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Torsional potential and nonlinear optical properties of phenyldiazines and phenyltetrazines

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ABSTRACT

In this research, the torsional potential and nonlinear optical properties of 2-,4-,5-phenylpyrimidine, 2-phenylpyrazine, 3-,4-phenylpyridazine, 3-phenyl-1,2,4,5-tetrazine(3-phenyl-s-tetrazine), 5-phenyl-1,2,3,4-tetrazine and 4-phenyl-1,2,3,5-tetrazine compounds were calculated by using HF theory and Becke three parameter functional(B3LYP) hybrid approaches within the density functional theory with 6-31++G(d,p) as the basis set. The effect of the dihedral angle on torsional potential and hyperpolarizability has been analyzed. The computations show that maximum hyperpolarizability is obtained at the planar conformation for all phenyl azabenzenes. The analysis of molecules studied shows that compounds with the same ortho substituent (including nitrogen lone pairs) have very similar conformational behavior. The calculated torsional potential, equilibrium dihedral angle and molecular dipole moment were compared with available experimental and other results determined from different computational methods.

Furthermore, static polarizability, polarizability anisotropy, first static hyperpolarizability and HOMO–LUMO molecular orbital energy difference were calculated at the stationary point on the energy surface.

1. Introduction

The barrier to rotation about the central C–C bond is an important factor in determining molecular properties. For example, for toxic polychlorinated biphenyls (PCBs), a lower barrier which leads to easy planarization, is associated with greater toxicity, whereas higher barriers are associated with reduced toxicity. Thus, the toxicity of a polychlorinated biphenyl seems to be determined by the barrier to rotation about the central C–C bond [1,2].

Nitrogen-rich substances have been attracting great interest as components for energetic applications like air-bags or metal-free combustion modificators [3]. Phenylazine molecules are attractive materials for a wide variety of applications in physical and chemical technology. Phenylpyridines are important intermediates in the synthesis of drugs, agrochemicals, herbicides, insecticides, desiccants, surfactant agents and anti-inflammatory agents [4]. 2-Phenylpyridine and its derivatives are widely used as ligands in the preparation of coordination complexes [4]. Phenylpyridine, phenylpyrimidine, phenylpyrazine and phenylpyridazines are usually used in liquid crystal and dye laser technology [5–8]. Triazine derivatives have widespread applications in the industries of polymer, pharmaceutical and dye stuffs [9].

Phenylazines have been the topic of many experimental [10–14] and quantum chemical investigations [15–20] due to their scientific and technological importance. In particular, many conformational analysis studies on 2-,3-,4-phenylpyridine and 2-,4-,5-phenylpyrimidine molecules have been performed, with the exclusion of phenylpyrazine, phenylpyridazine and phenyltetrazine molecules. In the first and second papers, we reported the torsional barrier and nonlinear optical properties of 2-,3-,4-phenylpyridine [19] and six phenyltriazine molecules [20]. In the present work, we extended our study to known phenyldiazines (phenylpyrimidines, phenylpyrazine and phenylpyridazines) and phenyltetrazines.

However, although the nonlinear optical properties of phenylpyridine and phenyltriazine molecules have been published, there have not yet been any publications on phenylpyrimidines, phenylpyrazine, phenylpyridazines and phenyltetrazines. All the azabiphenyl molecules are listed in Fig. 1.

2. Computational method

In the present work, torsional energy calculations were performed at intervals of 10° between 0° and 180°, by using the HF and DFT/B3LYP methods with 6-31++G(d,p) basis set [21–23]. The static polarizability, anisotropy of polarizability, first static hyperpolarizability depending on dihedral angle and HOMO–LUMO frontier molecular orbital energy calculations were performed with the B3LYP method [24–26] and 6-31++G(d,p) basis set. The adequacies of the HF/6-31++G(d,p) and B3LYP/6-31++G(d,p) level of theories for the calculation of torsional barriers

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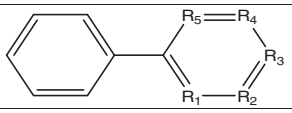

No	R_1	R_2	R_3	R_4	R_5	Upac Name
1	C	C	C	C	C	Biphenyl(bp)
2	N	C	C	C	C	2-phenylpyridine (2pp)
3	C	N	C	C	C	3-phenylpyridine (3pp)
4	C	C	N	C	C	4-phenylpyridine (4pp)
5	N	C	C	C	N	2-phenylpyrimidine (2pprmd)
6	N	C	N	C	C	4- phenylpyrimidine (4pprmd)
7	C	N	C	N	C	5- phenylpyrimidine (5pprmd)
8	N	C	C	N	C	2-phenylpyrazine (2ppyz)
9	N	N	C	C	C	3-phenylpyridazine (3pprdz)
10	C	N	N	C	C	4-phenylpyridazine (4pprdz)
11	N	C	N	C	N	2-phenyl-1,3,5-triazine (2ph-s-trz)
12	N	N	N	C	C	4-phenyl-1,2,3-triazine (4ph123trz)
13	C	N	N	N	C	5-phenyl-1,2,3-triazine (5ph123trz)
14	N	N	C	N	C	6-phenyl-1,2,4-triazine (6ph124trz)
15	C	N	N	C	N	5-phenyl-1,2,4-triazine (5ph124trz)
16	N	N	C	C	N	3-phenyl-1,2,4-triazine (3ph124trz)
17	N	N	C	N	N	3-phenyl-1,2,4,5-tetrazine (3ph-s-tetrazine)
18	N	N	N	N	C	5-phenyl-1,2,3,4-tetrazine (5ph1234ttrz)
19	N	N	N	C	N	4-phenyl-1,2,3,5-tetrazine (4ph1235ttrz)

Fig. 1. Structures and IUPAC names of phenylazines.

and NLO properties for similar compounds are discussed in detail [19,20]. All calculations were performed using the Gaussian 98/03W program [27]. Input data were prepared for Gaussian 98/03W using the Gauss View 04 graphical program.

3. Results and discussion

3.1. Torsional energy profile

The equilibrium geometry of the molecules results from a balance between two effects. One of these effects is conjugation interaction between phenyl and azabenzene rings which raises a tendency to a planar structure. The other one is steric repulsion between atoms in ortho positions which favors a nonplanar structure. Studies up to now have shown that azabiphenyls with the same local environment around the central C–C bond (i.e. the same ortho groups) have very similar equilibrium conformations [19,20]. The conformational behavior of 2-,4-,5-phenylpyrimidines was studied using the HF/STO-3G level by Barone et al. [28]. The results of both Barone et al. and our study are presented in Table 1. The optimized dihedral angle values obtained using the HF and B3LYP methods are compatible with the HF/STO-3G method for 2-,5-phenylpyrimidine [28], but not for 4-phenylpyrimidine. Furthermore, only some of the torsional potential values are compatible with the results for 2-,4-,5-phenylpyrimidine. The differences between the HF and B3LYP values can be explained as resulting from the slight overestimation of the DFT calculations on π electron delocalization across the two rings, which leads to smaller bond lengths and twist angles [17] (see Table 1).

The variation of the dipole moment of 2-phenylpyrimidine with a dihedral angle was investigated by Wells et al. using the CNDO/2 method [29]. Additionally, we investigated the variation of the dipole moment of 2-phenylpyrimide with a dihedral angle using the HF/6-31++G(d,p) and B3LYP/6-31++G(d,p) methods. These results are presented in Table 2. From this table we can infer that the HF method produces larger dipole moments than the B3LYP and CNDO/2 methods. The ground state dihedral angle, electronic energy, zero point energy and dipole moment values of all phenylazines are presented in Table 3.

In Table 4, the ranges of optimized dihedral angles and energy barriers ΔE_0 and ΔE_{90}, are listed according to the method and according to the basis set for all phenylazines. As can be seen from Table 4, twist angles calculated by HF methods are always high, but the angles calculated by the DFT method are always low due to the reason stated above. The same trends apply to ΔE_0, too. In contrast to the trends shown for ΔE_0, HF results for ΔE_{90} are quite low and DFT results are high.

In Figs. 2–4 the torsion potentials as a function of the torsion angle are presented as relative torsion potential where the optimized

Table 1
Dihedral angles (°), C–C interring bond lengths (Å) and relative energies (kJ/mol) for the 2,4,5-phenylpyrimidines.

	ΔE_{30}	ΔE_{60}	ΔE_{90}	Θ (°)	R (Å)
2-Phenylpyrimidine					
STO-3G (Ref. [28])	2.5	14.7	22.5	0.00	
HF/6-31++G(d,p)	5.0	19.7	28.6	0.00	1.489
B3LYP/6-31++G(d,p)	6.6	20.8	29.7	0.00	1.486
CNDO/2 (Ref. [29])	2.12	3.38	3.09	0.00	
4-Phenylpyrimidine					
STO-3G (Ref. [28])	4.9	2.2	9.2	34.9	
HF/6-31++G(d,p)	1.5	8.8	16.4	25.4	1.489
B3LYP/6-31++G(d,p)	0.9	11.8	20.1	17.4	1.486
5-Phenylpyrimidine					
STO-3G (Ref. [28])	14.7	14.2	8.2	47.7	
HF/6-31++G(d,p)	11.0	3.03	5.0	46.8	1.487
B3LYP/6-31++G(d,p)	9.9	1.12	8.5	40.0	1.481

Table 2
Variation of dipole moment with dihedral angle for 2-phenylpyrimidine at in the Debye unit.

Θ (°)	CNDO/2(Ref. [29])	HF	B3LYP
0(180)	1.57	1.87	1.69
10(170)	1.58	1.87	1.69
20(160)	1.60	1.87	1.69
30(150)	1.63	1.89	1.73
40(140)	1.65	1.90	1.77
50(130)	1.69	1.97	1.83
60(120)	1.73	2.02	1.89
70(110)	1.75	2.06	1.94
80(100)	1.77	2.09	1.98
90(90)	1.78	2.10	1.99

Table 3
Ground state electronic energy, zero point energy and dipole moment values of all phenylazines.

Molecule	E_{Scf} (a.u.)		E_{Zp} (k cal/mol)		μ (D)	
	HF	B3LYP	HF	B3LYP	HF	B3LYP
Biphenyl	−460.28524959	−463.33910383	121.51189	113.82322	0.00	0.00
2-phenylpyridine	−476.27880999	−479.37710415	113.79696	106.43714	1.91	1.83
3-phenylpyridine	−476.27588212	−479.37428713	113.84544	106.48200	2.44	2.46
4-phenylpyridine	−476.27689765	−479.37496374	113.88063	106.50861	2.85	2.91
2-phenylpyrimidine	−492.25241205	−495.40857210	105.99933	98.95777	0.64	0.83
4-phenylpyrimidine	−492.23126053	−495.37889905	105.65774	98.53872	4.03	3.89
5-phenylpyrimidine	−492.22981280	−495.37737301	105.75791	98.62508	5.14	5.18
2-phenylpyrazine	−492.27930135	−495.41556463	106.1179	99.0574	1.87	1.69
3-phenylpyridazine	−492.27624685	−495.41624681	106.2533	99.1651	2.67	2.79
4-phenylpyridazine	−492.27181287	−495.41223104	106.2453	99.1371	2.93	3.09
2-phenyl-1,3,5-triazine	−508.28228151	−511.46099959	98.63210	91.80665	1.24	1.56
4-phenyl-1,2,3-triazine	−508.19324225	−511.38860998	97.53938	90.64374	5.46	5.55
5-phenyl-1,2,3-triazine	−508.22200272	−511.41304178	97.94505	91.10722	3.06	3.13
6-phenyl-1,2,4-triazine	−508.22621079	−511.41648658	97.83357	91.02217	2.42	2.22
5-phenyl-1,2,4-triazine	−508.19036285	−511.38586750	97.59525	90.65266	6.35	6.55
3-phenyl-1,2,4-triazine	−508.22433450	−511.41504014	98.03338	91.18662	4.17	4.32
3-phenyl-1,2,4,5-tetrazine	−524.17593119	−527.41552630	89.51284	83.01713	1.20	1.72
5-phenyl-1,2,3,4-tetrazine	−524.14922519	−527.39325791	89.33302	82.53576	6.15	6.38
4-phenyl-1,2,3,5-tetrazine	−524.19390141	−527.42915360	89.79558	83.14485	3.76	4.09

Table 4
Dihedral angles (°) and relative energies (kJ/mol) for the phenylazines.

Molecule	Θ (°)		ΔE_0		ΔE_{90}	
	HF	B3LYP	HF	B3LYP	HF	B3LYP
Biphenyl (Ref. [19])	46.62	40.19	14.20	8.90	5.60	7.70
2-phenylpyridine (Ref. [19])	29.00	21.76	3.62	0.68	13.96	15.85
3-phenylpyridine (Ref. [19])	46.70	40.27	16.66	10.17	5.64	8.46
4-phenylpyridine (Ref. [19])	44.51	38.50	14.20	8.87	6.66	9.88
2-phenylpyrimidine	0.00	0.00	0.00	0.00	28.66	29.71
4-phenylpyrimidine	25.36	17.40	2.13	0.86	16.40	20.13
5-phenylpyrimidine	46.80	40.00	14.89	10.03	4.97	8.50
2-phenylpyrazine	30.50	23.69	3.56	1.67	13.57	17.52
3-phenylpyridazine	31.24	24.41	4.05	0.52	13.16	15.31
4-phenylpyridazine	44.15	37.49	13.48	8.53	6.55	10.22
2-phenyl-1,3,5-triazine(Ref. [20])	0.00	0.00	0.00	0.00	32.20	32.96
4-phenyl-1,2,3-triazine (Ref. [20])	25.50	18.20	2.13	1.05	15.86	19.98
5-phenyl-1,2,3-triazine (Ref. [20])	44.00	36.50	9.95	7.43	7.93	10.58
6-phenyl-1,2,4-triazine (Ref. [20])	31.42	24.31	3.56	1.77	12.42	16.73
5-phenyl-1,2,4-triazine (Ref. [20])	25.37	17.84	2.08	0.89	17.00	21.07
3-phenyl-1,2,4-triazine (Ref. [20])	0.00	0.00	0.00	0.00	27.27	29.22
3-phenyl-1,2,4,5-tetrazine	0.00	0.00	0.00	0.00	28.63	29.18
5-phenyl-1,2,3,4-tetrazine	25.00	18.16	1.69	0.97	15.94	21.35
4-phenyl-1,2,3,5-tetrazine	0.00	0.00	0.00	0.00	31.93	33.91

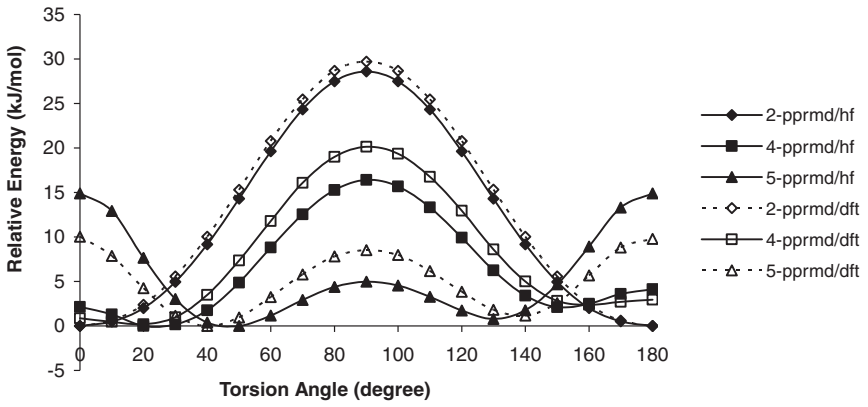

Fig. 2. Comparison of relative torsion energies with HF/6-31++G(d,p) and B3LYP/6-31++G(d,p) levels for 2,4,5-phenylpyrimidine compounds.

global minimum energy structure is taken as a zero level. Due to the symmetry of the molecules, it is sufficient to study torsion angles from 0° to 180°. As it can be seen from these figures, both methods produce qualitatively similar forms of the torsion potential. 2-phenylpyrimidine and 3-phenyl-s-tetrazine have the same relative energies at 0° and 90° because both molecules have similar vicinities

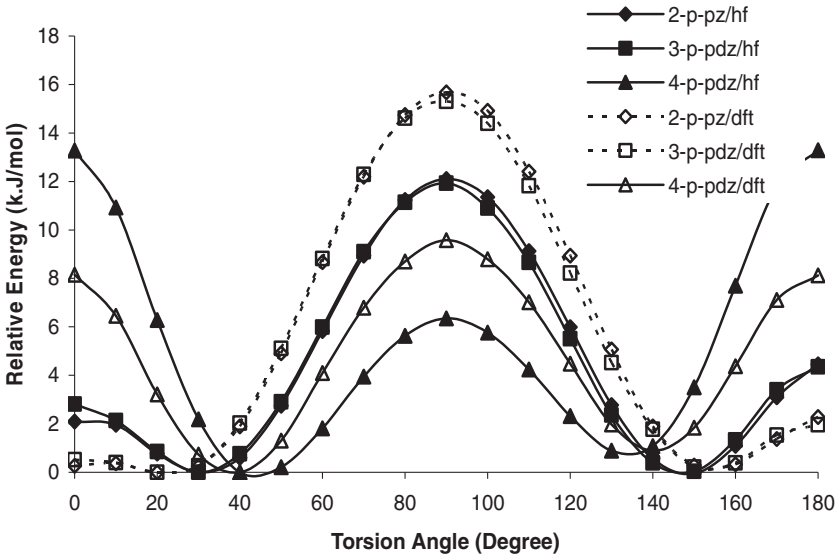

Fig. 3. The relative torsion energies with HF/6-31++G(d,p) and B3LYP/6-31++G(d,p) levels for 2-phenylpyrazine and 3,4-phenylpyridazine compounds.

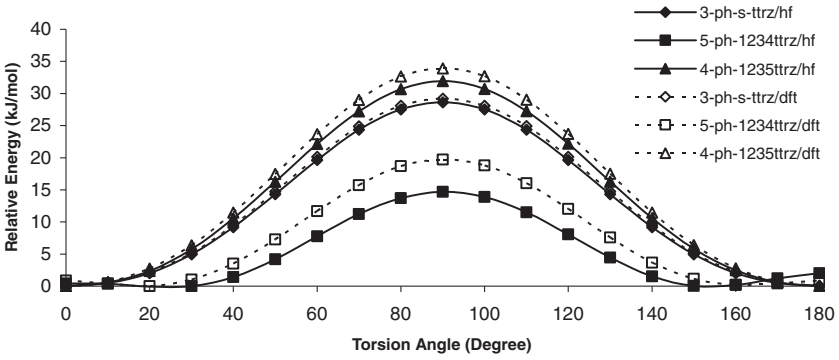

Fig. 4. The relative torsion energies with HF/6-31++G(d,p) and B3LYP/6-31++G(d,p) levels for 3-phenyl-s-tetrazine, 5-phenyl-1,2,3,4-tetrazine and 4-phenyl-1,2,3,5-tetrazine compounds.

around the central C–C bond, which includes two C–H and N interactions. The same is true for 4-phenylpyrimidine and 5-phenyl-1,2,3,4-tetrazine.

If we compare the results of the HF and DFT methods used in the calculation of torsional potentials, the DFT results are higher than the HF results for orthogonal conformation. This situation is reversed in planar conformations where HF torsional energy is noticeably higher (see Figs. 3 and 4). The DFT methods give few kJ/mol lower barriers for the planar conformations than the ab initio methods. This is in agreement with earlier studies of conjugated systems, which indicate that DFT methods somewhat overestimate the delocalization energy [30,31], and therefore produce more planar structures and lower orthogonal barriers than ab initio methods.

3.2. Nonlinear optical properties

During the past decade, people have shown great interest in studying many different types of nonlinear optical NLO matter [32–40] in order to design excellent NLO materials. Owing to their vital role in describing NLO properties, hyperpolarizabilities have recently received much attention. Many experimental [41–43] and theoretical efforts [44–47] have been devoted to the investigation of the first hyperpolarizability.

The electric dipole moment of a molecule is a quantity of fundamental importance in structural chemistry [48]. It is well known that the nonlinear optical response of an isolated molecule in an electric field E_i can be presented as a Taylor series expansion of the total dipole moment, μ_{tot}, induced by the field:

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

where α is the linear polarizability, μ_0 is the permanent dipole moment and β is the first hyperpolarizability tensor component. The calculations of mean static polarizability ($\langle\alpha\rangle$), polarizability of anisotropy ($\Delta\alpha$) and first static hyperpolarizability (β_{tot}) from the Gaussian output have previously been outlined in detail [49] as follows:

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

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

The complete equation for calculating the total static first hyperpolarizability magnitude from the Gaussian output is given as follows [50],

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

Ground state values of mean static polarizability, polarizability of anisotropy, first static hyperpolarizability and HOMO–LUMO energy difference are presented in Table 5. The polarizability and

Table 5
Ground state values of mean static polarizability, polarizability of anisotropy, first static hyperpolarizability and HOMO–LUMO energy difference.

Molecule	α_{ave} (a.u.)	$E_{H\text{-}L}$(eV)	$\Delta\alpha$ (a.u.)	β_{tot} (a.u.)
Biphenyl (Ref. [1])	142.17	5.27	75.35	12.1
2-phenylpyridine (Ref. [19])	138.97	4.99	81.75	439.1
3-phenylpyridine (Ref. [19])	136.35	5.26	74.00	125.5
4-phenylpyridine (Ref. [19])	135.93	5.31	68.33	204.4
2-phenylpyrimidine	133.84	4.81	80.83	584.9
4-phenylpyrimidine	132.93	4.80	78.37	546.8
5-phenylpyrimidine	131.22	4.59	71.20	360.8
2-phenylpyrazine	130.10	5.07	78.83	834.7
3-phenylpyridazine	132.53	4.96	78.45	676.6
4-phenylpyridazine	130.05	5.26	71.21	131.8
2-phenyl-1,3,5-triazine (Ref. [20])	123.70	5.04	74.55	989.7
4-phenyl-1,2,3-triazine (Ref. [20])	128.48	4.70	77.32	877.2
5-phenyl-1,2,3-triazine (Ref. [20])	127.71	4.37	76.64	648.3
6-phenyl-1,2,4-triazine (Ref. [20])	129.16	4.33	77.30	1025.0
5-phenyl-1,2,4-triazine (Ref. [20])	126.72	4.75	70.63	552.0
3-phenyl-1,2,4-triazine (Ref. [20])	128.76	4.22	78.72	895.4
3-phenyl-1,2,4,5-tetrazine	121.11	3.52	74.96	1151.6
5-phenyl-1,2,3,4-tetrazine	124.66	4.27	77.03	1086.6
4-phenyl-1,2,3,5-tetrazine	120.89	4.15	74.87	1229.4

anisotropic polarizability of azabenzene molecules (i.e.: benzene, pyridine, pyrazine, pyridazine, pyrimidine, 1,2,3-triazine, s-triazine and s-tetrazine) were experimentally studied and by using different theoretical methods [51–56]. The literature values are presented in Table 6. As can be seen from Tables 5 and 6, the polarizability of azabenzenes and phenylazabenzenes decreases when the number of nitrogen atoms on the benzene ring increases. Furthermore, the polarizability of azabenzenes and phenylazines increases as the distance between the nitrogen atoms on the benzene ring rises. The general trend of polarizability values, according to the Tables 4 and 5, for the azabenzene and phenylazine molecule groups is as follows:

benzene ≫ pyridine ≫ diazines ≫ triazines ≫ tetrazines

The order of polarizability for diazines is as follows:

pyrazine > pyridazine > pyrimidine

The order of polarizability for triazines is as follows:

1,2,3-triazine > s-triazine

as reported in Ref. [50]. The order of polarizability for phenylazines is as follows:

biphenyl ≫ phenylpyridines ≫ phenyldiazines ≫ phenyl triazines ≫ phenyltetrazines

This order is very similar to that of azabenzenes. In addition, as can be seen from Table 5, the order of polarizability between the phenylpyridine, phenyldiazine, phenyltriazine and phenyltetrazine groups is as follows:

2-phenylpyridine > 3- phenylpyridine > 4- phenylpyridine
2-phenylpyrazine > 3-phenylpyridazine > 4-phenylpyridazine > 2-phenylpyrimidine > 4- phenylpyrimidine > 5- phenylpyrimidine
3-phenyl-1,2,4-triazine > 5-phenyl-1,2,4-triazine > 4-Phenyl-1, 2,3-triazine > 6-phenyl-1,2,4-triazine > 5-phenyl-1,2,3-triazine > 2-phenyl-s-triazine
5- phenyl -1,2,3,4-tetrazine > 3- phenyl -s-tetrazine > 4- phenyl-1,2,3,5-tetrazine

As can be seen from Tables 5 and 6, the polarizability of azabenzenes is obtained approximately twofold large when the displacement of H and benzene on the azabenzenes occurs. Variations of the first static hyperpolarizabilities with dihedral angle are presented in Fig. 5.

The following conclusions can be drawn from Fig. 5 and Table 5.

(i) The largest first static hyperpolarizabilities (β_{tot}) were obtained from planar conformation for all phenylazines.
(ii) When the number of nitrogen atoms increase on the azabenzene ring, β_{tot} increases.
(iii) β_{tot} increases when the distance of the nitrogen atoms on the azabenzene ring from the vicinity of the single bond between two rings gets greater.

Table 6
Literature values of mean polarizabilities, polarizability of anisotropies for azabenzenes. Polarizabilities and polarizability of anisotropies are in (a.u.) unit.

Molecule	DFT geometries[a]		MISINDO geometries[a]		MP2/6-31G* geometries[b]		Exp. values	
	α_{ave}	$\Delta\alpha$	α_{ave}	$\Delta\alpha$	α_{ave}	$\Delta\alpha$	α_{ave}	$\Delta\alpha$
Benzene	70.17	38.44	69.63	37.80	69.28	36.16	71.5[c]	37.9[e]
Pyridine	64.97	36.51	65.00	36.27	63.95	34.31	64.1[d]	
Pyrazine	60.25	35.59	60.25	35.09	59.06	32.59	60.6[d]	
Pyridazine	59.98	33.54	59.90	33.30	59.63	32.73	59.3[d]	
Pyrimidine	59.36	33.22	59.37	33.05	58.65	31.82		
1,2,3-Triazine	54.74	30.06	54.85	29.28	54.52	29.31		
s-Triazine	53.59	29.31	53.96	29.26	53.33	28.69		
s-Tetrazine	50.42	27.22	50.58	27.31	49.97	26.20		

[a] Ref. [52].
[b] Ref. [53].
[c] Ref. [54].
[d] Ref. [55].
[e] Ref. [56].

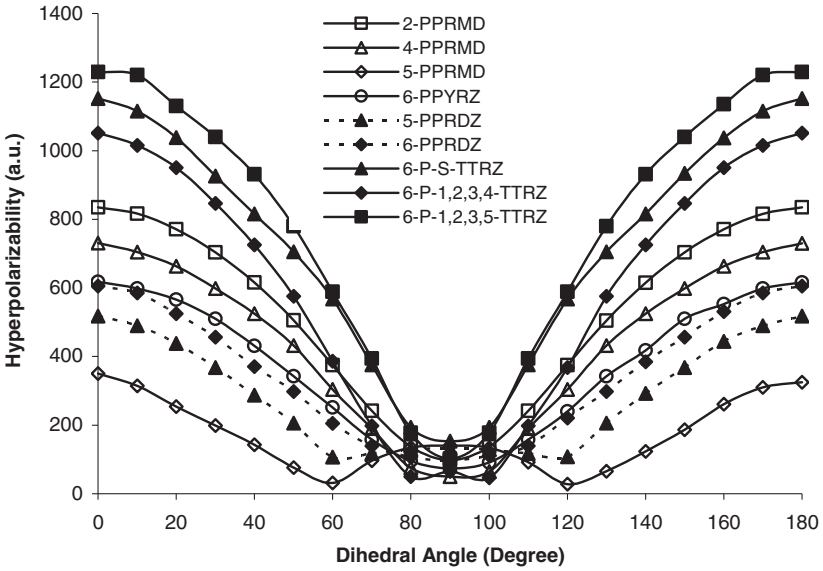

Fig. 5. Variation of first static hyperpolarizability with the dihedral angle for phenyldiazine and phenyltetrazine molecules using B3LYP/6-31++G(d,p) level.

(iv) β_{tot} is very sensitive to changes in the dihedral angle between two rings and as the value of the twist angle increases, the value of β_{tot} decreases.

(v) The following a rough order was obtained from Table 5 and Fig. 5 by using the B3LYP optimized structures for the calculation of first static hyperpolarizabilities:

phenyltetrazines > phenyltriazines > phenylpyrimidines > phenylpyridazines > phenylpyrazine > phenylpyridines > biphenyl

4. Conclusion

In this paper, torsional potential and nonlinear optical properties of phenyldiazines and phenyltetrazines were studied using the HF theory and Becke three parameter functional(B3LYP) hybrid approaches within the density functional theory with the 6-31++G(d,p) basis set. From the calculations, it can be concluded that the ortho-nitrogen substituents determine the rotational barriers and twist angles, while meta-nitro substituents have less influence on these parameters. Furthermore, the DFT methods produces larger rotational barriers than the HF methods for orthogonal conformation due to the fact that DFT methods somewhat overestimate the delocalization energy.

The polarizability of azabenzenes and phenylazines is related to the number of nitrogen atoms on the benzene ring and the distance between the nitrogen atoms. The polarizabilities of azabenzes are approximately two times larger than that of phenylazines. Planarity is one of the important factors in nonlinearity, and the largest first static hyperpolarizabilities were obtained from planar conformation for all phenylazines. As the number of nitrogen atoms on the azabenzene ring increases, the value of β_{tot} is increased. The value of β_{tot} is very sensitive to changes in the dihedral angle between two rings.

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