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Structural Properties and Nonlinear Optical Responses of Halogenated Compounds: A DFT Investigation on Molecular Modelling

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Abstract: Computational chemistry is used to evaluate structures of different compounds by using principles of theoretical and quantum chemistry integrated into useful computer programs. It is used to determine energies, dipole moments and thermodynamic properties of different compounds. The present work reports the computational study of six donor-acceptor dyes. The computational method CAM-B3LYP with 6-31G(d,p) was used in this research to determine the effect of halogens on non-linear optical compounds. HOMO-LUMO energy gaps, dipole polarizabilities, first hyperpolarizabilities, and absorption spectra of six studied compounds (**dye 1**: 4-(2-(4-fluorophenyl)ethynyl)benzenamine; **dye 2**: 4-(2-(4-chlorophenyl)ethynyl)benzenamine; **dye 3**: 4-(2-(4-bromophenyl)ethynyl)benzenamine; **dye 4**: 5-(2-(4-fluorophenyl)ethynyl)benzene-1,2,3-triamine; **dye 5**: 5-(2-(4-chlorophenyl)ethynyl)benzene-1,2,3-triamine; **dye 6**: 5-(2-(4-bromophenyl)ethynyl)benzene-1,2,3-triamine) with aniline and halo phenyl segments were computed by using density functional theory (DFT) and time-dependent density functional theory (TDDFT). Results indicate that all dyes showed wavelengths of maximum absorbance in the visible region. Small HOMO-LUMO energy gaps were observed in all investigated dyes. The present calculations on these dyes (1-6) offer an understanding of the direction of charge transfer (CT) and how NLO behavior can be explained. The aniline-to-halo phenyl CT, caused by the combination of the donor amino group and the acceptor halo group, could be a reason for NLO behavior of these sorts of compounds. These compounds exhibit significant molecular second-order NLO responses, especially dyes (6) and (5), with second-

order polarizability determined to be approximately 4600 a.u.

Keywords: DFT; hyperpolarizability; NLO compounds; Halogens; Amino group.

1 Introduction

Computational chemistry is the branch of chemistry that uses the results of theoretical chemistry to solve computer related problems of chemistry. It is a helpful way to investigate materials that are too difficult to purchase or are unstable. This discipline also involves analytical theory, which deals with the performing of simulations using fundamental equations that are derived from the Schrodinger equation or from classical mechanics. Computational chemistry also has to do with obtaining the equations that relate laboratory data (e.g., heat capacities, spectra, reaction cross-sections, phase diagrams, conductivity) to molecular properties (e.g., geometries, activation energies, bond energies, energy levels, intermolecular potentials). This analytical side of theory is also where the equations of statistical mechanics that correlate macroscopic properties of matter to the microscopic properties of the constituent molecules are constructed [1-7].

Donor (D)-acceptor (A) substituted organic molecules with large second-order nonlinear optical (NLO) properties have been the emphasis of many research efforts due to their possible applications in areas such as optical memory, molecular switching, optical modulation, and frequency doubling [8-11]. A key objective in the progress of materials for nonlinear optical applications is to find highly active materials with large second-order polarizabilities (β). The first hyperpolarizability and, hence, the second-order NLO response is related to an electronic intramolecular charge transfer (ICT) within the molecule. Both theoretical and experimental studies have shown that large hyperpolarizabilities generally arise

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from the merger of a strong electron donor and acceptor positioned at opposite ends of a suitable conjugation path [12-19]. Thus, a variety of donor-acceptor organic molecules containing different acceptor units have been reported previously [20-31]. However, the structure-property relationship indicates that the β value also increases with π -conjugating length [32-34]. On the basis of experimental and theoretical explorations, the design of molecule with good second-order NLO properties has primarily focused on the following points: (a) the planar D- π -A model [35], (b) bond length alternation (BLA) theory [36], (c) auxiliary donors and acceptors model of heterocycle [37-39], and (d) twisted π -electron systems [40-42].

The successes of these approaches encouraged the calculation of the large second-order NLO responses for the halogenated D-A dyes studied in this article. The bridge mediated donor-acceptor electron interaction is large enough to maximize the strength of the transition matrix element (associated with the oscillator strength) of the charge-transfer transition. Thus, computational approaches are of high interest in the field of nonlinear optics dealing with π -systems and halogens. Here, for the first time, the detailed DFT calculations and electronic and nonlinear optical responses of amino and halogenated D-A compounds are reported. This work may deliver useful results in developing new amino-halogenated NLO compounds.

2 Methods of calculation

When a molecule is placed in a uniform static electric field, its electronic energy can be written as a series involving coefficients identified as permanent multi-pole moments and polarizabilities (Eq. 1)

$$E = E^0 - \mu_i F_i - \frac{1}{2} \alpha_{ij} F_i F_j - \frac{1}{6} \beta_{ijk} F_i F_j F_k - \frac{1}{24} \gamma_{ijkl} F_i F_j F_k F_l \quad (1)$$

Where F_i , F_j , etc. denote the field at the origin.

The Gaussian 09 program package [28] was used to perform all calculations. All systems were optimized using density functional theory (DFT). CAM-B3LYP level of theory with 6-31G(d,p) basis set was adopted for geometry optimization, calculation of non-linear optical properties and UV/Vis spectra. This computational approach has been used successfully to study the non-linear optical properties of investigated dyes (1-6). Absorption spectra of dyes were simulated by using time dependent density

functional theory (TDDFT) calculations at CAM-B3LYP level of theory. DFT functional and basis sets are reliable, as these were used in our previous published data, where experimental parameters were reproduced by using the same basis sets [16-18]. Ten lowest singlet-singlet excitation energies were computed. Symmetry constraints are not considered in all calculations. The following formulas are used to calculate average polarizability.

$$\alpha = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3} \quad (2)$$

The output file of the Gaussian 09 program contains the following ten hyperpolarizability (β_{tot}) components: β_{xxx} , β_{xxy} , β_{xyy} , β_{yyy} , β_{xxz} , β_{xyz} , β_{yyz} , β_{zzz} , β_{zxx} and β_{zyy} . The relationship between hyperpolarizability and these components is given in following formula:

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

The use of functional and basis sets for the studied organic compounds (with a halogen group as acceptor and an amino group as donor) were inspired by previously published work [16-18].

Ethical approval: The conducted research is not related to either human or animal use. Yes. Agreed

3 Results and discussion

3.1 Dye structure

The dye structures studied in the present research work are shown below

3.2 Dipole Polarizabilities

To gain an idea about the second-order polarizability (β), it is important to have some knowledge of dipole polarizability (α). The coefficients of dipole polarizabilities for dyes (1-6) were calculated using equation 2, and the results are listed in Table 1.

Due to C_{2v} symmetry, α_{ii} ($i=x, y, z$) are not zero. The α_{xx} component has the highest value among α_{ii} components. However, the α_{xy} and α_{yz} constituents are less important. Therefore, the characteristics of systems 1-6 are

Figure 1: Structures of investigated dyes (1-6).

Table 1: Computed dipole polarizabilities (a.u) for dyes (1-6) at CAM-B3LYP level of theory with the 6-31G(d,p) basis set.

Dye	α_{xx}	α_{xy}	α_{yy}	α_{xz}	α_{yz}	α_{zz}	$\langle\alpha\rangle$
1	348.26	-10.00	170.01	3.00	4.00	62.21	193.49
2	390.89	-25.16	172.67	7.08	8.87	64.74	209.43
3	404.44	-26.27	173.33	-6.52	18.55	65.08	214.28
4	340.71	-13.89	167.09	-4.94	19.81	50.81	186.2
5	383.43	-13.05	169.80	-6.12	-5.70	53.33	202.19
6	396.92	-17.09	170.45	1.23	-16.78	53.68	207.02

predominantly calculated by transitions in the x-direction, so the formula in the x-direction can be written as shown below:

$$\alpha \propto \frac{(M_x^{gm})^2}{E_{gm}} \quad (4)$$

In the above equation (4), alpha is directly related to the transition moment and is directly proportional to 1/Energy of transition. Consequently, the system with a robust electronic absorption would acquire a bigger α value. The transition wavelengths (λ_{gm}), transition moment (M_x^{gm}) and related frontier molecular orbital (FMO) of studied systems 1-6 are given in Table 4. Average polarizability (α) decreases in the order $6 > 5 > 3 > 2 > 1 > 4$, as shown in Table 1.

3.3 HOMO-LUMO analysis

The HOMO-LUMO band gap is an important value for understanding the reactivity index [43, 44]. In TDDFT studies, the electron transitions of dye 1 mainly localized around the π -spacer (HOMO) to (LUMO) along the x-direction. A similar phenomenon happens on dye 2 from HOMO to LUMO, dye 3 from HOMO to LUMO and alike configuration in dyes 4, 5, and 6. The frontier molecular orbitals taking part in the main electronic transitions in

dyes 1-6 are given in Figure 2. The transition of system 6 is valuable, as it shows the leading NLO value. With C_{2v} symmetry restraints, the transitions are the singlet A1 along the x-direction. In these systems (1-6), the main transitions have an A1 symmetry value. Though the alterations of structures in molecules adjust the involvement of various orbitals to the transitions, major electronic transitions for the investigated compounds have symmetry that can be denoted as A₁; it is vital that CT coins from the methyl aniline to the halo phenyl segment along the direction of the x-axis. These patterns point out that the halo phenyl fragment is working as an acceptor and methyl aniline is behaving as a donor. In dye 1, methyl aniline is working as a donor while halo phenyl is serving as an acceptor via pi-conjugated connections.

The CT of dye 2 starts from the methyl aniline and connects to the halogen group (-X) through a conjugation bridge consisting of an ethylene fragment. For dye 3, the amino group (-NH₂), a strong donor at the end of organic ring, transfers charge density towards the halogen group. Dyes 4, 5, and 6 confirm that the halogenated phenyl fragment works as an acceptor and pi-conjugated connection as well when an amino moiety (-NH₂) is added on the outside side of the aniline ring. The bonding behavior between the halo phenyl and methyl aniline showed that a strong triple bond can be formed through C $\rightarrow$ C σ -donation, C $\rightarrow$ C π -donation and π -back donation in the formation of the various compounds. This strong interaction between σ -overlap and π -overlap produces a sturdy electronic connection between halo phenyl and methyl aniline.

In systems/compounds 1 to 6, resonance of π -electrons between phenyl rings has been increased with the involvement of the C $\equiv$ C triple bond, and the C-C π -bond is not localized but instead takes part in conjugation of the two phenyl/organic rings. So π -conjugation and delocalization are increased from system 1 to system 2 through the addition of the chlorine electron acceptor. This electron withdrawing group helps to increase the amount of CT by lowering the transition energy. Thus, a substantially higher β_{tot} value has been produced in system 2 relative to system 1. The conjugation has been lengthened in systems 4, 5, and 6, which leads to a lower transition energy and higher CT. In the HOMO-LUMO of systems 1-6, the methyl aniline can modify the HOMO and spread its π -electronic conjugation to the end of phenyl ring in the halogenated phenyl fragment, which enhances the CT from the methyl aniline to the halogenated phenyl segment of the molecule.

Figure 2: HOMO-LUMO transition plot and corresponding energy difference of dyes (1-6).

Table 2: Calculated HOMO-LUMO energy values and corresponding energy gaps.

Dye	HOMO	LUMO	Energy Gap
1	-4.962	-0.877	4.085
2	-5.036	-1.043	3.993
3	-5.005	-1.011	3.994
4	-4.703	-0.868	3.835
5	-4.764	-1.034	3.730
6	-4.74	-1.003	3.738

3.4 The second-order polarizabilities

The first hyperpolarizability, or second-order polarizability (β_{tot}), relates to the second-harmonic generation (SHG). Accordingly, β_{tot} of the methyl aniline, with its dipole moment along the x-axis, can be expressed in following equation;

$$\beta_{\text{tot}} = \frac{1}{3} \sum_{i=xyz} (\beta_{xii} + \beta_{ixi} + \beta_{iix}) \quad (5)$$

The second-order polarizability is denoted as the zero-frequency hyper-polarizability and is an approximation

of the core molecular hyperpolarizability without consideration of resonance effects. There are seven tensors of the second-order polarizability in molecules with C_{2v} symmetry. The β_{xxx} tensor has the most significant value. Therefore, the majestic part and the main charge transfer are also in the direction of x-axis. As given in Table 3, all systems under study have high values of second order polarizability tensors. This correlation suggests that all of the studied systems, other than system 1, have strong second-order NLO prospects. In system 1, the D-A-A layout, the CT can be observed from HOMO to LUMO. Here, the NH_2 works with fluoro group (F) and, due to electron-donating power of NH_2 and electron accepting behavior of F, the CT design is towards the F, resulting in a relatively low NLO value (see Table 3).

The direction of CT is along x-axis in systems 1-6, and the values of β_{tot} of these systems show that NLO behavior is decreasing in the order $6 > 5 > 2 > 4 > 1 > 3$. The β_{xxx} value of system 2 is more than that of system 1 due to presence of a nitro group, which suggests a D-D-A arrangement. The β_{zzz} value of system 4 is higher than that of system 3, leading to a D-D-A-A arrangement. System 3 shows minimal β_{xxx} and β_{tot} values due to poor CT.

The addition of a chlorine electron acceptor at the end of phenyl/organic ring in system 2 enhances the donating power. System 5 has a reasonably high NLO value because of the strong power of the NH_2 . There are three NH_2 moieties surrounding the phenyl ring and a chloro (-Cl) moiety competing on the opposite end. Thus, the β_{tot} value is increased from 3570.49 a.u in system 4 to 4527.82 a.u in system 5. System 6 has the highest NLO value of all six systems, as the donating power of aniline has been increased by adding three amino groups on the outside of the phenyl/organic ring, which indicates that addition of an amino group ($-\text{NH}_2$) on the outside of aniline and an electron acceptor (in this case, bromine) at the end of the phenyl ring concurrently is an important way to induce high nonlinearity. System 6 is an excellent example, as compared to systems 4 and 5, as it exhibits the highest NLO value among all tested systems because it has a D-D-A-A pattern. This latter result confirms our idea that aniline is working as a donor in the compounds under study.

The three amino groups ($-\text{NH}_2$) at the outer side of the aniline ring (see dye 6) increased CT and NLO value. The NLO responses of all the systems have been altered through the increase of the pi-conjugation length and by using donors and acceptors. Principally, the NLO values have been tuned by the addition of the donors on the outside of the aniline ring. This addition of donors is useful as it boosts the degree of CT by lowering the excited energy level, which leads to a significant increase in the first

Table 3: Computed second-order hyperpolarizabilities and their individual components for dyes 1-6.

dyes	β_{xxx}	β_{xxy}	β_{xyy}	β_{yyy}	β_{xxz}	β_{yyz}	β_{xzz}	β_{zzz}	β_{tot}
1	-3076.19	0.001	-45.27	60.00	-10.05	10.00	56.60	0.014	3178.69
2	3964.94	-0.032	93.41	78.000	-30.01	12.51	59.96	-11.8	4119.64
3	-27976.6	-534.35	929.3	106.6	-43.10	-3.67	76.86	-9.41	2899.02
4	-3380.21	-171.20	-171.2	43.86	12.373	0.59	11.97	-9.99	3570.49
5	4355.55	-312.33	126.88	73.60	36.72	13.30	-27.84	11.97	4527.82
6	-4293.19	-204.78	-117.3	70.78	30.14	-44.67	156.12	12.23	4576.57

hyperpolarizability. This effect is observable in system 6, which has a β_{tot} value of 4576.57 a.u. To better understand the basis of the second-order NLO phenomenon of the studied compounds, a determination of the structure-property relationship is also important. How does the structure lead to changes in the determined β_{tot} values? From the complex sum-over-states (SOS) formulation, the two-state model that expresses low-lying charge transfer transition has been studied. In this case, the following relation can be used to note CT.

$$\beta_{CT} = \frac{\Delta\mu_{gm} f_{gm}}{E_{gm}^3} \quad (6)$$

For any non-centro-symmetric system, the small value of the transition energy (<1 a.u.) is the critical element for the large NLO response. Therefore, for the studied compounds, a low excitation energy is likely the critical element leading to large β values. As can be seen in Table 4, the λ_{gm} values are related to the structural arrangement within the studied compounds. The λ_{gm} values increase in the order system $1 < 2 < 3 < 4 < 6 < 5$. The λ_{gm} value of system 1 is only 298.05 nm, while it is larger for systems 4 (305.84 nm) and 6 (313.03 nm), and a bit larger still for system 5 (313.12 nm). The red shift of the absorption band relates the addition/alteration of a donor and acceptor. Interestingly, the excitation energy will have a tendency to make a prevailing impact on the β_{tot} values of the studied compounds. A low energy value is a vital element in the value; as has been noted in systems 1-6, a low transition energy is a crucial factor to the determination of the NLO response, as shown in Table 4.

3.5 Absorption analysis

The absorption spectra, including λ_{max} , and molecular orbitals involved in transitions state were calculated for

Table 4: Excitation energies (λ_{gm} , nm; E, a.u.), oscillator strengths (f_{gm}) and corresponding dominant MO Transitions of Systems 1-6.

Dye	λ_{max}	E_{gm}	f_{gm}	MO transition
1	298.05	4.16	1.257	HOMO→LUMO (92%)
2	304.91	4.07	1.359	HOMO→LUMO (91%)
3	305.11	4.06	1.405	HOMO→LUMO (91%)
4	305.84	4.05	1.089	HOMO→LUMO (90%)
5	313.12	3.96	1.177	HOMO→LUMO (89%)
6	313.03	3.96	1.220	HOMO→LUMO (89%)

all six dyes by CAM-B3LYP/6-31G(d,p) in gas phase and in methanol solution. The calculated absorption spectra (λ_{max}) of dyes were found in the range of 270-350 nm. UV-Vis absorption spectra of dyes are shown in Figure 3. The spectra of dyes are red-shifted in the gas phase: the λ_{max} shifted from 298 in methanol to 313 nm in the gas phase. The overall spectral red-shift was in the following order: dye-6 > dye-5 > dye-4 > dye-3 > dye-2 > dye-1. This order is reverse of the order of the HOMO-LUMO energy gap. Dyes that have low energy gaps require less energy for electronic transitions. Low energy transitions result in red shifted absorption wavelengths. These dye are also environment friendly because they absorb in the UV region, which should mitigate a primary cause of global warming [45,46].

The UV-Visible spectra of the dyes is given in Table 4. The experimental spectra for such types of dyes possess peaks at the range of 240 nm to 300 nm wavelength [47]. The experimental spectra of such types of dyes, then, are in close agreement with simulated spectra, ranging from 298 nm to 313 nm.

4 Conclusions

The compounds with the lesser transition energy values have longer wavelengths, exhibited by the high ratio of

Figure 3: Simulated absorption Spectra of dyes (1-6) calculated in gas phase at DFT/CAM-B3LYP/6-31G(d, p) level of theory

beta. The studied systems that have amino donors and halogen acceptors have considerably large values of second-order polarizabilities. Detailed studies of HOMO-LUMO orbitals show that the CT from aniline donor to halo acceptor group plays a practical role in the NLO response. As per the two-state model, a small excitation energy value is a primary contributor to large values of beta.

Following points can be summarized after this theoretical study:

1. Structure-property interactions are critical, and this study provides several strategies to increase NLO responses.
2. The addition of an electron acceptor group (-X) at the termination of phenyl/organic ring leads to a greater value, as it creates a D – A – A arrangement.
3. The most important way to increase optical nonlinearity was seen in system 6, where a D-D-A-A arrangement coupled with the donating power of aniline substantially increased the NLO response. The involvement of an amino donor on the outside of aniline and a halogen electron acceptor on the terminal part of the organic ring led to a significantly larger value of beta.
4. System 6 is an excellent example of a D-D-A-A structural layout as it shows the maximal NLO response among all the studied systems.
5. Dyes with donor-acceptor configurations can become an excellent kind of material in the second-order NLO field. The present calculations on these dyes give us an understanding of the direction of CT and reason for NLO properties. The charge transfer from aniline to halogenated phenyl could be a vital factor explaining the NLO properties of such compounds.

Conflict of Interest: This manuscript has not been published previously and is not under consideration for publication in another journal at the time of submission. There is no conflict of interest as well.

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