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 preformed 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.
Keywords: Ethylene dioxythiophene; thiophene; hyperpolarizability; density functional theory; non-linear optics.

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 Cs2, 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, $\beta_{vec}$ (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 $\beta_{tot}$ 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 $\beta_{tot}$ values using density functional theory (DFT). Moreover, the study compares two different DFT methods for their agreement between the calculated $\beta_{tot}$ 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 $\beta_{tot}$ 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, \( \beta \), 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. \( \beta \) reflects the effect that external electromagnetic radiation field imparts on the 10 components in the order of tetrahedral. The GAUSSIAN98W output gives the representation in the lower tetrahedral format (EDOT) oligomers possessing NH₂ and NO₂ groups on either side of each molecule, using GAUSSIAN98W.

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

\[
\beta_{\text{tot}} = \sqrt{\left(\beta_{xx}^2 + \beta_{yy}^2 + \beta_{zz}^2 + \beta_{xy}^2 + \beta_{xz}^2 + \beta_{yz}^2 + \beta_{zx}^2 + \beta_{zy}^2 + \beta_{zy}^2 + \beta_{zz}^2\right)}
\]

In GAUSSIAN98W, output \( \beta \) values are reported in atomic units (a.u.). To convert these values into electrostatic units (esu) the appropriate conversion factor 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 \( \mathbf{a} \) to \( \mathbf{k}_1 \) 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 \( \mathbf{k}_2 \) to \( \mathbf{m} \) 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 \( \pi \)-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 $\beta_{\text{tot}}$ 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 $\beta_{\text{tot}}$ values exceed $1000 \times 10^{-30}$ 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 ($\beta_{\text{tot}}$) values for all the molecules

| Molecule | Number of Thiophene rings | Method   | $\beta_{\text{tot}} \times 10^{-30}$ (esu) |
|----------|---------------------------|----------|------------------------------------------|
|          |                           | B3LYP    | B3PW91                                   |
| 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 k$_2$
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 k₂ 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 k₁ and k₂ possess five thiophene moieties while k₂ is substituted by an ethylhexyl group. The reduction in the hyperpolarizability for molecules k₂ 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 k₃ to molecule m possess βₜₗ values exceeding 1000 x 10⁻³⁰ esu. However, even with a corresponding reduction of βₜₗ (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 βₜₗ value that is greater than k₁ to k₃.
than 7 times (greater than $5000 \times 10^{-30}$ 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 $\pi$-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.

### Table 2. HOMO LUMO energies of the optimized structures

| Molecule (Number of Thiophene rings) | HOMO (Hartrees) | LUMO (Hartrees) | HOMO - LUMO gap (Hartrees) | $1 / (\text{HOMO} - \text{LUMO} \text{ gap})$ (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                                          |
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 ~7.3rd power of the inverse HOMO-LUMO gap (with coefficient of determination ($R^2$) being almost 1.000). Since larger molecules are
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 Slepkov 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 \( \beta_{tot} \) or \( \beta_1 \) 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 \( \pi \)-conjugated D – \( \pi \) - 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 $\beta_{tot}$ value significantly. Nevertheless, even after such reductions they show very high first hyperpolarizabilities (e.g., for $k_2$, $\beta_{tot}$ is greater than $1000 \times 10^{-30}$ 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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