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Applying Density Functional Theory to Study NLO Properties of Benzyne-Based Chromophores

Reza Ghiasi*, Azadeh Heidarbeigi

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

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Abstract

Density Functional Theory (DFT) calculations were employed to investigate the structural characteristics, electronic properties, and nonlinear optical properties of Benzyne-Based Chromophores at B3LYP/6-31G(d,p) level. The effects on the hyperpolarizabilities of various donor and acceptor substituent (H, F, Cl, Br, Me, NH_2, OH, NH_3^+, COOH, CHO, CN, NO, NO_2) were studied. The results revealed a significant influence of the substituent on the first hyperpolarizability of this compound.

Key words: *Benzyne-Based Chromophores, Nonlinear optics, Density functional theory.*

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 has been studied for NLO activity [2-10].

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

* ***Corresponding author:*** *Dr. Reza Ghiasi, Professor, Department of Chemistry, East Tehran Branch, Qiam Dasht, Islamic Azad University, Tehran, IRAN. E-mail: rghiasi@iauet.ac.ir.*

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 [12-14]. Geometry optimization was performed using Becke's hybrid three-parameter exchange functional and the nonlocal correlation functional of Lee, Yang, and Parr (B3LYP) [15]. 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:

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

upon calculating the individual static components

$$\beta_i = \beta_{ii} + \frac{1}{3}\sum_{i \neq j}(\beta_{ij} + \beta_{ji} + \beta_{jj})$$

Due to the Kleinman symmetry [16]:

$$\beta_{xyy} = \beta_{yxy} = \beta_{yyx} ; \beta_{yyz} = \beta_{yzy} = \beta_{zyy}, \ldots$$

one finally obtains the equation that has been employed:

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

The electronic spectra for the studied compounds were calculated by TD-DFT[17] 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

Structural analysis

The optimized geometries of Benzyne-Based Chromophores studied in work with atom labeling are depicted in Figure 1. All studied molecules are essentially planar. Table 1 shows the B3LYP/6-31G (d,p) selected structural data for the optimized structures with various X-groups along with their Hammett constants (σ_p) [18].

Table 1. Optimized Bond Lengths (Å) of Benzyne-Based Chromophores with Various X-Groups.

X	12	23	34	45	56	67	78	89	910	BLA
H	1.416	1.401	1.428	1.459	1.349	1.465	1.407	1.393	1.395	0.00816
F	1.416	1.401	1.428	1.459	1.349	1.464	1.408	1.392	1.389	0.00616
Cl	1.416	1.401	1.428	1.459	1.349	1.464	1.407	1.392	1.393	0.00781
Br	1.416	1.401	1.428	1.459	1.349	1.464	1.407	1.392	1.392	0.00747
Me	1.416	1.401	1.428	1.458	1.350	1.463	1.405	1.393	1.398	0.00873
OH	1.416	1.401	1.428	1.458	1.350	1.462	1.406	1.392	1.398	0.01078
NH_2	1.416	1.401	1.429	1.457	1.351	1.459	1.408	1.388	1.405	0.018095
NH_3^+	1.419	1.399	1.428	1.455	1.352	1.458	1.411	1.391	1.389	0.009355
CN	1.416	1.401	1.428	1.458	1.350	1.463	1.409	1.388	1.404	0.01852
NO	1.417	1.400	1.428	1.457	1.351	1.461	1.416	1.384	1.402	0.0253
NO_2	1.417	1.400	1.428	1.458	1.350	1.462	1.410	1.389	1.393	0.012915
COOH	1.416	1.401	1.428	1.458	1.350	1.463	1.409	1.390	1.401	0.01509
CHO	1.416	1.401	1.428	1.458	1.350	1.462	1.409	1.390	1.400	0.014765

These values indicate 1-2, 3-4, 8-7, and 9-10bonds are longer, while 2-3 and 8-9 bonds 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. The concept of bond-length-alternation (BLA), defined as the difference between the average carbon–carbon adjacent bond lengths along a conjugated backbone, was found to be a significant parameter that correlates with the optical nonlinearities of organic and organometallic/coordination complexes [19-23].

The BLA parameter for all molecules is given in Table 1. The positive sign of BLA indicates that zwitterionic resonance form is the dominant contributor to the ground-state (the neutral and charge-separated resonance forms for the complexes are illustrated in Figure 1).

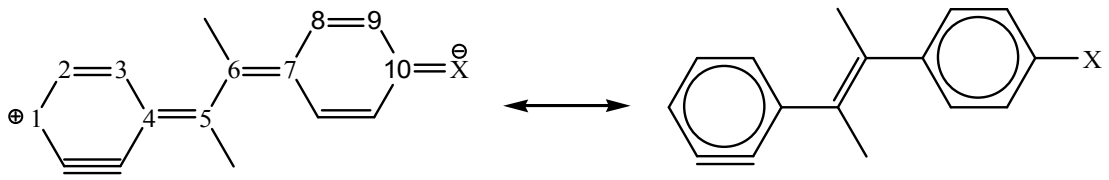

Figure 1. Resonance Forms of Benzyne-Based Chromophores with Various X-Groups.

Dipole moment

The dipole moment values have been gathered in Table 2. A good correlation between μ and Hammett constants (σ_p) has been shown (except for NH_3^+ that induces a very large dipole moment of 18 D not reflected by its σ_p value of 0.6 and Me, OH, NH_2). (See Figure 2)

Table 2. Hammet constant ($_p$), dipole moment (μ, Debye) of Benzyne-Based Chromophores with Various X-Groups.

X	p	x	y	z	tot
H	0.00	0.8743	1.3603	0.0044	1.6170
F	0.15	-0.4569	1.5037	0.0043	1.5716
Cl	0.24	-1.3469	1.5389	0.0038	2.0451
Br	0.26	-1.2534	1.5149	0.0034	1.9662
Me	-0.14	1.4845	1.2886	-0.0186	1.9659
OH	-0.38	1.7592	2.6834	0.0014	3.2086
NH_2	-0.57	-3.5538	1.2259	0.9994	3.8899
NH_3^+	0.60	18.6046	0.5217	0.0216	18.6120
CN	0.70	-4.9415	1.7784	0.0024	5.2518
NO	0.91	-4.6345	1.3922	0.0043	4.8391
NO_2	0.81	-5.4104	1.7614	0.0034	5.6899
COOH	0.44	-1.2992	2.8053	0.0021	3.0916
CHO	0.42	-3.0458	3.1743	0.0009	4.3992

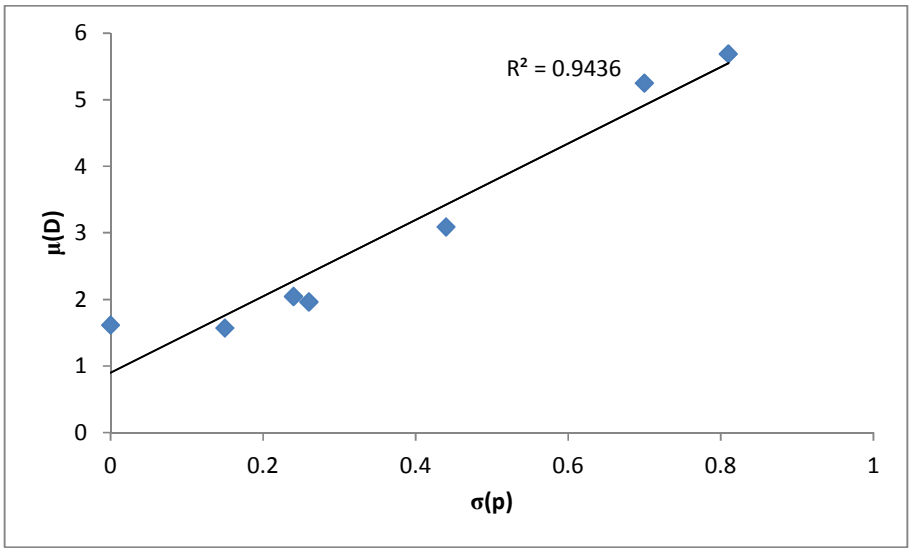

Figure 2. Dipole moment (μ)versus σ_p Hammett constants (σ_p) (except for NH_3^+ that induces a very large dipole moment of 18 D not reflected by its σ_p value of 0.6). The line has a linear correlation coefficient of R^2) 0.94.

Electronic spectra

We found the most intense electronic transition (λ_{max}) of molecules. The wave length, oscillator strength and the composition of the transitions were obtained by TD-DFT calculations given in Table 3. There is a good correlation between σ_p and λ_{max} for all substituent, except X=Me, NH_2^+, OH NH_3^+, CN (Figure 3).The most intense electronic transition for X=NH_3^+, COOH, CHO, CN is attributed to HOMO→LUMO transition, and for other substituent is HOMO→LUMO+1.

Table 3. Maximum Absorption wavelength (λ_{max}), Oscillator strength (f), and its character for Benzyne-Based Chromophores with Various X-Groups.

X	max	f	character
H	315.53	1.0184	HOMO→LUMO+1
F	317.39	1.0156	HOMO→LUMO+1
Cl	322.70	1.1331	HOMO→LUMO+1
Br	325.62	1.1677	HOMO→LUMO+1
Me	320.98	1.1148	HOMO→LUMO+1
OH	327.43	1.0490	HOMO→LUMO+1
NH_2	343.13	1.0624	HOMO→LUMO+1
NH_3^+	351.60	0.9164	HOMO→LUMO
CN	333.35	1.2141	HOMO→LUMO
NO	384.21	0.8387	HOMO→LUMO+1
NO_2	365.76	0.8752	HOMO→LUMO
COOH	335.04	1.1794	HOMO→LUMO
CHO	343.81	1.1441	HOMO→LUMO

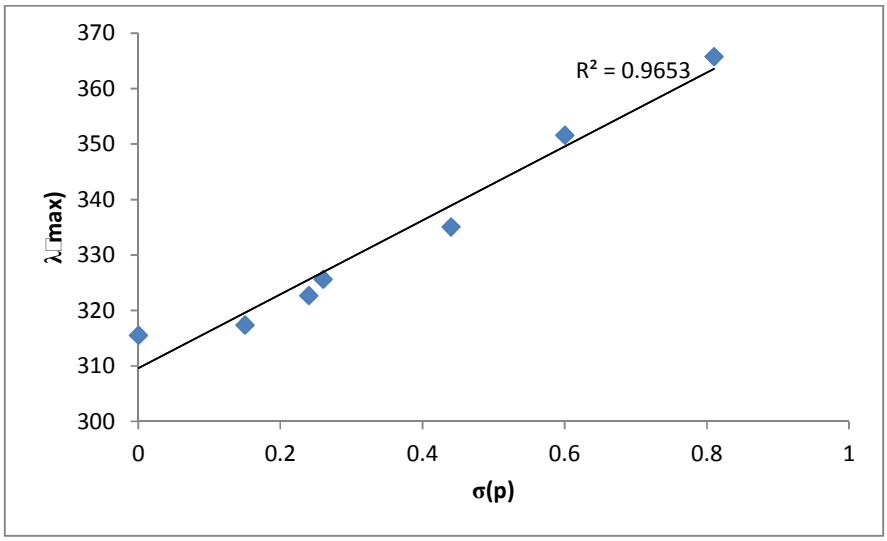

Figure 3. Maximum Absorption wavelength (λ_{max}) versus Hammett constants (σ_p) (except for Me, OH, NH_2, CN).

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. Table 4displays the HOMO-LUMO gaps of all structures. These values indicate substitution causes decreasing of energy gaps.

Table 4. Frontier orbital energies (Hartree), HOMO-LUMO gap energy (eV), hardness (eV), and chemical potential (eV) for Benzyne-Based Chromophores with Various X-Groups.

X	E(HOMO)	E(LUMO)	E
H	-0.20966	-0.06876	3.834114
F	-0.21041	-0.07054	3.806086
Cl	-0.21427	-0.07314	3.840373
Br	-0.21368	-0.07314	3.824318
Me	-0.20495	-0.06696	3.754929
OH	-0.19858	-0.06543	3.623225
NH2	-0.18657	-0.06112	3.413695
NH_3^+	-0.31696	-0.18297	3.646082
CN	-0.22600	-0.08588	3.812889
NO	-0.21548	-0.10664	2.961711
NO_2	-0.23094	-0.10030	3.554923
COOH	-0.21978	-0.07968	3.812345
CHO	-0.22245	-0.08643	3.701322

The frontier orbitals are depicted in Figure 5. The largest contributions of HOMO arise from the benzene moiety in X=H, Me, and the benzene moiety in X=F, Cl, CN, NH_3^+, COOH, NO_2. On the other hand, LUMO is mostly spread over the molecules (Except X=NO). There is a good correlation between E(HOMO) and E(LUMO) with σ_p for all substituent, except X= NH_3^+ (Figure 4).

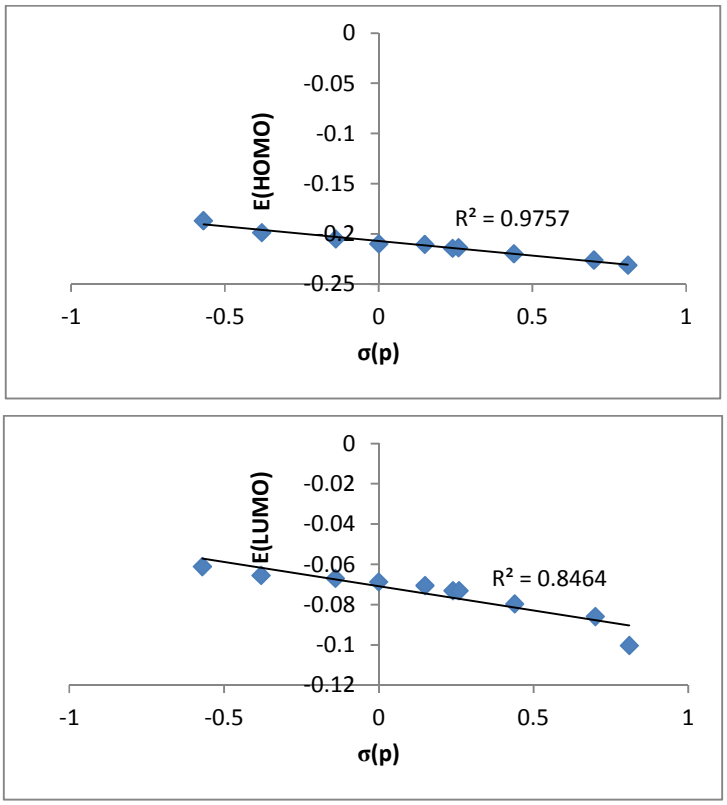

Figure 4. Frontier orbitals energiesversus Hammett constants (σp) (except for NH_3^+).

X	HOMO	LUMO
H		
F		
Cl		
Br		

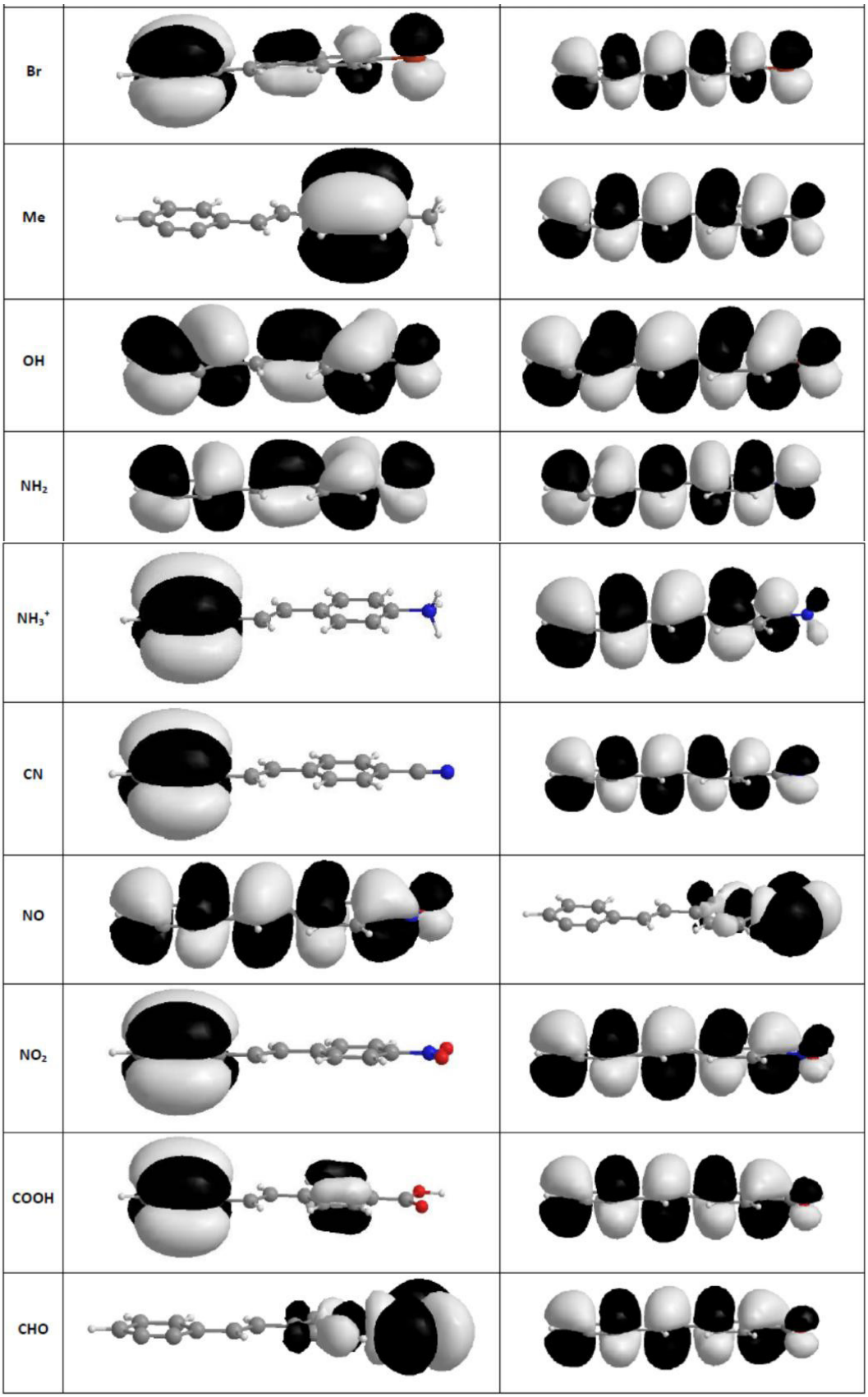

Figure 5. Representation of frontier orbitals of Benzyne-Based Chromophores with Various X-Groups.

Table 5. β components and β_{tot} values (10^{-30} esu) for Benzyne-Based Chromophores with Various X-Groups.

X	H	F	Me	OH	NH_2	CN	NO_2	COOH	CHO	NH_3^+	Cl	Br	NO
β_{XXX}	388.89	592.39	665.66	1174.41	1955.76	-498.95	-2241.24	-887.18	-1293.17	-2368.30	701.28	825.12	-2104.64
β_{XXY}	-22.71	0.04	-2.28	1.54	-62.52	-0.55	-1.98	0.81	-0.63	-1.94	-0.01	0.79	-2.81
β_{XYY}	-3.50	-3.91	-37.45	-1.68	-4.19	0.00	0.30	0.38	0.02	-37.60	-2.92	-11.96	-0.89
β_{YYY}	7.81	-0.45	5.57	-0.47	-1.45	0.26	0.04	-0.70	-0.30	3.51	-0.62	-1.68	0.35
β_{XXZ}	-317.52	-591.66	-641.04	-1167.48	-1915.85	548.50	2156.70	910.61	1219.18	2207.32	-624.98	-724.42	2158.03
β_{XYZ}	10.92	-1.46	-4.49	-1.46	53.25	1.06	0.07	0.46	1.45	-3.93	-0.90	-0.18	0.53
β_{YYZ}	21.39	-3.92	1.99	-5.82	-3.60	-4.39	-6.08	-4.73	-7.07	14.63	-5.39	5.09	-6.16
β_{XZZ}	249.99	548.37	587.23	1079.74	1724.76	-494.86	-1869.68	-783.11	-1024.11	-1995.74	567.40	661.23	-2046.07
β_{YZZ}	13.32	-1.88	-2.69	-1.65	-53.91	-6.20	-2.83	-1.95	1.09	-1.32	3.24	-2.85	-3.32
β_{ZZZ}	-186.32	-385.97	-426.77	-816.52	-1349.08	439.55	1524.63	599.91	899.28	1790.37	-459.34	-545.82	1817.23
β_{tot}	6.89E-30	1.30E-29	1.40E-29	2.60E-29	4.25E-29	1.21E-29	4.76E-29	1.94E-29	2.71E-29	5.15E-29	1.44E-29	1.68E-29	4.96E-29
$\beta_{tot}\ 10^{+}_{30}$	6.89	12.98	13.97	25.97	42.51	12.08	47.64	19.43	27.08	51.46	14.43	16.79	49.62

Hyperpolarizability

The first static hyperpolarizability (β_{tot}) values for the organic molecules are shown in Table 5. The results showed that the magnitude of the first hyperpolarizability tensor of all molecules is rather moderate, these values decrease in the following order:

$$NH_3^+ > NO > NO_2 > NH_2 > CHO > OH > COOH > Br > Cl > F > CN$$

in accordance with the electron accepting strength of subsituents. A good correlation has been shown between β_{tot} and σ(p) for X= H, F, Cl, Br, CN (Figure 6).

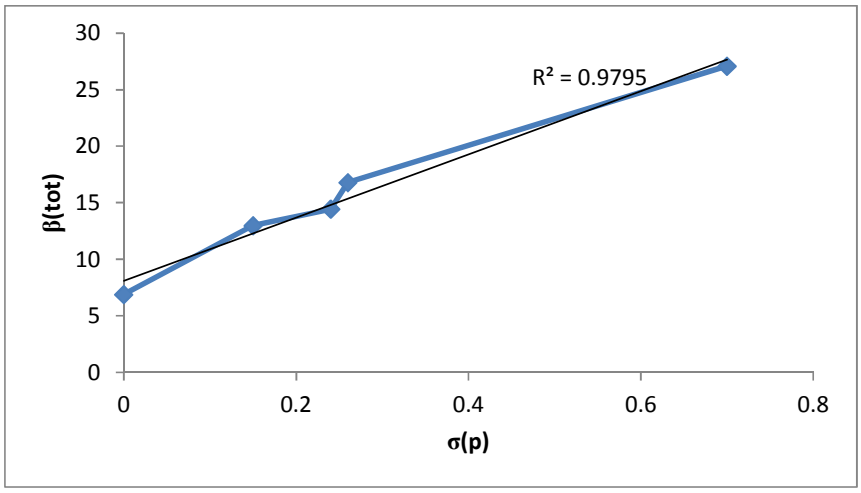

Figure 6. The first static hyperpolarizability (β_{tot}) versus and σ(p) for X= H, F, Cl, Br, CN.

There is a good correlation between β_{tot} and λ_{max} for all subtituents, except X=NH_2, NH_3^+, CN (Figure 7). The correlation suggested that this transition participate a significant role in determining β.

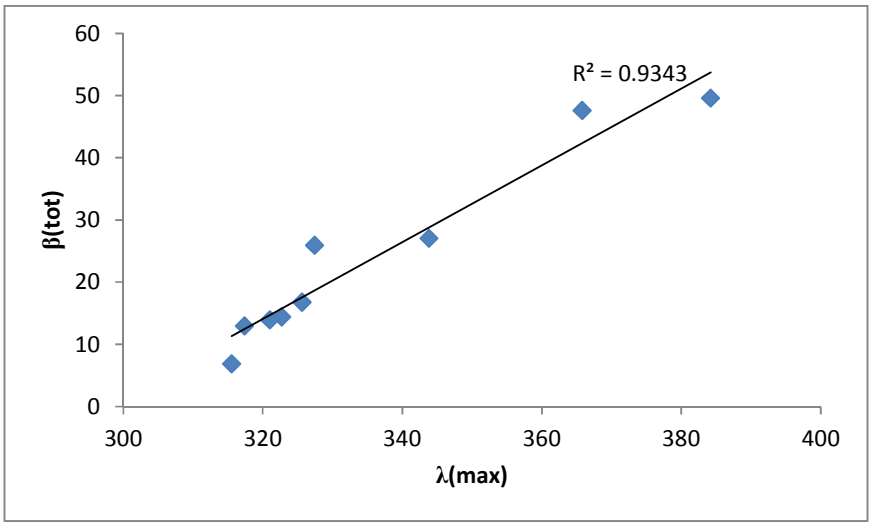

Figure 7. The first static hyperpolarizability (β_{tot}) versus λ_{max} for all subtituents, except X=NH_2, NH_3^+, CN.

On the other hand, a good correlation between BLA and β_{tot} values has been shown max for all subtituents, except X= NH_3^+, CN, NO_2, COOH (Figure 8).

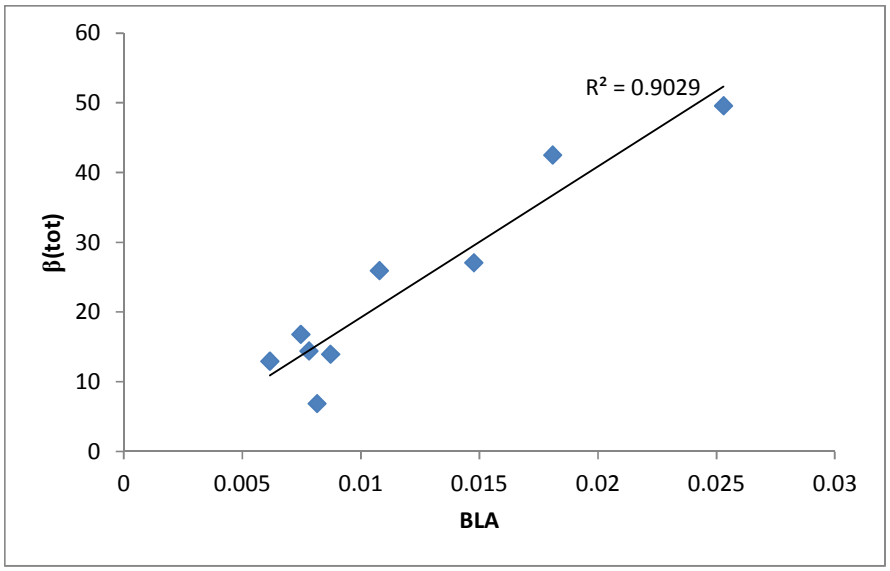

Figure 8. The first static hyperpolarizability (β_{tot}) versus BLA for all subtituents, except X= NH_3^+, CN, NO_2, COOH.

Conclusion

The electronic, structural and spectroscopic properties as well as the static first hyperpolarizabilities of the Benzyne-Based Chromophores have been investigated by means of B3LYP/6-31G (d,p) level calculations. Theoretical studies indicated donor and acceptor substituent increase first static hyperpolarizability. The good correlations have been found between β_{tot} values with BLA, λ_{max} and σ(p) for some of the substituent.

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