

Second-order nonlinear optical properties of dithienophenazine and TTF derivatives: A butterfly effect of dimalononitrile substitutions



Shabbir Muhammad^{a,b,*}

^a Department of Physics, College of Science, King Khalid University, P.O. Box 9004, Abha 61413, Saudi Arabia

^b Research Center for Advanced Materials Science (RCAMS), King Khalid University, P.O. Box 9004, Abha 61413, Saudi Arabia

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ABSTRACT

Using density functional theory (DFT) methods, the nonlinear optical (NLO) properties have been calculated with strong donor- π -conjugation-acceptor configurations. The static first hyperpolarizability (β_0) and dynamic (frequency dependent) electric field induced second harmonic generation (EFISHG) first hyperpolarizability ($\mu\beta$) are calculated for all designed systems. Our DFT calculations show dithienophenazine merged TTF (**2**) holds larger β_0 amplitudes ($\beta_0 = 21.04 \times 10^3$ a.u.) as compared to its corresponding compounds of TTF merged-difurophenazine (**1**), dicyclopentaphenazine (**3**) and dipyrrolophenazine (**4**) derivatives having β_0 amplitudes of 16.25×10^3 , 12.69×10^3 , and 18.38×10^3 a.u., respectively. Furthermore, substitution of dimalononitrile $[\text{C}(\text{CN})_2]_2$ groups at acceptor end of these compounds results in new derivatives **1a–4a**, respectively. Interestingly, a butterfly effect on first hyperpolarizability of all systems **1a–4a** has been spotted, which not only results in their robustly larger β_0 amplitudes but also changes the increasing order of β_0 amplitudes from systems **3** < **1** < **4** < **2** to **1a** < **2a** < **3a** < **4a** at both PBE0/6-31G* and CAM-B3LYP/6-31+G* levels of theory. For example, the increase in β_0 amplitudes of systems **1a**, **2a**, **3a** and **4a** are 3, 3, 5, and 19 times as compared with their corresponding non dimalononitrile derivatives at PBE0/6-31G* level of theory, respectively. Remarkably, unlike the static first hyperpolarizability, the dynamic EFISHG hyperpolarizability ($\mu\beta_\omega$) has the largest value for system **4a** with its amplitudes of 1378.59×10^{-46} and 1349.40×10^{-46} esu, at PBE0/6-31G* and CAM-B3LYP/6-31+G* levels of theory, respectively. TD-DFT calculations have been performed to trace the origin of first hyperpolarizability. It has been found that the lower transition energy and higher oscillator strengths cause robustly large amplitudes especially in systems **3a** and **4a**, which consequently stems in strong donor- π -conjugation-acceptor configuration of these systems. Thus the present results intrigue the butterfly effect of a two-step substitution on NLO properties of TTF merged dithienophenazine compounds that can be used as an efficient NLO material.

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1. Introduction

Materials exhibiting NLO response are currently of great scientific and technological interest because of their potential applications spanning from optical telecommunications, signal processing, data storage, logic technologies and sensor protection to modern optical computing, etc. [1]. A large number of reports have been presented up till now on NLO materials with different conventional strategies to enhance NLO response. These strategies mainly include the use of the molecules with the extended π -electron systems [2–4], bond length alternation (BLA) theory

[5], twisted π -electron systems [6,7], intercalation of lithium metal into cage compounds [8–11], non-covalent charge transfer [12] and donor- π -conjugated-acceptor (D- π -A) models [13–17], etc. Several organic molecules with D- π -A configurations have been remaining a great potential for designing efficient second-order nonlinear optical (NLO) materials. In order to optimize the second-order nonlinear optical response (β) in such molecules, it is important to know the influence of different donors and acceptors, the spatial molecular structure and degree of conjugation. Usually, the nonlinear optical chromophores are designed using donor and acceptor units connected through a π -conjugated bridge. From a recent literature survey, it has been found that many different donor groups have also been studied including benzylidene aniline [18,19], thiophenes [20], ferrocenes [21] and thiafulvalenes [22], etc. all of which are of clear interest in the fields of electro-active and/or conducting materials. Due to the

* Correspondence to: Department of Physics, College of Science, King Khalid University, P.O. Box 9004, Abha 61413, Saudi Arabia. Tel.: +966 568761658.

E-mail address: mshabbir@kku.edu.sa

applications of NLO materials in ultra fast networking and hi-tech laser processes, it is important to realize the NLO materials having exceptional amplitudes of first hyperpolarizability. Nevertheless, the effect of a tetrathiafulvalene (TTF) group on the second-order NLO properties of D- π -A model systems has been already studied [23]. The electron-donor properties of TTF derivatives have led to wealth of organic conductors and super conductors [24–26]. However, Guegano and co-workers [27] have recently reported a strong push–pull combination of dithieno phenazine and dithiolodithieno phenazine moieties merged with TTF units. They described a high-lying HOMO with a low-lying LUMO and a fairly low-lying LUMO+1 on the bridging units, giving rise to strong optical charge transfer transitions, which might have potential to get robustly large NLO response. In the light of previous reports, the above organic chromophores can be excellent candidates for NLO applications due to their low cost, large nonlinear response over a broad frequency range, inherent synthetic flexibility, low dielectric constant, high optical-damage threshold, and intrinsic tailorability. In present investigation, we will not only investigate the remarkable dithieno phenazine and dithiolodithieno phenazine chromophores but also explore the potential of their derivatives for NLO properties by changing the hetro-atom in five-membered thiophene rings.

2. Computational details

The density functional theory (DFT) methods have been applied in all calculations. Geometry optimizations for all systems were performed using PBE0/6-31G* level of theory. There are many recent reports, which clearly indicate that among DFT functionals, PBE0 provides more accurate approximation about structural, optical and nonlinear optical properties of molecules bearing thiophene rings [20,28–30]. All the molecular geometries have been optimized using PBE0/6-31G* level of theory. In a semi-quantitative way, to see the effect of functionals on dipole moment, polarizability and first hyperpolarizability, we have initially applied some well-known DFT functionals having different ranges of exchange and correlation on system **2**, which is experimentally synthesized and is considered as parent system in present investigation (see Table S1 of supporting information). It can be seen from Table S1 that PBE0 and mPW1PW91 have shown reasonably good agreement with a recently developed M06 functional while others (B3LYP, O3LYP and B3P86) have shown slightly larger values for the dominant components of dipole moment, polarizability and hyperpolarizability. To further address the long-range charge-transfer effects in our studied systems, we have also added the results of static and dynamic first hyperpolarizabilities at an advanced long-range corrected functional CAM-B3LYP with a larger basis set 6-31+G*. A graphical comparison of static first hyperpolarizability at PBE0/6-31G* and CAM-B3LYP/6-31+G* levels of theory is illustrated in Fig. S1 of supporting information. From Fig. S1 of supporting information, it can be seen that the β_0 amplitudes calculated at PBE0/6-31G* level of theory are relatively larger than those calculated at CAM-B3LYP/6-31+G* level of theory. These overestimations are slightly larger in case of chromophores (**3a** and **4a**) having larger extends of intramolecular charge transfers. Nevertheless, overall similar trends can be seen in the change of β_0 amplitudes for all adopted systems at both PBE0/6-31G* and CAM-B3LYP/6-31+G* levels of theory (see Fig. S1). The overestimation of β_0 amplitudes at PBE0/6-31G* level of theory is about two times than those β_0 amplitudes calculated at CAM-B3LYP/6-31+G* level of theory. To see the origin of difference among β_0 amplitudes (either from change of functional or basis set), we have further calculated β_0 amplitudes at PBE0/6-31+G* level of theory. A comparison of results at PBE0/6-31G* and PBE0/6-31+G* levels of theory has been elucidated in Table S2 of supporting information. It can

be seen from Table S2 of supporting information that there is no significance difference between β_0 amplitudes calculated at both 6-31G* and 6-31+G* basis sets for all adopted systems in present study. Thus the difference of β_0 amplitudes calculated at both PBE0/6-31G* and CAM-B3LYP/6-31+G* levels of theory is due to the use of CAM-B3LYP functional with long-range charge transfer effects. Absorption energies have been calculated using TD-PBE0/6-31G* level. The static first hyperpolarizability β_0 of all compounds were calculated by finite field (FF) method. The FF method has been broadly applied to investigate NLO properties because this methodology can be used in concert with the electronic structure method to compute β values [31,32]. In some very recent reports, β_0 amplitudes calculated by FF method are found substantiated with experimental structure property relationship. In FF method, a molecule is subjected to a static electric field (F), the energy (E) of the molecule is expressed by Eq. (1)

$$E = E^{(0)} - \mu_1 F_1 - \frac{1}{2} \alpha_{ij} F_i F_j - \frac{1}{6} \beta_{ijk} F_i F_j F_k - \frac{1}{24} \gamma_{ijkl} F_i F_j F_k F_l - \dots \quad (1)$$

where $E^{(0)}$ is the energy of molecule in the absence of an electronic field, μ is the components of the dipole moment vector, α is the linear polarizability tensor, β and γ are the first and second hyperpolarizability tensors respectively, while i, j and k label the x, y and z components, respectively. It is clear that $\mu, \alpha, \beta, \gamma$ can be obtained by differentiating E with respect to F . In our present investigation, we have calculated the electronic dipole moment, and molecular first hyperpolarizability. For a molecule with C_{2v} structure, its total dipole moment (μ_0) is defined as:

$$\mu_0 = \mu_z \quad (2)$$

Similarly, the first hyperpolarizability can be calculated using the following Eq. (3)

$$\beta_0 = \frac{3}{5} (2\beta_{yyz} + \beta_{zzz}) \quad (3)$$

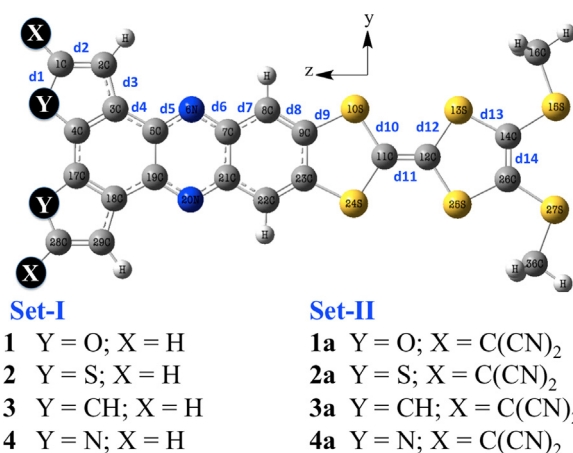
The components of first hyperpolarizability (β) are calculated using analytical third energy derivatives that are more efficient and less expensive method [33]. All the calculations have been performed on GAUSSIAN 09 [34]. It should be noted that the default settings i.e. energy convergence criteria and field strength for all methods were chosen in the present calculations. In addition to static first hyperpolarizability values, we have also calculated the dynamic (frequency dependent) electric field induced second harmonic generation (EFISHG) first hyperpolarizabilities ($\mu\beta_\omega$). The frequency dependent coupled-perturbed Kohn-Sham (CPKS) method with the PBE0 functional has been applied to calculate the dynamic first hyperpolarizability values. In case of EFISHG experiments, the measurement provide information on the projection of the vector part of β on the dipole moment vectors as given by following Eq. (4)

$$\beta_\omega(-2\omega; \omega, \omega) = \beta_\omega = \frac{3}{5} \sum_{\xi}^{x,y,z} \frac{\mu_\xi \beta_\xi}{||\mu||} \quad (4)$$

where μ is the norm of dipole moment vector and μ_ξ and β_ξ are the components of μ and β vectors. The EFISHG first hyperpolarizability ($\mu\beta_\omega$) values can be finally calculated using following relationship:

$$\mu\beta_\omega = \frac{5}{3} \mu \cdot \beta_\omega \quad (5)$$

All the $\mu\beta_\omega$ values have been given in electrostatic units (10^{-46} esu) within T-convention of reference [35]. In CPKS method, the matrices of CPKS equation are expanded in Taylor series of external dynamic electric field and are solved analytically order by order. According to usual experimental setup for EFISHG first hyperpolarizability ($\mu\beta_\omega$) measurement, the frequency dependent



Scheme 1. Schematic diagram and general labeling for molecular structure of all adopted chemical models.

calculations are carried out within T-convention using an incident wavelength of 1064 nm. The solvent (n,n-dimethyl formamide) effects were taken into account using polarized continuum method (PCM).

3. Results and discussion

3.1. Molecular geometries

In the present study, we have categorized adopted chemical models into two sets i.e. Set-I and Set-II depending on the nature of acceptor group in donor- π -conjugation-acceptor (D- π -conjugation-A) configurations. In each molecule the donor fragment is tetrathiafulvalene (TTF) fused with different acceptor fragments of phenazine derivatives. The Set-I consists of four systems including 10-(4,5-bis(methylthio)-1,3-dithiol-2-ylidene)-[1,3]dithiolo[4,5-*i*]difuro[3,2-*a*:2',3'-*c*]phenazine system **1**, 10-(4,5-bis(methylthio)-1,3-dithiol-2-ylidene)-[1,3]dithiolo[4,5-*i*]dithieno[3,2-*a*:2',3'-*c*]phenazine (system **2**), 10-(4,5-bis(methylthio)-1,3-dithiol-2-ylidene)-2,6a-dihydrodicyclopenta[*a*,*c*] [1,3]dithiolo[4,5-*i*]phenazine (system **3**) and 10-(4,5-bis(methylthio)-1,3-dithiol-2-ylidene)-2,6a-dihydro[1,3]dithiolo[4,5-*i*]dipyrrolo[3,2-*a*:2',3'-*c*]phenazine (system **4**), respectively. In Set-II, the acceptor fragments of these derivatives have been further modified by the substitution of dimalononitrile [C(CN)₂]₂ groups at phenazine part as shown in Scheme 1. The chemical systems **1a**, **2a**, **3a** and **4a** of Set-II are the dimalononitrile derivatives of systems **1**, **2**, **3** and **4** of Set-I, respectively. The systems **2** and **2a** are experimentally synthesized compounds [27] where pentamethyl chain of system **2a** has been replaced with methyl group to reduce the computational cost. It is reported in several previous studies that the alkyl branched chain has negligible effect on electronic structure and electro-optical properties of materials [28–30]. In Scheme 1, a general labeling pattern has been illustrated for all chemical structures. A comparative analysis has been made among the important bond lengths in all chemical systems as shown in Table 1 according to the structural labeling in Scheme 1. From Table 1, it can be seen that the heteroatom substitutions have primarily affected the geometrical parameters of acceptor part (phenazine moiety) while TTF has does not show noticeable structural changes. The d₁ bond distance, which involves heteroatoms, increases slightly in systems of Set-II by substituting dimalononitrile strong-withdrawing groups. The increases in d₁ bond distances between systems of Set-I and Set-II are 0.001, 0.022, 0.097 and 0.091 Å, respectively. Analysis of bond lengths shows that by substituting dimalononitrile groups,

Table 1

The optimized bond distances (Å) of all chemical systems where labeling is according to Scheme 1 calculated at PBE0/6-31G* level of theory.

Bond length	Set-I				Set-II			
	1	2	3	4	1a	2a	3a	4a
d ₁	1.365	1.733	1.356	1.302	1.366	1.755	1.453	1.393
d ₂	1.355	1.359	1.466	1.467	1.426	1.427	1.455	1.455
d ₃	1.431	1.426	1.359	1.356	1.367	1.366	1.356	1.356
d ₄	1.434	1.439	1.45	1.453	1.452	1.455	1.447	1.450
d ₅	1.328	1.328	1.318	1.317	1.321	1.322	1.325	1.321
d ₆	1.341	1.341	1.353	1.353	1.346	1.345	1.344	1.347
d ₇	1.418	1.418	1.412	1.412	1.413	1.413	1.413	1.412
d ₈	1.369	1.37	1.374	1.375	1.373	1.373	1.373	1.374
d ₉	1.752	1.752	1.754	1.751	1.745	1.745	1.746	1.746
d ₁₀	1.764	1.764	1.763	1.764	1.763	1.763	1.76	1.76
d ₁₁	1.349	1.349	1.349	1.349	1.351	1.351	1.353	1.355
d ₁₂	1.762	1.762	1.762	1.762	1.758	1.759	1.757	1.756
d ₁₃	1.763	1.763	1.763	1.763	1.762	1.763	1.761	1.760
d ₁₄	1.349	1.349	1.349	1.349	1.349	1.349	1.351	1.352

the cyclopentadiene and pyrrole rings of system **3a** and **4a** are expanded more than thiophene and furan rings of systems **1a** and **2a**. Similar bond length increasing trends have been also found in d₂, d₃ and d₄ bond lengths of all systems by dimalononitrile substitutions.

3.2. Dipole moment and first hyperpolarizability

The dipole moments of all chemical systems have been calculated in their optimized ground state and excited state geometries using PBE0/6-31G* and TD-PBE0/6-31G* level of theories, respectively. As all the molecules are in C_{2v} symmetry, only the z-components of dipole moments are found significant both in ground state (μ^z_{gg}) and first excited state (μ^z_{ee}) as shown in Table 2. From Table 2, it can be seen that all the systems in Set-II have significantly larger ground state dipole moments as compared to the systems in Set-I. The ground state dipole moments of systems **1a**, **2a**, **3a** and **4a** are –15.34, –11.34, –11.98 and –17.58 D, respectively. The larger amplitudes of dipole moments are due to the strong terminal with drawing nitrile groups, which have perhaps induced significant charge separation in ground state molecular geometries and resulted in larger amplitudes of dipole moments.

It is important mention here that negative signs are only related with definition of z-axis and has nothing to do with amplitude of dipole moments. There are no significant changes in dipole moments of all systems while moving from ground to excited state geometries with only a slight reduction in amplitudes in excited state dipole moments. This is because the π -conjugation is almost same in all the systems, the difference between ground and excited states dipole moments are not very significant. We have also reported the first hyperpolarizabilities (β_0) for all the eight

Table 2

The calculated ground state dipole moments (μ^z_{gg}) and excited state (μ^z_{ee}) dipole moments and the difference between them $\Delta\mu^z$ (Debye*) for all adopted systems.

Components	μ^z_{gg}	μ^z_{ee}	$\Delta\mu^z$ (D)
Set-I			
Sys. 1	–0.47	–0.01	0.46
Sys. 2	–2.84	–2.85	0.01
Sys. 3	–2.49	–3.27	0.77
Sys. 4	–4.03	–3.66	0.37
Set-II			
Sys. 1a	–15.34	–14.90	0.43
Sys. 2a	–11.34	–11.04	0.29
Sys. 3a	–11.98	–11.45	0.53
Sys. 4a	–17.53	–17.09	0.44

* 1 Debye = 0.393456 a.u.

Table 3

The calculated values of static first hyperpolarizabilities ($\beta_0 \times 10^3$ a.u.^a) along with their individual components as well as dynamic EFISHG hyperpolarizability ($\beta_\omega \times 10^{-30}$ esu) and product $\mu\beta_\omega$ ($\mu\beta_\omega = 5/3 \mu \beta_\omega$, in $\times 10^{-46}$ esu) for all study systems.

Chem. Sys.	CAM-B3LYP/6-31+G*			PBE0/6-31G*		
	$\beta_0 \times 10^3$ a.u.	$\beta_\omega \times 10^3$ a.u.	$\mu\beta_\omega \times 10^{-46}$ esu	$\beta_0 \times 10^3$ a.u.	$\beta_\omega \times 10^3$ a.u.	$\mu\beta_\omega \times 10^{-46}$ esu
Set-I						
1	7.000	17.48	1.52	16.25	61.14	4.14
2	8.506	20.72	2.82	21.04	81.80	4.83
3	5.142	10.76	6.05	12.69	86.94	31.17
4	7.664	20.11	13.76	18.38	67.15	38.97
Set-II						
1a	11.66	237.58	570.73	53.12	276.10	609.96
2a	20.89	238.51	366.16	58.49	300.18	490.23
3a	82.62	560.87	700.24	320.41	513.38	885.74
4a	120.94	621.34	1349.4	343.44	546.06	1378.59
PNA	0.839	2.913	3.912	0.870	1.899	2.488

Value of frequency is $\omega = 1064$ nm.

^a No factor has been applied for β_ω and $\mu\beta_\omega$ T-convention values.

systems in Set-I and Set-II. For a chromophore with C_{2v} symmetry, there are three nonzero components of the β tensor i.e. β_{zzz} , β_{xxz} and β_{yyz} . According to Eq. (3), we have collected all types of β values in Table 3. The static first hyperpolarizabilities for systems **1**, **2**, **3** and **4** are 16.25×10^3 , 21.04×10^3 , 12.69×10^3 , 18.38×10^3 a.u. at PBE0/6-31G* level and 7.04×10^3 , 8.50×10^3 , 5.14×10^3 and 7.66×10^3 a.u., at CAM-B3LYP/6-31+G* level theory. A comparable similar trend of varying the β_0 amplitudes for all the systems of Set-I has been found at both PBE0/6-31G* and CAM-B3LYP/6-31+G* levels of theory, which is $3 < 1 < 4 < 2$ for cyclopentadiene, furan, pyrrole and thiophene containing molecules, respectively. Among the systems of Set-I, the system **2** containing thiophene ring in acceptor moiety showed relatively larger amplitude of first hyperpolarizability that is about 4.084×10^3 , 7.645×10^3 , 1.930×10^3 a.u. larger than those of systems **1**, **3** and **4**, respectively, at PBE0/6-31G* level of theory. These amplitudes of first hyperpolarizability of all the systems in Set-I are significantly larger than that of the typical prototype para-nitroaniline (PNA) molecule. In present calculations, the first hyperpolarizability of PNA is found to be 0.870×10^3 and 0.839×10^3 a.u. at PBE0/6-31G* and CAM-B3LYP/6-31+G* levels theory, respectively.

A comparison of first hyperpolarizability amplitudes of all systems in Set-I with PNA shows that the amplitudes of systems **1**, **2**, **3** and **4** are about 19, 23, 14 and 21 times larger than that of PNA at PBE0/6-31G* level of theory. Interestingly, the effects on β_0 amplitudes for systems in Set-II are more robust as compared to systems in Set-I as well as to standard PNA molecule. In Set-II, the systems **1a–4a** with dimalononitrile $[C(CN)_2]_2$ groups register significantly larger β_0 amplitudes, which are 53.12×10^3 , 58.49×10^3 , 320.41×10^3 and 343.44×10^3 a.u., respectively, at PBE0/6-31G* level of theory. For systems in Set-II, a comparison of β_0 amplitudes show a similar trend of increasing their amplitudes as $1a < 2a < 3a < 4a$ calculated at both PBE0/6-31G* and CAM-B3LYP/6-31+G* levels of theory. It is important to note that the systems **1a–4a** with dimalononitrile $[C(CN)_2]_2$ groups show about 3, 3, 27 and 18 times larger β_0 amplitudes than those of their respective systems in Set-I without dimalononitrile substitutions at PBE0/6-31G* level of theory. Remarkably, the β_0 amplitudes of systems in Set-II are much more larger than that of PNA. For example, the β_0 amplitude of system **4a** is about 400 times larger than that of PNA molecule as calculated at PBE0/6-31G* level of theory. Furthermore, we have also calculated frequency dependent first hyperpolarizability β_ω and $\mu\beta_\omega$ using 1064 nm laser frequency with n,n-dimethyl formamide solvent effects at PBE0/6-31G* and CAM-B3LYP/6-31+G* levels theory. These amplitudes can be directly compared with experimental EFISHG measurements. The amplitudes of β_ω values are comparatively larger than their

respective static values. The trend of change in amplitudes among all the systems has been found semi-quantitatively similar to static trends as shown in Fig. 1 at PBE0/6-31G* level theory.

3.3. Origin of first hyperpolarizability

TD-DFT calculations have been performed to trace the origin of first hyperpolarizability. In case of static hyperpolarizability a well-known two-level approximation that has been often used in literature to roughly trace the origin of first hyperpolarizability. In two-level approximation, the nonlinear optical response is calculated including the transition parameters of ground and one excited state in sum-over-state expression. However, care should be taken while applying two-level model to the molecules with significantly populated excited states [36]. Despite the fact that the general validity of two-level model has been also questioned for extrapolating β value to zero frequency, it is widely used in experimental studies of nonlinear optical properties of organic molecules. Unlike the sum-over-state approximation, two-level model is simple representation of molecular response including wavelength dependence. This model is also the origin of the most widely applied push–pull technique for designing efficient NLO chromophore. Oudar and Chemla have first used two-level model to

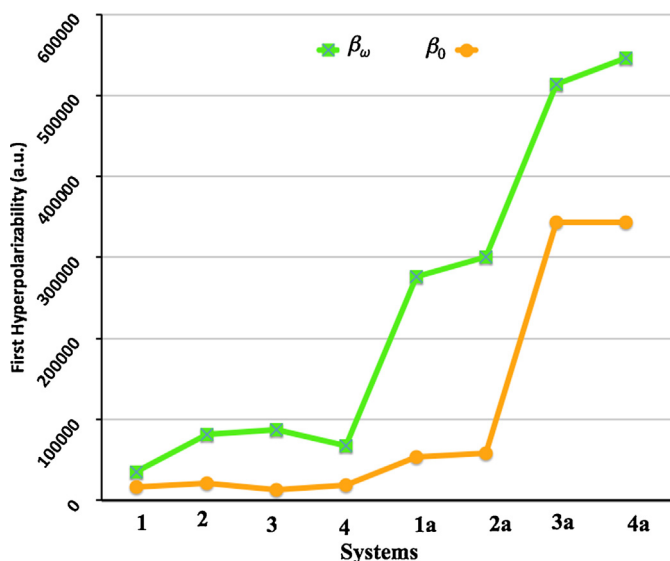


Fig. 1. The graph between static first hyperpolarizability and dynamic EFISHG responses calculated at PBE0/6-31G* level of theory.

study the first hyperpolarizability of nitroanilines [37]. In two-level expression the β_0 value is expressed as:

$$\beta_0 = \left(\frac{3}{2}\right) \Delta\mu \frac{f_0}{\Delta E^3}$$

where ΔE , f_0 , $\Delta\mu$ are transition energy, oscillator strength and change in dipole moment between ground and crucial exited state. As the amplitude of β_0 is inversely proportional to the third power of transition energy, it might be considered as the decisive factor to control the β_0 amplitudes in our all derived compounds. For a more comprehensive understanding of transition energy dependence of β_0 amplitudes, a graph has been drawn between β_0 amplitudes and transition energies of all adopted systems as shown in Fig. 2. From the graph it can be seen that the order of decreasing transition energy is in semi quantitative agreement with the order of increasing β_0 amplitudes for our all adopted systems. For example, among all the adopted systems, the systems **3a** and **4a** with lower transition energies have the larger β_0 amplitudes of 320.41×10^3 and 343.44×10^3 a.u., respectively. A similar trend but in vice versa order i.e. with higher transition energies and lower β_0 amplitudes can be also seen for other systems as illustrated in Fig. 2. Furthermore, between the other two factors, oscillator strengths also have constructive effect on the β_0 amplitudes. For example, the systems **3a** and **4a** have the highest oscillator strengths with the largest β_0 amplitudes among all systems as seen from Table 4. The third factor in two-level i.e. the change in dipole moment between ground and crucial exited state for all the systems does not show any significant change. This is because usually by increasing π -conjugation results in increase of dipole moment between ground and crucial exited

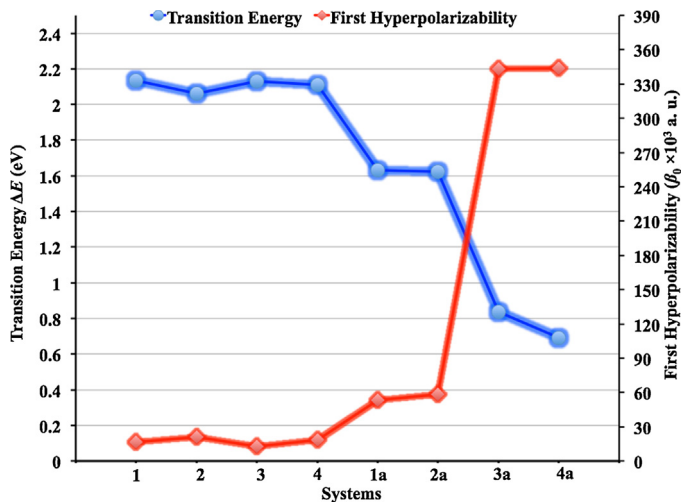


Fig. 2. The graph between static first hyperpolarizability and transition energy of all adopted systems at PBE0/6-31G* level of theory.

state, which is not the case in present derivatives that have been made only by the substitution of single hetro-atoms.

3.4. Frontier molecular orbitals (FMOs) analysis

The frontier molecular orbitals involved in crucial transitions are illustrated in Fig. 3. The FMOs can provide significant insights into the transition nature as well as in the origin of transition energy

Table 4
TD-DFT results for all adopted chemical models including the computed ground state (μ_{gg}) and excited state (μ_{ee}) dipole moments (D), dipole moment differences ($\Delta\mu^z = \mu_{ee} - \mu_{gg}$), oscillator strengths (f_0), transition energies ΔE (eV), and major orbital contributions.

Systems	$\Delta\mu^z$	Electronic Excitation	ΔE	f_0	Major contribution	%
Set-I						
1	0.09	$S_0 \rightarrow S_1$	2.135	0.277	H \rightarrow L	70%
2	0.01	$S_0 \rightarrow S_1$	2.062	0.308	H \rightarrow L	70%
3	0.77	$S_0 \rightarrow S_3$	2.130	0.017	H-2 \rightarrow L	70%
4	0.37	$S_0 \rightarrow S_3$	2.109	0.218	H \rightarrow L+1	69%
Set-II						
1a	0.43	$S_0 \rightarrow S_2$	1.630	0.317	H \rightarrow L+1	71%
2a	0.29	$S_0 \rightarrow S_2$	1.623	0.320	H \rightarrow L+1	71%
3a	0.53	$S_0 \rightarrow S_1$	0.837	0.332	H \rightarrow L	71%
4a	0.44	$S_0 \rightarrow S_1$	0.692	0.323	H \rightarrow L	73%

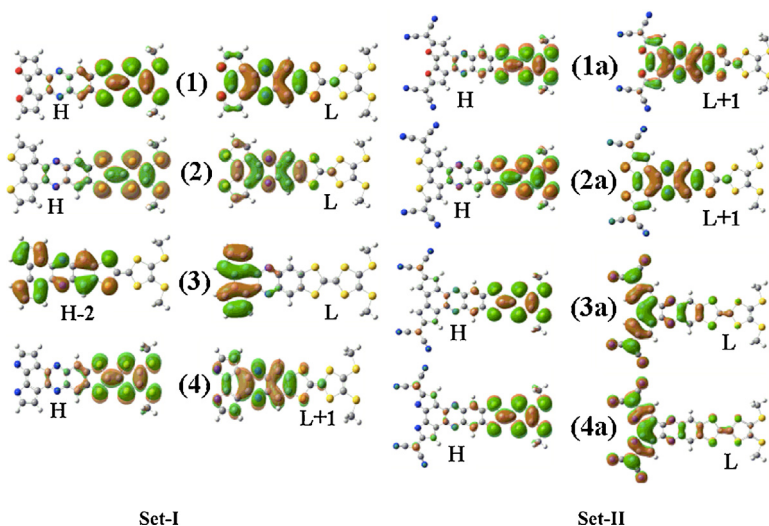


Fig. 3. The frontier molecular orbitals involved in crucial transitions for all adopted systems.

and first hyperpolarizability. Among the systems 1, 2, and 3 in Set-I, the transition nature is donor- π -conjugation-acceptor (D- π -A) type where HOMOs and LUMO + i ($i = 1$) orbitals are present on TTF and quinoxaline moieties, respectively. These transitions have sizable oscillator strengths of 0.277, 0.308 and 0.218 for systems 1, 2 and 3, respectively. Unlike the other systems in Set-I, the system 3 has the lowest β_0 amplitude and larger transition energy of 2.130 eV with oscillator strength of 0.017. This very weak oscillator strength of 0.017 might be attributed to the small charge redistribution between HOMO and LUMO + 1 orbitals limited only on quinoxaline moiety as seen in Fig. 3. The FMOs patterns for systems 1a–4a of Set-II are also D- π -A type where the LUMOs of systems 3a and 4a are also extended over dimalononitrile [C(CN)₂]₂ groups at phenazine part as shown in Fig. 3. This perhaps results a strong D- π -A configuration having the lowest transition energies and larger oscillator strengths as compared with other systems.

4. Conclusions

Thus a comprehensive structure-NLO property relationship has been investigated in TTF merged dithienophenazine (2) derivatives. A two-step approach has been applied to designed different derivatives of TTF merged dithienophenazine compound i.e. by replacing heteroatom (sulfur) with oxygen, carbon and nitrogen as in systems of Set-I and by further addition of dimalononitrile [C(CN)₂]₂ groups at acceptor end as in systems of Set-II. It is found that TTF merged-difurophenazine (1), dithienophenazine (2), dicyclopentaphenazine (3) and dipyrrolophenazine (4) derivatives have significant β_0 amplitudes of 16.25×10^3 , 21.04×10^3 , 12.69×10^3 , and 18.38×10^3 a.u., respectively. An additional substitution of dimalononitrile groups at acceptor end of these compounds results in a butterfly effect on their first hyperpolarizability amplitudes as large as 53.12×10^3 , 58.49×10^3 , 320.41×10^3 , 343.44×10^3 a.u. for systems 1a–4a respectively. Furthermore, a comparison between β_0 amplitudes of all the chemical systems at PBE0/6-31G* and CAM-B3LYP/6-31+G* levels of theory showed important differences among their respective amplitudes, which are perhaps due to the log-range intramolecular charge transfer effects especially larger in systems 3a and 4a. The TD-DFT calculations along with FMOs analysis indicate the lowest energy transitions as well as the strong donor- π -conjugation-acceptor configuration of these systems, which results in the larger amplitudes of NLO responses. Thus the present results show that the two-step substitution in dithienophenazine merged TTF compounds is an important strategy to design efficient NLO material.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jmngm.2015.03.003>.

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