Chemically Modified Quinoidal Oligothiophenes for Enhanced Linear and Third-Order Nonlinear Optical Properties

Amna Bibi, Shabbir Muhammad, Shafiq UrRehman,* Shamsa Bibi,* Shahid Bashir, Khurshid Ayub, Muhammad Adnan, and Muhammad Khalid*

ABSTRACT: In the present investigation, quantum chemical calculations have been performed in a systematic way to explore the optoelectronic, charge transfer, and nonlinear optical (NLO) properties of different bis(dicyanomethylene) end-functionalized quinoidal oligothiophenes. The effect of different conformations (linking modes of thiophene rings) on conformational, optoelectronic, and NLO properties are studied from the best-performed dimer to octamer. The optical and NLO properties of all the selected systems (1–7) are calculated by means of density functional theory (DFT) methods. Among all the designed compounds, the largest linear isotropic (δnIsotrop) polarizability value of 603.1 × 10⁻²⁴ esu is shown by compound 7 which is ∼ 12, ∼ 16, ∼ 9, ∼ 11, ∼ 10, and ∼ 4 times larger as compared to compounds 1–6, respectively. A relative investigation is performed considering the expansion in third-order NLO polarizability as a function of size and conformational modes. Among all the investigated systems, system 7 shows the highest value of static second hyperpolarizability (γ) with an amplitude of 7607 × 10⁻²⁰ esu at the M06/6-311G(2d,2p) level of theory, which is ∼ 521, ∼ 505, ∼ 38, ∼ 884, ∼ 185, and ∼ 15 times more than that of compounds 1–6, respectively. The extensively larger (γ) amplitude of compound 7 with higher oscillator strength and lower transition energy indicates that NLO properties are remarkably dependent upon linking modes of thiophene rings and its chain length. Furthermore, to trace the origin of higher nonlinearities, TD-DFT calculations are also performed at the same TD-M06/6-311G(2d,2p) level of theory. Additionally, a comprehensive understanding of the effect of structure/property relationship on the NLO polarizabilities of these investigated quinoidal oligothiophenes is obtained through the inspection of Frontier molecular orbitals, the density of states (TDOS and PDOS), and molecular electrostatic potential diagrams including the transition density matrix. Hence, the current examination will not just feature the NLO capability of entitled compounds yet additionally incite the interest of experimentalists to adequately modify the structure of these oligothiophenes for efficient optical and NLO applications.

1. INTRODUCTION
A nonlinear optical (NLO) material is considered as one of the most influential applications of science which originated from extremely acute laser systems.¹ NLO materials are playing a significant role in revolutionizing the modern time hi-tech community²−⁴ which creates the demand for potentially efficient NLO materials.⁵ These materials are incredibly fascinated by scientists and researchers because of their potential applications in optical computing,⁶ quantum optics,⁷ optical data processing devices,⁸ color display,⁹ particle accelerator,¹⁰ fluorescence imaging, dynamic holography,¹¹ telecommunication processes, and so forth.¹² Over the last couple of years, numerous types of NLO materials have been investigated in theory and experiment for their valuable electro-optical characteristics.¹³ These materials include organic polymers,¹⁴,¹⁵ semiconductors,¹⁶−¹⁸ organometallics,¹⁹ organic–inorganic hybrid, and inorganic materials. Every class of materials has its own advantages and disadvantages associated with it. For example, it is easy to grow bulk inorganic crystals with higher thermal stability, but optical nonlinearities of these molecules are not sufficient as required by modern time technological applications.⁵ In contrast, organic NLO materials with larger NLO susceptibilities are highly favored over their counterpart inorganic materials because of their diverse structural features, ease of fabrication, low dielectric constant, electro-optic modulation, quick response time, and low production cost.¹¹ A considerable amount of research interest has been focused on developing organic NLO materials with larger values of second- and third-order NLO properties.²⁰,²¹ Possibility in tuning the absorption wavelengths and chemical structures of organic materials is a key factor to design these materials with tremendously efficient NLO characteristics to be used in integrated optics, optical switching, and organic light-emitting diodes.²²−²⁴ To increase the efficiency of NLO materials, different strategies have been
adopted to address the issue of novel arising innovations. Conventionally, these strategies included the D–π–A (donor–π–acceptor) model, bond length alteration (difference between the distance of average single and double bonds in the conjugated framework) theory, switching perturbations, molecules with auxiliary donor and acceptors model, noncovalent charge transfer, chromophores with twisted-π electron systems, extension in π-conjugation of the molecular structure, and so on. A lot of theoretical and experimental investigations have shown that extending the length of π-conjugation can dramatically enhance the NLO response in organic molecules, making them leading candidates for NLO materials. Much great attention has been given to predict and perceive the optical polarizability (second- and third-order nonlinear polarizability) of different types of π-conjugated polymeric systems including polycyanes, polycetylene, and polyi thiophenes. Among these, considerable research interest is focused on sulfur-containing heterocyclic polythiophenes with rigid polymeric structures. These molecules show enhanced NLO activity under the influence of the applied electric field which results in greater redistribution of electric charge over the entire length of π-conjugation responsible for the polarization of molecules. Conjugated molecules with quinoidal structures are very important in determining the optoelectronic characteristics as these types of structures show effective electron delocalization, subsequently displaying reduced band gaps contrasted with their aromatic analogue. Over the last several decades, many quinoidal oligothiophene derivatives were reported to have NLO response characteristics. For example, Kishi et al. reported the linear and third-order NLO polarizability of phenoxyl-based derivatives of quinoidal oligothiophenes. Similarly, Vikramaditya et al. reviewed the electronic structure–property relationship of α-oligothiophenes substituted with electron-donating and electron-withdrawing groups. Dependence of linear and third-order NLO polarizability of oligothiophenes upon the type, number, and position of different substituents was explored by van Keuren et al.

An in-depth interpretation of NLO properties at both microscopic and macroscopic levels is required for the establishment of efficient materials to be used in NLO devices. In the field of science, integrative research efforts have been made in both theory and experiment for the improvement of organic NLO compounds. Quantum-chemical characterization provides significant information in order to understand electronic polarization and to establish structure–property interaction through molecular NLO approaches. In the present investigation, we have theoretically designed and explored the structure–property relationship of seven novel oligothiophene compounds (1–7) based on different numbers and connecting patterns of thiophene rings. All the compounds possess terminal dicyanomethylene acceptor groups as strong acceptors. Among these compounds, compounds 1 and 2 are designed by connecting two thiophene rings through two and three carbon–carbon bonds, respectively. Compounds 3 and 4 are composed of fusion of two and three thiophene rings, while compound 5 is designed by incorporation of a benzo group fused with two side thiophene rings. While, on the other hand, compounds 6 and 7 are extensions of compound 1 having four and eight thiophene rings.

After such key modifications, our work aims to explain the impact of conformational changes on optical and NLO properties of the oligothiophenes as moving from compound 1 to compound 7 having different conformations. Furthermore, the impact of increasing the chain length and insertion of bridging groups on the optical and NLO properties and energy band gaps will be studied for the designed geometries. Consequently, the present examination will not just feature the capability of chosen compounds as proficient third-order NLO materials yet also includes a relative investigation of the total and partial density of states (TDOS/PDOS), molecular electrostatic potential (MEP) diagrams, and transition density matrix (TDM) to tune such compounds for their possible use in linear and nonlinear optics and so on. To the best of our knowledge, an in-depth theoretical investigation of these quinoidal oligothiophenes is carried out for the first time which is the basic requirement to design new and improved organic NLO materials (Scheme 1).

2. COMPUTATIONAL METHODOLOGY

All the quantum-chemical calculations have been performed using Gaussian 16 package, whereas the visualization of the results is obtained using GaussView 5.0. The ground-state optimized geometries of all the designed compounds were obtained in the gas phase at the density functional theory (DFT) level of theory using the M06 method (Minnesota density functional) with 6-311G** basis sets. The recently developed M06 functional has provided satisfactory results in many computational investigations. To further test the functional for the current type of systems, we performed some test calculations for linear polarizability and third-order nonlinear (NLO) polarizability through the use of three different functionals including B3LYP, PBE0, and M06 with the 6-311G** basis set for compound 1. The calculated average static second hyperpolarizability (γ) of system 1 at B3LYP, PBE0, and M06 are found to be 31.14 × 10−36, 35.34 × 10−36, and 14.59 × 10−36 esu, respectively. As usual, B3LYP and PBE0 overestimated (γ) amplitudes in contrast to the M06 method. For example, the (γ) amplitude of compound 1 computed at the M06 functional is 2.13 and 2.42 times lesser as compared to B3LYP and PBE0 functionals, respectively (see Table S1 of Supporting Information). In the present study, in view of our test computations and some previously reported literature on M06 efficiency, we preferred to perform calculations using the M06 method for all compounds.

The stability of optimized molecular geometries was further confirmed as a global minimum by running vibrational
frequency calculation with no negative values of frequency. Transition properties were calculated using TD-DFT (time-dependent density functional theory) with the M06 functional and 6-311G** basis sets, which is the most accepted method for screening electronic transition characteristics because of its proficiency and accuracy. The linear polarizability and average third-order nonlinear polarizability along its tensor components were evaluated using the finite field (FF) method at the same M06/6-311G** level of theory. The well-known FF approach which was initially developed by Kurtz et al. is used to estimate polarizability and second hyperpolarizability. The FF approach is exploited by many computational and experimental scientists to characterize the properties of different types of NLO materials. In the FF approach, molecular systems were subjected to a static electric field to formulate the energy of the systems as expressed by the following equation

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

where the energy of the molecules in the absence of an electronic field is represented by \( E^{(0)} \), \( \mu \) is the vector component of dipole moments, \( \alpha \) is the linear polarizability, and \( \beta \) and \( \gamma \) are second- and third-order nonlinear (NLO) polarizabilities, respectively, where i, j, k, and l tensor components label the x, y, and z-axis, respectively. From the abovementioned equation, it is clearly shown that values of \( \mu, \alpha, \beta, \) and \( \gamma \) can be obtained by differentiating \( E \) with respect to \( F \). The dipole moment \( \mu \), isotropic (\( \alpha_{iso} \)) and anisotropic (\( \alpha_{aniso} \)) linear polarizability, and average third-order nonlinear polarizability (\( \gamma \)) of a system can be calculated using the expressions given below

\[ \mu = (\mu_x^2 + \mu_y^2 + \mu_z^2) \]

\[ \text{The average polarizability (} \alpha_0 \text{) can be calculated using the following equation} \]

\[ \alpha_0 = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \]

Anisotropic polarizability, which shows that potential energy is dependent upon the direction of electronic cloud with reference to the collision axis, can be estimated by the following expression

\[ \Delta \alpha = \frac{1}{\sqrt{2}} \sqrt{[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xyz}^2]} \]

The second hyperpolarizability is estimated using the following equations

\[ \gamma = \frac{1}{15} \sum_{i=j=k} (\gamma_{ijj} + \gamma_{iij} + \gamma_{iii}) \]

According to Kleinman symmetry, the abovementioned components can be reduced to six components for at least third-order nonlinear (NLO) polarizability.

\[ \gamma = \frac{1}{5}(\gamma_{xxxx} + \gamma_{yyy} + \gamma_{zzz} + 2(\gamma_{xyy} + \gamma_{xzr} + \gamma_{yyz})) \]

The specified components of (\( \gamma \)) in terms of their Cartesian coordinates are calculated from Gaussian 16 output files.
3. RESULTS AND DISCUSSION

3.1. Optimized Molecular Geometries. The optimized geometries of all the selected systems in the gas phase at M06/6-311G** computational methodology with labeled bond lengths and angles are depicted in Figure 1. All the investigated neutral molecules are rigid and planar (dihedral angle \( \theta \approx 180^\circ \)). The planarity of quinoidal oligothiophenes might be attributed to the contribution of quinoidal resonance forms since the quinoidal forms offer a double-bond contribution to the linker \( \text{C}_n-\text{C}_o \) bonds. The C-C single- and C=C double-bond lengths of terminal thiophene rings are found in the range of 1.41–1.45 and 1.36–1.39 Å lie in between typical carbon single- (1.54 Å) and double-bond distance (1.33 Å). The lengths of linker \( \text{C}_n-\text{C}_o \) bonds lie in the range of 1.36–1.39 Å which are also in between standard C-C single and double bonds. The bond angle between C−S−C of thiophene rings is found in the range 91.1–91.7° in \( \alpha-\alpha' \)-linked thiophenes, whereas it is reduced to 89.9° in all fused thiophene rings in order to maintain fused ring structures by decreasing the angle strain. The difference in the geometrical structures mainly comes from alteration in the bond length. Therefore, to deeply demonstrate the dependence of geometrical parameters on the chain length and different conformation modes, first of all, we calculated the bond length alternation (BLA) to assess the geometrical variations. Here, the value of BLA of each thiophene ring is calculated by subtracting the bond length of \( \text{C}_n-\text{C}_o \) from the average bond lengths of \( \text{C}_n-\text{C}_o \) and \( \text{C}_n-\text{C}'_o \) bonds. Since our main consideration is on the thiophene backbone, therefore, terminal C(CN)_2 groups and their connected bonds to thiophene are excluded from the BLA computation. In compounds 1, 2, and 3, both thiophene rings show a BLA value of \( \sim 0.09 \) (Å), whereas all three thiophene rings of compound 4 show a BLA value of \( \sim 0.08 \) (Å). A BLA value of \( \sim 0.07 \) (Å) is shown by both the terminal thiophene rings of compound 5. All the thiophene rings of compound 6 possess a BLA value of \( \sim 0.06 \) (Å). In compound 7, both terminal thiophene rings show a BLA of \( \sim 0.05 \) (Å), and rings next to terminal rings show a BLA of \( \sim 0.01 \) (Å), whereas middle rings show a BLA of \( 0.01 \) (Å). Terminal and central thiophene rings are found to be similar to each other in molecules with a smaller number of \( n \) (\( n = \) number of thiophene rings). In both \( \alpha-\alpha' \)-linked and fused thiophene rings, BLA values are found to be negative for terminal rings and remain negative for all \( n \), while it becomes positive for the central rings with \( n \geq 8 \) as in the case of compound 7. The positive values of BLA as shown by central rings of compound 7 indicate the appearance of the aromatic character in middle rings of quinoidal oligothiophenes with an extended chain length. From the above-mentioned results, it can be seen that all investigated compounds possess variable BLA values which could be beneficial for enhancing charge transfer properties.

3.2. Linear Polarizability (\( \alpha \)). Linear molecular polarizability plays a vital role to comprehend the electronic charge distribution. When the external electric field is applied to the molecules, it creates negative and positive poles resulting in the polarizability of molecules. The linear isotropic (\( \alpha_{\text{iso}} \)) and anisotropic (\( \alpha_{\text{aniso}} \)) polarizabilities of all the designed compounds along with individual tensor components calculated at the M06/6-311G** level of theory are given in Table 1. Among the individual tensor components, \( \alpha_{\text{iso}} \) shows larger values, showing that polarizability mainly occurred along the x-axis. Compound 7 shows the larger polarizability value of \( 1693 \times 10^{-24} \) esu, which is \( 
abla \sim 16, \sim 22, \sim 12, \sim 15, \sim 15, \sim 5 \) times greater than compounds 1–6, respectively. The trend of increasing the linear polarizabilities of all the compounds is as \( 2 \times 1 < 4 = 5 < 3 < 6 < 7 \). The graphical analysis of \( \alpha_{\text{iso}} \) and \( \alpha_{\text{aniso}} \) of all the compounds has been shown in Figure 2. From Figure 2, it can be seen that amplitudes of \( \alpha_{\text{iso}} \) and \( \alpha_{\text{aniso}} \) increase efficiently upon increasing the degree of \( \pi \)-conjugation in all the compounds. Among all the designed compounds, compound 2 shows the least value of isotropic and anisotropic polarizability, which is \( 38.51 \times 10^{-24} \) and \( 59.72 \times 10^{-24} \) esu, respectively, while, on the other hand, compound 7 shows the largest isotropic and anisotropic polarizability of \( 603.1 \times 10^{-24} \) and \( 1642 \times 10^{-24} \) esu, respectively. Moreover, the larger difference between isotropic and anisotropic polarizability values of all the compounds shows that polarizability significantly depends on the direction of the applied electric field.

3.3. Third-Order NLO Polarizability. From the chemical point of view, the most vital NLO theoretical computation characteristic is that they provide a critical understanding of...
shows the largest \( \gamma \) amplitude of third-order nonlinear polarizability \( \gamma \) values of all the compounds is represented in Figure 3. Among the individual tensor components computed at the M06/6-311G** level of theory are organized in Table 2. Among the individual tensor components, \( \gamma_{xxxx} \) shows the largest amplitude of third-order NLO polarizability because the x-axis is oriented along the direction of the intramolecular charge transfer axis in these molecules. From Table 2, it can be seen that values of \( \gamma_{xxxx} \) are even larger than that of average \( \langle \gamma \rangle \) amplitudes. A comparative study of the designed systems designates that compound 7 shows the largest \( \gamma_{xxxx} \) value of 38.591 \( \times 10^{-36} \) esu, which is about \( \sim 771, \sim 1054, \sim 50, \sim 202, \sim 548, \) and \( \sim 13 \) times greater as compared to compounds 1–6, respectively. On the other hand, the lowest \( \gamma_{xxxx} \) value of 36.61 \( \times 10^{-36} \) esu is shown by compound 2. The increasing trend of \( \gamma_{xxxx} \) values of all the compounds is \( 2 < 1 < 5 < 4 < 3 < 6 < 7 \). Furthermore, the graphical comparison of average third-order nonlinear polarizability \( \langle \gamma \rangle \) of all the compounds is represented in Figure 3.

![Figure 3](https://doi.org/10.1021/acsomega.1c03218)  
Figure 3. Plot of average third-order nonlinear polarizability \( \langle \gamma \rangle \) of all the selected compounds computed at M06/6-311G** levels of theory.

From Figure 3, it is observable that compound 7 shows the highest \( \langle \gamma \rangle \) amplitude of 7607 \( \times 10^{-36} \) esu, which is \( \sim 521, \sim 505, \sim 38, \sim 884, \sim 185, \) and \( \sim 15 \) times more than that of compounds 1–6, respectively. To make a comparative analysis of the average third-order polarizability of our designed compounds, \( \langle \gamma \rangle \) values of para-nitroaniline (p-NA) were also computed at the same M06/6-311G** level of theory to make the comparison more reliable. The average third-order polarizability of p-NA is found to be 7.29 \( \times 10^{-36} \) esu. The comparison shows that all the studied compounds possess larger \( \langle \gamma \rangle \) values as compared to the p-NA molecule. For example, investigated \( \langle \gamma \rangle \) amplitudes of all the designed compounds (1–7) are \( \sim 2 \) to \( \sim 1043 \) times more than that of p-NA. Consequently, this comparison of \( \langle \gamma \rangle \) amplitudes of p-NA and our compounds revealed that our natively designed compounds are potential contenders for NLO and can be utilized for potential NLO applications.

### 3.4. TD-DFT Calculations and Origin of NLO Response

In order to trace the origin of the substantial NLO response of the above-entitled compounds, we have also performed TD-DFT computations at the TD-M06/6-311G** level of theory. All the spectroscopic parameters including oscillator strength \( (f_g) \), transition energy \( (\Delta E) \), crucial excited states, % configuration interaction (C.I.), and transition moment \( (\mu_{ng}) \) from TD-DFT calculations have been collected in Table 3. In fact, transition dipole moment and transition energy are considered as two of the most important parameters to trace the origin of higher third-order nonlinear polarizability values. Based on the perturbative formula, a simple three-state approximation is considered here by employing these spectroscopic parameters to trace the origin and trend of higher third-order NLO polarizability for the static longitudinal \( \gamma_1 \) value as follows:

\[
\gamma_1 = 24 \left( \frac{\mu_{ng}^2 f_{ng}^2}{\Delta E_{ng}} - \frac{\mu_{ng}^4}{4 \Delta E_{ng}^3} \right)
\]

(7)

\[
\gamma_1 = 18 \left[ \frac{\Delta \mu_{ng}^2 f_{ng}^4}{2 \Delta E_{ng}^5} - \frac{3 f_{ng}^2}{\Delta E_{ng}^5} \right]
\]

(8)

where transition moment is represented by \( \mu_{ng} \) transition energy involved in crucial excited states is shown by \( \Delta E_{ng} \) and \( \Delta \mu_{ng} = \mu_{ng} - \mu_{ng} \)(the change in dipole moment from the ground \( (|g\rangle) \) to the crucial excited \( (|n\rangle) \) state. In addition, \( f_{ng} \) is the oscillatory strength which relates the transition energy and transition momentum as shown by the following equation

\[
f_{ng} = \frac{2}{3} \Delta E_{ng} \mu_{ng}^2
\]

(9)

A careful analysis of the abovementioned expressions shows that all of these parameters are closely related to each other and mainly depend upon the electronic characteristics of NLO compounds. This three-level approximation has been broadly utilized by many computational and experimental scientists to explain the modifications in NLO response of several push–pull systems. For additional subtleties of the abovementioned approximations, we recommend the reader to the studies of Nakano et al., Bredas et al., and similar other investigators.

It is apparent from eqs 7 and 8 that \( \gamma \) has a direct relation with the transition dipole moment and oscillator strength, while inverse relation with transition energy \( \Delta E \). Obviously,
lower transition energy accompanied by higher transition dipole moment and oscillator strength will lead to greater charge transfer, which consecutively results in robust NLO-response (third-order NLO polarizability) properties. From Table 3, it can be seen that all the compounds possess considerably lower values of transition energies which decrease upon increasing the extent of conjugation. For better understanding, a graphical comparison between average third-order polarizability $\langle \gamma \rangle$ and transition energies of all the designed compounds is represented in Figure 4. It is clear from Tables 2 and 3 that compound 7 exhibits the largest $\gamma_{xxxx}$ value of $38,591 \times 10^{-36}$ esu which is attributed to its higher oscillator strength of 2.1959 and relatively lower transition energy of 0.714, showing that extension in $\pi$-conjugation incredibly enhanced the NLO response in these compounds. These outcomes are very encouraging with the previously mentioned three-level approximation.

3.5. Frontier Molecular Orbitals. At the molecular level, internal charge transfer (ICT) characteristics are mainly governed by the nature of molecular orbitals (MOs). The energy level and spatial distribution of MOs help us to predict the stability and chemical reactivity of compounds. Qualitative Frontier MO (FMO) representation of all the investigated compounds has been depicted in Figure 5 (representation of other MOs is given in Figures S1–S7 of Supporting Information). The transition nature of FMOs (HOMOs/LUMOs) is a key factor in determining the optoelectronic properties of the molecules. From Figure 5, it can be seen that all the designed compounds have almost the same pattern of electronic distribution on the highest occupied MO (HOMO) and lowest unoccupied MO (LUMO) and both orbitals are of $\pi$-nature with the electronic densities distributed over the whole $\pi$-conjugated backbone of oligothiophenes along with participation from nitrogen atoms of dicyanomethylene (C(CN)$_2$) groups except for compound 7 where the electron densities are localized more on the terminal thiophene ring and dicyanomethylene groups attributed to the spatial distribution of unpaired electron density (odd-electron density) which increases upon increasing the number of thiophene rings. Moreover, sulfur atoms of the thiophene ring largely contributed to the formation of the HOMO, and during the transition from the HOMO to LUMO, this electron density is distributed over the entire molecular framework. Notably, larger contribution of the 3p-orbital of the sulfur atom to the HOMO should be effecive for efficient intramolecular overlapping which is beneficial for the charge transfer process.

Table 3. Transition Energies $\Delta E$ (eV), Oscillator Strength ($f_0$), Transition Dipole Moments ($\mu_{ng}$), and Percentage Configuration Interactions (C.I) of All the Designed Compounds Calculated at the M06/6-311G** Level of Theory

| compounds | electronic excitation | $\Delta E$ (eV) | $f_0$ | $\mu_{ng}$ | transitions | % C.I. |
|-----------|------------------------|----------------|-------|------------|-------------|-------|
| 1         | $S_0 \rightarrow S_1$  | 2.398          | 1.158 | 4.441      | H $\rightarrow$ L      | 71    |
|           | $S_0 \rightarrow S_1$  | 3.566          | 0.227 | 1.614      | H $\rightarrow$ 2 $\rightarrow$ L | 70    |
|           | $S_0 \rightarrow S_1$  | 2.717          | 0.000 | 0.000      | H $\rightarrow$ 1 $\rightarrow$ L | 70    |
| 2         | $S_0 \rightarrow S_1$  | 2.871          | 1.196 | 4.116      | H $\rightarrow$ L      | 72    |
| 3         | $S_0 \rightarrow S_1$  | 2.341          | 1.780 | 5.570      | H $\rightarrow$ L      | 72    |
|           | $S_0 \rightarrow S_1$  | 3.681          | 0.142 | 1.258      | H $\rightarrow$ 2 $\rightarrow$ L | 69    |
| 4         | $S_0 \rightarrow S_1$  | 2.371          | 0.417 | 2.680      | H $\rightarrow$ 1 $\rightarrow$ L | 53    |
| 5         | $S_0 \rightarrow S_1$  | 2.647          | 1.020 | 3.966      | H $\rightarrow$ L      | 54    |
|           | $S_0 \rightarrow S_1$  | 2.017          | 0.000 | 0.000      | H $\rightarrow$ 1 $\rightarrow$ L | 70    |
| 6         | $S_0 \rightarrow S_1$  | 2.390          | 1.441 | 4.947      | H $\rightarrow$ L      | 72    |
| 7         | $S_0 \rightarrow S_1$  | 1.649          | 2.266 | 7.488      | H $\rightarrow$ L      | 74    |
|           | $S_0 \rightarrow S_1$  | 3.469          | 0.131 | 1.243      | H $\rightarrow$ 5 $\rightarrow$ L | 47    |
|           | $S_0 \rightarrow S_1$  | 0.714          | 2.195 | 11.19      | H $\rightarrow$ L      | 97    |
|           | $S_0 \rightarrow S_1$  | 2.060          | 1.930 | 6.184      | H $\rightarrow$ L + 2 | 55    |

Figure 4. Graphical comparison between average third-order nonlinear polarizability $\langle \gamma \rangle$ and transition energy.

Figure 5. Three-dimensional illustration of FMOs of all the compounds involved in crucial transitions obtained at M06/6-311G** levels of theory.
The terminal electron-withdrawing C(CN)₂ groups equally participate in both FMOs and lowering the energy levels of the LUMO, showing an overall redistribution of charge density. To quantitatively analyze the effect of different conformations and chain length on FMO energy, the energy level diagram of the HOMO and LUMO is represented in Figure 6. It is apparent from Figure 6 that compound 7 possessed the lowest energy gap (ΔEₚ) of 0.35 eV. The energy gap (ΔEₚ) between the MOs is an imperative parameter to control the electronic and optical properties of the systems by changing the process of ICT. Consequently, the lower orbital energy gap facilitates the electronic transitions promoting ICT processes with lower transition energy and greater oscillator strength as accompanied by compound 7. The decreasing trend of orbital band gaps of all the compounds is 2 > 4 > 1 > 3 > 5 > 6 > 7. Table 3 illustrates the nature, oscillator strength, and energy of electronic transitions (singlet−singlet) for all the selected compounds computed at the TD-DFT M06/6-311G** level of theory. From Table 3, it can be observed that the most intense electronic transitions are occurring from the HOMO to LUMO, which are crucial for currently designed compounds.

3.6. Molecular Electrostatic Potentials. The MEP maps are very important in illustrating the reactivity of chemical compounds by anticipating their electrophilic and nucleophilic sites. MEP analysis of all the selected systems is carried out at the same M06/6-311G** level of theory, and three-dimensional MEP plots representing total electron density distribution are shown in Figure 7. In MEPs, nuclear and electronic charge distribution is represented by a wide range of color bands, which is an appropriate physical feature to comprehend the reactivity of different chemical species. Regions with higher negative potentials are specified by a red color, indicating the site for an electrophilic attack, whereas the higher positive potential region is distinguished by blue color, which is a favorable site for nucleophilic attack. From Figure 7, it can be seen that terminal dicyanomethylene C(CN)₂ groups confined the maximum negative potential (red) region which increases upon increasing the degree of conjugation. Hence, terminal C(CN)₂ groups are the favorable sites for an electrophilic attack, while, on the other hand, the maximum positive potential (blue) region is confined by the central thiophene core which is the beneficial site for nucleophilic attack in all above-entitled compounds.

3.7. Density of States. In order to comprehensively understand the structure−NLO property relationship of designed compounds, the explicit contribution of an individual fragment in the form of their PDOSs and total density of states (TDOS) has also been calculated using AOMix software at the M06/6-311G** level of theory. Plots of TDOS and PDOS are generated by splitting the whole molecule into two fragments, that is, central core containing the central thiophene backbone and the C(CN)₂ fragment consisting of terminal dicyanomethylene groups (see Figure 8). The plots of PDOS and TDOS offer insights into optical and electronic characteristics. The TDOS plots seem to show the population evaluation of each orbital over the entire molecule, while, on the other hand, the contribution of each molecular fragment toward the whole orbital make-up of the final molecule is determined by the plots of PDOS. From Figure 8, it can be seen that both fragments of the central core and C(CN)₂ show somewhat similar patterns of contributions in PDOS and TDOS in all designed molecules. In the ground state, the HOMO energy of compound 1 is −7.03 eV, which upon excitation increases to −4.54 eV, and the band gap between the HOMO and LUMO is found to be 2.48 eV. Similarly, the HOMO and LUMO of compound 2 have an energy of −7.51 eV and −4.61 eV, respectively, with a band gap of 2.90 eV. The
remaining compounds 3, 4, 5, 6, and 7 have an energy of −6.78, −7.08, −6.02, and −5.08 eV, respectively, in the ground state (HOMO), while their excited state energies (LUMO) are found to be −4.38, −4.59, −4.49, and −4.73 eV, respectively, with a band gap ($\Delta E_g$) of 2.40, 2.49, 2.27, 1.53, and 0.35 eV, respectively. The following trend is observed when these compounds are placed in the ascending order of their band gap: 7 < 6 < 5 < 3 < 4 < 1 < 2. In all compounds, the major contribution of the central core and C(CN)$_2$ fragment in the valence band occurs at ~12 to ~10 eV and ~14 to ~12 eV, respectively, while for the conduction band, major contribution is shown at ~1 to ~6 eV and ~1 to ~4 eV by the central core and C(CN)$_2$ fragment, respectively. From the DOS graph of compounds 6 and 7, it is apparent that the contribution of central thiophene rings increases in the HOMO and in the LUMO with an extension in the length of $\pi$-conjugation results in enhanced charge transfer characteristics. Furthermore, Mulliken’s analysis as representative of the
percentage (%) contribution of each fragment to DOS in terms of FMOs also confirmed that different conformations, linking modes, and chain lengths affect the distribution patterns of charge density around the HOMO and LUMO (see Table S4 of Supporting Information). The significant contribution of both fragments in PDOS and TDOS maps without significant donor/acceptor trend reported a good intramolecular charge transfer particularly for compound 7 with the lowest band gap of 0.3 eV, which is additionally in line with the abovementioned good optical transition and NLO-response properties of this compound.

3.8. Transition Density Matrix. We have specifically calculated the colored 3D TDM plots of our designed molecules using multiwfn 3.8 software at the M06/6-311G** level of theory to estimate the charge transfer behavior that happens in between the lower and middle energy peaks. Moreover, it also provides information related to the specific positioning of electrons, holes, and electron−hole overlap. The TDM plots provide a great deal of information about the intramolecular charge transfer phenomenon. Therefore, we have also estimated these for our calculated molecules for the very first time in order to explore their hidden potential, as shown in Figure 9. Interestingly, we have realized that all of our calculated molecules show a significant ICT behavior. It is interesting to see that electron−hole pairs are likely to localize along with the diagonal element, but still, some are delocalized with the same element, while also the electron−hole coherence is delocalized over the whole molecule, ensuring a specific delocalized transition. From Figure 9, it can be viewed that α-α’-linked oligothiophenes show more dissociation of charge along with the diagonal component as compared to fused oligothiophenes, and the extent of dissociation increases with increasing the conjugation in both oligothiophenes and oligothienoacenes. Among all the selected compounds, compound 7 shows substantial intramolecular charge transfer followed by smaller electron−hole coherence, resulting in easy dissociation of excitations. Furthermore, there is also the probability of transformation of electrons seen in the off-diagonal part which could also be helpful to further improve the charge transfer behavior of the molecules.

Figure 9. TDM analysis of all the designed compounds associated with low-energy electronic transitions at the M06/6-311G** level of theory (effect of hydrogen atoms has been neglected because of their little contribution in electronic transitions). Here, C represents the central oligothiophene ring and A represents the terminal C(CN)2 acceptor groups.
4. CONCLUSIONS

Thus, in the current quantum chemical investigation, we have successfully calculated isotropic and anisotropic linear polarizabilities and third-order NLO polarizabilities for all designed compounds by utilizing DFT and TD-DFT methodology. Among all the studied compounds, the highest linear polarizability ($\alpha_{x}$) is found to be $1693 \times 10^{-24}$ esu for compound 7. Static third-order NLO polarizabilities ($\gamma$) shown by compounds 1–7 are found to be $14.59 \times 10^{-36}$, $15.04 \times 10^{-36}$, $197.8 \times 10^{-36}$, $8.662 \times 10^{-36}$, $41.10 \times 10^{-36}$, $492.4 \times 10^{-36}$, and $7607 \times 10^{-36}$ esu, respectively, at the M06/6-311G** level of theory. According to the relative investigation of ($\gamma$) of all the compounds, the lowest ($\gamma$) amplitude of $8.662 \times 10^{-36}$ has been shown by compound 4, whereas compound 7 expressed an extensively larger ($\gamma$) amplitude of $7607 \times 10^{-36}$ esu. Static second hyperpolarizability ($\gamma$) of all the designed systems has also been compared with that of the prototype p-NA molecule. Intriguingly, the largest ($\gamma$) amplitude of $7607 \times 10^{-36}$ esu exhibited by our best-considered compound 7 is $\approx 1043$ times greater as compared to p-NA ($7.29 \times 10^{-36}$ esu) calculated at the same M06/6-311G** level of theory, which manifests significant NLO potential characteristic of compound 7. Furthermore, TD-DFT computations have also been carried out to examine the effect of chain length upon transition properties. The results of FMOs revealed that compound 7 with an extensive quinoidal conjugative strand exhibits the lowest band gap ($\Delta E_i$) of 0.35 eV, promoting the extensive ICT from the HOMO–LUMO, which is also in good agreement with TDM results where compound 7 shows the greater extent of charge dissociation which is a characteristic feature of these compounds. The lower linear and nonlinear polarizability values along with a larger band gap of compounds 2, 4, and 5 as compared to compounds 6 and 7 contributed to destabilization of the HOMO and LUMO in these compounds show that $\alpha_{x}$-linked oligothiophenes possess greater NLO response as compared to fused oligothiophenes. All of these observations clearly manifest the extremely larger effect of the position, nature, and extent of the chain length upon linear and nonlinear polarizability of our designed compounds.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c03218.

Table for comparison of third-order nonlinear polarizability of compound 1 using different methods, MO energy values (HOMO + i and LUMO – i where i = 0, 1, 2, 3, 4, and 5), band gap ($\Delta E_i$), percentage composition of building fragments in FMOs, and 3-D FMO plots of all the designed compounds (PDF)

AUTHOR INFORMATION

Corresponding Authors
Shafiq UrRehman — Department of Chemistry, University of Agriculture Faisalabad, Faisalabad 38000, Pakistan; Email: shafiq.urrehman@uaf.edu.pk
Shamsa Bibi — Department of Chemistry, University of Agriculture Faisalabad, Faisalabad 38000, Pakistan; orcid.org/0000-0003-2936-4716; Email: shamsa.shafiq@uaf.edu.pk

Muhammad Khalid — Department of Chemistry, Khwaja Faried University of Engineering & Information Technology, Rahim Yar Khan 64200, Pakistan; Email: khalidhej@hotmail.com

Authors
Amna Bibi — Department of Chemistry, University of Agriculture Faisalabad, Faisalabad 38000, Pakistan
Shabbir Muhammad — Department of Physics, College of Science, King Khalid University, Abha 61413, Saudi Arabia; orcid.org/0000-0003-4908-3313
Shahid Bashir — Centre for Ionic University of Malaya, Department of Physics, University of Malaya, Kuala Lumpur 50603, Malaysia
Khurshid Ayub — Department of Chemistry, COMSATS University, Islamabad 22060, Pakistan; orcid.org/0000-0003-0990-1860
Muhammad Adnan — Graduate School, Department of Chemistry, Chosun University, Gwangju 501-759, Republic of Korea; orcid.org/0000-0001-9224-3824

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acsomega.1c03218

Notes

The authors declare no competing financial interest.

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