

Density Functional Theory Predictions of the Nonlinear Optical (NLO) Properties in Triphenylamine based α -Cyanocinnamic Acid Compounds: Effect of Fluorine on NLO Response

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Abstract. In this study, the energy gaps, second-order nonlinear optical (NLO) properties and dipole polarizabilities of triphenylamine based α -cyanocinnamic acid acetylene derivatives have been investigated by employing time-dependent density functional theory (TD-DFT). These compounds were designed theoretically by substitution of fluorine (F) atom at different positions of phenyl ring of the α -cyanocinnamic acid segment. The results have indicated that the systems substituted by fluorine show remarkable NLO response, especially D4 system with static second-order polarizability (β_{tot}) computed to be 70537.95 (a.u). Hence, these compounds have the likelihood to be an excellent second-order nonlinear optical compounds. The β_{tot} value suggests that along the x-axis the charge transfer (CT) from triphenylamine to α -cyanocinnamic acid (D-A) plays a key role in NLO response; whereas α -cyanocinnamic acid acts as an acceptor (A) and triphenylamine acts as a donor (D) in all the studied compounds (D0-D4). Incorporation of an electron acceptor (F) at the end phenyl ring of the α -cyanocinnamic acid segment increases the β value. The LUMO-HOMO energy gaps of all dyes have been found smaller which results in large NLO response. The present investigation therefore provides an important insight into the remarkably greater NLO properties of α -cyanocinnamic acid and triphenylamine attached via acetylene.

Keywords: DFT; Nonlinear Optics; Molecular modeling.

Resumen. En este estudio, las brechas de energía, las propiedades ópticas no lineales de segundo orden (NLO) y las polarizabilidades dipolares de los derivados de acetileno del ácido α -cianocinámico a base de trifenilamina se han investigado empleando la teoría funcional de la densidad dependiente del tiempo (TD-DFT). Estos compuestos se diseñaron teóricamente mediante la sustitución del átomo de flúor (F) en diferentes posiciones del anillo fenilo del segmento del ácido α -cianocinámico. Los resultados han indicado que los sistemas sustituidos por flúor muestran una notable respuesta NLO, especialmente el sistema D4 con una polarizabilidad estática de segundo orden (β_{tot}) calculada para que sea 70537.95 (a.u). Por lo tanto, estos compuestos tienen la probabilidad de ser un excelente compuesto óptico no lineal de segundo orden. El valor de β_{tot} sugiere que a lo largo del eje x la transferencia de carga (CT) de la trifenilamina al ácido α -cianocinámico (D-A) desempeña un papel clave en la respuesta NLO; mientras que el ácido α -cianocinámico actúa como un aceptor (A) y la trifenilamina actúa como un donante (D) en todos los compuestos estudiados (D0-D4). La incorporación de un aceptor de electrones (F) en el extremo del anillo fenilo del segmento de ácido α -cianocinámico aumenta el valor β . Los huecos de energía LUMO-HOMO de todos los tintes se han encontrado más pequeños, lo que resulta en una gran respuesta NLO. Por lo tanto, la presente investigación proporciona una visión importante de las propiedades NLO notablemente mayores del ácido α -cianocinámico y la trifenilamina unidas a través del acetileno.

Palabras clave: DFT; No-lineal; Modelado Molecular.

Introduction

Organic non-linear optical (NLO) materials during last two decades are subject of considerable research owing to their potential applications in optoelectronic technologies field for optical switching, signal processing, information storage and telecommunication [1, 2].

Organic compounds are widely focused as NLO materials due to their fabrication ease, low cost, facile synthesis and tailoring ability thus tuning their structure chemically according to desired properties of NLO [3]. Owing to recent developments in NLO field, second-order based NLO materials are finding practical applications due to combination of various synthetic strategies and their chemical tenability [4]. Intramolecular charge transfer (ICT) basically influences NLO material properties which originate mainly because of acceptor to donor moieties linked via π -conjugated bridge [5-8]. High performance NLO materials can be designed via modification of substituent's properties such as acceptor, donor or π -conjugated bridge within acceptor- π -conjugated bridge- donor systems [9, 10].

Singer et al. in 1989 explored organic NLO molecule series with π -conjugation. They advocated property-structure relationship which affects β because of substituents, molecular configuration, π -conjugation system length and its type [11,12].

Janjua et al. in 2010 used quantum chemical methods for investigating halogen atoms effect on dipole polarizabilities and NLO second order response of hexa-molybdates derivatives like organoimido. It has been studied that NLO second order response of fluorine can be tuned due to its electron withdrawing ability [13]. Janjua et al. 2010 computed β value of terpyridine substituted hexamolybdates by studying halogens effect on NLO properties. The increase in computed β value is due to halogens incorporation (F, Br, I and Cl) in terpyridine ligand at the terminus [14].

An NLO response exhibit by organic compounds is often superior to those of pure inorganic materials [15,16]. Therefore, in this field organometallic compounds possessing NLO properties have opened new doors of achievement whereas search of new materials with greater NLO response are still in progress. Recently, POM-based inorganic-organic hybrid materials with large NLO properties have made great progress [17]. Janjua et al. concluded different results by studying electron withdrawing group effects on hexamolybdates and thus determined following aspects:

- The NLO second-order response can be enhanced remarkably via introducing electron acceptors at terpyridine-substituted hexamolybdates end which is attributed to increase in charge transfer between hexamolybdate and terpyridine.
- The large nonlinear second-order response is obtained via immediate introduction of CN and CF₃ at the terpyridine-substituted hexamolybdates end.
- The compounds containing CN and CF₃ exhibits larger second- order polarizabilities as compared to those having Cl and F.
- These compounds when electrons transition occurs to crucial excited states can turned to be an excellent 2-dimensional NLO candidates. It is due to off-diagonal second-order polarizability tensor (β_{zyy}) which originates via contribution of y polarized transition.
- One of advantageous features of acceptors is that they contributes in enhancement of NLO response by strengthening bridge conjugation [9].

For obtaining better nonlinear optical properties, LUMO-HOMO energy gap should be low. By increasing conjugation energy gap between LUMO and HOMO can be decreased. Another strategy used for lowering energy gap is structural modification. Similarly, more fluorine (F) atoms incorporation also results in decreasing LUMO-HOMO energy gap [18].

The NLO properties of acetylene derivatives (triphenylamine based α -cyanocinnamic acid) have been examined in this article. The author has designed triphenylamine based α -cyanocinnamic acid derivatives of acetylene via incorporation of fluorine (F) atom/atoms at phenyl ring of α -cyanocinnamic acid segment (see Fig. 1). Where, α -cyanoainnamic acid and triphenylamine act as acceptor (A) and donor (D) respectively. Effect of Fluorine atom on absorption and NLO properties has been tested by using density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations. It is anticipated that obtained results may open a new gateway in providing useful mean for designing triphenylamine- α -cyanocinnamic acid segment based NLO compounds with tunable performance.

Computational details

Optimization of dyes structure in gas phase have been done via using B3LYP functional and 6-31+G* basis set [19]. Gaussian 09 program package was used for performing all calculations with the help of 10^{-8} integration grid and convergence criteria (SCF 10^{-8} au) [20]. However, frequency calculations have been performed for verification of optimized molecule's nature [21,22]. Frequency analysis was performed to confirm that all structures in potential energy surfaces are present at local minima and there is no presence of imaginary frequency. Therefore, choosing appropriate functional absorption spectra of such organic dyes are calculated carefully. Coulomb-attenuating method CAMB3LYP functional, which is long-range corrected form of B3LYP, was used to calculate absorption spectra of dyes.[19] Success of this functional for determination of transition energies for a series of organic dyes is already proven.[23] The absorption spectra of the dyes were simulated by TD-DFT. Solvent effect (acetone) was undertaken using conductor-like polarizable continuum model (CPCM).[24]

Reproducible results of material's optical properties are obtained using TDDFT/ DFT computational methods [25-29]. For studying acetone effect as solvent, CPCM (conductor-like polarizable continuum) model has been used [24]. Equation (1)[30] has been used for calculating average polarizability (α):

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

Ten hyperpolarizability (β_{tot}) components shown by Gaussian 09 program output file are as follows: β_{xxx} , β_{xxy} , β_{xyy} , β_{yyy} , β_{xxz} , β_{xyx} , β_{yyz} , β_{xzz} , β_{yzz} and β_{zzz} . Equation (2) represents the relation between these components and hyperpolarizability as under:

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

Molecular geometry

Substituted acetylene systems are used in this research. Two compounds such as α -cyanocinnamic acid and triphenylamine are used for substitution of acetylene. Fig. 1 shows the structures of these compounds D0-D4. Triphenylamine with formula $(\text{C}_6\text{H}_5)_3\text{N}$ is an organic compound which as compared to most amines is non-basic in nature. Triphenylamine derivatives exhibit useful properties in electro-luminescence, electrical conductivity [31] and as hole-transporters in OLEDs [32].

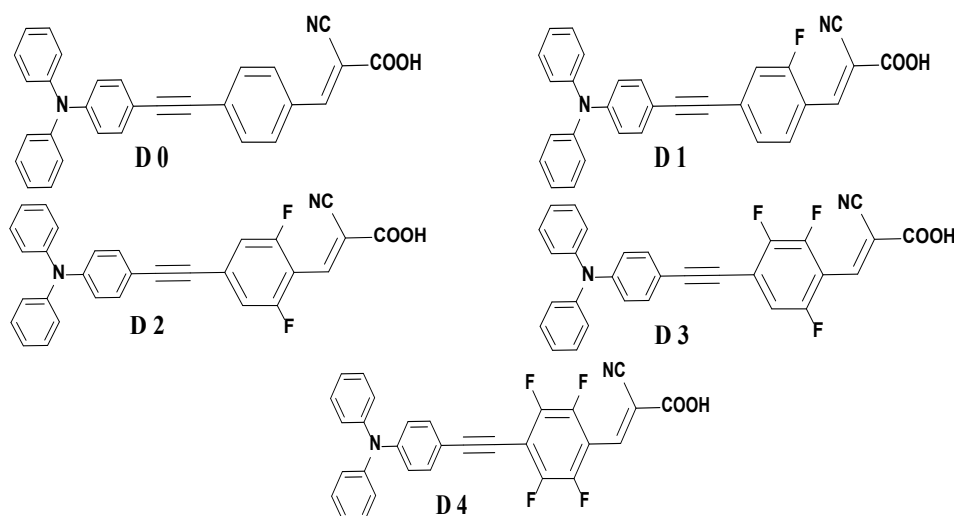


Fig. 1. Structures of D0-D4

Results and discussion

Effect of Fluorine (F) on LUMO and HOMO Energy Gap

LUMO and HOMO frontier molecular orbital's determines molecular reactivity. Whereas, molecule's chemical reactivity depends upon frontier energy gap as molecule becomes more polarizable with small energy gap. However, LUMO stabilization was higher which means LUMO energy decreased greatly as compared to HOMO. Hence, it results in lowering the energy gap between LUMO and HOMO. Table 1 shows calculated LUMO-HOMO energy gaps of D0-D4 are in following order; $D4 < D1 < D0 < D3 < D2$.

Table 1: HOMO, LUMO and energy gap (eV) of D0-D4.

Systems	HOMO	LUMO	Energy Gap
D0	-5.206	-2.678	2.528
D1	-5.273	-2.760	2.513
D2	-5.277	-2.655	2.622
D3	-5.290	-2.761	2.529
D4	-5.304	-2.864	2.440

The energy gap of D3 and D2 systems is greater than D0 system whereas that of D4 and D1 is less than that of D0 system (the un-substituted system). Thus, D2 system is highly stabilized as compared to all other compounds. Largest energy gap is exhibited by D2 and smallest by D4. And with first fluorine substitution decrease in energy gap was observed. However, energy gap increases with second fluorine atom substitution and with third fluorine atom substitution, energy gap increases further. But remarkable decrease in energy gap is observed with subsequent substitution of fourth F atom.

Dipole Polarizability

Dipole polarizabilities are of important consideration for having better understanding of NLO second-order response (β). The average polarizability exhibits three major components i.e. α_{xx} , α_{yy} and α_{zz} . Equation 3 is used for calculation of average polarizability (α_0) and obtained results are shown by Table 2.

Table 2: The computed dipole polarizabilities (a.u) of systems D0-D4.

Systems	α_{xx}	α_{yy}	α_{zz}	α_0
D0	985.55	333.04	178.82	499.14
D1	993.21	333.29	179.93	502.14
D2	912.62	337.74	179.19	476.52
D3	929.74	338.55	180.04	482.78
D4	944.44	339.77	180.99	488.40

Table 2 shows components of dipole polarizability calculated for D0-D4. The (α_{xx}) component exhibits maximal value in studied compounds. That is why the property of studied compounds is determined dominantly via x -axis transition. Following formula is used for dipole polarizability along x -direction.

$$\alpha \propto \frac{(M_x^{\text{gm}})^2}{E_{\text{gm}}} \quad (3)$$

Where, in above equation α_{xx} relates directly to transition moment and inverse relation to transition energy. According to analysis of TDDFT, the generation of crucial excited state in D0-D4 occur along x -direction. Fig. 2 depicts frontier molecular orbitals.

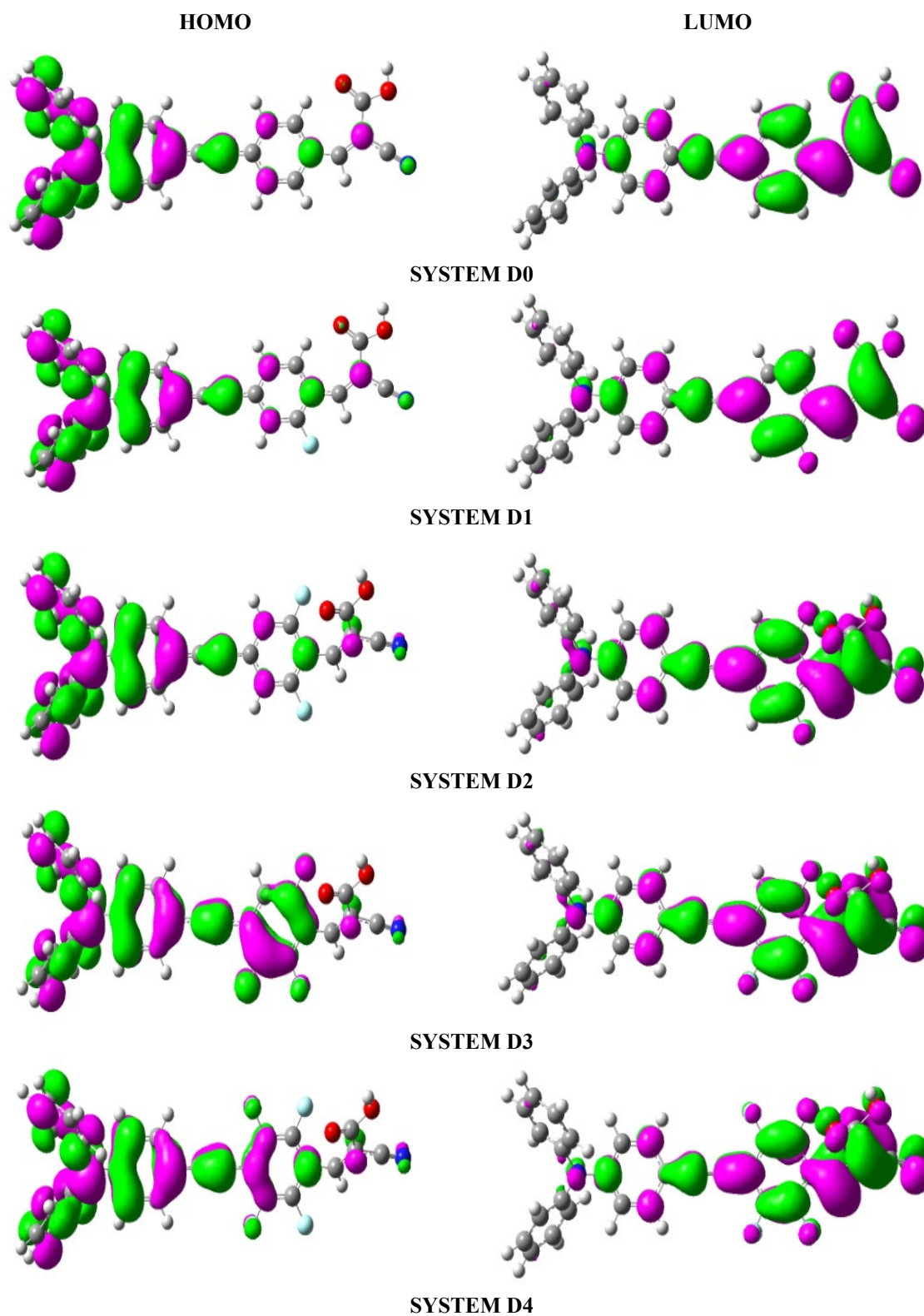


Fig. 2. HOMO and LUMO orbitals of D0-D4 calculated by employing CAM-B3LYP functional.

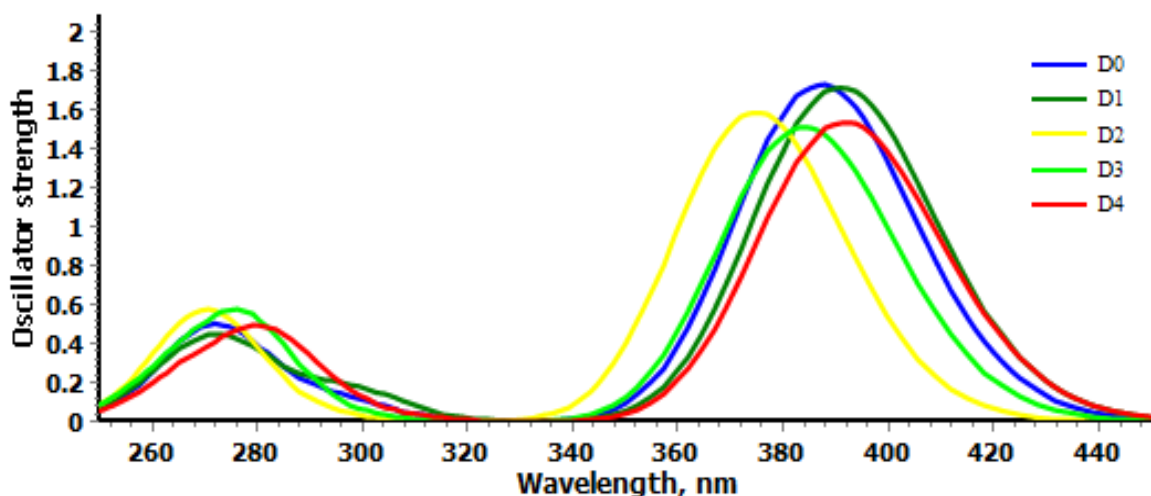


Fig. 3. UV-Vis Spectrum of D0–D4.

Fig. 3 shows that D3 and D2 possess blue shift whereas D1 exhibits bathochromic shift and D4 system shows no change in the λ_{max} .

Static Second Order Polarizability.

Second-harmonic generation (SHG) is related to second-order polarizability. The static second-order polarizability (β_{tot}) is defined as hyperpolarizability with zero-frequency and is therefore an estimate of molecular intrinsic hyperpolarizability in resonance effect. Individual components of D0–D4 and computed values of β_{tot} are given in Table 3. Owing to C_1 symmetry, the second-order polarizability possesses ten components. It is evident from Table 3 that largest value is shown by β_{xxx} component in all studied compounds. Therefore, β_{xxx} component mainly contributes for second-order polarizability and major transfer of charge is along the x-direction. According to Table 3, it is clear that D0–D4 exhibit larger coefficients of second-order polarizability. For instance, the β_{tot} computed value for D4 is greater than average second-order polarizability of all D0–D3. Therefore, it indicates that except D3 and D2 all are showing excellent NLO second order response. Due to charge transfer from HOMO to LUMO the transition is assigned in system D3 and D2 (D- π -A configuration).

Table 3: The Computed hyperpolarizabilities (a.u) of D0–D4

System	β_{xxx}	β_{xxy}	β_{xyy}	B_{yyy}	β_{xxz}	β_{xyz}	β_{xzz}	β_{tot}
D0	-66312.19	-1567.89	882.49	217.35	-532.10	-144.81	49.00	65396.08
D1	-68670.21	-803.72	926.50	245.35	-191.70	-141.87	70.95	67674.93
D2	-56755.17	-1369.73	949.26	271.29	29.12	181.34	113.45	55703.17
D3	-64027.63	-1172.20	971.58	293.37	114.51	172.52	94.50	62967.51
D4	-71538.75	-1512.33	924.05	273.60	5.55	159.941	87.50	70537.95

In D0–D4, due to CT along x-axis, the β_{tot} computed values indicate decrease in NLO response as follows: D4 > D1 > D0 > D3 > D2 whereas, calculated LUMO–HOMO energy gaps of D0–D4 are in following order; D4 < D1 < D0 < D3 < D2.

In D1 system, the β_{xxx} component is greater as compared to D0 system because of fluorine atom presence and D-A-A configuration establishment. β_{xxx} largest value is shown by D4 system. Among all five compounds, D4 system exhibits highest NLO response which is attributed to enhancement in α -cyanocinnamic acid donating ability (It is due to incorporation of four F atoms at outer side of benzene ring which in turns favors the conclusion that F atom substitution is important for enhancing the optical nonlinearity). According to Tables 1 and 4, it is interesting to note that a correlation exists between HOMO-LUMO gaps and β values; lower is the gap, higher is β . In (D0-D4) studied compounds, demonstrating the structure-property relationship is mandatory to throw light for origin of NLO second-order properties. Through complex sum-over-states (SOS) expression, the two-state model has been established which linked between low-lying charge transfer transition and β [33]. The following model expression is applied for estimating β_{CT} in terms of static case.

$$\beta_{CT} = \frac{\Delta\mu_{gm}f_{gm}}{E_{gm}^3} \quad (4)$$

Where,

E_{gm} , f_{gm} , and $\Delta\mu_{gm}$ represents transition energy, oscillator strength and dipole moment difference between the ground state (g) and the m th excited state (m), respectively.

The second-order polarizability in terms of two-state model expression resulted due to charge transfer (β_{CT}) is directly proportional to optical intensity whereas inversely related to transition energy in cubic form. Thus, in calculating β value for the studied compounds the decisive factor is low excitation energy. In terms of Table 4, the values of λ_{gm} for studied compounds are related with structural character. Increase in computed λ_{gm} values are shown as follows: D2 < D3 < D1 < D0 = D4.

The λ_{gm} value is larger for D1 and D3 whereas for D2 its value is only 374 nm and for D4 and D0 it increases a bit further i.e. upto 391 nm. By substituting electron withdrawing atom the absorption band shows bathochromic shift. The significant enhancement in β_{tot} value is observed because of this behavior as shown by equation 4. Therefore, dominant contribution is attributed to excitation energy towards β_{tot} values of studied compounds. It has been demonstrated already that β value is directly proportional to $\Delta\mu$ (difference between excited and ground state dipole moment) and oscillator strength. However, it shows inverse relation towards transition energy. In D0-D4, for larger β value the low excitation energy is considered to be decisive factor for determining NLO response as given in Table 4. Thus, oscillator strength (f_{gm}) for D0-D4 systems is 1.538, 1.719, 1.595, 1.516 and 1.538, respectively. D4 and D0 systems exhibit same oscillating strength such that (1.583). In D0 system the excitation energy is higher than that of D4 system (which is a key factor in assigning NLO response in comparison of both compounds). Hence, in these systems the principle factor is low-lying excitation energy for increasing the value of β_{tot} . The strong oscillation strength is responsible for large β_{tot} values. In a nut shell, transition energy should be small but there are also some other factors which can influence NLO response including charge transfer and transition moments. Thus, following is the NLO response of D0-D4; D4 > D1 > D0 > D3 > D2

Table 4. Maximum absorption wavelengths (λ_{max} in nm), Excitation energy (eV), oscillator strengths (f_{gm}), and molecular orbital (MO) transitions

Dye	λ_{max}	E_{gm}	f_{gm}	MO transition
D0	391	3.202	1.538	HOMO \rightarrow LUMO (74%)
D1	390	3.171	1.719	HOMO \rightarrow LUMO (76%)
D2	374	3.308	1.595	HOMO \rightarrow LUMO (73%)
D3	383	3.229	1.516	HOMO \rightarrow LUMO (75%)
D4	391	3.164	1.538	HOMO \rightarrow LUMO (74%)

It is obvious that D4 system offers maximum β value via D- π -A configuration. It is also understandable that electron withdrawing substitution has a potential influence on NLO second-order property in our studied compounds. Thus, it can be concluded from these results that by incorporating electron withdrawing atom at benzene ring β value can be increased.

In D0-D4 another important factor is extension of π -conjugation via $C\equiv C$ lengthening; and it also improved the delocalization. Generally, small energy difference is observed between charge transfer (CT) excited states (also enhances charge transfer degree accordingly) and ground states due to extended conjugation. It is well known that transition energy values governed NLO second-order property. Similarly, through introduction of an electron-withdrawing group (F) the LUMO-HOMO energy gap is decreased generally as in case of D4 and D1. However, D2 and D3 exhibit larger LUMO-HOMO energy gaps than D0. In terms of energy gaps of D0-D4, the D4 has least HOMO-LUMO energy gap value of 2.440.

Therefore, it is noticed that maximal NLO response is possessed by compound having smallest band gap (i.e. system D4 with band gap 2.440 eV). This band gap strongly influences the optical and electrical properties of material and is also a useful aspect of band structure. Generally, with increase in molecular size the band gap decreases. Transfer of electrons from one band to the other is done by means of recombination processes and carrier generation. Thus, due to generation of defect states within band gap via doping is useful in materials science for creating devices such as transistors, diodes, laser diodes, solar cells and others.

Conclusions

The α -cyanocinamic acids substituted with triphenylamine are found to possess considerably large static second-order polarizabilities. A compound having an electron acceptor (F) exhibits remarkably large second-order static polarizabilities. In terms of frontier MOs, the optical excitation analysis shows that the NLO response is attributed to charge transfer (CT) from triphenylamines to benzene ring with α -cyanocinamic acid. In D0-D4, CT along x -axis towards organic segment plays a key role in determining NLO response. According to the two-state model, the strong oscillation strength and the low excitation energy are the decisive factors in generating large β value. Compounds with longer wavelength transition possess higher computed β value. This research work reveals the NLO behavior of α -cyanocinamic acid-triphenylamine substituted compounds and therefore opens new doors for experimentalists in terms of designing NLO functional compounds with tunable performance. The present investigation provides an insight for NLO responses of triphenylamine substituted α -cyanocinamic acids and thus discloses the trend of NLO response. Our research presents vital confirmation for controlling the kinds of fluorinated rings that is a significant approach for the design of new appealing NLO compounds. This theoretical framework also highlights the NLO properties of organic dyes that can be valuable for their uses in modern hi-tech applications.

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