DMNP and DENP leads to the displacement of electronic cloud from

pyridine, which in turn leads to the increase in dipole moment, as predicted by HF/6-31G and B3LYP/6-31G methods. The similar results have been obtained for DMOP and DEOP with B3LYP/6-31G method. The positive charge on dimethylaniline at pyridine in DMNPA, on expected ground showed the donor behavior as predicted by results of ab initio as well as with DFT calculations. The strong conjugation predicted in DMNPA manifested the high dipole moment and large value of hyperpolarizability of DMNPA, and is attributed to electron releasing and accepting ability of donor and acceptor substituent, thus influencing the charge transfer.
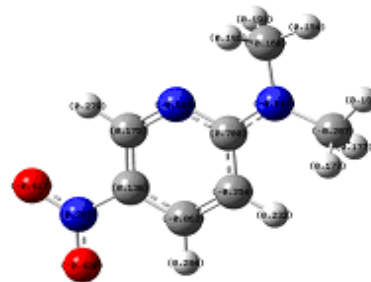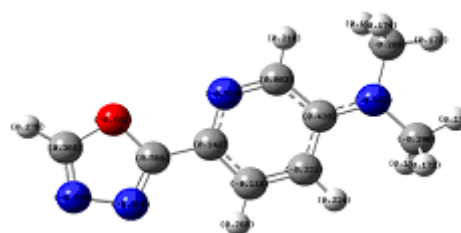

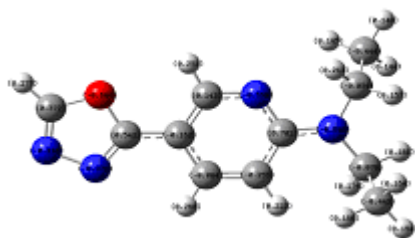N,N-dimethyl-5-nitropyridin-2-amine (DMNP)
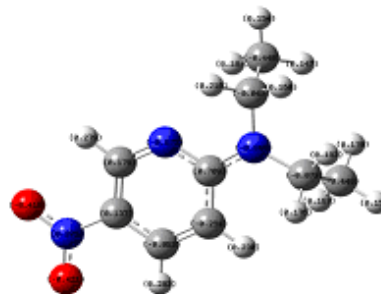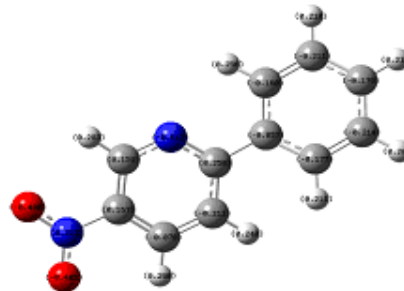
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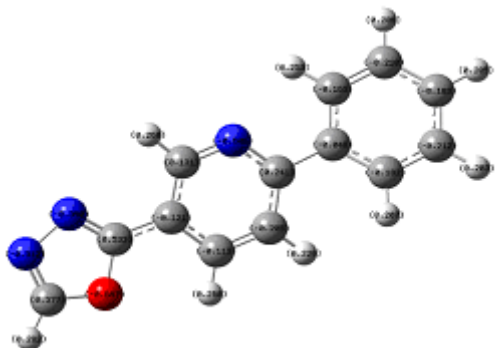

5-nitro-2-phenylpyridine (NPP)

N,N-dimethyl-5-(1,3,4-oxadiazole-2-yl)pyridine-2-amine (DMOP)

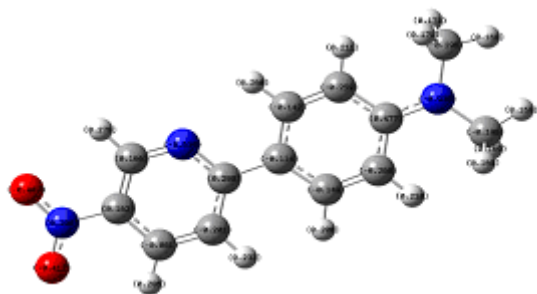N,N-diethyl-5-(1,3,4-oxadiazole-2-yl)pyridine-2-amine
(DEOP)

N,N-diethyl-5-nitropyridin-2-amine (DENP)

5-(1,3,4-oxadiazole-2-yl)-2-phenylpyridine(OPP)

5-nitro-2-phenylpyridine (NPP)

N,N-dimethyl-4-(5-nitropyridin-2-yl)aniline (DMNPA)

Fig.1. Optimized geometries and Mulliken atomic charges
for pyridine based pyridine D-A molecular structures
obtained by using HF/6-31G. The red, blue spheres
correspond to oxygen and nitrogen atom. The grey and
white corresponds to carbon and oxygen.

N,N-dimethyl-5-(1,3,4-oxadiazole-2-yl)pyridine-2-amine
(DMOP)

N,N-diethyl-5-(1,3,4-oxadiazole-2-yl)pyridine-2-amine
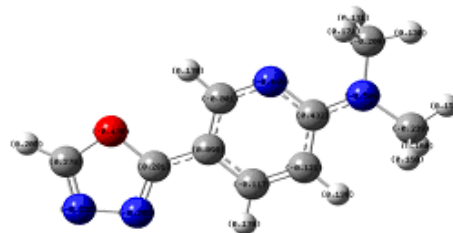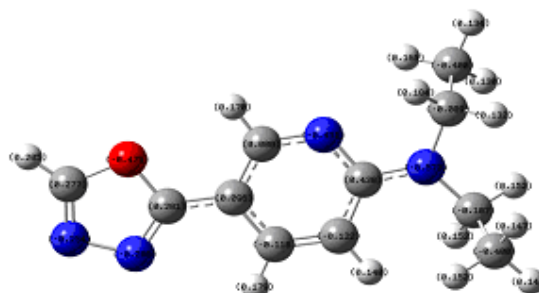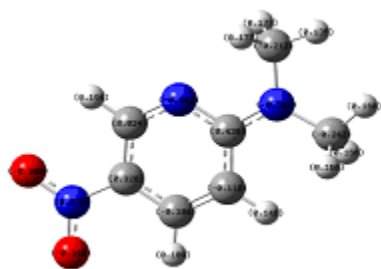(DEOP)

N,N-dimethyl-5-nitropyridin-2-amine (DMNP)

5-(1,3,4-oxadiazole-2-yl)-2-phenylpyridine(OPP)
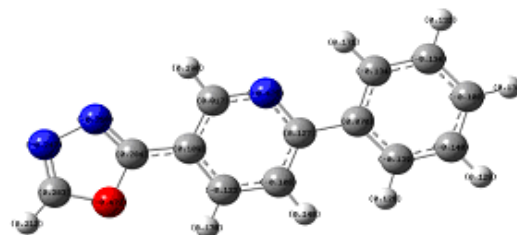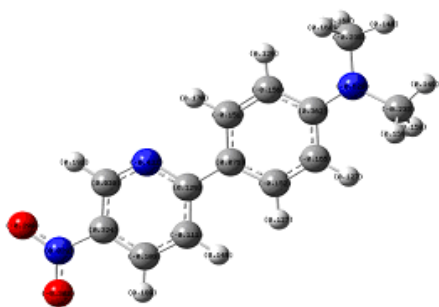
N,N-dimethyl-4-(5-nitropyridin-2-yl)aniline (DMNPA)

Fig. 2. Optimized geometries and Mulliken atomic charges for pyridine based pyridine D-A molecular structures obtained by using B3LYP/6-31G. The red, blue spheres correspond to oxygen and nitrogen atom. The grey and white corresponds to carbon and oxygen.

The NLO properties of these molecular systems can be understood by examining the frontier molecular orbitals, viz HOMO and LUMO energies. The values of HOMO and LUMO energies as predicted by ab initio/HF method and DFT/B3LYP method for all molecular structures are summarized in table 4. The variation of calculated HOMO and LUMO energies and the variation of

(a)
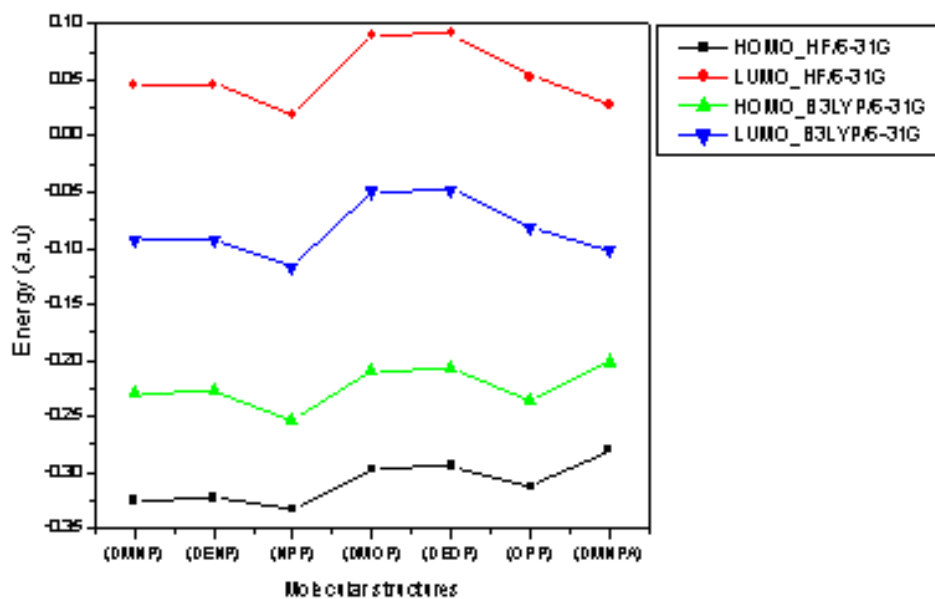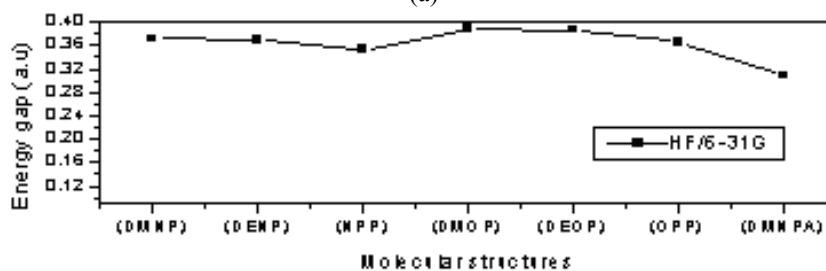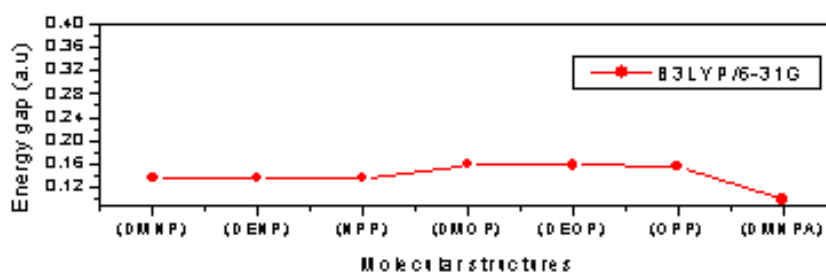
(b)

Fig. 3. Variation of (a) HOMO and LUMO energies and (b) HOMO-LUMO energy difference of the molecular structures using HF/6-31G and B3LYP/6-31G methods.
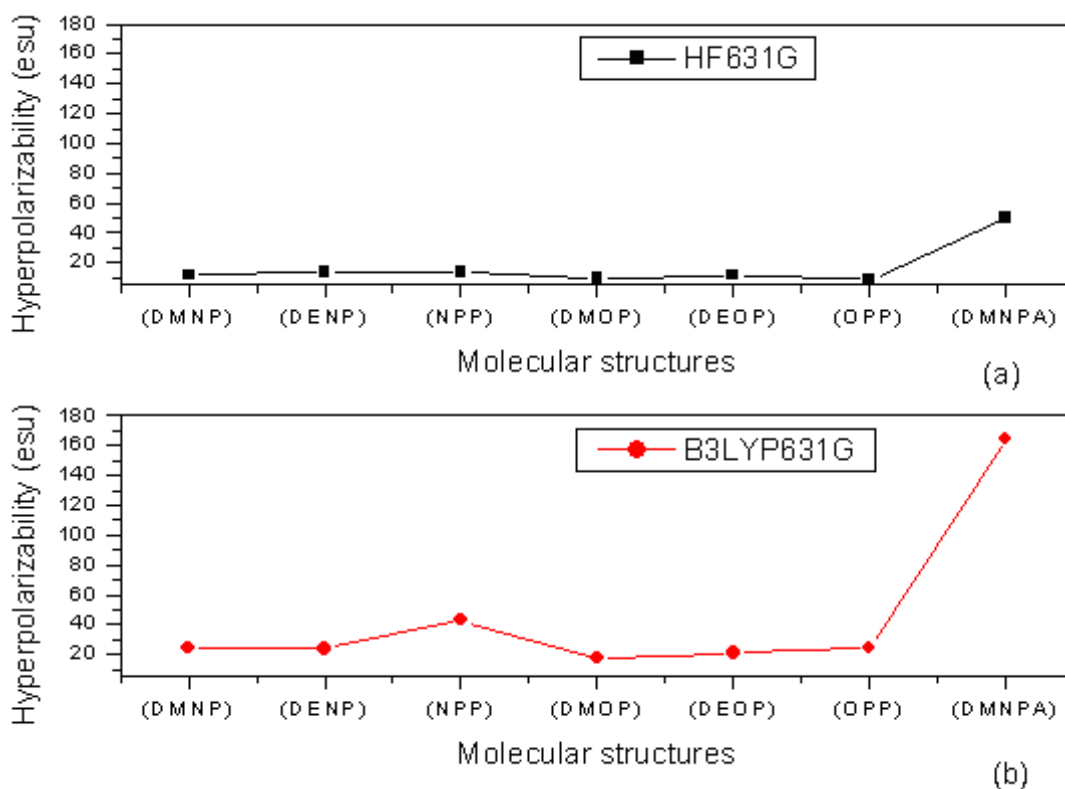
Fig. 4. Variation of theoretical hyperpolarizability of all molecules obtained by using (a) HF/6-31G and (b) B3LYP/6-31G methods.

calculated HOMO- LUMO energy gap are shown in figure 3, whereas the variation of values of hyperpolarizability of all the molecular structures estimated by using HF/631G method is depicted in figure 4. The graphical representation of HOMO and LUMO energies calculated with ab initio/HF method, indicates that HOMO energy for the molecular structures with same acceptors changes slightly except for DMNPA, for which a significant change in HOMO energy on change of donor is observed. The LUMO energies for the molecular

systems DMNP, DENP, DMOP, DEOP are found to increase due to different donors $N(Me)_2$ and $N(Et)_2$. As a result, the energy gap in these systems is larger and a correlation between the higher energy gap and low value of hyperpolarizability is observed. The values of HOMO and LUMO are found to be slightly increased and reduced respectively due to the substitution of phenyl and that led to a reduced energy gap which in turn is manifested as the increased value of hyperpolarizability. Of all the molecular structures, only OPP is not found to obey the inverse relationship between energy gap and the low value of hyperpolarizability (8.83×10^{-30} esu) is estimated despite for its low energy gap, as predicted by HF/6-31G. It can be observed from Fig. 3 that there is a steady change in HOMO and LUMO energies calculated with

DFT. The molecular systems containing nitro as an acceptor, having low difference in HOMO-LUMO energies are found to have large value of β as in NPP, DMNP, DENP, while molecular systems OPP, DMOP and DEOP having oxadiazole as an acceptor have large band gap as predicted using HF/6-31G and DFT/B3LYP methods and thus low values of their hyperpolarizability. A large value of hyperpolarizability for DMNPA as obtained with DFT/B3LYP method can be attributed to the decrease in LUMO energy and an increase in HOMO energy thus reducing the energy gap drastically.

CONCLUSIONS

The seven Donor-Acceptor type conjugated molecular structures based on pyridine have been designed and studied theoretically for examining their non-linear optical behavior. Among seven molecular systems studied in this work only N, N-dimethyl-5-nitropyridine (DMNP) has been synthesized by Arumugam Kodi-muthali (Kodimuthali *et al*., 2010). The NLO properties of this molecule and other molecular structures in the study have not been predicted yet to the best of our knowledge. The ground state dipole moment (μ), polarizability (α) and hyperpolarizability (β) for these seven molecular systems have been investigated by employing ab initio/ HF 6-31G

Table 1. Designed pyridine based donor-acceptor type molecular structures.

N,*N*-dimethyl-5-nitropyridin-2-amine (DMNP)

N,*N*-dimethyl-5-nitropyridin-2-amin (DENP)

5-nitro-2-phenylpyridine (NPP)

N,*N*-diethyl-5-(1,3,4-oxadiazol-2-yl)pyridin-2-amine (DMOP)

N,*N*-diethyl-5-(1,3,4-oxadiazol-2-yl)pyridin-2-amine (DEOP)
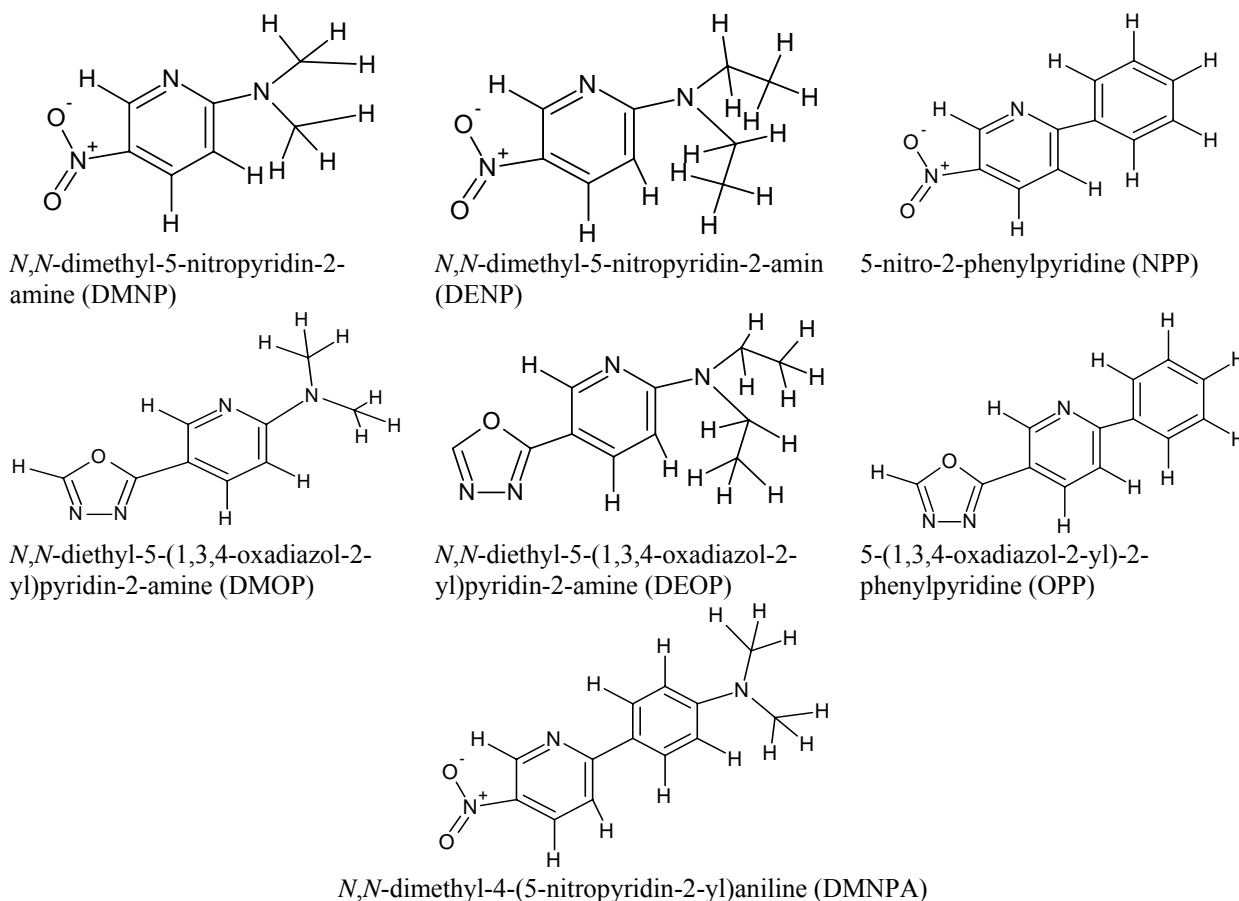
5-(1,3,4-oxadiazol-2-yl)-2-phenylpyridine (OPP)

N,*N*-dimethyl-4-(5-nitropyridin-2-yl)aniline (DMNPA)

Table 2. Calculated ground state dipole moment (μ in Debye), polarizability (α in a.u), hyperpolarizability (β x 10^{-30} esu) using ab- initio/ HF and DFT/ B3LYP with 6-31G basis set.

Molecule	Ab-initio HF/6-31G			DFT B3LYP/6-31G		
	μ	α	β	μ	α	β
N,N-dimethyl-5-nitropyridin-2-amine (DMNP)	8.02	96.48	12.00	8.13	111.05	24.56
N,N-diethyl-5-nitropyridin-2-amine (DENP)	7.99	118.15	13.58	8.14	134.80	23.62
5-nitro-2-phenylpyridine (NPP)	6.02	125.74	13.93	5.70	145.52	42.95
N,N-dimethyl-5-(1,3,4-oxadiazol-2-yl)pyridin-2-amine (DMOP)	4.38	115.18	9.94	5.07	132.85	17.83
N,N-diethyl-5-(1,3,4-oxadiazol-2-yl)pyridin-2-amine (DEOP)	4.35	137.38	11.63	5.09	157.31	21.14
5-(1,3,4-oxadiazol-2-yl)-2-phenylpyridine (OPP)	5.11	146.46	8.83	4.83	169.60	24.84
N,N-dimethyl-4-(5-nitropyridin-2-yl)aniline (DMNPA)	9.13	169.40	49.92	10.15	215.94	164.61

and DFT/B3LYP 6-31G methods. The value for hyperpolarizability predicted for DMNPA, 49.92 X 10^{-30} and 164.61 X 10^{-30} esu by HF/6-31G and B3LYP/6-31G methods, respectively, are two orders larger in order as compared to pyridine based structures reported in literature (Atalay *et al*., 2008). An inverse relationship

Table 3. Theoretical Mullikien charge analysis over fragments by HF/6-31G and B3LYP/6-31G -R= dimethylamine, diethylamine[b], Phenyl[c], dimethylaniline[d]

Molecular Structure	HF/6-31G			DFT/6-31G		
	HOMO	LUMO	Energy Gap	HOMO	LUMO	Energy Gap
DMNP	-0.32548	0.04565	0.37113	-0.22954	-0.09271	0.13683
DENP	-0.32292	0.04629	0.36921	-0.22768	-0.09194	0.13574
NPP	-0.33343	0.01861	0.35204	-0.25314	-0.11649	0.13665
DMOP	-0.29730	0.09022	0.38752	-0.20922	-0.04961	0.15961
DEOP	-0.29485	0.09140	0.38625	-0.20714	-0.04861	0.15853
OPP	-0.31294	0.05313	0.36607	-0.23649	-0.08094	0.15555
DMNPA	-0.28016	0.02809	0.30825	-0.20121	-0.10184	0.09937

Table 4. Theoretical predicted HOMO (a.u), LUMO (a.u), HOMO-LUMO energy gap (a.u) by HF/6-31G and B3LYP/6-31G

Molecular structure	Ab initio/ Acceptor	HF PY	- R	DFT/ Acceptor	B3LYP PY	-R
DMNP	-0.630	0.831	-0.199[a]	-0.591	0.647	-0.054[b]
DENP	-0.633	0.828	-0.197[b]	-0.594	0.644	-0.048[c]
NPP	-0.593	0.496	0.097[c]	-0.541	0.407	0.132[a]
DMOP	-0.184	0.413	-0.227[a]	-0.249	0.333	-0.085[b]
DEOP	-0.185	0.415	-0.231[b]	-0.252	0.332	-0.081[c]
OPP	-0.157	0.084	0.074[c]	-0.209	0.105	0.104[a]
DMNPA	-0.611	0.485	0.124[d]	-0.572	0.367	0.205[d]

between energy gap and hyperpolarizability is established on the basis of the results of calculations based on both HF/6-31G and DFT/B3LYP/6-31G. The large β values predicted theoretically for the designed molecular systems suggest the potential applications of these systems in nonlinear optical devices.

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