Torsional barriers and nonlinear optical properties of 2-, 3-, 4-phenylpyridine molecules

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The torsional barriers and nonlinear optical properties for all phenylpyridine molecules were calculated by using Hartree–Fock (HF) theory and Becke three-parameter functional (B3LYP) hybrid approaches within the density functional theory framework with the 6-31++G(d, p) basis set, and via the GAUSSIAN 98W. The torsional barrier computations show that dihedral angle between the two rings increases with the number of H–H vicinal interactions and torsional barriers with dihedral angles for 3-, 4-phenylpyridines are too similar for both HF and B3LYP level calculations. Also, HOMO-LUMO energy gaps, polarizabilities, anisotropy of polarizabilities, and static hyperpolarizabilities are calculated as a function of dihedral angle between benzene and pyridine rings. The study reveals that the phenylpyridines show very low nonlinear optical properties. The calculated torsional barrier, equilibrium dihedral angle and molecular dipole moment results for these molecules were compared with available experimental and other results determining from different computational methods.

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Key words: phenylpyridine, torsional barrier, nonlinear optics, hyperpolarizability, B3LYP

1 Introduction

Phenylazines have been the subject of many experimental [1–5] and semi-empiri cal quantum-mechanical [6–10] investigations in view of the considerable interest of organic bases in several fields of physical and chemical technology (for example homogenous catalysis or liquid crystal and dye laser technology) [11–13]. Phenylpyridines are important intermediates in synthesis of drugs, agrochemicals, herbicides, insecticides, desiccants, surfactant agents and anti-inflammatory agents [14]. 2-phenylpyridine and its derivatives are widely used as ligands in the preparation of coordination complexes [14]. Our aim is, firstly, to perform ab initio computations for the most significant phenylpyridines and to analyze, on these grounds,

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the interplay of conjugative, steric and electrostatic interactions in determining torsional barriers of these molecules. Up to now many calculations on the torsional behaviour of phenylpyridines have been made with different methods; however, we have not seen density functional calculations for 3-, 4-phenylpyridines in the literature. Previous experimental and theoretical studies have been mainly concerned with determination of rotational conformation of the phenyl and pyridine rings around the inter-ring bond, represented by the dihedral angle 1-6-R6-R1 (see Fig. 1).

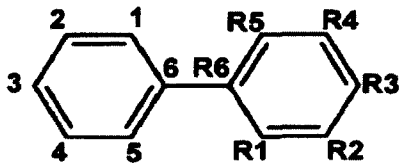

Fig. 1. Numbering scheme: 2-phenylpyridine **2PP**: 1 = C, R1 = N; 3-phenylpyridine **3PP**: 1 = C, R2 = N; 4-phenylpyridine **4PP**: 1 = C, R3 = N.

In the gas phase, without any intermolecular interaction, the torsional angle and barriers to internal rotation depend on the balance of two interactions: (i) the π-electronic conjugation in favor of a coplanar conformation, in which the π-electrons are delocalized between the phenyl and pyridine fragments; and (ii) the steric repulsion of the other hydrogens (with respect to the inter-ring bond) in favor of a non-planar structure, in which the steric hindrance is minimized. The equilibrium geometry of the molecule results from a balance between these two effects, the relative contributions of which are measured by the value of dihedral angle (1-6-R6-R1).

At second step of our study, we calculate nonlinear optical (NLO) properties these molecules using Hartree–Fock theory and Becke three-parameter functional (B3LYP) hybrid approaches within the density functional theory (DFT) framework with the 6-31++G(d, p) basis set. Although the torsional behaviour and electronic properties of phenylpyridines has been experimental and theoretically characterized [5, 7, 9–11, 15], no report has been published so far about the NLO properties of these molecules.

Organic NLO materials have attracted a keen interest in recent years owing to their potential applications in various photonic technologies [16–19]. Significant efforts have focused on studying the electronic and structural properties of donor-acceptor substituted π-conjugated organic molecules with large molecular nonlinear optical response (β, first-order hyperpolarizability) [20]. Polarizability of organic materials is generally due to the contribution from the components of system (atoms, molecules) because of the weak intermolecular bonding (Van der Waals, dipole–dipole interactions, hydrogen bonds). Nonlinear optical properties of molecular systems depend on the polarizability of electrons in the π bonding orbitals.

The present study is dedicated to a theoretical investigation of the torsional barrier calculations. We report and highlight the influence of dihedral angle on highest occupied molecular orbital (HOMO) energy and lowest unoccupied molecular orbital (LUMO) energy differences and NLO properties of phenylpyridines, represented as dipole polarizability (α), anisotropy of polarizability ($\Delta\alpha$) and first hyperpolarizability (β). The polarizabilities and hyperpolarizabilities of these molecules are compared with previous biphenyl results obtained in detail in literature [21, 22].

2 Methods

The equilibrium torsional angle of all phenylpyridines has been obtained through full geometry optimization within the framework of two different theoretical ap-

Table 1. Energies in kJ mol^{-1} relative to (global) minimum and angles for (relative) minimum, and dipole moment (μ) values Debye (D) units.

Method	1-6-R6-R1	E_0	E_{90}	μ
2-Phenylpyridine 2PP				
HF/6-31G(d)[a]	27.90	2.09	12.39	
HF/6-31++G(d, p)[e]	28.97	4.43	12.65	1.91
STO-3G[b]	30.70	4.50	13.00	1.83
B3LYP/6-31+G(d)[a]	21.89	0.68	14.97	
B3LYP/6-31++G(d, p)[e]	21.69	0.67	15.85	1.83
BPW91/6-31+G(d)[a]	21.69	0.63	15.10	
MP2(fc)/6-31G(d)[a]	31.49	4.22	13.28	
CNDO/2[c]				2.50
Exp.[d]				1.94
3-Phenylpyridine 3PP				
STO-3G[b]	43.00	15.00	7.00	2.05
HF/6-31++G(d, p)[e]	46.00	16.54	5.52	2.44
B3LYP/6-31++G(d, p)[e]	40.27	10.17	8.46	2.46
CNDO/2[c]				2.71
Exp.[d]				2.45
3-Phenylpyridine 4PP				
STO-3G[b]	41.00	11.00	8.00	2.34
HF/6-31++G(d, p)[e]	44.51	14.20	6.42	2.85
B3LYP/6-31++G(d, p)[e]	38.50	8.60	9.34	2.91
CNDO/2[c]				3.04
Exp.[d]				2.57

[a] From Ref. [10]
[b] From Ref. [11]
[c] From Ref. [7]
[d] From Ref. [5]
[e] Our study

proaches: Hartree–Fock (HF) theory and density functional theory (DFT). For both sets of calculations the molecular wave functions were represented in terms of the Pople split-valence plus polarization 6-31++G(d, p) basis set [23–25]. Computation of dipole polarizabilities requires a more flexible basis set. Furthermore, basis set appropriate for polarizability computations involve additional diffuse polarization functions. In the DFT calculations we used B3LYP [26–28] hybrid exchange-correlation energy functional to represent the exchange and correlation energy potentials.

The equilibrium dihedral angle, torsional energies at 0° and 90° and dipole moment values of all molecules obtained by two methods and theoretical and experimental values in the literature are shown in Table 1. All molecules were optimized without any constraint. Also all torsional barriers, polarizability and hyperpolarizability calculations of phenylpyridines were performed using GAUSSIAN 98W [29]. The variation of static hyperpolarizabilities against the dihedral angle was scanned by full optimization of the rest of the geometry at every point. The points were selected at intervals of 10° for dihedral angle (1-6-R6-R1) ranging from 0° to 180°.

3 Results and discussion

3.1 Torsional barriers

This section of results reports the optimized geometries, dipole moments, and torsional dependence of relative energies, calculated at HF and B3LYP levels using the 6-31++ G(d, p) basis set, together with earlier theoretical calculations [7, 9–11] are shown in Table 1. The symmetry of the molecules imposes two strictly equivalent minima at theta and 180-theta. Thus, HF/6-31++ G (d, p) level of theory calculations predicted the inter-ring dihedral angle to be 28.97° (**2PP**), 46.0° (**3PP**), and 44.5° (**4PP**), while the corresponding predictions of DFT B3LYP/6-31++G(d, p) level of theory are 21.69° (**2PP**), 40.24° (**3PP**) and 38.5° (**4PP**). Equilibrium value of dihedral angle of phenylpyridines had been calculated with RHF/6-31G* method by R. da Silva et al.[9] to be 27.9° (**2PP**), 45.6° (**3PP**), and 43.5° (**4PP**), while DFT B3LYP/6-31G* methods are 20.7° (**2PP**), 37.9° (**3PP**), and 36° (**4PP**). The accuracy of the above results can be assessed from the estimated inter-ring dihedral angles (45.7° and 40.19°) obtained in this work for biphenyl molecule. These values compare very well with the experimental gas-phase values of 44.1°±1.2° obtained from electron diffraction measurements [30], even though DFT calculations seem to overestimate slightly the π electron delocalization across two rings, thus leading to smaller dihedral angle.

The adequacy of B3LYP/6-31++G (d, p) scheme may be assessed by comparing the calculated structural data for 4-phenylpyridine with the experimental and theoretical values of biphenyl and 4,4'-bipyridyl. The experimental data from electron diffraction on dihedral angle values of biphenyl and 4,4'-bipyridyl in the gas phase are 44.1° and 37.2° for gas phase, respectively [30, 31]. The experimental mean value for biphenyl and 4-4'-bipyridyl is 40.7° and calculated mean value of these molecules is 38° at the B3LYP/6-31G(d) level of theory [32]. The mean value for biphenyl and

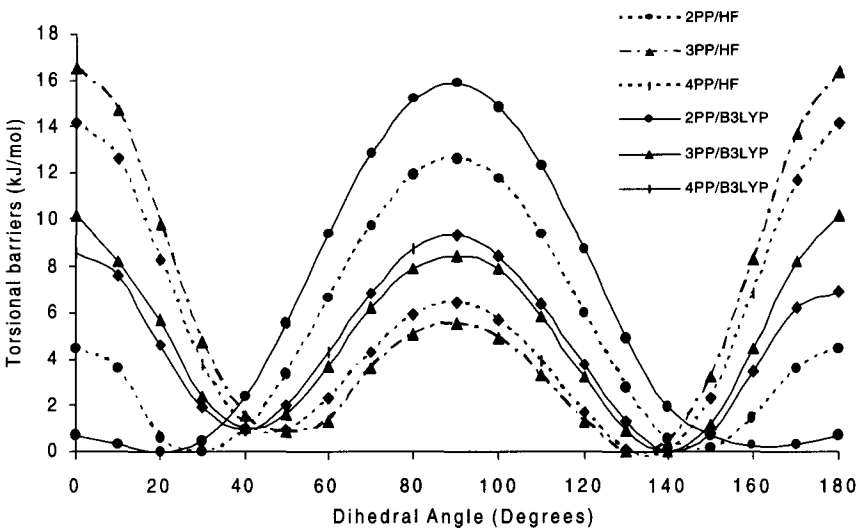

Fig. 2. Rotational barriers for **2PP**, **3PP** and **4PP**. Energies are relative to global minimum.

4-4'-bipyridyl may be expected also for 4-phenylpyridine. The corresponding value calculated at B3LYP/6-31++G (d, p) level is 39°. On the other hand, the calculated polarizabilities of biphenyl and 4-4'-bipyridyl are 142 and 129 a.u., respectively, and the mean value is 135.5 a.u. The calculated value for 4-phenylpyridine is 136 a.u. This comparison indicates adequacy of the B3LYP/6-31++G (d, p) method for the phenylpyridines studied.

Our calculations and previous results [10, 11] show that the calculated values of barriers strongly depend on the levels of theory. The variation of torsional barriers with the dihedral angle for all phenylpyridines is shown in Fig. 2.

The calculated torsional barrier and dipole moment results are shown in Table 1. It is well known that current functionals overemphasize conjugative interactions leading to 'too-planar' energy minima for biphenyl-like molecules. This is confirmed by comparison between MP2 and DFT results for **2PP** (Table 1). The ring-ring dihedrals are larger for HF than for B3LYP method.

3.2 Nonlinear optical (NLO) properties

In this work, we will focus our attention on NLO properties because the torsional barrier calculations of phenylpyridines previously had been studied [3, 7, 10]. In this section we report the calculation of dipole polarizability, anisotropy of polarizability and first static hyperpolarizability by changing the dihedral angle (1-6-R6-R1) for phenylpyridines. The calculations of these properties were carried out with the HF and B3LYP methods and 6-31++G (d, p) basis set. The dipole polarizability is a fundamental molecular property that is related to many chemical and physical

processes and can be experimentally determined or theoretically calculated. This property represents the response of the molecular charge distribution to the action of an external electric field. The mean polarizability and anisotropy of polarizability, α_{ave} and $\Delta\alpha$, respectively; were calculated from the polarizability components as

$$\alpha_{\text{ave}} = \tfrac{1}{3}\left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right) , \tag{1}$$

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

The calculation of first static hyperpolarizability from the GAUSSIAN 98W output has been explained previously [33]. The magnitude of the total first hyperpolarizability from GAUSSIAN 98W output is given by

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

There are no experimental and theoretical determinations for α_{ave} and β_{tot} of the studied molecules. These three molecules were investigated as a function of dihedral angle and their polarizability, anisotropy of polarizability, and hyperpolarizability was calculated for all the dihedral angles ranging from 0° to 180°. However, the study deals with the variation of polarizability and hyperpolarizability as functions of the dihedral angle are available in literature [34–36].

The variation of static polarizability and anisotropy of polarizability with the dihedral angle for phenylpyridines is graphically shown in Fig. 3. Although no report has been published so far about the NLO properties of the molecules studied here, polarizability of biphenyl has been calculated with HF/6-31++G(d, p) and B3LYP/6-31++G(d, p) Spackman's basis sets by S.T. Howard et al. [21]. In fact, our mean value for 2-, 3-, 4-phenylpyridines with HF method 127.2, 125.43, and 125 au, for B3LYP 139, 136.4, 135.9 a.u. Mean polarizability results for biphenyl computed by S.T. Howard et al. for HF and B3LYP methods 138.9 and 144.8 a.u.,

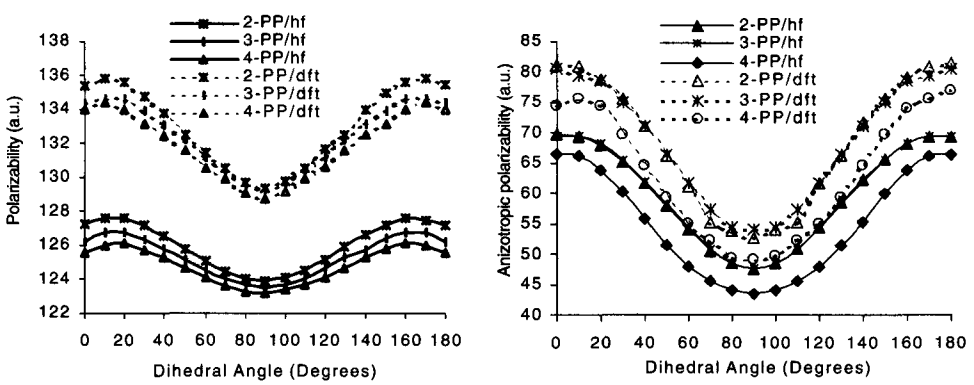

Fig. 3. The variation of polarizability and anisotropy of polarizability with the dihedral angle for 2-, 3-, 4-phenylpyridine molecules.

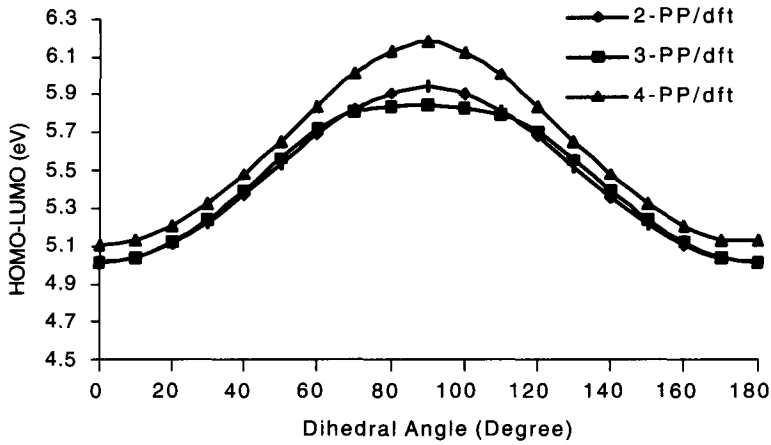

Fig. 4. The variation of HOMO-LUMO energy gap with the dihedral angle for phenylpyridine molecules.

respectively [21]. The other NLO properties for these molecules, anisotropy of polarizability are also found as 69.41, 69.44, and 66.47 a.u. values for HF methods and as 81.14, 80.68, and 74.30 a.u. values for B3LYP methods, respectively.

The variation of HOMO–LUMO energy gap with the dihedral angle for all molecules is given in Fig. 4. Polarizability is associated with molecular electronic distribution under the influence of the electrical field depending on loosely or tightly bound electrons. Therefore there is an inverse relationship between the polarizability and HOMO–LUMO energy gaps [37] can be seen from Figs. 3 and 4.

Maximum total hyperpolarizability β_{tot} for 2-, 3- and 4-phenylpyridine are obtained, as 220.2, 86.4, and 141.2 a.u., using HF method, and as 456.7, 199.9, and 303.8 a.u. using B3LYP method, respectively.

As shown in Fig. 5, the calculated hyperpolarizability values by B3LYP method are two times larger than those calculated with HF method for all molecules. And

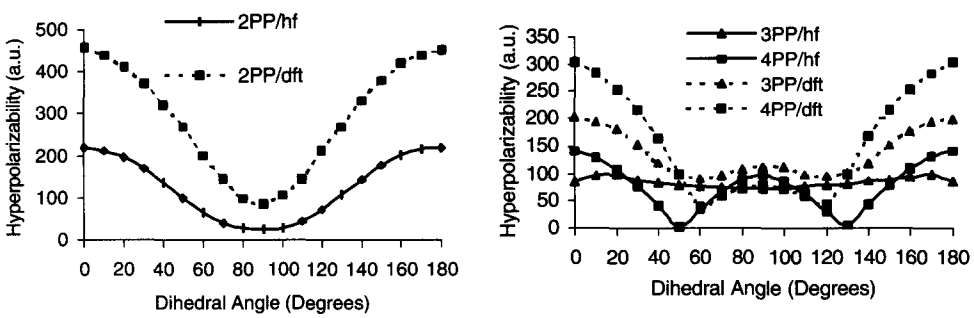

Fig. 5. The variation of first static hyperpolarizability with the dihedral angle for 2-phenylpyridine, 3-phenylpyridine and 4-phenylpyridine molecules.

also we can see from the Fig. 3 that magnitude of polarizability and anisotropy of polarizability are less affected than hyperpolarizability on changing the dihedral angle. The variation of first static hyperpolarizability with the dihedral angle for phenylpyridines is graphically shown in Fig. 5. M. Rumi and G. Zerbi computed the first hyperpolarizability of biphenyl with HF/3-21G level of theory [22]. As it can be expected, the calculated β values are quite small ($\approx$ 1.16–11.57 a.u.) and only β_{xxz}, β_{yyz}, and β_{xyz} components are different from zero. Our results are quite agreeing with previous calculations of polarizability and hyperpolarizability of biphenyl [21, 22]. Substitution of one CH group by one N atom lowers the mean polarizability and, on the contrary, hyperpolarizabilities of the system increase [38].

If we examine variations of β components with the dihedral angle for **2PP**, only β_{xxx} component is different from zero. Its computed values vary from 255 to 40 a.u. between 0° and 90° dihedral angles for HF method and from 480 to 113 a.u. for DFT B3LYP method, respectively. The other components of β are quite small. Mainly the values of variation of β_{xxx} components are sensitive to variation of dihedral angle between all components for **3PP**. Only the magnitudes of four of the 10 components, viz. β_{xxz}, β_{xyz}, β_{yyz}, and β_{zzz}, are different from zero for **4PP**, whereas values of the other components are exactly zero. Computed values of the β_{zzz} vary on from 262 to 4 a.u. between 0° and 90° dihedral angles for HF method and from 410 to 6 a.u. for DFT B3LYP method, respectively. Both calculation methods show the same trend and are in good quantitative agreement.

4 Conclusions

We have presented a theoretical study of torsional barriers, dipole moment, HOMO–LUMO energy gap, average polarizability, anisotropy of polarizability and static hyperpolarizability of phenylpyridines. Our torsional barrier and dipole moment results are in good agreement with previous theoretical and experimental studies. We have also observed that the hyperpolarizability is heavily dependent on the dihedral angle. However, average polarizability and anisotropy of polarizability depend only slightly on the dihedral angle.

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