

Non-linear Optical (NLO) Properties of Conjugated Thiophene and Ethylene Dioxy Thiophene (EDOT) Oligomers: A Density Functional Theory (DFT) Study

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Authors' contributions

This work was carried out in collaboration between all authors. Authors KMNdS, RMdS and NA designed the study. Author NA performed the DFT calculations, analysis, managed the literature search and wrote the first draft of the manuscript with the assistance from authors RMdS and KMNdS. All three authors read and approved the final manuscript.

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ABSTRACT

We report accurate nonlinear optical (NLO) properties of mixed thiophene and ethylene dioxythiophene oligomers using Density Functional Theory at the B3LYP and B3PW91 levels of theory using 6-31G basis set using Gaussian98 software package. The geometry optimizations of all molecules were performed using the same level of theory. The first static hyperpolarizabilities (β) of these molecules were calculated using B3LYP and B3PW91/6-31G using the same software package. The HOMO-LUMO gaps of these molecules were also calculated using the same level of theory. The calculation of hyperpolarizabilities of these molecules could prove useful owing to the recent reports of the synthesis of these molecules for optoelectronic applications.

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1. INTRODUCTION

Nonlinear optics captured the attention of the scientists in 1875 with the publication by J. Kerr of his observations of a quadratic electric field induced change in the refractive index of CS_2 , now known as the Kerr effect. This discovery was followed shortly in 1883 by the observation of a similar but linear electric field effect in quartz, now known as the Pockels effect. Nonlinear effects had remained almost in obscurity until the discovery of the laser in 1960 by Maiman [1], followed by the observation by P. Franken et al. of second harmonic generation (SHG) in quartz [2]. Following these events, the field of nonlinear optics developed dramatically, with ever increasing enthusiasm into the 21st century. Consequently, a large number of nonlinear optical (NLO) effects have been discovered ranging from third harmonic generation (THG), stimulated Raman scattering, saturable absorption etc [3-5].

Current investigations in the field of chemical physics invest a significant degree of effort in the direction of nonlinear optical phenomena (both experimental and theoretical) due to its growing number of applications in data processing and imaging technologies, optical switching (optical computing), sensing, microfabrication, medicinal applications (cancer therapy) etc [3-8]. This extraordinary promise demonstrated is due to the range of possible modifications that NLO active media can impart on incident electromagnetic radiation (e. g., phase modifications, frequency changes etc).

Conjugated polymers (in their doped state) are well known for their high electrical conductivity that can be regarded as one of the primary reasons for their utilization in organic semiconductor devices [9]. However, polymer thin film materials are gaining increased attention not only as semiconductor devices but also as bifunctional photonic devices [10], possessing multiple functionalities.

Polythiophenes belong to a class of compounds that have captured the interest of many photophysicists and theoretical and synthetic chemists for their favourable properties in electro-optic technologies such as polymer LEDs, electrochromic or smart windows, electromagnetic shielding materials, solar cells etc [9-12].

Due to the complications faced in the measurement of NLO properties of SHG materials and due to high labor-intensive and facilities-intensive synthetic procedures required in NLO material synthesis [3], it is a good idea for chemical physicists turn to theoretical prediction of hyperpolarizabilities well before scheming synthetic routes. Some computational efforts have been carried out on polythiophenes, polypyrroles, polyfurans etc at the semi-empirical level of theory to show slowly increasing first hyperpolarizability, β_{vec} (that lies in the direction of the dipole moment) with saturation effects [13-15]. Even though many ab-initio calculations investigating NLO properties of small organic molecules to oligomeric systems were carried out previously [12,16,17], calculations of second order NLO properties of substituted oligothiophene systems were not reported until now.

The objectives of the current investigation are to study the β_{tot} first static hyperpolarizability, of a set of oligothiophenes and oligomers of 3,4-Ethylenedioxythiophenes (EDOTs) equipped with NH_2 and NO_2 groups (as donor and acceptor groups respectively) on either side of each molecule, to calculate the frontier orbital (HOMO, LUMO) energies and to study their relationship with β_{tot} values using density functional theory (DFT). Moreover, the study compares two different DFT methods for their agreement between the calculated β_{tot} values. Eventually, the possibility of predicting the hyperpolarizability values for longer oligomers (or polymers) is also investigated which could largely reduce the computational efforts required in calculating β_{tot} for longer oligomers.

2. THEORETICAL METHODOLOGY

All the geometry optimizations and hyperpolarizability and frontier orbital calculations were performed using GAUSSIAN98W [18] on an Intel Pentium IV, 0.99 GHz processor with 1.5 GB RAM and Microsoft Windows XP as the operating system.

The calculations were performed on the molecules 'a' to 'm' (Fig. 1), each of which is substituted by NH_2 and NO_2 (as donor and acceptor groups respectively) on either side of the conjugated thiophene moiety as illustrated in the Fig. 1.

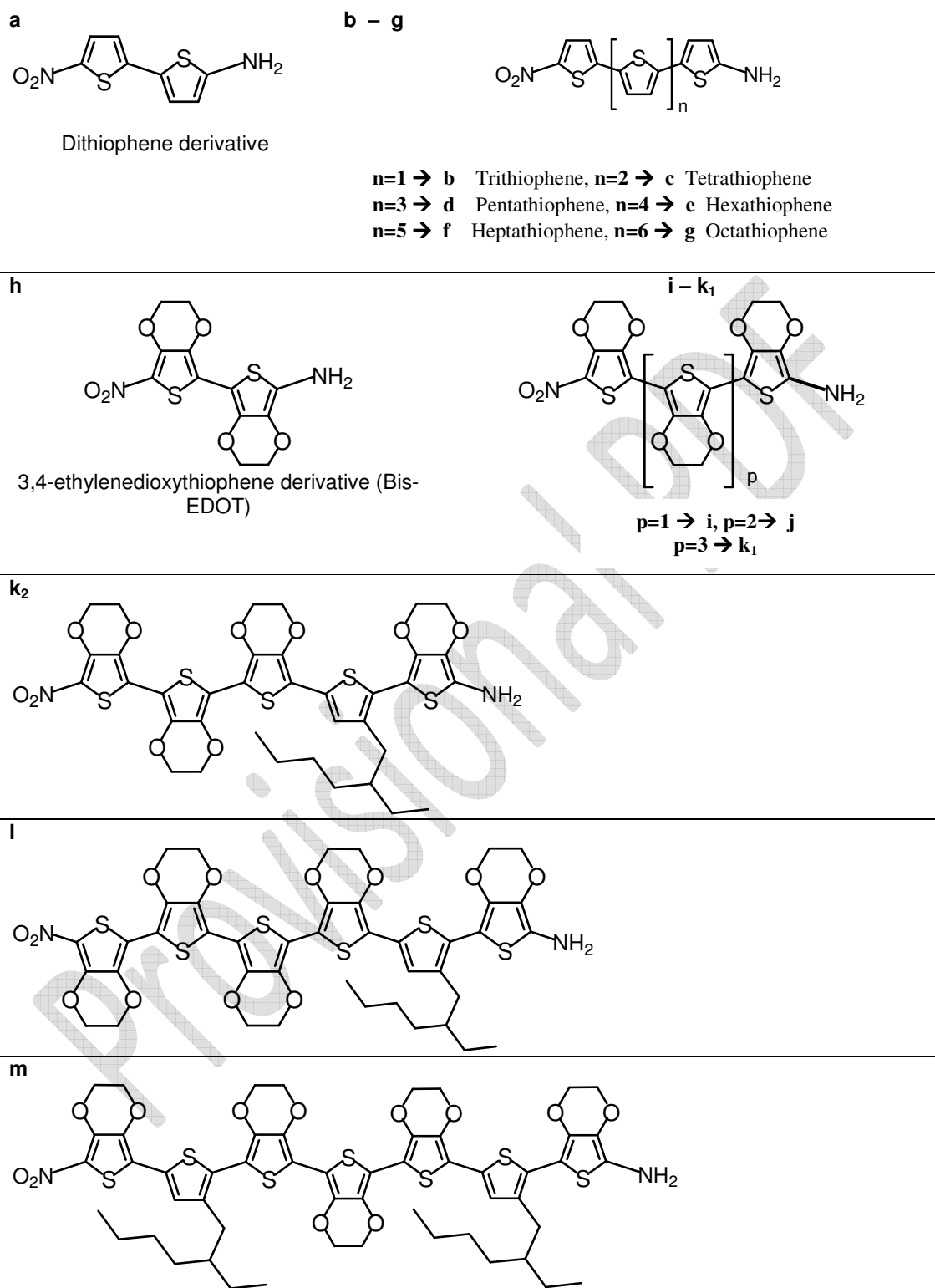


Fig. 1. Thiophene and EDOT oligomers

Initial geometry optimization was carried out at the Hartree-Fock level using '# HF/3-21G' in the route section followed by '# HF/6-31G' level of theory, whose resultant structure was optimized using '# B3LYP/6-31G' prior to the hyperpolarizability calculation. The final optimized structure thus obtained was used to calculate the first static hyperpolarizability, β , using '#P B3LYP/6-31G POLAR = ENONLY' and '#P B3PW91/6-31G POLAR = ENONLY' in the route section. Frontier orbital energies were obtained by using '#P B3LYP/6-31G POP = FULL' calculation on the optimized output.

3. RESULTS AND DISCUSSION

The gas phase (*in vacuo*) hyperpolarizability tensor was calculated for all of the thiophene oligomers and 3,4-ethylenedioxythiophene (EDOT) oligomers possessing NH₂ and NO₂ groups on either side of each molecule, using GAUSSIAN98W.

Since the first hyperpolarizability is a third rank tensor it can be explained and described by a 3 x 3 x 3 matrix. β reflects the effect that external electromagnetic radiation field imparts on induced dipole moment vectors (μ_x , μ_y , μ_z) due to the external electric field along the *a*-axis (*a*= x, y or z) and the external electric field along the *b*-axis (*b*= x, y or z). Therefore, β can be considered as a value based on a single quantum mechanical process involving two photons, indicating the application of frequency doubling in molecules inheriting large β values. The 27 components of the 3 x 3 x 3 matrix can be reduced to 10 components due to Kleinman symmetry ($\beta_{xyy} = \beta_{yyx} = \beta_{yyx}$, $\beta_{yyz} = \beta_{zyy} = \beta_{zyy}$, --- likewise 27 components are reduced to 10).

Kleinman Symmetry is a consequence of the full permutation symmetry condition that allows the indices of the hyperpolarizability components to be interchanged under the interchange of the input and output frequency terms (in a lossless medium) and under conditions where optical frequencies involved are much smaller than the lowest resonance frequency of the material system [4].

Therefore, the hyperpolarizability tensor can be represented in the lower tetrahedral format where lower part of the 3 x 3 x 3 cube matrix is tetrahedral. The GAUSSIAN98W output gives the 10 components in the order of β_{xxx} , β_{xxy} , β_{xyy} , β_{yyy} , β_{xxz} , β_{xyz} , β_{yyz} , β_{xzz} , β_{yzz} , β_{zzz} respectively. Several types of hyperpolarizabilities are available in the literature namely β_{vec} (β vector),

$\beta_{||}$ (β parallel), β_{tot} (β total). β_{vec} , the component along the dipole moment is measured experimentally by Stark Spectroscopy. $\beta_{||}$ is the component parallel to the ground state CT direction (mostly used by theoretical chemists). β_{tot} is the hyperpolarizability type that is used for the calculation in this investigation [19].

β_{tot} can be derived as follows,

$$\beta_i = \beta_{iii} + \frac{1}{3} \sum_{i \neq j} (\beta_{ijj} + \beta_{jij} + \beta_{jji}) \quad (3.1)$$

The magnitude of the first hyperpolarizability tensor can be calculated using x, y and z components by using the following equation.

$$\beta_{tot} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad (3.2)$$

The complete equation to calculate the magnitude of the total first hyperpolarizability tensor from GAUSSIAN98W is,

$$\beta_{tot} = \left[\begin{aligned} &(\beta_{xxx} + \beta_{yyy} + \beta_{zzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{zyy})^2 \\ &+ (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2 \end{aligned} \right]^{1/2} \quad (3.3)$$

In GAUSSIAN98W, output β values are reported in atomic units (a.u.). To convert these values into electrostatic units (esu) the appropriate conversion should be done using the following conversion factor [19]

$$1 \text{ a.u.} = 8.6393 \times 10^{-33} \text{ esu.}$$

The optimized structures obtained for molecules **a** to **k₁** possess perfectly planar thiophene moieties which could give unhindered conjugation extending from the donor group to the acceptor as shown in Fig. 2.

However, molecules from **k₂** to **m** possess (Fig. 3) optimized geometries with a loss of planarity due to the steric effects of the ethyl hexyl groups attached. This results in a consequent reduction in the degree of conjugation that could reduce the π -electron communication across the molecule from the donor to the acceptor.

By using the equation 3.3 first static hyperpolarizabilities were calculated for all the 14 molecules under B3LYP and B3PW91 levels of theory. The current level of theory was chosen to keep the computational accuracy at a reasonable

level while reducing the computational cost. Also, since these functionals can be used with lower costs in many theoretical studies of potential optoelectronic materials, future comparisons of material properties (with different heteroatoms) will be facilitated. The values that were obtained from the GAUSSIAN98W output (in atomic units) for the components of the hyperpolarizability tensor were used to calculate β_{tot} values (in electrostatic units).

A summary of the results thus obtained for the two DFT methods employed are listed in Table 1. It can be observed that β_{tot} values exceed 1000×10^{-30} esu as the number of thiophene rings exceeds four.

Since both the values obtained from B3LYP and B3PW91 are in fair agreement with each other, the hyperpolarizability values obtained for the two methods map virtually on top of each other as illustrated in Fig. 4.

Therefore, it can be suggested that for hyperpolarizability calculations involving fairly small to moderate sized oligomers (from 2 to 8 repeating units), any one of the two methods would yield more or less the same value. i.e.,

both B3LYP functional and B3PW91 appear to behave in a similar manner [20]. Consequently, from here on, unless stated otherwise, only hyperpolarizability values obtained from the B3LYP method will be used for further discussion.

Table 1. Calculated hyperpolarizability (β_{tot}) values for all the molecules

Molecule	Number of Thiophene rings	Method	
		B3LYP $\beta_{\text{tot}} \times 10^{-30}$ (esu)	B3PW91 $\beta_{\text{tot}} \times 10^{-30}$ (esu)
a	2	70.99	71.44
b	3	256.50	258.27
c	4	660.43	664.30
d	5	1352.34	1357.29
e	6	2344.30	2345.73
f	7	3605.72	3595.54
g	8	5126.22	5094.32
h	2	68.45	68.96
i	3	247.00	249.19
j	4	660.10	666.32
k ₁	5	1402.72	1416.26
k ₂	5	1078.54	1086.80
l	6	1738.73	1751.36
m	7	2875.60	2901.00

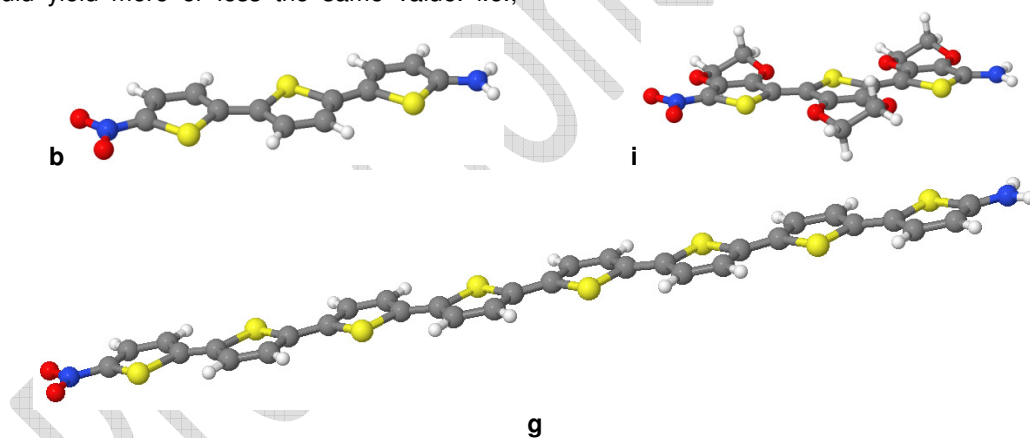


Fig. 2. Optimized structures of three molecules b, i and g

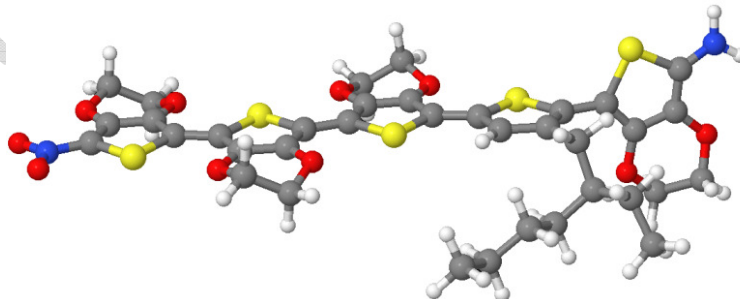


Fig. 3. Optimized structure of k₂

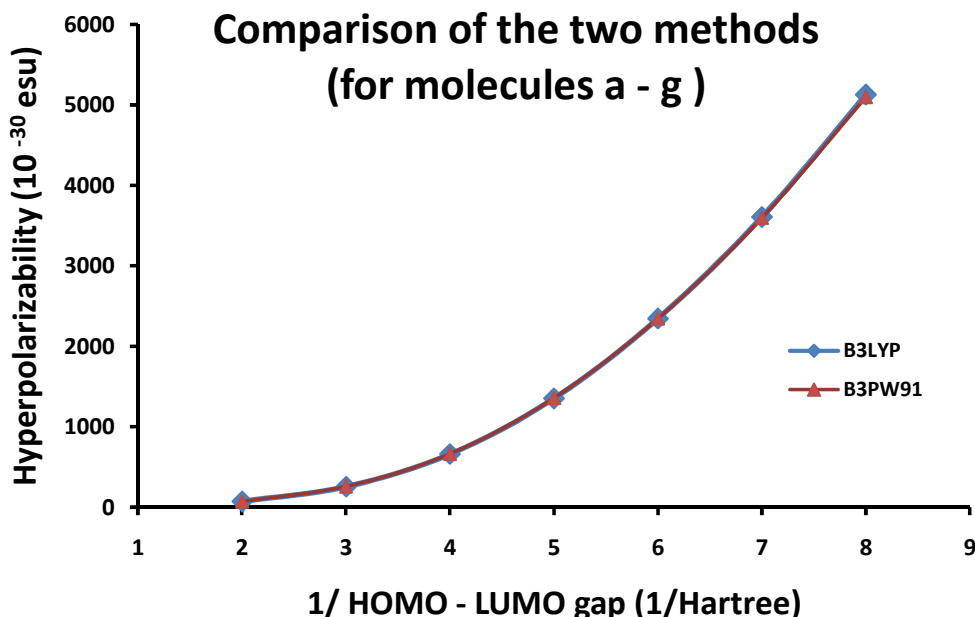


Fig. 4. Comparison between the two methods B3LYP and B3PW91

As can be observed from the Fig. 4, total first static hyperpolarizability values of thiophene oligomers increase exponentially with increasing chain length. Nevertheless, as Schulz et al. [14] report, the experimental third order polarizability values reach an asymptotic maximum value as the chain length is increased [13,15]. Nonetheless, thiophene-based oligomers appear to show very high NLO responses, compared to their furanyl, benzenyl and pyrrolyl counterparts [13]. Since molecules **a** to **g** do not possess inversion symmetry, their practical application could yield greater nonlinear responses. However, as reported by Hutchings et al. [15] some thiophene based molecules fail to give SHG response since the crystallization of the material has occurred in a centrosymmetric manner. Moreover, the strong colors of thiophenes obviate their use as SHG materials since optical transparency in the green and blue regions of the visible spectrum becomes a technical requirement. Therefore, if one intends to design a SHG NLO material a tradeoff between optical transparency and hyperpolarizability must be taken into account. Nevertheless, this requirement does not apply to electro-optic applications which results from Pockels effect [19].

The 3,4-ethylenedioxythiophenes (EDOTs) are employed in organic thin film semiconductor devices and to facilitate their incorporation into

such materials, as the chain length is increased, alkyl groups are substituted. Molecules **k**₂ to **m** are substituted by ethylhexyl groups as depicted in Fig. 1. Fig. 5 illustrates the variation in total first static hyperpolarizability for all the molecules under investigation against the number of thiophene rings present.

As the Figure depicts there is a significant change in the hyperpolarizability value when the molecules were substituted by alkyl groups. Both **k**₁ and **k**₂ possess five thiophene moieties while **k**₂ is substituted by an ethylhexyl group. The reduction in the hyperpolarizability for molecules **k**₂ to **m** can be explained by the fact that steric effects caused by the alkyl group results in the loss of planarity (as depicted in Fig. 3) in the π -conjugated structure which causes a significant loss of conjugation. This loss of conjugation disrupts the facile intramolecular charge transfer (ICT) from the donor to the acceptor across the conjugated system. Similar reductions in first hyperpolarizabilities with torsional angles were previously reported by Antipin and coworkers [21]. Even with such distortions in the structure, molecule **k**₂ to molecule **m** possess β_{tot} values exceeding 1000×10^{-30} esu. However, even with a corresponding reduction of β_{tot} (compared to a thiophene counterpart), the EDOTs seem to follow a similar exponential increase of the total first static hyperpolarizability. Nonetheless, molecule **g** possesses a β_{tot} value that is greater

than 7 times (greater than 5000×10^{-30} esu) the value of c , clearly indicating a highly favorable charge transfer across the molecule. The planar structure that is adopted by the molecule facilitates the charge transfer during the incidence of high intensity radiation. Table 2 lists HOMO, LUMO energies in atomic units and the HOMO LUMO gap and the inverse of the latter.

As depicted in Fig. 3 the thiophene ring that is adjacent to the alkyl substituent and that bears the electron donor group has undergone rotation around the rest of the planar moiety of the molecule. This in turn reduces the effective electronic communication via the π -conjugated

system. Thus intramolecular charge transfer (ICT) is interrupted, resulting in a reduced NLO response.

Even though the first static hyperpolarizability increases as the HOMO – LUMO gap [19,22] decreases, the inverse relationship between the two are not in the first order. i.e., the reciprocal of the HOMO – LUMO gap does not hold direct proportionality to the first static hyperpolarizability. Instead, the relationship appears to be exponential, as depicted in Fig. 6 of the plot of hyperpolarizability values calculated by the B3LYP method against the inverse of the HOMO – LUMO gap.

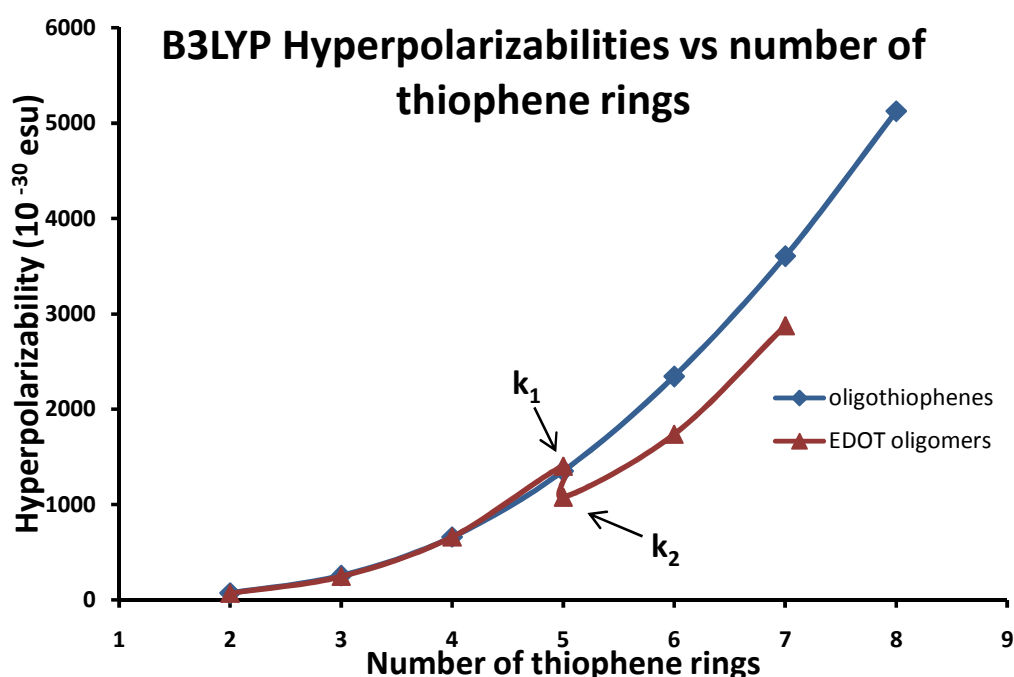


Fig. 5. Plot of B3LYP hyperpolarizability against the number of thiophene units

Table 2. HOMO LUMO energies of the optimized structures

Molecule (Number of Thiophene rings)	HOMO (Hartrees)	LUMO (Hartrees)	HOMO - LUMO gap (Hartrees)	1 / (HOMO - LUMO gap) (1/ Hartrees)
a (2)	-0.20419	-0.10287	0.10132	9.8697
b (3)	-0.19289	-0.10830	0.08459	11.822
c (4)	-0.18617	-0.11173	0.07444	13.434
d (5)	-0.18170	-0.11410	0.06760	14.793
e (6)	-0.17850	-0.11582	0.06268	15.954
f (7)	-0.17616	-0.11709	0.05907	16.929
g (8)	-0.17441	-0.11805	0.05636	17.743
h (2)	-0.18378	-0.08344	0.10034	9.9661
i (3)	-0.16091	-0.08547	0.07544	13.256
j (4)	-0.16008	-0.08673	0.07335	13.633
k ₁ (5)	-0.15424	-0.08765	0.06659	15.017
k ₂ (5)	-0.16565	-0.09369	0.07196	13.897
l (6)	-0.16089	-0.09293	0.06796	14.715
m (7)	-0.15927	-0.09573	0.06354	15.738

Hyperpolarizability vs Inverse HOMO/LUMO gap

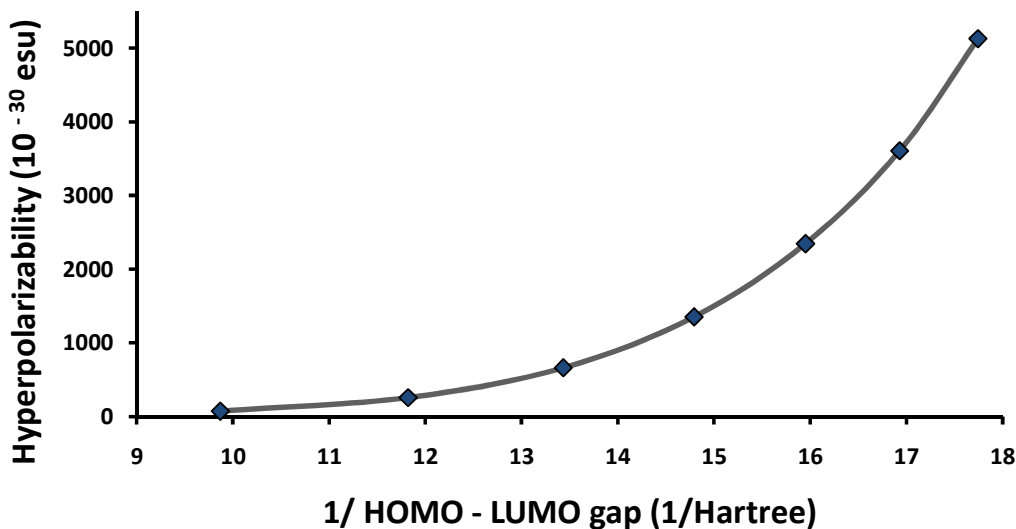


Fig. 6. Plot of hyperpolarizability against the inverse of the HOMO - LUMO gap

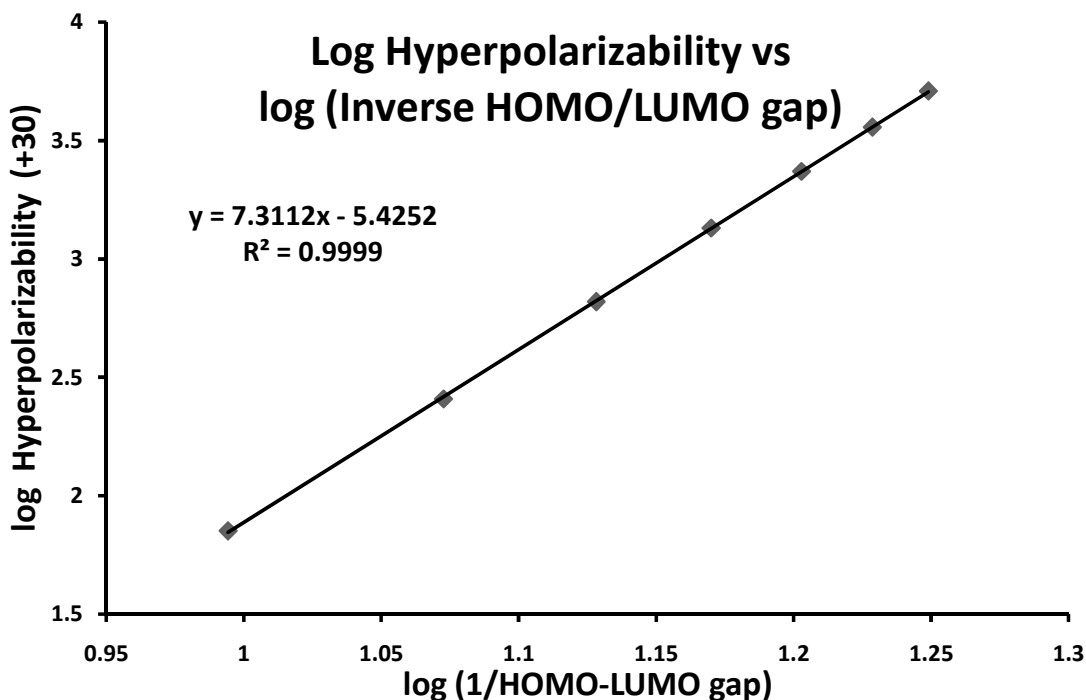


Fig. 7. Log Hyperpolarizabilities vs log (Inverse HOMO LUMO gap)

As depicted in Fig. 7 the logarithmic plot appears to be linear with a ~ 7.3 gradient indicating that the exponential rise is occurring to the $\sim 7.3^{\text{rd}}$ power of the inverse HOMO-LUMO gap (with coefficient of determination (R^2) being almost 1.000). Since larger molecules are

computationally more expensive due to the greater computational effort required, the prediction of first order nonlinear susceptibility of polymer materials could prove useful both for the theoretical chemist and to the synthetic chemist. Therefore, finding a relationship between the HOMO – LUMO gap and β_{tot} , could be a significant step forward. However, this assumed linearity in no way implies that a universal predictor is established. Further investigation on many such oligomeric materials as well as on longer polymer materials may lead to a better understanding of the relationship that was discussed above [15]. If the aforementioned general relationship (across many heteroatoms) was established a significant amount of computational time could be preserved since the time required for the calculation of HOMO, LUMO values are relatively shorter than the time required for a hyperpolarizability calculation.

Use of DFT for hyperpolarizability calculations is justified by the fact that, DFT methods incorporate correlation effects in their model Hamiltonians unlike many *ab initio* (HF) calculations. This in turn suggests that methods like HF require polarized or diffused basis sets to facilitate the consideration of electron correlation effects. This basis set requirement is significantly relaxed when the molecule under consideration is large, because, typically, the change in the charge cloud upon excitation becomes progressively smaller as the size of the system increases; i.e. for atoms and small molecules the change in the charge cloud is proportionately larger requiring greater polarized and diffused basis sets to account for the electronic charge distribution [3]. On the other hand semi-empirical methods are too arbitrary due to the inherent parametrization problem which makes them less accurate compared to DFT or HF. Therefore, DFT can be adopted instead of HF consuming relatively the same amount of computational time with increased accuracy. Furthermore, the use of 6-31 G basis set thus appear sufficient to produce results with an acceptable degree of accuracy with moderate computational effort, since the molecules become very large as the number of repeating units are increased.

The design and the practical adoption of SHG materials impose a barrier as the molecules become colored and thus non-transparent hindering their application in the technically viable region of the visible spectrum. Therefore, a tradeoff between transparency and hyperpolarizability is vital. This conundrum may

be circumvented by adopting an appropriate spacer group which could preserve planarity as well as the conjugation without driving/ limiting the absorption spectrum of the molecule towards the visible region. It can be suggested that polyyne oligomers as one such spacer group which could rather improve the NLO response while circumventing the aforementioned problem [23], which requires further investigations.

Therefore, thiophene moieties spaced by diyne or triyne groups could be a suitable model to start with. Nevertheless, it should be noted that the synthesis of such materials could be challenging as reported by Slepков et al. [23]. However, the synthesis of few oligo ethylene dioxythiophenes with side arms to enhance the solubility, has been reported in the recent literature [24].

Since the use of polymeric/oligomeric thin film materials for NLO applications are becoming increasingly popular, establishing a rule of thumb if not a solid theory to predict their hyperpolarizability values could prove useful. The linear dependence of hyperpolarizability against $\sim 7.3^{\text{rd}}$ power of the inverse HOMO – LUMO gap observed for thiophene oligomers may provide a predictive rule of thumb to know the hyperpolarizability values of longer oligomers/polymers, since HOMO – LUMO energy calculations require much less computational effort than a hyperpolarizability calculation. (e.g For octathiophene calculation times; HOMO-LUMO ~ 10 minute, Hyperpolarizability ~ 4 hours [~ 240 minutes]) However, this dependence requires further scrutiny as well as endorsement by experimental observations in order for it to be practically useful. Moreover, oligomeric material classes may be tested for such relationships (e.g., polyfurans, polypyrroles etc.), to see if the pattern observed can be extended over to all such oligomeric materials as a general trend.

4. CONCLUSIONS

In summary, in the current work, we report accurate calculations of static hyperpolarizabilities of thiophene-based oligomers including 3,4-ethylenedioxythiophenes (EDOTs). These molecules appear to give exceptionally large calculated hyperpolarizabilities due to their extensively π -conjugated D – π - A planar structure which facilitates direct electronic communication from the donor to the acceptor. However, the

hyperpolarizabilities of molecules from k_2 to m deviate from the trend observed in oligothiophenes, primarily due to the loss of planarity and consequent loss of conjugation of the optimized structures due to the presence of substituted alkyl groups. Such loss of conjugation disrupts the facile intramolecular charge transfer (ICT) across the system reducing the β_{tot} value significantly. Nevertheless, even after such reductions they show very high first hyperpolarizabilities (e.g., for k_2 , β_{tot} is greater than 1000×10^{-30} esu). The complete description of the hyperpolarizability values entails the consideration of the molecular orbital picture of the HOMO and LUMO, since it supplements HOMO-LUMO energy gap argument by adding the spatial aspect into perspective. Finally, if a general trend was found, our observation of a predictable trend between log-inverse of HOMO-LUMO gap and the log hyperpolarizability for the oligomers studied could prove useful for less expensive predictions of nonlinear optical properties for organic optoelectronic materials.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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