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Investigation of torsional barriers and nonlinear optical (NLO) properties of phenyltriazines

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Abstract

In this study, electronic and nonlinear optical properties of six phenyltriazine isomers were calculated. The calculated properties are electronic energy, HOMO–LUMO energies, static polarizability α, anisotropy of polarizability $\Delta\alpha$, and first static hyperpolarizability β at equilibrium geometry and their torsional dependence. The torsional barriers and potential energy curves were calculated at HF/6-31++G(d,p) and B3LYP/6-31++G(d,p) methods. The number of ortho hydrogen atoms mainly determines the torsional barriers of these molecules, while the meta hydrogen atoms have a small influence on the equilibrium torsional angles and barriers. Nonlinear optical properties (NLO)-dihedral angle θ correlations of phenyltriazine isomers were calculated at the B3LYP/6-31++(d,p) level. Polarizabilities of phenyltriazines decrease with shifting the nitrogen atoms to the para position. On the contrary, hyperpolarizabilities of phenyltriazines increase with shifting the nitrogen atoms to the ortho position.
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1. Introduction

The torsional behaviour and nonlinear optical properties (NLO) of biphenyl like molecules has been subject of many experimental and theoretical studies [1–14] due to their potential scientific and technological importance [14–16]. Phenyltriazine isomers and derivatives have widespread applications in polymer, pharmaceutical and dye stuffs industry [17,18].

Although many calculations on the torsional behaviour of biphenyl, phenylpyridines and phenylpyrimidines have been made with different methods [1–14] there have been no calculations on phenyltriazine isomers. Despite NLO properties of azabenzenes [19–21], biphenyl [22,23] and phenylpyridines [11] has been theoretically characterized, no report has been published so far about the NLO properties of phenyltriazines. In our previous paper [11], we presented the results of ab initio study of torsional barrier and NLO properties of 2-,3-,4-phenylpyridine molecules. Now, we are reporting torsional barrier and NLO properties (static polarizability, anisotropy of polarizability and first static hyperpolarizability) of phenyltriazines (Fig. 1) by using HF and DFT methods.

The polarizabilities and hyperpolarizabilities of phenyltriazines are compared with those reported for biphenyl [22,23] and 2-,3-,4-phenylpyridine [11], 1,2,3-triazine, 1,2,4-triazine, 1,3,5-triazine and *s*-triazine [19–21].

2. Methods

The equilibrium torsional angle of all phenyltriazines has been obtained through full geometry optimization within the framework of two different theoretical approaches, HF and DFT theory. For both methods 6-31++G(d,p) basis set [24–26] was used. In our previous paper we showed the adequacies of HF/6-31++G(d,p) and B3LYP/6-31++G(d,p) schemes for the calculations

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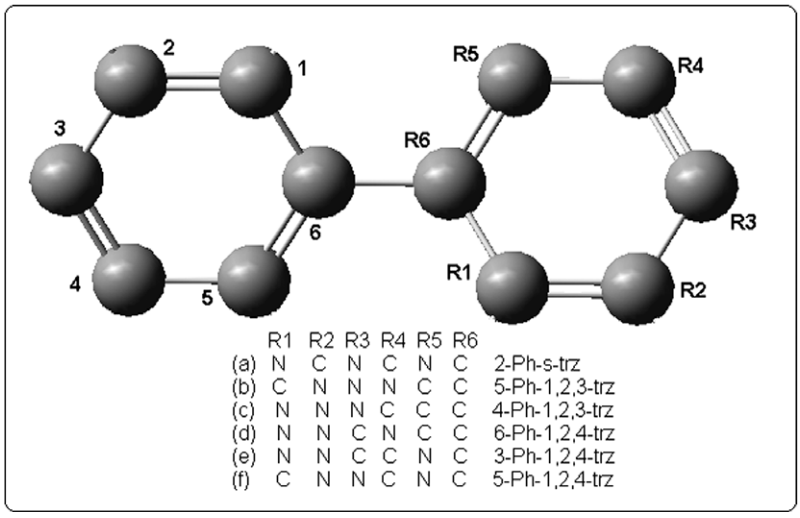

	R1	R2	R3	R4	R5	R6	
(a)	N	C	N	C	N	C	2-Ph-s-trz
(b)	C	N	N	N	C	C	5-Ph-1,2,3-trz
(c)	N	N	N	C	C	C	4-Ph-1,2,3-trz
(d)	N	N	C	N	C	C	6-Ph-1,2,4-trz
(e)	N	N	C	C	N	C	3-Ph-1,2,4-trz
(f)	C	N	N	C	N	C	5-Ph-1,2,4-trz

Fig. 1. Structure of phenyltriazine isomers.

of torsional barriers and NLO properties of phenylpyridines, respectively. Therefore these methods have also been used in this work. The variation of NLO properties against the dihedral angle between 0° and 180° in 19 steps was obtained.

All calculations were performed using GAUSSIAN 98W [27] program on an Intel Pentium IV and Microsoft windows 98 as the operating system. Input data were prepared for GAUSSIAN 98W using Gauss View 2.1 graphical program.

3. Results and discussion

3.1. Torsional barriers

While the conjugation interaction between phenyl and triazine rings tends to prefer a planar structure, the steric repulsion between the ortho-ring hydrogens favors a non-planar structure. The equilibrium geometry of the molecule results from a balance between these two effects. Fig. 2 shows the variation of torsional barriers with the dihedral angles. The calculated relative energies for torsional angle 0° and 90° are given in Table 1.

As seen from Fig. 2 the maximum values of the relative energies for all molecules are reached at 90°, but the equilibrium torsional angles are ranged from 0° to ca. 38°. This is not unexpected result since there are two equilibrium torsional angles about 90°.

As can be seen from Table 1 relative energies obtained from the B3LYP calculations are larger than those from the HF calculations. It is well known that the HF calculation under-estimates the relative energies and the inclusion of electron correlation make them larger. Similar results have also been obtained for phenylpyridine isomers [7]. The twist angles are become smaller at B3LYP level than the HF (Table 1). DFT calculation seems to over-estimate

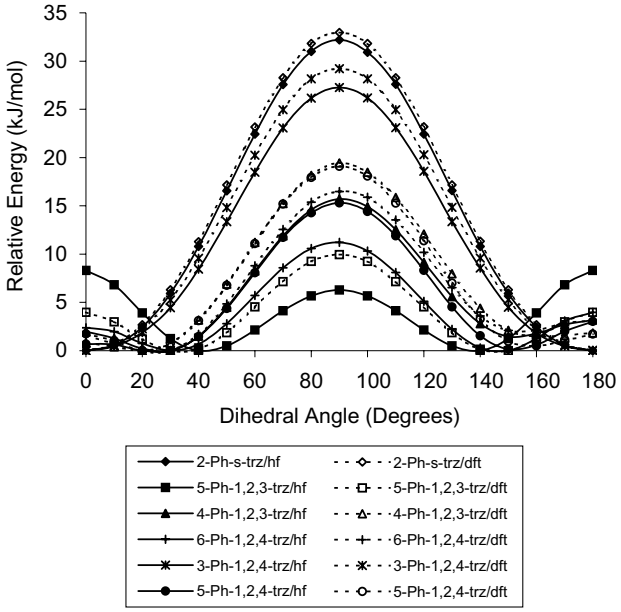

Fig. 2. Torsional barriers for phenyltriazines. Energies are relative to minimum.

the π electron delocalization across two rings, thus leading to smaller dihedral angle.

The respective values of ΔE_0 and ΔE_{90} are in the following orders. For ΔE_0: 5-phenyl-1,2,3-triazine >> 6-phenyl-1,2,4-triazine > 4-phenyl-1,2,3- triazine > 5-phenyl-1,2,4-triazine > 3-phenyl-1,2,4-triazine = 2-phenyl-*s*-triazine and for ΔE_{90}: 2-phenyl-*s*-triazine > 3-phenyl-1,2,4-triazine >> 4-phenyl-1,2,3-triazine > 5-phenyl-1,2,4-triazine > 6-phenyl-1,2,4-triazine > 5-phenyl-1,2,3-triazine.

From these calculations, it is clear that the number of ortho H atoms has a major influence on the torsional barrier of phenyltriazines, whereas the effect of adjacent meta H atoms is much smaller. The shapes of torsional barrier curves for phenyltriazines with the same number of ortho

Table 1
The equilibrium dihedral angle (in degree) and energies in kJ mol^{-1} relative to global minimum

Molecule	HF/6-31++G(d,p)			B3LYP/6-31++G(d,p)		
	1-6-R6-R1	E_0	E_{90}	1-6-R6-R1	E_0	E_{90}
2-Ph-*s*-triazine	0.00	0.00	32.20	0.00	0.00	32.96
4-Ph-1,2,3-triazine	25.50	2.13	15.86	18.20	1.05	19.98
6-Ph-1,2,4-triazine	31.42	3.56	12.42	24.31	1.77	16.73
3-Ph-1,2,4-triazine	0.00	0.00	27.27	0.00	0.00	29.22
5-Ph-1,2,3-triazine	44.00	9.95	7.93	36.50	7.43	10.58
5-Ph-1,2,4-triazine	25.37	2.08	17.00	17.84	0.89	21.07

H atoms are very similar (Fig. 2). The 2-phenyl-*s*-triazine and 3-phenyl-1,2,4-triazine molecules, which have no ortho H atoms, have an energy minimum at 0°. This is due to that the presence of meta H atom adjacent to ortho H-atom causes further increase in ΔE_0 and decrease in ΔE_{90} values.

3.2. Nonlinear optical (NLO) properties

This section reports the α_{ave}–θ, $\Delta\alpha$–θ and β_{tot}–θ correlations and the positional effects of the nitrogen atoms on the NLO properties of compounds (Fig. 1).

The mean static polarizability α_{ave}, anisotropy of polarizability ($\Delta\alpha$) and first static hyperpolarizability (β_{tot}) formulas are as follows:

$$\alpha_{ave} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (1)$$

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

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

The calculated values of these parameters are given by the output of GAUSSIAN 98W program.

There has been neither experimental nor theoretical calculation for the α_{ave} and β_{tot} values of the molecules studied. The variation of static polarizability and HOMO–LUMO energy gap with the dihedral angle for phenyltriazines is graphically shown in Fig. 3. Although no report has been found so far about the NLO properties of the molecules studied here, polarizability of biphenyl has been calculated using HF/6-31++G(d,p) and B3LYP/6-31++G(d,p) levels by Howard et al. [12]. However, first hyperpolarizability of biphenyl has been report by Zerbi at al. [13] and NLO properties of phenylpyridines have been studied by Alyar et al. [11].

The calculated NLO values of phenyltriazines are shown in Table 2, along with those of biphenyl and phenylpyridine molecules. The notable futures arising from Table 2 and Figs. 3 and 4 are as follows:

(i) On going from free phenyl and triazine moieties to phenyltriazine compounds (Table 2) polarizabilities and hyperpolarizabilities increase, while the HOMO–LUMO energy difference decreases. These are due to that according to the frontier orbitals concept, phenyl group which is simple conjugated system, is an electron drawing substituent, which will raise the energy of the HOMO and lowers that of the LUMO [28], resulting in softer phenyltriazine molecule which possessing higher polarizability and higher hyperpolarizability.

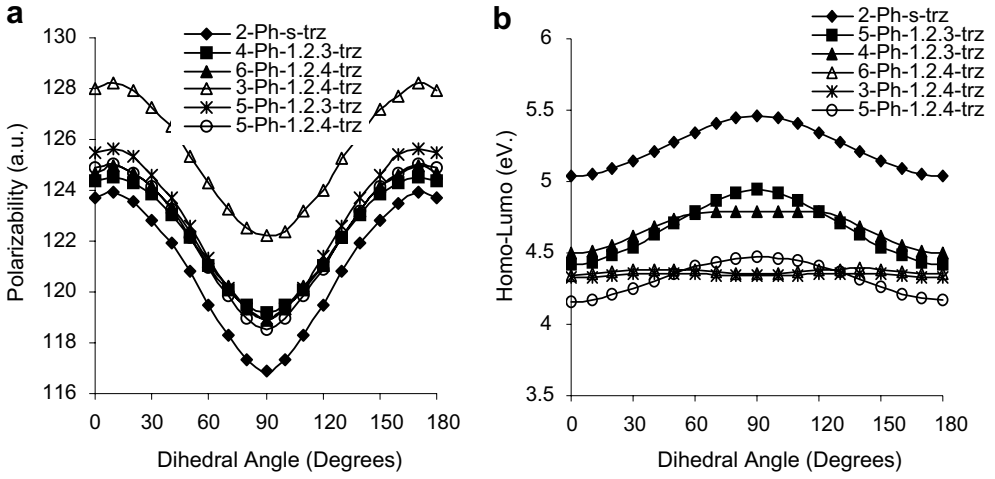

Fig. 3. The variation of static polarizability (a) and HOMO–LUMO energy gap (b) with the dihedral angle for phenyltriazine isomers.

Table 2
Average polarizability, anisotropic polarizability and first hyperpolarizability values of biphenyl, phenylpyridine and phenyltriazine molecules

NLO properties	Methods	Phenyl moiety	1,2,3-trz	1,2,4-trz	1,3,5-trz	BP	2-PP	3-PP	4-PP	3-Ph-1,2,4-trz	5-Ph-1,2,4-trz	4-Ph-1,2,3-trz	6-Ph-1,2,4-trz	5-Ph-1,2,3-trz	2-Ph-1,3,5-trz (2-Ph-*s*-trz)
α_{ave}	BLYP/6-31G[a]	70.17	54.74		53.59										
	MP2/6-31G(d)[b]		54.52	54.22	53.33										
	HF/6-31++G(d,p)[c]					138.90									
	B3LYP/6-31++G(d,p)[c]					144.80									
	B3LYP/6-31++G(d,p)[d]					142.00	139.00	136.40	135.90	129.10	128.70	128.50	127.70	126.70	123.70
	Exp.	71.5													
$\Delta\alpha$	BLYP/6-31G[a]	38.44	30.06		29.31										
	B3LYP/6-31++G(d,p)[d]					75.35	81.70	74.00	68.00	77.30	78.70	77.30	76.60	70.60	74.50
	Exp.	37.90													
β_{tot}	HF/3-21G[e]					1.16–11.57									
	B3LYP/6-31++G(d,p)[d]					12.10	439.00	125.50	204.40	1025.00	895.40	877.00	648.30	552.00	990.00
HOMO–LUMO	B3LYP/6-31++(G(d,p)[d]	6.59	5.00	4.45	5.95	5.27	4.99	5.26	5.31	4.33	4.22	4.70	4.37	4.75	5.04
μ	B3LYP/6-31++G(d,p)[d]	0.00	5.23	2.74	0.00	0.00	1.83	2.46	2.91	2.22	4.32	5.55	3.13	6.55	1.56
	Exp.						1.94	2.45	2.57						

All α_{ave}, $\Delta\alpha$, β_{tot}values are in atomic units.
[a] From Ref. [21].
[b] From Ref. [20].
[c] From Ref. [12].
[d] From Ref. [11].
[e] From Ref. [13].

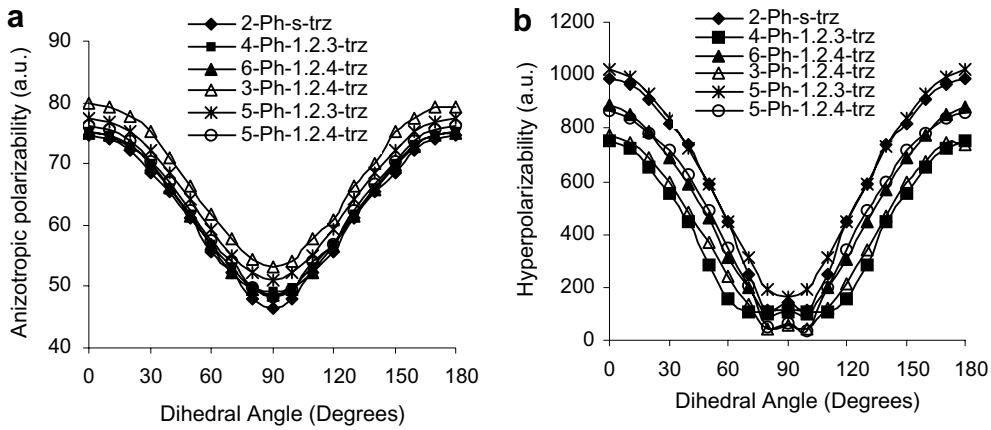

Fig. 4. The variation of anisotropy of polarizability (a) and first static hyperpolarizability (b) with the dihedral angle for phenyltriazine isomers.

(ii) As the twist angles change from the equilibrium values to 90°, the HOMO–LUMO energy difference increase (Fig. 3b) suggesting that the molecules tend to approach to the separation into phenyl and triazin moieties. In this context, we report some calculations which may support this view: The results of the optimization calculations performed at each of 19 steps for 4-Ph-1,2,3-, 6-Ph-1,2,4-, 3-Ph-1,2,4- and 5-Ph-1,2,4-triazine molecules show that interring bonds increase with increasing twist angles.
(iii) Static polarizability, anisotropy of polarizability and first static hyperpolarizability values decrease with increasing the interring angles to 90° (Fig. 3a, Fig. 4a and Fig. 4b). These observations may be interpreted interms of frontier orbitals and hard–soft acid base concepts: As was mentioned in (i), HOMO–LUMO gap increases with increasing the twist angle, resulting in harder phenyltriazine bases [28]. This implies that the harder the base, the lower the polarizability, anisotropy and hyperpolarizability values.
(iv) As seen from Table 2, the equilibrium polarizability, anisotropy and hyperpolarizability values decrease with increasing the equilibrium angles. This may be due to the change in the degree of conjugation depending on the angle.
(v) A final notable is that similar trends of the parameters in Tables 1 and 2, and Figs. 2–4 are also obtained from the energy calculations following the step-wise optimizations for 2-Ph-*s*-triazine, 4-Ph-1,2,3-triazine, 6-Ph-1,2,4-triazine, 3-Ph-1,2,4-triazine, 5-Ph-1,2,3-triazine and 5-Ph-1,2,4-triazine.

The conclusion to be drawn from the above considerations is that the phenyltriazine molecules may be the candidate systems for use in the areas related to the nonlinear optical activity.

References

[1] A. Almeningen, O. Bastiansen, L. Fernholt, B.N. Cyvin, S.J. Cyvin, J. Mol. Struct. 128 (1985) 59.
[2] S. Samdal, O. Bastiansen, J. Mol. Struct. 128 (1985) 115.
[3] F. Lelj, N. Russo, G. Chidichimo, Chem. Phys. Lett. 69 (1980) 530.
[4] V. Barone, F. Lelj, C. Cauletti, M.N. Piancastelli, N. Russo, Mol. Phys. 49 (1983) 599.
[5] E.R. Lippincott, J.E. Katon, Spectrochim. Acta 15 (1959) 627.
[6] W.B. Wise, R.J. Kurland, J. Am. Chem. Soc. 86 (1964) 1877.
[7] M.A.V. Riberio da Silva, M.A.R. Matos, C.A. Rio, V.M.F. Morais, J. Wang, G. Niclos, J.S. Chickos, J. Phys. Chem. A 104 (2000) 1774.
[8] A. Göller, U.W. Grummt, Chem. Phys. Lett. 321 (2000) 399.
[9] S. Arulmozhiraja, T. Fujii, J. Chem. Phys. 115 (23) (2001) 10591.
[10] F. Grein, J. Mol. Struct. (Theochem) 624 (2003) 23.
[11] H. Alyar, M. Bahat, E. Kasap, Z. Kantarci, Czech. J. Phys. 56 (4) (2006) 349.
[12] S.T. Howard, I.A. Fallis, D.J. Willock, Mol. Phys. 97 (1999) 913.
[13] M. Rumi, G. Zerbi, Chem. Phys. 242 (1999) 123.
[14] V. Barone, F. Lelj, C. Cauletti, M.N. Piancastelli, N. Russo, Mol. Phys. 49 (1983) 599.
[15] D. Vizitiu, C. Lazar, J.P. Radke, C.S. Harley, M.A. Glaser, R.P. Lemieux, Chem. Mater. 13 (2001) 1692.
[16] R.P. Lemieux, Acc. Chem. Res. 34 (2001) 845.
[17] W.M. Boesveld, P.B. Hitchcock, M.F. Lappert, J. Chem. Soc., Perkin Trans. 1 (2001) 1103.
[18] D.R. Goldsmith, A.J. Wagstaff, T. Ibbotson, C.M. Perry, CNS Drugs 18 (1) (2004) 63.
[19] A. Hinchliffe, H.J. Soscun, J. Mol. Struct. (Theochem) 304 (1994) 109.
[20] R.J. Doerksen, A.J. Thakkar, Int. J.Quantum Chem. Quantum Chemistry Symposium 30, 1996, p. 1633.
[21] P. Calaminici, K. Jug, A.M. Köster, V.E. Ingamells, M.G. Papadopoulos, J. Chem. Phys. 112 (2000) 6301.
[22] S.T. Howard, I.A. Fallis, D.J. Willock, Mol. Phys. 97 (1999) 913.
[23] M. Rumi, G. Zerbi, Chem. Phys. 242 (1999) 123.
[24] P.C. Hariharan, J.A. Pople, J. Chem. Phys. 27 (1974) 209.
[25] R. Ditchfield, W.J. Hehre, J.A. Pople, J. Chem. Phys. 54 (1971) 724.
[26] W.J. Hehre, R. Ditchfield, J.A. Pople, J. Chem. Phys. 56 (1972) 2257.
[27] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheesemann, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S.Dapprick, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M.Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Cliffort, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi,R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al- Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, M. Head-Gordon, E:S. Replogle, and J.A. Pople.; Revision A.9 ed.; Gaussian, Inc: Pittsburgh, PA, 1998.
[28] I. Fleming, Frontier Orbitals and Organic Chemical Reactions, John Wıley&Sons, Chichester, New York, Brisbane, Toronto, Singapore, 1978, p. 47.