A DENSITY FUNCTIONAL THEORY STUDY ON STRUCTURE AND PROPERTIES OF BENZENE AND BORAZINE-BASED CHROMOPHORES

REZA GHIASI*, SARA AKBARI

Department of Chemistry, East Tehran Branch, Qiam Dasht, Tehran, Islamic Azad University, IRAN

ABSTRACT

Density functional theory (DFT) calculations were employed to investigate the structural characteristics, electronic properties, and nonlinear optical properties of borazine-based chromophores at B3LYP/ 6-311G(d,p) level. We studied the effects of various donor and acceptor substituents (H, F, Cl, Br, Me, NH₂, OH, COOH, CHO, CN, NO₂) on the stability, dipole moment, polarizability, frontier orbitals, structure, the most intense electronic transition, and hyperpolarizabilities. These calculations indicate B-isomer is more stable than N-isomer. On the other hand, the most stable isomer confirms the minimum polarizability and maximum hardness principles in the most molecules. Also, we obtained good linear relations between some of the studied properties. The predicted first hyperpolarizability also shows that the substituted molecules might have a reasonably good nonlinear optical (NLO) behavior.

Keywords: Borazine-Based Chromophores, Substituent effect, Frontier orbitals analysis, Nonlinear optics.

INTRODUCTION

There is growing attention in materials with high non-linear optical (NLO) properties due to their potential application in technologies such as lasers, telecommunications, photovoltaic cells, organic light emitting diodes, and semiconductor layers in field-effect transistors [1] information processing and holography. Organic π -conjugated oligomers and polymers represent an excellent alternative to traditional inorganic NLO crystals because they can be easily synthesized and chemically modified. Extremely fast switching times, resistance to high intensity radiation, possibility of thin-layer fabrication, and low electric permittivity (related to low-frequency dependence in nonresonant regime) are important properties in favor of organic NLO materials. A variety of inorganic, organic, and organometallic molecular systems have been studied for NLO activity [2-10].

We report here on a systematic computational investigation of the NLO properties of borazine-based chromophores. The main purpose here is to assess the use of borazine moieties for the design of molecular NLO chromophores and to obtain insight into the structure-function relationships of these systems.

Computational Methods

All calculations were carried out with the Gaussian 03 suite of program [11]. All molecules were described by the standard 6-31G(d,p) basis set [12-15]. Geometry optimization was performed using Becke's hybrid three-parameter exchange functional and the nonlocal correlation functional of Lee, Yang, and Parr (B3LYP) [16]. A vibrational analysis was performed at each stationary point which corresponds to an energy minimum.

Geometries were optimized at this level of theory without any symmetry constraints followed by the calculations of the first order hyperpolarizabilities. The total static first hyperpolarizability β was obtained from the relation:

$$\beta_{tot} = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2}$$

upon calculating the individual static components

$$\beta_i = \beta_{iii} + \frac{1}{3} \sum_{i \neq j} (\beta_{ijj} + \beta_{jij} + \beta_{jji})$$

Due to the Kleinman symmetry [17]:

$$\beta_{xyy} = \beta_{yyx} = \beta_{yyx} ; \beta_{yyz} = \beta_{zyz} = \beta_{zyy}, \dots$$

one finally obtains the equation that has been employed:

$$\beta_{tot} = \sqrt{(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyx} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzx} + \beta_{zyy} + \beta_{zyx})^2}$$

The electronic spectra for the studied compounds were calculated by TD-DFT [18] using the same hybrid functionals and basis sets as used for the calculation of the hyperpolarizabilities. The

10 lowest excitation energies were computed.

RESULTS AND DISCUSSION

1. Energetic aspects

Figure 1 shows benzene and borazine-Based chromophores investigated in this paper. Table 1 presents the computed energies, relative energies, for all molecules. The relative energies show that B-isomer is more stable than N-isomer in all species. We believe the added stability of the B- isomer systems is due to the degree of polarization of the B-C bond is greater than the N-F bond. For example, in B-isomer (X=H) the charges on B1 and C2' are +0.920e and -0.480e respectively. In N-isomer, the charges on N1 and C2' are -0.888e and +0.064 (Table 1). There is a good linear relation between the relative energies values and along with their Hammett constants (σ_p) [19]. (Figure2).

Figure 1. Resonance forms of Borazine-based chromophores with various X-groups. For acceptors, the zwitterionic form has the opposite charge separation.

Table 1. Absolute energy (Hartree), relative energy (kcal/mol), Hammett constant (σ_p), dipole moment (μ , Debye) and NBO Charges of C2', N1, and B1 atoms of borazine-based chromophores with various X-groups.

	Energy		ΔE	σ_p	μ_{tot}		N-isomer		B-isomer	
	N-isomer	B-isomer			N-isomer	B-isomer	Q(C2')	Q(N1)	Q(C2')	Q(B1)
H	-551.261	-551.287	16.01	0.00	1.62	1.13	0.064	-0.888	-0.480	0.920
F	-650.525	-650.551	16.07	0.15	1.57	0.39	0.063	-0.888	-0.482	0.919
Cl	-1010.884	-1010.909	15.71	0.24	2.05	1.05	0.070	-0.887	-0.473	0.919
Br	-3124.804	-3124.829	15.68	0.23	1.97	0.93	0.065	-0.891	-0.459	0.918
OH	-626.504	-626.531	16.70	-0.38	3.21	2.28	0.053	-0.888	-0.494	0.920
NH ₂	-606.634	-606.661	17.19	-0.57	3.89	3.83	0.046	-0.889	-0.506	0.919
Me	-590.589	-590.615	16.28	-0.14	1.97	1.74	0.060	-0.888	-0.486	0.920
CN	-643.528	-643.552	14.81	0.70	5.25	4.39	0.087	-0.884	-0.454	0.917
CF ₃	-888.402	-888.426	15.15	0.53	5.24	2.41	0.082	-0.885	-0.461	0.918
CHO	-664.618	-664.642	14.91	0.42	4.40	2.98	0.087	-0.884	-0.457	0.917
COOH	-739.894	-739.918	15.11	0.44	3.09	1.55	0.084	-0.884	-0.461	0.917
NO ₂	-755.820	-755.843	14.48	0.81	5.69	4.65	0.094	-0.883	-0.447	0.916

Figure 2. Relative energy ($=E^{N\text{-isomer}} - E^{B\text{-isomer}}$) versus Hammett constants (σ_p).

2. Dipole moment

The dipole moment values have been gathered in Table 1. These values present N-isomer has a larger dipole moment rather than B-isomer. A good correlation between μ and Hammett constants (σ_p) has been shown. See Figure 3. As a consequence, dipole moment values also increases with an increase in the accepting strength of the X-group.

3. Polarizability

Polarizabilities describe the response of a system in an applied electric field [20]. They determine not only the strength of molecular interactions (such as the long range intermolecular induction, dispersion forces, etc.) as well as the cross sections of different scattering and collision processes, but also the nonlinear optical properties of the system [21].

The isotropic polarizability $\langle \alpha \rangle$ is calculated as the mean value as given in the following equation:

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

And the polarizability anisotropy invariant is:

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

The calculated isotropic and anisotropic polarizability values indicate these values decrease in the stable complexes, as expected from the principles of minimum energy and minimum polarizability in most cases (except, $X = \text{NH}_2$, OH; Table 2) [22]. On the other hand, there is a good correlation between isotropic and anisotropic polarizability values with relative energy values (Figure 4).

Figure 3. Dipole moment (μ) versus σ_p Hammett constants (σ_p).

Table 2. Isotropic polarizability $\langle\alpha\rangle$ and anisotropy polarizability ($\Delta\alpha$) of borazine-based chromophores with various X-groups.

N-isomer					
X	α_{xx}	α_{yy}	α_{zz}	$\langle\alpha\rangle$	$\Delta\alpha$
H	260.787	139.702	73.940	158.14	164.16
F	260.859	139.051	74.100	158.00	164.22
Cl	304.180	144.030	76.048	174.75	202.87
Br	320.349	147.513	79.458	182.44	215.10
OH	277.676	141.719	76.158	165.18	178.03
NH ₂	297.112	144.446	79.753	173.77	193.31
Me	292.308	148.750	83.391	174.82	185.10
CN	335.430	147.450	74.208	185.70	233.39
CF ₃	292.318	150.503	78.867	173.90	188.15
CHO	331.835	155.859	73.325	187.01	228.70
COOH	330.595	156.577	75.493	187.56	225.76
NO ₂	334.723	158.126	72.087	188.31	231.91

B-isomer					
	α_{xx}	α_{yy}	α_{zz}	$\langle\alpha\rangle$	$\Delta\alpha$
H	255.713	146.889	69.021	157.21	162.42
F	257.317	146.220	69.067	157.53	163.91
Cl	298.592	150.047	72.492	173.71	199.00
Br	314.962	153.435	75.963	181.45	211.20
OH	278.632	149.437	70.213	166.09	182.22
NH ₂	304.095	152.919	72.381	176.47	203.75
Me	289.339	155.586	78.542	174.49	184.74
CN	317.687	150.197	75.197	181.03	215.03
CF ₃	278.756	153.745	79.259	170.59	174.61
CHO	310.828	158.578	74.321	181.24	207.62
COOH	312.534	160.044	75.681	182.75	207.93
NO ₂	307.255	160.322	74.236	180.60	204.08

4. Frontier orbital analysis

A particularly interesting property for these molecules is the energy gap (E_g) between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The energy gap is considered as a reflection of the molecule's chemical activity. The frontier orbital energies values have been gathered in Table 3. These values display HOMO and LUMO energy values decrease in substituted molecules, except X=Me, NH₂, OH. Also, these values decrease in more stable isomer. Figure 5 presents linear correlation between frontier orbital energies and hammet constant values. A good correlation found suggests that the electron withdrawing/donating groups influences the E(HOMO), and this correlation may be used as a tool to predict E(HOMO) for other substituents for which σ_p is known. The same correlation is observed for E(LUMO) energies.

Table 3 exhibits the HOMO-LUMO gaps of all structures. These values indicate substitution causes decreasing of energy gaps. On the other hand, the calculated the HOMO-LUMO gaps values indicate these values increase in the stable isomer, as expected from the principles of minimum energy and

maximum hardness in most cases (expect, X=NH₂, OH; Table 3). There is a good correlation between relative hardness values with constant values (Figure 6).

Figure 4. $\alpha(\text{iso})_{\text{N-isomer}} - \alpha(\text{iso})_{\text{B-isomer}}$ and $\alpha(\text{aniso})_{\text{N-isomer}} - \alpha(\text{aniso})_{\text{B-isomer}}$ values versus relative energy.

To evaluate the chemical potential (μ) of these complexes, these values can be calculated from the HOMO and LUMO orbital energies using the following approximate expression [23-29]:

$$\mu = \frac{E_{\text{HOMO}} + E_{\text{LUMO}}}{2}$$

The chemical potential characterizes the tendency of electrons to escape from the equilibrium system. As expected, more stable isomer has less chemical potential.

To evaluate the electrophilicity of these complexes, we have calculated the electrophilicity index, ω , using the expression:

$$\omega = \frac{\mu^2}{2\eta}$$

The values of electrophilicity index in Table 3 indicate more stable isomer has the largest electrophilicity.

5. Structural analysis

The optimized geometries of borazine-based chromophores studied in work with atom labeling are depicted in Figure 1. All studied molecules are essentially nonplanar. Table 4 shows the B3LYP/6-311G(d,p) selected structural data for the optimized structures with various X-groups.

These values indicate bonds C1C2, C3C4, and C5C6 are longer, while bonds B1N2 and B3N3 are shorter. These changes in the bond lengths indicate a larger contribution of the zwitterionic (nonaromatic) resonance structure to the ground state of these derivatives.

Table 3. Frontier orbital energies (Hartree), HOMO-LUMO gap energy (eV), hardness (eV), and chemical potential (eV) for Borazine-Based Chromophores with Various X-Groups.

N-isomer							
	HOMO	LUMO	ΔE	η	S	μ	ω
H	-0.209	-0.038	4.66	2.33	0.21	-3.37	2.43
F	-0.211	-0.040	4.65	2.32	0.22	-3.42	2.51
Cl	-0.214	-0.047	4.54	2.27	0.22	-3.55	2.78
Br	-0.214	-0.048	4.52	2.26	0.22	-3.55	2.79
OH	-0.198	-0.031	4.53	2.26	0.22	-3.11	2.14
NH ₂	-0.185	-0.026	4.35	2.17	0.23	-2.87	1.90
Me	-0.204	-0.035	4.60	2.30	0.22	-3.26	2.31
CN	-0.225	-0.070	4.24	2.12	0.24	-4.01	3.80
CF ₃	-0.222	-0.057	4.50	2.25	0.22	-3.80	3.21
CHO	-0.221	-0.074	4.02	2.01	0.25	-4.01	4.00
COOH	-0.219	-0.065	4.20	2.10	0.24	-3.86	3.54
NO ₂	-0.230	-0.092	3.76	1.88	0.27	-4.38	5.10

B-isomer							
	HOMO	LUMO	ΔE	η	S	μ	ω
H	-0.231	-0.059	4.68	2.34	0.21	-3.94	3.31
F	-0.232	-0.061	4.65	2.33	0.21	-3.98	3.40
Cl	-0.235	-0.067	4.56	2.28	0.22	-4.10	3.69
Br	-0.233	-0.067	4.52	2.26	0.22	-4.09	3.70
OH	-0.216	-0.051	4.47	2.24	0.22	-3.64	2.95
NH ₂	-0.200	-0.045	4.23	2.11	0.24	-3.34	2.64
Me	-0.224	-0.055	4.60	2.30	0.22	-3.80	3.15
CN	-0.248	-0.087	4.38	2.19	0.23	-4.57	4.76
CF ₃	-0.246	-0.076	4.63	2.32	0.22	-4.38	4.14
CHO	-0.244	-0.089	4.22	2.11	0.24	-4.54	4.89
COOH	-0.242	-0.081	4.37	2.18	0.23	-4.40	4.43
NO ₂	-0.255	-0.105	4.07	2.03	0.25	-4.89	5.89

6. Electronic spectra

We found the most intense electronic transition ($\lambda_{\max}$) of molecules. The wavelength, oscillator strength and the composition of the transitions obtained by TD-DFT calculations are given in Table 5. The most intense electronic transition for all molecules is attributed to HOMO@LUMO transition. The $\lambda_{\max}$ is a function of substituent, the stronger the donor character of substituent, the more electron push into the molecule, the less $\lambda_{\max}$. These calculations illustrate the decreasing of $\lambda_{\max}$ in B-isomer, which is compatible with larger HOMO-LUMO gap in this isomer. There is a good correlation between HOMO-LUMO gap and $\lambda_{\max}$ (Figure 7).

7. Hyperpolarizability

The first static hyperpolarizability (β_{tot}) values for the all molecules are shown in Table 6. The results show that the magnitude of the first hyperpolarizability tensor of all molecules is rather moderate, and NO₂ and NH₂ substations have the most value in N- and B-isomers, respectively. Also, these values indicate the first hyperpolarizability values of N-isomer are more than B-isomer with withdrawing substitutions. On the other hand, these values of N-isomer are less than B-isomer with donor substitutions.

This chromophore exhibits larger non-linearity and its $\lambda_{\max}$ is red-shifted in B-isomers (except β in X=Me, CN) and N-isomers when compared with unsubstituted molecule. Therefore, it is clear that the hyperpolarizability is a

strong function of the absorption maximum. Since even a small absorption at the operating wavelength of optic devices can be detrimental, it is important to make NLO chromophores as transparent as possible without compromising the molecule's non-linearity.

A good correlation has been shown between β_{tot} and $\lambda_{\max}$ in N-isomer for all substituents (Figure 8). But, there is similar correlation in B-isomer for donor substituents and withdrawing substituents.

CONCLUSION

The study of electronic, structural and spectroscopic properties as well as the static first hyperpolarizabilities of the borazine-based chromophores indicated stability of B-isomer species is more than N-isomer. The decreasing of isotropic and anisotropic polarizability values and increasing of HOMO-LUMO gaps values in the stable complexes is compatible with the principles of minimum energy and minimum polarizability in most cases (expect, X=NH₂, OH). Calculations showed that the most intense electronic transition is due to HOMO→LUMO transition in all molecules. Theoretical studies indicated acceptor substitutions causes to increasing the first hyperpolarizability values in N-isomer rather than B-isomer, whilst, these values of N-isomer are less than B-isomer with donor substitutions.

Table 4. Optimized Bond lengths (Å) of Borazine-Based Chromophores with Various X-Groups.

N-isomer															
X	N1 B1	B1N2	N2B2	B2N3	N3B3	B3N1	N1C2'	C1'C2'	C1'C1	C1C2	C2C3	C3C4	C4C5	C5C6	C6C1
H	1.445	1.424	1.428	1.429	1.425	1.447	1.417	1.340	1.468	1.405	1.391	1.393	1.395	1.389	1.406
F	1.445	1.424	1.428	1.429	1.425	1.447	1.417	1.340	1.468	1.405	1.391	1.385	1.388	1.389	1.406
Cl	1.446	1.423	1.428	1.429	1.424	1.448	1.415	1.341	1.466	1.405	1.390	1.389	1.392	1.388	1.406
Br	1.446	1.423	1.428	1.429	1.424	1.448	1.415	1.341	1.466	1.405	1.391	1.390	1.392	1.389	1.406
OH	1.444	1.425	1.428	1.428	1.426	1.446	1.420	1.340	1.467	1.403	1.391	1.394	1.398	1.386	1.408
NH ₂	1.443	1.425	1.428	1.428	1.427	1.445	1.421	1.340	1.466	1.404	1.388	1.402	1.404	1.386	1.406
Me	1.444	1.425	1.428	1.429	1.425	1.446	1.418	1.340	1.467	1.402	1.392	1.396	1.402	1.387	1.407
CN	1.448	1.422	1.428	1.430	1.422	1.450	1.411	1.343	1.463	1.407	1.386	1.402	1.405	1.384	1.409
CF ₃	1.447	1.423	1.428	1.430	1.423	1.449	1.413	1.342	1.465	1.405	1.389	1.393	1.397	1.386	1.408
CHO	1.448	1.422	1.428	1.430	1.423	1.450	1.412	1.343	1.462	1.407	1.388	1.397	1.404	1.381	1.413
COOH	1.447	1.423	1.428	1.430	1.423	1.449	1.413	1.342	1.464	1.407	1.387	1.398	1.401	1.383	1.409
NO ₂	1.449	1.422	1.428	1.430	1.422	1.451	1.410	1.343	1.462	1.409	1.386	1.391	1.394	1.384	1.410

B-isomer															
X	B1 N1	N1B2	B2N2	N2B3	B3N3	N3B1	B1C2'	C1'C2'	C1'C1	C1C2	C2C3	C3C4	C4C5	C5C6	C6C1
H	1.439	1.428	1.429	1.430	1.427	1.438	1.559	1.345	1.469	1.404	1.391	1.392	1.396	1.388	1.406
F	1.438	1.428	1.429	1.430	1.427	1.438	1.559	1.345	1.469	1.404	1.391	1.385	1.389	1.387	1.406
Cl	1.438	1.428	1.429	1.430	1.427	1.438	1.560	1.345	1.469	1.403	1.391	1.389	1.393	1.387	1.405
Br	1.438	1.428	1.429	1.430	1.427	1.438	1.560	1.345	1.469	1.403	1.391	1.390	1.394	1.388	1.405
OH	1.440	1.427	1.430	1.430	1.426	1.440	1.557	1.346	1.466	1.402	1.390	1.395	1.400	1.384	1.408
NH ₂	1.441	1.426	1.430	1.431	1.425	1.441	1.555	1.348	1.463	1.405	1.387	1.403	1.407	1.383	1.407
Me	1.439	1.427	1.429	1.430	1.426	1.439	1.558	1.346	1.468	1.402	1.392	1.396	1.403	1.386	1.406
CN	1.436	1.429	1.429	1.430	1.428	1.436	1.563	1.345	1.469	1.405	1.387	1.401	1.405	1.384	1.406
CF ₃	1.437	1.429	1.429	1.430	1.428	1.437	1.562	1.344	1.470	1.403	1.390	1.393	1.398	1.385	1.406
CHO	1.437	1.429	1.429	1.430	1.428	1.437	1.562	1.345	1.468	1.405	1.389	1.397	1.403	1.382	1.410
COOH	1.437	1.429	1.429	1.430	1.428	1.437	1.562	1.345	1.469	1.405	1.388	1.398	1.401	1.384	1.407
NO ₂	1.436	1.480	1.429	1.430	1.429	1.436	1.564	1.345	1.469	1.406	1.388	1.390	1.393	1.388	1.407

Table 5. Maximum Absorption wavelength ($\lambda_{\max}$), Oscillator strength (f), and its character for borazine-based chromophores with various X-groups.

	character	N-isomer		B-isomer	
		$\lambda_{\max}$	f	$\lambda_{\max}$	f
H	HOMO→LUMO	286.95	0.6877	277.81	0.8117
F	HOMO→LUMO	288.60	0.5803	279.87	0.7579
Cl	HOMO→LUMO	294.37	0.7667	286.60	0.8986
Br	HOMO→LUMO	296.29	0.8082	290.02	0.9224
OH	HOMO→LUMO	296.39	0.5979	290.45	0.8057
NH ₂	HOMO→LUMO	308.24	0.6218	306.66	0.8390
Me	HOMO→LUMO	290.82	0.7622	283.37	0.9175
CN	HOMO→LUMO	309.30	0.9708	295.71	0.9774
CF ₃	HOMO→LUMO	294.60	0.8166	281.36	0.8660
CHO	HOMO→LUMO	323.59	0.9312	306.52	0.9179
COOH	HOMO→LUMO	313.42	0.9459	298.05	0.9504
NO ₂	HOMO→LUMO	352.16	0.6839	326.03	0.6617

Figure 5. Frontier orbital values versus relative energy.

Figure 7. HOMO-LUMO gap versus $\lambda_{\max}$. Figure 6. (a) Hardness (except for Me, NH₂, OH) and (b) chemical potential values versus Hammett constant.

Table 6. β components and β_{tot} values (10^{-30} esu) for Borazine-Based Chromophores with Various X-Groups.

N-isomer												
X	H	F	Cl	Br	Me	NH ₂	CN	COOH	CHO	NO ₂	CF ₃	OH
β_{XXX}	247.31	-62.44	-70.46	-71.57	-72.78	-52.44	-78.01	-84.23	-28.74	-83.25	-73.97	-54.15
β_{XXY}	56.14	1.42	8.41	10.24	-10.93	0.55	19.91	25.08	1.05	23.13	18.90	-7.18
β_{XYY}	-118.15	6.78	-0.60	-1.83	14.06	10.16	-6.89	-4.92	5.59	-2.67	-7.83	9.90
β_{YYY}	10.69	1.80	9.41	11.30	14.80	10.00	4.63	1.12	-4.83	2.69	5.99	1.17
β_{XXZ}	-16.83	130.47	168.08	183.09	121.68	124.45	205.88	231.36	196.48	2.22	191.36	124.20
β_{XYZ}	55.60	32.42	15.30	6.60	15.46	46.48	-19.69	-35.69	-19.04	-47.56	-14.32	48.57
β_{YYZ}	-4.49	-3.04	16.05	20.13	-32.96	-17.82	33.65	33.20	21.67	41.72	31.66	-9.35
β_{XZZ}	-24.05	-10.19	13.26	10.97	-1.53	-104.13	152.54	207.31	219.93	324.39	81.17	-56.11
β_{YZZ}	1.08	10.43	-1.62	-0.20	1.07	172.54	-117.38	-169.26	-174.82	-266.02	-73.68	27.66
β_{ZZZ}	7.03	234.41	79.71	157.52	59.52	1848.99	-2007.88	-2856.46	-3397.78	-5040.28	-1030.40	979.37
β_{tot}	1.09E-30	3.18E-30	2.34E-30	3.17E-30	1.38E-30	1.70E-29	1.53E-29	2.25E-29	2.76E-29	4.33E-29	6.99E-30	9.50E-30
$\beta_{\text{tot}} \cdot 10^{-30}$	1.09	3.18	2.34	3.17	1.38	17.02	15.31	22.45	27.57	43.27	6.99	9.5

B-isomer												
X	H	F	Cl	Br	Me	NH ₂	CN	COOH	CHO	NO ₂	CF ₃	OH
β_{XXX}	27.92	26.61	21.49	20.99	29.33	57.02	15.42	4.93	68.14	3.67	10.33	48.85
β_{XXY}	-9.91	-13.85	-11.08	-10.08	-33.26	-24.01	-6.88	-1.79	-25.08	-4.08	-7.31	-21.73
β_{XYY}	4.12	1.54	-0.66	0.10	10.95	7.76	-1.39	3.56	14.93	3.49	1.20	4.83
β_{YYY}	4.43	7.11	10.78	9.09	16.90	10.21	7.00	0.90	-5.81	3.09	3.94	3.26
β_{XXZ}	-42.46	-46.68	-19.80	-7.01	-63.98	-78.85	-6.25	20.84	-24.35	22.80	0.61	-65.60
β_{XYZ}	22.02	30.45	21.38	13.69	22.40	35.23	14.20	0.84	23.86	-1.27	14.17	39.39
β_{YYZ}	17.17	21.99	33.30	37.40	-13.14	32.28	43.58	47.38	30.67	47.21	41.22	24.84
β_{XZZ}	-73.27	-125.84	-127.38	-144.89	-119.27	-341.15	49.14	127.63	158.15	247.97	-0.65	-214.01
β_{YZZ}	44.32	74.29	86.67	94.46	76.66	298.37	-25.12	-83.97	-92.64	-156.04	-0.49	96.98
β_{ZZZ}	702.19	1222.74	1411.03	1642.97	1291.75	3344.65	-265.34	-959.81	-1360.79	-2515.21	192.77	2159.49
β_{tot}	5.87E-30	1.04E-29	1.24E-29	1.45E-29	1.05E-29	2.87E-29	2.06E-30	7.83E-30	1.19E-29	2.13E-29	2.03E-30	1.84E-29
$\beta_{\text{tot}} \times 10^{-30}$	5.87	10.4	12.36	14.52	10.53	28.7	2.06	7.83	11.93	21.28	2.03	18.37

Figure 8. The first static hyperpolarizability (β_{tot}) versus λ_{max} .

REFERENCES

1. C.D. Dimitrakopoulos, P. Malenfant, *Adv. Mater.* 14, 29, (2002).
2. D.R. Kanis, M.A. Ratner, T.J. Marks, *Chem. Rev* 94, 195, (1994).
3. P.J. Mendes, T.J.L. Silva, A.J.P. Carvalho, J.P.P. Ramalho, *Journal of Molecular Structure: THEOCHEM* 946, 33,
4. D. Avci, A. Basoglu, Y. Atalay, *Struct Chem* 21, 213, (2010).
5. M. Medved, S. Budzák, I. Cernušák, *Journal of Molecular Structure: THEOCHEM* 961, 66, (2010).
6. W. Bartkowiak, K. Strasburger, *Journal of Molecular Structure: THEOCHEM* 960, 93, (2010).
7. L.A.D. Souza, A.M.D.S. Jr., G.M.A. Junqueira, A.C.M. Carvalho, H.F.D. Santos, *Journal of Molecular Structure: THEOCHEM* 959, 92, (2010).
8. A. Karton, M.A. Iron, M.E.v.d. Boom, J.M.L. Martin, *J. Phys. Chem. A* 109, 5454, (2005).
9. P.C. Ray, *Chemical Physics Letters* 354, (2004).
10. A. Hameed, A. Rybarczyk-Pirek, J. Zakrzewski, *Journal of Organometallic Chemistry* 656, 102, (2002).
11. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, *Gaussian 03*, Gaussian, Inc., Pittsburgh PA, 2003.
12. M.J.S. Dewar, C.H. Reynolds, *J. Comp. Chem.* 2, 140, (1986).
13. K. Raghavachari, J.A. Pople, E.S. Replogle, M. Head-Gordon, *J. Phys. Chem. A* 94, 5579, (1990).
14. A.D. McLean, G.S. Chandler, *J. Chem. Phys.* 72, 5639, (1980).
15. R. Krishnan, J.S. Binkley, R. Seeger, J.A. Pople, *J. Chem. Phys.* 72, 650, (1980).
16. A.D. Becke, *J. Chem. Phys.* 98, 5648, (1993).
17. D.A. Keleiman, *Phys. Rev.* 126, 1977, (1962).
18. E. Runge, E.K.U. Gross, *Phys. Rev. Lett.* 52, 997, (1984).
19. C. Hansch, A. Leo, R.W. Taft, *Chem. Rev.* 97, 165, (1991).
20. C.R. Zhang, H.S. Chen, G.H. Wang, *Chem. Res. Chinese* 20, 640, (2004).
21. H. Cheng, J. Feng, A. Ren, J. Liu, *Acta Chim. Sin.* 60, 830, (2002).
22. D.R. Roy, P.K.r. Chattaraj, *J. Phys. Chem. A* 112, 1612, (2008).
23. P. Geerlings, F.D. Proft, W. Langenaeker, *Chem. Rev.* 103, 1793, (2003).
24. H. Chermette, *J. Comput. Chem.* 20, 129, (1999).
25. C.-G. Zhan, J.A. Nichols, D.A.J. Dixon, *J. Phys. Chem. A* 107, 4184, (2006).
26. R.G. Parr, Z. Zhou, *Acc. Chem. Res.* 26, 256, (1993).
27. L.G. Arnaut, S.J. Formosinho, *Chem. Eur. J.* 14, 6578, (2008).
28. R.G. Pearson, *J. Chem. Educ.* 64, 561, (1987).
29. R.G. Parr, P.K. Chattaraj, *J. Am. Chem. Soc.* 113, 1854, (1991).