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Key Electronic, Linear and Nonlinear Optical Properties of Designed Disubstituted Quinoline with Carbazole Compounds

Bakhat Ali 1,2,*, Muhammad Khalid 2,*, Sumreen Asim 3, Muhammad Usman Khan 3,*, Zahid Iqbal 2,*, Ajaz Hussain 4, Riaz Hussain 3, Sarfraz Ahmed 5, Akbar Ali 6, Amjad Hussain 3, Muhammad Imran 7,*, Mohammed A. Assiri 7, Muhammad Fayyaz ur Rehman 6,*, Chenxi Wang 8,* and Changrui Lu 1,*

1 Department of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai 201620, China; bakhat.ali@kfueit.edu.pk
2 Department of Chemistry, Khwaja Fareed University of Engineering & Information Technology, Rahim Yar Khan 64200, Pakistan; sumreen.asim@kfueit.edu.pk (S.A.); mrzahidiqbal77@gmail.com (Z.I.)
3 Department of Chemistry, University of Okara, Okara 56300, Pakistan; usman.chemistry@gmail.com (M.U.K.); riazhusain@uo.edu.pk (R.H.); amjadhusain@uo.edu.pk (A.H.)
4 Institute of Chemical Sciences, Bahauddin Zakariya University, Multan 60800, Pakistan; ajaz_hussain11@yahoo.com
5 KBCMA College of Veterinary and Animal Sciences, Narowal 51600, Pakistan; sarfraz.ahmed@uvas.edu.pk
6 Institute of Chemistry, University of Sargodha, Sargodha 40100, Pakistan; akbarchm@gmail.com (A.A.); fayyaz9@gmail.com (M.F.u.R.)
7 Department of Chemistry, Faculty of Science, King Khalid University, P.O. Box 9004, Abha 61413, Saudi Arabia; imranchemist@gmail.com (M.I.); maassiri@kku.edu.sa (M.A.A.)
8 Department of Cardiovascular Surgery, Renji Hospital, School of Medicine, Shanghai Jiaotong University, Shanghai 200240, China
* Correspondence: Khalid@iq.usp.br (M.K.); wangchenxir@yeah.net (C.W.); crlu@dhu.edu.cn (C.L.)

Abstract: Organic materials development, especially in terms of nonlinear optical (NLO) performance, has become progressively more significant owing to their rising and promising applications in potential photonic devices. Organic moieties such as carbazole and quinoline play a vital role in charge transfer applications in optoelectronics. This study reports and characterizes the donor–acceptor–donor–π–acceptor (D–A–D–π–A) configured novel designed compounds, namely, Q3D1–Q3D3, Q4D1–Q1D2, and Q5D1. We further analyze the structure–property relationship between the quinoline–carbazole compounds for which density functional theory (DFT) and time-dependent DFT (TDDFT) calculations were performed at the B3LYP/6-311G(d,p) level to obtain the optimized geometries, natural bonding orbital (NBO), NLO analysis, electronic properties, and absorption spectra of all mentioned compounds. The computed values of λmax, 364, 360, and 361 nm for Q3, Q4, and Q5 show good agreement of their experimental values: 349, 347, and 323 nm, respectively. The designed compounds (Q3D1–Q5D1) exhibited a smaller energy gap with a maximum redshift than the reference molecules (Q3–Q5), which govern their promising NLO behavior. The NBO evaluation revealed that the extended hyperconjugation stabilizes these systems and caused a promising NLO response. The dipole polarizabilities and hyperpolarizability (β) values of Q3D1–Q3D3, Q4D1–Q1D2, and Q5D1 exceed those of the reference Q3, Q4, and Q5 molecules. These data suggest that the NLO active compounds, Q3D1–Q3D3, Q4D1–Q1D2, and Q5D1, may find their place in future hi-tech optical devices.

Keywords: carbazole; quinoline; NLO response; density functional theory; acceptor units

1. Introduction

Recently, the demand for more efficient optoelectronic materials has skyrocketed. Numerous theoretical and experimental research groups focus on the development of nonlinear optical (NLO) materials [1–6] owing to their overwhelming potential in photonic-based...
technologies [7,8], including two-photon excitation fluorescence imaging [9], multidimensional optical-based data storage devices [10], optical communication [11], and numerous other optical devices [12]. Studies have also reported different NLO active materials, including molecular dyes and organic and inorganic polymers, as well as nanomaterials [13–17]. Among the NLO active compounds described above, organic compounds, especially with a π-extended skeleton [18], attract more interest in NLO studies due to their efficient intra-molecular charge transfer (ICT) process. Organic compounds synthesis is relatively easily, and these compounds possess higher photothermal stability, structural flexibility, and quick response time [19,20].

Recently, the electronic properties for photonic applications have extended to many organic compounds with donor–π–acceptor (D–π–A) chemical systems where the donor (D) plays the role of hole transport and the acceptor (A) plays a role as an electron transporter [21]. Usually, non-centrosymmetric organic compounds show a second-order nonlinear polarizability response [22]. Specifically, the compounds consisting of electron donor (D) and electron acceptor (A) moieties connected by a π-conjugated bridge led to a considerable increment in the ICT process [23–28]. Consequently, the transfer of electron density from D to A units via a π-bridge imparts NLO properties to D–π–A organic compounds [29]. The literature has reported many different configurations of π-conjugated systems: D–π–A, D–π–π–A, A–π–D–π–A, D–π–A–π–D, D–D–π–A, D–A–π–π–A, and D–A–π–A [30–34], showing an enhancement in ICT that might eventually result in a significant NLO response. One such compound is quinoline, which plays many roles in optoelectronic applications.

Quinoline and its derivatives have applications in various fields, such as organic light-emitting diode (OLED) [35] and solar cell (SC) technologies [36]. Quinoline-based compounds possess high thermal and chemical stability, electron-transporting capability, and easy structural modification. These key properties are highly desired in optoelectronic applications [37,38]. The electron-withdrawing nature of quinoline also plays a significant role in the electron transportation process. On the other hand, carbazole, with an electron-rich moiety, has many applications and is frequently used in hole-transporter materials [39,40]. Quinoline derivatives have been prepared by diverse synthetic routes, especially cross-coupling reactions using different catalysts [41–43]. Kiymaz et al. [44] reported that the substitution effect on a carbazole ring results in better performance of dyes with a C4 atom alkyl chain than dyes containing an alkyl chain with C2, C6, and C12 atoms. Recently, Slodek et al. [45] presented a vital synergistic experimental–computational report on how the different lengths of the alkyl chain, substituted at the 3-position (N atom) of a carbazole ring, affect the electrochemical and optical properties of the entire system. This report also confirms that different substitutions at the nitrogen (N) atom of the carbazole ring can tune the overall characteristics of compounds [45]. However, no study has reported the NLO-based properties of these synthesized molecules. Consequently, we utilized synthesized Q3 (2,2′-(quinoline-2,4-diyl)bisis(9-methyl-9H-carbazole), Q4 (2,2′-(quinoline-2,4-diyl)bisis(9-octyl-9H-carbazole), and Q5 (2,2′-(quinoline-2,4-diyl)bisis(9-decyl-9H-carbazole) compounds by Slodek et al. and designed 2,4-dicarbazoyl-substituted quinoline-based D–A–D–π–A-type novel compounds: Q3D1(2-(5′-(2-(4-(9-methyl-9H-carbazol-2-yl)quinolin-2-yl)-9H-carbazol-9-yl)(E)-2-cyano-3-(5′-(2-(4-(9-methyl-9H-carbazol-2-yl)quinolin-2-yl)-9H-carbazol-9-yl)-(E)-2-cyano-3-(5′-(2-(4-(9-octyl-9H-carbazol-2-yl)quinolin-2-yl)-9H-carbazol-3-yl)-(2,2′-bithiophenyl)-5-yl)acrylic acid), Q4D1(2-(5′-(2-(4-(9-methyl-9H-carbazol-2-yl)quinolin-2-yl)-9H-carbazol-9-yl)-(2,2′-bithiophenyl)-5-yl)methylene)malonicitrile), Q3D2(2-(5′-(2-(4-(9-methyl-9H-carbazol-2-yl)quinolin-2-yl)-9H-carbazol-9-yl)-(2,2′-bithiophenyl)-5-yl)methylene)malonicitrile), Q3D3(2-(5′-(2-(4-(9-methyl-9H-carbazol-2-yl)quinolin-2-yl)-9H-carbazol-9-yl)-(2,2′-bithiophenyl)-5-yl)methylene)malonicitrile), Q4D2(2-(5′-(2-(4-(9-octyl-9H-carbazol-2-yl)quinolin-2-yl)-9H-carbazol-3-yl)-(2,2′-bithiophenyl)-5-yl)methylene)malonicitrile), and Q5D1(2-(5′-(2-(4-(9-decyl-9H-carbazol-2-yl)quinolin-2-yl)-9H-carbazol-3-yl)-(2,2′-bithiophenyl)-5-yl)methylene)malonicitrile). This study investigates the NLO properties of synthesized Q3, Q4, and Q5 and their designed Q3D1–Q3D3, Q4D1–Q4D2, and Q5D1 compounds. In a nutshell, the optimization with frequency
analysis revealed that all compounds were found at a true minimum in the potential surface. Further, frontier molecular orbitals (FMOs), natural bonding orbitals (NBOs), UV/Vis analyses, and global reactivity parameters, as well as a two-level model, were performed to support the NLO results of all compounds. Furthermore, our results show that 2,4-dicarbazolyl-substituted quinoline compounds may help to develop potent NLO compounds for future hi-tech applications.

2. Results and Discussion

2.1. Modeling and Designing of Compounds

This quantum chemical calculation work aims to analyze the NLO of novel 2,4-disubstituted quinoline–carbazole-based compounds. For designing novel organic chromophores (Q3D1–Q3D3, Q4D1–Q4D2, and Q5D1), recently synthesized compounds (Q3, Q4, and Q5) are used. These parent compounds (Q3, Q4, and Q5) have a donor-acceptor-donor (D-A-D) structure in which carbazole, acting as a D moiety, is present at both termini of the molecules. At the same time, quinoline is an acceptor moiety present at the center core of the molecules (Figure 1). The different electron-donating groups (alkyl groups), such as CH₃, C₈H₁₇, and C₁₀H₂₁, are attached to the N atom of the carbazole (D) in Q3, Q4, and Q5, respectively [45]. Studies have shown that the extent of the π-conjugated system and nature of D, A moieties play a crucial role in ICT characteristics, the HOMO–LUMO energy gap and absorption spectrum, which lead to fine-tuning of the NLO response properties of materials. Both theoretical and experimental studies have shown that the significant second-order NLO response originates from the union of strong D and A groups held at the opposite ends of a proper π-conjugated system. Thus, we designed compounds from synthesized reference molecules (Q3, Q4, and Q5) with the addition of a donor–acceptor–donor–π–acceptor (D–A–D–π–A) model. The selected compounds, Q3D1, Q3D2, and Q3D3, retained the carbazole–quinoline–carbazole-based D–A–D part, while we modified the architecture of the synthesized Q3 molecule (Figure 1) by connecting it with 2-(thiophen-2-yl) thiophene (TTP) as a spacer linker and different terminal units such as 2-ethylidenemalonic acid (EMA), 2-ethylidenemalononitrile (EMN), and (Z)-2-cyanobut-2-enoic acid (BEA) to act as acceptor units (Figure 1). Similarly, Q4D1–Q4D2 structures combined the synthesized Q4 molecule with TTP as a spacer and BEA, EMN as A segments (Figure 1). However, Q5D1 was modeled by connecting the Q5 architecture with TTP and BEA as a π-conjugated system and A moiety, respectively (Figure 1). The chemical structures of reference molecules (Q3, Q4, and Q5) and designed compounds (Q3D1–Q3D3, Q4D1–Q4D2, and Q5D1) are displayed in Figure 2. Next, we performed DFT and TDDFT computations on synthesized (Q3–Q5) and designed compounds (Q3D1–Q3D3, Q4D1–Q4D2, and Q5D1) to predict their NLO response properties. These calculations aimed to elucidate the definite guidelines for designing novel NLO compounds and describe how π-conjugated linkers and different A units affect the photochemical, electronic, and NLO responses. For the present probe, basic parameters such as (i) electronic properties, (ii) NBO investigation, (iii) polarizability (α), (iv) hyperpolarizability (β), (v) absorption wavelength, and (vi) light-harvesting efficiency (LHE) are calculated. We believe this work will aid future research on the synthesis of proficient NLO materials.
2-(thiophen-2-yl)thiophene (TTP)
2-ethylidenemalononitrile (EMN)
2-ethylidenemalonic acid (EMA)
(Z)-2-cyanobut-2-enoic acid (BEA)

Figure 1. Scheme and structures of spacer and different terminal acceptors used in the designed compounds Q3, Q4, and Q5.

Figure 2. Cont.
2.2. Frontier Molecular Orbital (FMO) Analysis

The frontier molecular orbital (FMO) analyses explain the chemical stability, electronic, and optical properties of understudied molecules [46]. FMOs collectively consist of a lower unoccupied molecular orbital (LUMO) and higher occupied molecular orbital.

Figure 2. Structures of studied compounds Q3D1–Q3D3, Q4D1–Q4D2, and Q5D1.
2.2. Frontier Molecular Orbital (FMO) Analysis

The frontier molecular orbital (FMO) analyses explain the chemical stability, electronic, and optical properties of understudied molecules [46]. FMOs collectively consist of a lower unoccupied molecular orbital (LUMO) and higher occupied molecular orbital (HOMO), which describe numerous interactions between conjugated systems, types of reaction, the UV–visible spectrum, and fluorescence [47]. Usually, the LUMO shows the ability to accept an electron, while the HOMO expresses the ability to donate an electron [48,49]. The $E_{\text{HOMO}} - E_{\text{LUMO}}$ explains the chemical softness, hardness, dynamic stability, and chemical reactivity of the compounds under investigation. Compounds with large $E_{\text{gap}}$ values exist as hard compounds in nature, offering resistance to change in their electronic configuration. Conversely, compounds with a small $E_{\text{gap}}$ value are softer, more reactive, and highly polarizable and show excellent NLO properties. The calculations for energies of the HOMO, LUMO, and energy gap of synthesized (Q3–Q5) and designed compounds Q3D1–Q3D3, Q4D1–Q4D2, Q5D1 are shown in Table 1.

### Table 1. $E_{\text{HOMO}}$, $E_{\text{LUMO}}$, and energy gap ($E_{\text{LUMO}} - E_{\text{HOMO}}$) of the investigated compounds in eV using B3LYP/6-311G (d,p) level of theory.

| Compounds | $E_{\text{HOMO}}$ | $E_{\text{LUMO}}$ | Bandgap ($E_{\text{LUMO}} - E_{\text{HOMO}}$) |
|-----------|------------------|------------------|-------------------------------|
| Q3        | -5.593           | -1.816           | 3.777                         |
| Q3D1      | -5.828           | -2.781           | 3.047                         |
| Q3D2      | -5.598           | -3.441           | 2.157                         |
| Q3D3      | -5.535           | -3.222           | 2.313                         |
| Q4        | -5.546           | -1.768           | 3.778                         |
| Q4D1      | -5.522           | -2.928           | 2.594                         |
| Q4D2      | -5.618           | -3.126           | 2.492                         |
| Q5        | -5.540           | -1.765           | 3.775                         |
| Q5D1      | -5.488           | -2.879           | 2.609                         |

H: HOMO, L: LUMO.

The experimental reported HOMO energy for the reference Q3 molecule, $-5.99$ eV [45], corresponds to a HOMO energy value of $-5.593$ eV of Q3 computed at the B3LYP/6–311G(d,p) level of theory. For Q4, the reported and DFT-computed HOMO energy values are $-5.83$ eV [45] and $-5.546$ eV, respectively. For Q5, the experimental reported value ($-5.90$ eV) [45] corresponds to the DFT-computed ($-5.540$ eV) energy value for HOMO. These results indicate that the adopted DFT method B3LYP and basis set 6–311G (d,p) combination warrants further computational calculations. From Table 1, $E_{\text{gap}}$ values of Q3, Q4, and Q5 are similar. Among all the synthesized molecules (Q3, Q4, and Q5), the Q4 molecule with values of $E_{\text{LUMO}}$ of $-1.768$ eV and $E_{\text{HOMO}}$ of $-5.546$ eV has the largest $E_{\text{gap}}$ value, while Q5 has the lowest $E_{\text{gap}}$ value of $3.775$ eV. Table 1 shows that all synthesized reported compounds (Q3, Q4, and Q5) have a larger $E_{\text{gap}}$ value than their designed compounds. Next, we examine the gap reduction in the designed species. In Q3 and its derivatives, Q3 has the highest value of $E_{\text{gap}}$ (3.777 eV) that dwindled to 3.047 eV in Q3D1. This 0.73 eV reduction in the $E_{\text{gap}}$ value of Q3D1 might result from the combined effect of extended conjugation of TTP spacers and the electron-withdrawing effect of EMA containing two COOH groups present in Q3D1 (absent in Q3). The $E_{\text{gap}}$ value was further reduced to 2.157 eV in Q3D2. The TTP spacer linker and two CN groups present in the EMN terminal acceptor collectively reduce the large energy gap in Q3D2 compared to Q3. A similar effect was observed in Q3D3, where CN, COOH groups present in the BEA acceptor and TTP spacer reduced the $E_{\text{gap}}$ value to 2.313 eV (1.464 eV less compared to Q3). The $E_{\text{gap}}$ order of Q3 and its derivatives is Q3D2 < Q3D3 < Q3D1 < Q3, which suggests the effectiveness of terminal acceptors in the order of EMN > BEA > EMA. A similar effect holds true for Q4 and its derivatives. Q4’s value of 3.778 eV, the greatest energy gap value, decreased to 2.594 eV in Q4D1 and then further decreased to 2.492 eV in Q4D2, reductions of 1.184 eV and 1.286 eV, respectively. The sharp narrowing of the energy gap in Q4D1
and Q4D2 results from the effect of TTP spacers and BEA, EMN terminal acceptor units present in Q4D1 and Q4D2 architectures which are absent in Q4. The efficiency in bridging the energy gap increases for EMN in Q4D2 over BEA in Q4D1. Therefore, the increasing Egap order of Q4 and its derivatives is Q4D2 < Q4D1 < Q4. Among Q5 and its derivative Q5D1, Q5’s largest value of Egap of 3.775 eV narrows down to 2.609 eV in Q5D1 due to the inclusion of TTP and BEA as the π-conjugated system and A moiety. The final increasing order for the energy gap ranks as follows: Q3D2 < Q3D3 < Q4D2 < Q4D1 < Q5D1 < Q3D1 < Q5 < Q3 < Q4. This reduction in the energy gap of the designed derivatives compared to synthesized (reported) compounds shows the effect of structural tailoring by introducing planar, electron-rich π-linkers and different suitable terminal acceptor units. These modifications can tailor the molecules to exhibit desired NLO characteristics.

Figure 3 shows the pictorial display of the HOMO and LUMO of synthesized (Q3–Q5) and designed compounds (Q3D1–Q3D3, Q4D1–Q4D2, and Q5D1). Most of the HOMO electron charge separation spread over the donor carbazole part of the compounds compared to the bridge part. Meanwhile, the LUMO largely spread over the terminal acceptors' units and partially on the π-spacer of the studied compounds. This analysis suggests that the charge shifted from a D moiety to A unit via π-linkers and demonstrates that these materials can have desired NLO properties.

![Figure 3. Cont.](image-url)
2.3. Global Reactivity Parameters (GRPs)

The strength of FMOs ($E_{\text{gap}} = E_{\text{LUMO}} - E_{\text{HOMO}}$) includes the global reactivity information, such as global hardness ($\eta$), global softness ($S$), global electrophilicity index ($\omega$) electron affinity (EA), ionization potential (IP), electronegativity (X), and the chemical potential ($\mu$). Equations (7)–(13) are utilized to calculate the global reactivity parameters (GRPs), and results are given in Table 2.

Table 2. Calculated global reactivity parameters using the energies of HOMO and LUMO.

| Compounds | I    | A    | X    | $\eta$ | $\mu$ | $\omega$ | S    |
|-----------|------|------|------|--------|-------|----------|------|
| Q3        | 5.593| 1.816| 3.704| 1.888  | −3.704| 3.633    | 0.2647|
| Q3D1      | 5.828| 2.781| 4.304| 1.523  | −4.304| 6.080    | 0.3280|
| Q3D2      | 5.598| 3.441| 4.519| 1.078  | −4.519| 9.469    | 0.4630|
| Q3D3      | 5.535| 3.222| 4.378| 1.156  | −4.378| 8.288    | 0.4320|
| Q4        | 5.546| 1.768| 3.655| 1.889  | −3.657| 3.539    | 0.2646|
| Q4D1      | 5.522| 2.926| 4.225| 1.297  | −4.225| 6.881    | 0.3850|
| Q4D2      | 5.618| 3.126| 4.372| 1.246  | −4.372| 7.670    | 0.4010|
| Q5        | 5.540| 1.765| 3.652| 1.887  | −3.652| 3.533    | 0.2649|
| Q5D1      | 5.488| 2.879| 4.183| 1.304  | −4.183| 6.708    | 0.3830|

IP = ionization potential, EA = electron affinity, X = electronegativity, $\mu$ = chemical potential, $\eta$ = global hardness, $S$ = global softness, and $\omega$ = global electrophilicity. Units in eV.

The GRPs illustrated the reactivity of Q3–Q5 (synthesized) and Q3D1–Q5D1 (designed) compounds. Ionization potential expresses the electron-donating ability and equals the energy compulsory to extract one electron from the HOMO. Electronegativity helps to explain the propensity of electron cloud interactions. Another chemical parameter, chemical potential, relates to the reactivity and stability of compounds. A direct relation between energy gap, hardness, chemical potential, and stability collectively contributes towards an inverse relationship towards chemical reactivity. Hence, molecules with a larger energy gap will show more kinetic stability, lower reactivity, and more resistance to any electronic configuration change. The value of $E_{\text{gap}}$ is highest in Q4 among the synthesized compounds (Q3, Q4, and Q5). The hardness value calculated for Q4 is higher (1.889) with a chemical reactivity of −3.657. Meanwhile, Q5 has the lowest value of calculated hardness of 1.887, and Q3 has a hardness value of 1.888, with a chemical reactivity of −3.652 and −3.701 for Q5 and Q3, respectively. These results show that Q4 is less reactive and more chemically stable than Q3 and Q5.

The Q3 derivatives show reduced hardness values compared to native Q3. The calculated value of hardness of 1.523 in Q3D1 decreased to 1.156 in Q3D3 and 1.078 in Q3D2. Similarly, Table 2 shows the diminishing chemical potential values. Among all the...
compounds studied, Q3D2 is the least chemically stable with the smallest calculated value of hardness and a minimum chemical potential value of −4.519. Similarly, the examined hardness and the potential chemical value also decreased in Q4 derivatives (Table 2). The hardness value for Q4D1 (1.297) further declined to 1.246 in Q4D2. Amongst all Q4 derivatives, Q4D2 showed the smallest chemical potential value of −4.372 and, hence, the least stability. The designed compounds of Q5 also showed diminishing hardness and chemical potential values. The decreasing order of hardness of all investigated compounds ranks as follows: Q4 > Q3 > Q5 > Q3D1 > Q5D1 > Q4D1 > Q4D2 > Q3D3 > Q3D2, similar to the HOMO–LUMO energy gap order.

Next, we evaluated softness which directly relates to the chemical reactivity of the molecules under investigation. The value of global softness is 0.264 in the reference compounds Q3, Q4, and Q5. Our designed compounds display extended softness values. In the designed compounds of Q3, Q3D1 expressed a value of 0.328 of softness, while Q3D3 shows 0.432 and Q3D2 further increases to 0.463. Similarly, among Q4 derivative molecules, Q4D1 showed a 0.385 value of global softness, which increases to 0.401 in Q4D2. This result shows that Q4D2 has the most reactivity. The value of softness also increased in the designed compound Q5D1 compared to its parent molecule Q5. From all investigated molecules, Q3D2 has the highest value of softness, thus the highest chemical reactivity. The decreasing order of softness among all the investigated molecules ranks as exactly the inverse to the increasing E\text{gap} order: Q3D2 > Q3D3 > Q4D2 > Q4D1 > Q5D1 > Q3D1 > Q4 > Q3 > Q5. All these global reactivity parameter investigations illustrate that the investigated compounds might hold promising NLO characteristics.

2.4. Natural Bond Orbital (NBO) Analysis

The NBO study provides the Lewis structures, atomic charge, hybridization, and diverse bonds (dative, ionic, covalent, \(\sigma\) and \(\pi\)) [28,50]. The stabilization energy \(E^{(2)}\) with a second-order perturbation method is calculated using Equation (10).

\[
E^{(2)} = q_i \left( \frac{F_{ij}}{\epsilon_j - \epsilon_i} \right)^2
\]

where \(q_i\) means occupancy of contributor orbital, \(\epsilon_j\) and \(\epsilon_i\) are the off-diagonal NBO Fock matrix elements, \(F_{ij}\) is the diagonal, and \(E^{(2)}\) is stabilization energy.

In this NBO study, electron acceptor–donor interactions are shown by the \(E^{(2)}\) value. Table S1 (Supplementary Information) shows hyperconjugative interactions of the acceptor moieties and electron-contributing moieties of the reference and designed compounds. We show that four major transitions, \(\sigma\rightarrow\sigma^*\), \(\pi\rightarrow\pi^*\), \(\sigma^*\rightarrow\pi^*\), and \(\pi^*\rightarrow\pi^*\), are observed for all the chemical compounds. The \((\pi\rightarrow\pi^*)\) transitions were extensively observed with a large \(E^{(2)}\), whereas \(\sigma\rightarrow\sigma^*\) and \(\pi^*\rightarrow\pi^*\) transitions were found with a small \(E^{(2)}\) in comparison to \(\pi\rightarrow\pi^*\). In addition, the lowest \(E^{(2)}\) values originate from \(\sigma\rightarrow\sigma^*\) transitions.

The electronic \(\pi\rightarrow\pi^*\) transitions of peak values are \(\pi(C8–C12)\rightarrow\pi^*(C11–N23), \pi(C70–C72)\rightarrow\pi^*(C74–C76), \pi(C8–C12)\rightarrow\pi^*(C11–N23),\) and \(\pi(C70–C72)\rightarrow\pi^*(C74–C76),\) with stabilization energy of 24.1, 24.53, 24.90, and 25.75 kcal/mol in Q3, Q3D1, Q3D2, and Q3D3, respectively. Some transitions with less stabilization energy were also observed, including \(\pi(C35–C36)\rightarrow\pi^*(C8–C12), \pi(C8–C12)\rightarrow\pi^*(C35–C36), \pi(C8–C12)\rightarrow\pi^*(C35–C36),\) and \(\pi(C8–N12)\rightarrow\pi^*(C3–C4),\) with 5.15, 5.58, 6.04, and 13.68 kcal/mol in Q3, Q3D1, Q3D2, and Q3D3, respectively.

In these compounds, transitions in accordance with the \(\sigma\rightarrow\sigma^*\) transitions were: \(\sigma(C26–C27)\rightarrow\sigma^*(N24–C25), \sigma(C74–C75)\rightarrow\sigma^*(S69–C72),\) \(\sigma(C76–C77)\rightarrow\sigma^*(C77–N80),\) and \(\sigma(C76–C77)\rightarrow\sigma^*(C77–N80). These interactions contribute the most among all \(\sigma\rightarrow\sigma^*\) transitions, with stabilization energy of 6.16, 9.45, 8.68, and 8.62 kcal/mol in Q3 and its derivative compounds (Q3D1–Q3D3), respectively. Some transitions with minimal energy are: \(\sigma(C27–H32)\rightarrow\sigma^*(C27–C28), \sigma(C12–H13)\rightarrow\sigma^*(C3–C8), \sigma(C28–C29)\rightarrow\sigma^*(C21–C30)\) and
σ(C60–S62)→σ*(C60–C61), with 0.54, 5.03, 5.01, and 0.55 kcal/mol in Q3, Q3D1, Q3D2, and Q3D3, respectively.

Moreover, we observed LP→π* transitions: LP(N54)→π*(C38–C42), LP2(O80)→π*(C77–O79), LP1(N54)→π*(C38–C42), and LP2(O80)→π*(C77–O79), with 36.87, 45.85, 37.92, and 45.47 kcal/mol stabilization energy in Q3, Q3D1, Q3D2, and Q3D3, respectively. These highest values of excitations from LP→π* transitions. Furthermore, we saw a small amount of stabilization energy in LP(N54)→π*(C56–H59), LP1(N23)→π*(C11–O12), LP1(N23)→π*(C11–O12), and LP1(S62)→π*(C60–C61), with 7.29, 10.53, 10.67, and 21.62 kcal/mol in Q3 and its derivative compounds (Q3D1–Q3D3), respectively.

Similarly, in the case of Q4, Q5 and their designed molecules (Q4D1, Q4D2, and Q5D1), we calculated π→π* electronic interactions: π(C8–C12)→π*(C11–N23), π(C8–C12)→π*(C11–C23), π(C14–C16)→π*(C19–C21), π(C8–C12)→π*(C11–C23), and π(C4–C5)→π*(C1–C6), with the highest stabilization energy of 24.23, 24.17, 21.69, 24.71, and 24.64 kcal/mol in Q4, Q5, Q4D1, Q4D2, and Q5D1, respectively. Meanwhile, transitions with less stabilization energy were also detected: π(C11–N23)→π*(C14–C16), π(C11–N23)→π*(C14–C16), π(C8–C12)→π*(C3–C4), π(C8–C12)→π*(C3–C4), and π(C8–C12)→π*(C3–C4), with 8.31, 8.58, 13.57, 13.57, and 13.57 kcal/mol in Q4, Q5 and their designed molecules (Q4D1, Q4D2, and Q5D1). Among the σ→σ* transitions, these molecules also showed transitions of σ(C47–C50)→σ*(C45–N54), σ(C47–C50)→σ*(C45–N54), σ(C106–C108)→σ*(C110–N112), σ(C26–C27)→σ*(N24–C25), and σ(C46–C49)→σ*(C44–N53), with the highest stabilization energy of 6.15, 6.13, 5.49, 5.80, and 6.13 kcal/mol in Q4, Q5 and their designed compounds Q4D1, Q4D2, and Q5D1, respectively. The lowest stabilization energy transitions were σ(C68–C71)→σ*(C71–H73), σ(C68–C71)→σ*(C71–H73), σ(C73–H76)→σ*(C73–C74), σ(C73–H76)→σ*(C73–C74), and σ(C73–H76)→σ*(C73–C74), with 0.50 kcal/mol in Q4, Q5 and their designed molecules (Q4D1, Q4D2, and Q5D1), respectively.

Last, but not least, the highest stabilization energy by the transitions by lone pairs LP1 (N54)→π*(C38–C42), LP1(N54)→π*(C38–C42), LP2(O123)→π*(C122–O123), LP1(N24)→π*(C25–C30), and LP2(O138)→π*(C136–C137) gave 37.08, 37.07, 41.89, 38.24, and 37.97 kcal/mol in Q4, Q5, Q4D1, Q4D2, and Q5D1, respectively. All these transitions had the highest stabilization energy among all transitions. The lowest value transitions were LP1 (N54)→σ*(C56–C62), LP1 (N54)→σ*(C56–C62), LP1(N23)→π*(C3–C4), LP1(N23)→π*(C3–C4), and LP1(N23)→π*(C3–C4), with 6.36, 6.33, 10.37, 10.36, and 10.37 kcal/mol in Q4, Q5 and their designed molecules (Q4D1, Q4D2, and Q5D1), respectively.

In conclusion, our NBO calculations show that intra-molecular interactions and extended hyperconjugation in the studied compounds provide more stability and a vital explanation of charge transfer properties. Hence, they might be useful for potential NLO features.

2.5. Nonlinear Optical (NLO) Properties

NLO compounds widely occur in signal processing, optical switches, communication technology, and optical memory devices. The polarizability or α (linear response) and hyperpolarizabilities or β (nonlinear response) relate to the optical response generated by the electrical characteristics of the compounds under investigation. We investigated both linear and nonlinear responses of quinoline–carbazole synthesized (Q3–Q5) and designed compounds (Q3D1–Q3D3, Q4D1–Q4D2, Q5D1) using the B3LYP/6-311G (d,p) functional. Tables 3 and 4 summarize the results for α and β values.
Table 3. Dipole polarizabilities and major contributing tensors (a.u.) of Q3–Q5D1.

| Systems  | αxx | αyy | αzz | <α>  |
|----------|-----|-----|-----|------|
| Q3       | 672.576 | 539.206 | 221.601 | 477.794 |
| Q3D1     | 993.607 | 751.135 | 324.147 | 689.629 |
| Q3D2     | 1055.229 | 741.468 | 312.972 | 703.223 |
| Q3D3     | 1019.920 | 750.156 | 319.464 | 696.513 |
| Q4       | 798.885 | 687.857 | 419.76 | 635.500 |
| Q4D1     | 1673.744 | 875.709 | 481.294 | 1010.249 |
| Q4D2     | 1707.951 | 868.809 | 482.809 | 1019.856 |
| Q5       | 730.898 | 855.859 | 467.796 | 684.851 |
| Q5D1     | 1688.74 | 930.010 | 526.738 | 1048.496 |

Table 4. The computed second-order polarizabilities (βtot) and major contributing tensors (a.u.) of Q3–Q5D1.

| System | βxxx | βxyy | βyxx | βyyy | βzzz | βyyy | βzzz | βtot |
|--------|------|------|------|------|------|------|------|------|
| Q3     | -1530.726 | 1871.795 | -474.090 | 730.504 | -51.232 | -50.945 | -77.808 | 3277.62 |
| Q3D1   | 713.938 | -602.979 | 413.750 | 2310.371 | 38.201 | 17.561 | -3.128 | 7811.75 |
| Q3D2   | 15,811.353 | -3037.588 | 490.217 | 1138.007 | -38.279 | -15.314 | -44.940 | 16,375.60 |
| Q3D3   | 13,250.577 | -884.401 | -113.490 | 1410.887 | -51.728 | -14.813 | -47.341 | 13,095.90 |
| Q4     | 1303.257 | -1614.86 | 461.9083 | -732.367 | 94.1197 | 16.408 | -3.3530 | 3000.35 |
| Q4D1   | -50,840.435 | 4690.332 | -737.360 | -762.310 | -469.516 | 105.223 | 63.545 | 52,662.1 |
| Q4D2   | -56,982.727 | 5969.852 | -1009.638 | -703.564 | -573.947 | 143.688 | 56.811 | 59,316.4 |
| Q5     | -595.429 | -141.705 | -1439.05 | -1813.59 | -43.2138 | -228.978 | 57.493 | 3103.51 |
| Q5D1   | -48,440.596 | 5639.601 | -697.923 | -541.280 | -884.401 | 1439.05 | 1614.86 | 50,156.00 |

Table 3 represents transitions predominantly contributing to average polarizability <α> values in all studied molecules observed along the x-axis (αxx). The <α> value of Q3, computed at 477.794 (a.u), was found to be the smallest, while the largest value of 648.851 (a.u) belongs to Q5 among all synthesized compounds (Q3–Q5). With the inclusion of different acceptor units and linker/spacer units, the designed species display increased polarizability <α> values. Specifically, structural modeling of Q3 by incorporating TTP spacers and electron-withdrawing units EMA, EMN, BEA in Q3D1–Q3D3 augmented the average polarizability in designed compounds compared to Q3. The <α> value increased from 477.794 (a.u) in Q3 to 689.629 (a.u) in Q3D1, 696.513 (a.u) in Q3D3, and 703.223 (a.u) in Q3D2 as their bandgap decreased. The order of <α> values in Q3 and its derivatives rank as follows: Q3D2 > Q3D3 > Q3D1 > Q3. We observed similar enhancement in Q4 and its designed compounds. The lowest value of average polarizability, 635.500 (a.u) in Q4, increased to 1010.249 (a.u) in Q4D1 and 1010.856 (a.u) in Q4D2. The increase in the <α> value in Q4D1 and Q4D2 results from the effect of TTP spacers and BEA, EMN terminal acceptor units present in Q4D1-Q4D2 architectures and their absence in Q4. The increasing order for <α> values of Q4 and its designed molecules is Q4 < Q4D1 < Q4D2. Similarly, the derivative of Q5 exhibits the largest value of <α> of 684.851 (a.u). Among all these investigated compounds, Q5D1 exhibits the largest value of average polarizability of 1048.496 (a.u). Overall, the decreasing order of average polarizability value of studied molecules ranks as follows: Q5D1 > Q4D2 > Q4D1 > Q3D2 > Q3D3 > Q3D1 > Q5 > Q4 > Q3.

Studies show that large β values correspond to narrow bandgap and large linear polarizability values [51,52]. The polarizability values are computed by employing y- or x-axis direction electronic transitions using Equation (2) (along x-direction).

\[
\alpha \alpha \propto \left(\frac{M_{X}^{gm}}{E_{gm}}\right)^{2}
\]  

(2)

In this equation, \(M_{X}^{gm}\) indicates the ground and \(m^{th}\) excited state transition moment. \(E_{gm}\) denotes transition energy. Equation (11) explains that \(\alpha\) is directly proportional to the
square of the transition moment and inversely proportional to transition energy. The square of the transition moment explains the power of interaction because of the distribution of charge density contained in the system. In general, a molecule with a large value of $M_X^{\text{gm}}$ and a smaller value of $E_{\text{gm}}$ will have a high hyperpolarizability value. Therefore, dipole polarizability quantitatively estimates the NLO response properties of compounds. Additionally, second-order polarizability or first hyperpolarizability ($\beta$) helps to compute the NLO response of materials. Table 4 shows the hyperpolarizabilities of synthesized (Q3–Q5) and designed compounds (Q3D1–Q3D3, Q4D1–Q4D2, and Q5D1) with $\beta_{\text{tot}}$ values, along with their major contributing tensors.

Table 5 shows that the NLO response in these compounds mainly results from the x-axis tensor $\beta_{xxx}$ containing larger values and contributing predominantly toward $\beta_{\text{tot}}$ among all contributing tensors. All the synthesized compounds showed smaller values of $\beta_{\text{tot}}$ than their designed derivatives. Among the synthesized compounds (Q3–Q5), Q3 exhibits the highest $\beta_{\text{tot}}$ value of 3277.62 (a.u), while Q4 exhibits the lowest $\beta_{\text{tot}}$ value of 3000.35 (a.u). The decreasing order of $\beta_{\text{tot}}$ values for reference compounds is Q3 > Q5 > Q4. The designed molecule Q3D1 shows an increase in hyperpolarizability value from 3277.62 (a.u) in Q3 to 7811.75 (a.u). Q3D3 and Q3D2 further increased the value to 13,095.90 (a.u) and 16,375.60 (a.u). This increase in $\beta_{\text{tot}}$ values compared to reference Q3 results from the insertion of TTP spacers and the electron-withdrawing effect of EMA containing two COOH groups present in Q3D1, two CN groups present in the EMN terminal acceptor of Q3D2, and CN, COOH groups present in the BEA acceptor of Q3D3. The result of the terminal acceptor enlarging the nonlinear response (in the order EMN > BEA > EMA) corresponds to the increase in the linear response and reduction in the energy gap. We observed similar phenomena for Q4 and Q5 derivatives. Q4 has the smallest value of 3000.35 (a.u). Q4D1 increases the value to 52,662.1 (a.u) due to the TTP spacer and BEA terminal acceptor unit effect. The TTP spacer and EMN terminal acceptor present in Q4D2 further enlarges the $\beta_{\text{tot}}$ value to 59,316.4 (a.u) in Q4D2. The Q5D1 derivatives containing TTP and BEA as a π-conjugated system and A moiety exhibited the higher value of hyperpolarizability of 50,156.00 (a.u) than their parent molecule Q5 (3103.51(a.u)). Overall, Q4D2 came first with the highest $\beta_{\text{tot}}$ value of 69,791.4 among all investigated compounds. The compound rank in decreasing order of $\beta_{\text{tot}}$ values is as follows: Q4D2 > Q4D1 > Q5D1 > Q3D2 > Q3D3 > Q3D1 > Q3 > Q5 > Q4.

Table 5. Computed transition energy (eV), maximum absorption wavelengths ($\lambda_{\text{max}}$/nm), oscillator strengths ($f_{\text{os}}$), light-harvesting efficiency (LHE), transition moment ($M_X^{\text{gm}}$) a.u., and transition natures of analyzed compounds.

| Compounds | $E_{\text{gm}}$ (eV) | $\lambda_{\text{max}}$ (nm) | $f_{\text{os}}$ | $\Delta\mu_{\text{gm}}$ (a.u) | Major MO Transitions |
|-----------|------------------|-----------------------------|-------------|-----------------------------|---------------------|
| Q3        | 3.397            | 364.97 (349)                | 1.026       | 0.905                       | 5.842               |
| Q3D1      | 2.699            | 459.35                      | 0.652       | 0.777                       | 7.088               |
| Q3D2      | 2.332            | 531.57                      | 0.707       | 0.803                       | 7.366               |
| Q3D3      | 2.445            | 507.09                      | 0.673       | 0.788                       | 7.611               |
| Q4        | 3.435            | 360.90 (347)                | 1.005       | 0.901                       | 3.854               |
| Q4D1      | 2.087            | 593.82                      | 1.479       | 0.966                       | 9.390               |
| Q4D2      | 2.019            | 613.87                      | 1.476       | 0.966                       | 9.345               |
| Q5        | 3.428            | 361.67 (323)                | 1.025       | 0.905                       | 3.658               |
| Q5D1      | 2.102            | 589.61                      | 1.454       | 0.964                       | 7.317               |

Our $\beta_{\text{tot}}$ findings for the investigated molecules are further strengthened by comparing them with an organic reference urea molecule [53]. All synthesized (Q3–Q5) and designed compounds (Q3D1–Q3D3, Q4D1–Q4D2, Q5D1) have greater $\beta_{\text{tot}}$ values than a urea molecule, indicating the potential NLO applicability of these compounds in future NLO applications.
2.6. UV–Vis Spectra Analysis

UV–visible spectroscopy explains the charge transfer of compounds under investigation. The absorption spectra of synthesized Q3–Q5 and designed compounds Q3D1–Q3D3, Q4D1–Q4D2, Q5D1 are computed using TDDFT at the B3LYP/6-311G(d,p) level of theory. During TDDFT computations, the six lowest singlet–singlet transitions were studied. Table 5 summarizes the results obtained from UV–visible spectral analysis, while Figure 4 shows the absorption spectra of the studied compounds.

![Simulated absorption spectra of studied compounds.](image)

The DFT-computed λ\text{max} value of Q3 (364.970 nm) corresponds to the experimental λ\text{max} value reported at 349 nm [45]. Similarly, DFT-computed λ\text{max} values of Q4 and Q5 (360.901 and 361.670 nm, respectively) also correspond to reported λ\text{max} values at 347 and 323 nm [45]. These matches validate our selection of the B3LYP/6-311G(d,p) functional for the calculations. Among all synthesized (Q3–Q5) compounds, Q4 shows the lowest λ\text{max} value of 360.90 nm, which is the lowest calculated λ\text{max}, while Q3 exhibits the highest value of maximum absorption of 364.97 nm. This shows that Q3 leans towards the bathochromic shift. All the designed molecules exhibited a larger value of maximum absorption than their parent compounds. The absorption maximum observed in the Q3 family reduces in transition energy, owing to the combined effect of TTP spacers and electron-withdrawing units EMA, EMN, BEA present in Q3D1–Q3D3. Consequently, λ\text{max} values of Q3D1–Q3D3 are increased by 95 nm, 167 nm, and 143 nm, respectively, compared to Q3. Q3D2 exhibits the largest λ\text{max} value of 531.57 nm with the smallest transition energy value of 2.332 eV among the Q3 family; hence, it is the most redshifted among Q3 and its designed derivatives. The decreasing order of λ\text{max} found in Q3 and its compounds is Q3D2 > Q3D3 > Q3D1 > Q3. We observed a similar redshift in Q4 designed derivatives due to similar structural modifications. Q4D1 and Q4D2 show an increase in absorption wavelengths at 593.82 nm and 613.87 nm compared to Q4, caused by the combined effect of TTP spacers and BEA, EMN terminal acceptor units present in Q4D1 and Q4D2 architectures, while they are absent in Q4. Similar to the Q4 family, Q5D1 has a higher value of maximum absorption at 589.61 nm with a lower value of transition energy, 2.102 eV, than Q5. This result shows that Q5D1 and Q5 are bathochromic and hypochromic, respectively. Among all the studied compounds, Q4D2 ranks highest in maximum absorption wavelength. The decreasing order for λ\text{max} values of studied compounds is: Q4D2 > Q4D1 > Q5D1 > Q3D2 > Q3D3 > Q3D1 > Q3 > Q5 > Q4. Table 5 indicates that major transitions among
synthesized and reported molecules Q3, Q4, and Q5 arose from HOMO-2→LUMO (≥92%). In the designed derivatives of Q4 and Q5, HOMO→LUMO (99%) transitions were observed and Q3 derivatives containing HOMO-1→LUMO (≥95%) transitions were observed. These characteristics render these compounds suitable for fine optoelectronic roles.

Excitation energy further enhances the electro-optic properties of NLO materials. The combined effect of TTP spacers and electron-withdrawing units EMA, EMN, BEA lowers the excitation energy value from 3.397 eV (Q3) to 2.699 eV, 2.332 eV, and 2.445 eV in Q3D1–Q3D3. In Q4D1 and Q4D2, excitation energy values decrease to 2.087 eV and 2.019 eV compared to the Q4 value of 3.435 eV due to the BEA, EMN terminal acceptors and TTP spacers present in Q4D1 and Q4D2. A similar effect was observed in Q5D1, where the excitation energy value, 2.102 eV, is lower than that of the parent Q5 excitation energy value of 3.428 eV. The lower excitation energy results in higher charge transfers and vice versa. Our all designed molecules exhibit low excitation energy compared to their parent compounds, ideal for NLO response properties.

Lastly, we quantified the optical efficiency of studied compounds by light-harvesting efficiency (LHE). We measured the photocurrent response of compounds by LHE using the $f_{\text{os}}$ value and Equation (3) [54].

$$\text{LHE} = 1-10^{-f_{\text{os}}}(3)$$

Table 5 reveals that Q3D1 has the lowest LHE value, while compounds like Q4D1, Q4D2, and Q5D1 have large LHE values.

We opted to explain the donor–acceptor unit effect on enhanced NLO characteristics by structure–property relationships. Chemla and Oudar [55] expressed the relationship between hyperpolarizability and electronic charge transfer transition using a two-level model based on complex sum-over-states (SOS):

$$\beta_{\text{CT}} = \frac{\Delta \mu_{\text{gm}} f_{\text{gm}}}{E_{3\text{gm}}^2} \quad (4)$$

Here, $E_{3\text{gm}}$, $\Delta \mu_{\text{gm}}$, $\beta_{\text{CT}}$, and $f_{\text{gm}}$ are the most crucial $m^{\text{th}}$ excited state excitation energy difference, dipole moment difference, first hyperpolarizability, and oscillator strength. These parameters are governed by the choice of suitable acceptor units, bridges, and inter-linked donors. A larger $\beta$ value can result from the most promising blend of these parameters. The product of $\Delta \mu_{\text{gm}}$ and $f_{\text{gm}}$ has a direct relation, as seen from Equation (4), which shows an inverse relationship between the cube of transition energy and $\beta_{\text{CT}}$. Thus, large $\Delta \mu_{\text{gm}}$, $f_{\text{gm}}$ magnitude, and low $E_{3\text{gm}}^2$ serve as vital gauges for the optimum design of proficient NLO compounds. From our spectral analysis, the values of $\Delta \mu_{\text{gm}}$, $f_{\text{gm}}$, and $E_{3\text{gm}}^2$ are calculated, and results are given in Table 5.

A graphical representation of a comparison between the computed $\beta_{\text{tot}}$ findings and $\beta_{\text{CT}}$ results (obtained from a two-level model) for synthesized (Q3–Q5) and designed compounds (Q3D1–Q3D3, Q4D1–Q4D2, Q5D1) is shown in Figure 5. The x-axis describes the studied systems, and the vertical y-axis indicates the magnitudes of $\beta_{\text{tot}}$ and $\beta_{\text{CT}}$ results. It is evident from Figure 5 that both $\beta_{\text{tot}}$ and $\beta_{\text{CT}}$ findings are in direct relation with each other. The preceding discussion concluded that $\beta_{\text{tot}}$ results are also confirmed by a two-level model, which implies that studied molecules can be recommended for future construction of high-performance NLO materials.
3. Computational Procedure

The Gaussian 09 program package [56] was applied to conduct all quantum chemical calculations in this study. All input files were generated using the GaussView 5.0 [57] program. All synthesized (Q3, Q4, and Q5) and designed chemical systems (Q3D1–Q3D3, Q4D1–Q4D2, and Q5D1) were optimized by employing density functional theory (DFT) computations. The B3LYP functional was utilized with a 6-311G(d, p) basis set for optimizing geometries, frequency analysis, NBO analysis, and computing the NLO parameters of entitled compounds. Time-dependent DFT (TDDFT) calculations with the B3LYP/6-311G(d,p) level was carried out for frontier molecular orbital (FMO) analysis and UV/Vis spectra estimation. Symmetry constraints were not adopted in all DFT- and TDDFT-based calculations. Six linear polarizability tensors, \( \alpha_{xx}, \alpha_{yy}, \alpha_{zz}, \alpha_{xy}, \alpha_{xz}, \) and \( \alpha_{yz}, \) and ten hyperpolarizability tensors, \( \beta_{xxx}, \beta_{xyy}, \beta_{xzz}, \beta_{yyy}, \beta_{xxy}, \beta_{yyz}, \beta_{xzz}, \beta_{zxx}, \beta_{yyz}, \) and \( \beta_{xyz}, \) along \( x-, y-, \) and \( z- \) directions, were collected from the Gaussian 09 output. The amplitudes of average polarizability \( < \alpha > \) and first hyperpolarizability \( (\beta_{\text{tot}}) \) are calculated by Equations (5) and (6) [58].

\[
< \alpha > = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{5}
\]

\[
\beta_{\text{tot}} = \left[ (\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{xxy} + \beta_{yyz})^2 + (\beta_{zxx} + \beta_{yyz} + \beta_{xyz})^2 \right]^{1/2} \tag{6}
\]

The highest occupied molecular orbital (HOMO) energy and the lowest unoccupied molecular orbital (LUMO) energy were used to explore the global reactivity parameters (GRPs), such as global hardness (\( \eta \)), global softness (\( S \)), global electrophilicity index (\( \omega \)), electron affinity (EA), ionization potential (IP), electronegativity (X), and the chemical potential (\( \mu \)) [59–63].

The ionization potential (I) and electronic affinity (A) values are calculated using Equations (7) and (8), respectively.

\[
I = -E_{\text{HOMO}} \tag{7}
\]

\[
A = -E_{\text{LUMO}} \tag{8}
\]

Electronegativity (X) and hardness (\( \eta \)) are attained using Equations (9) and (10).

\[
X = \frac{I + A}{2} \tag{9}
\]
\[ \eta = \frac{I - A}{2} \]  

To calculate the chemical potential (\( \mu \)), Equation (11) is used.

\[ \mu = \frac{E_{\text{HOMO}} + E_{\text{LUMO}}}{2} \]  

The relation between energy variation and maximum electrons transferred can be determined by the magnitude of the electrophilicity (\( \omega \)), which is calculated according to Equation (12).

\[ \omega = \frac{\mu^2}{2\eta} \]  

For calculating the value of softness (\( S \)), Equation (13) is used.

\[ \sigma = \frac{1}{2\eta} \]  

4. Conclusions

This study explores the effect of different substitutions of the \( \pi \)-conjugated linker and diverse acceptor units in carbazole units on NLO properties of Q3–Q5. We observed differences in NLO behavior, which is strongly dependent on diverse acceptor units, the length of the alkyl chains, and the \( \pi \)-conjugated linker attachment in carbazole to the quinoline skeleton. NBO analysis shows that hyperconjugative interactions, occurring among bonds and intra-molecular charge transfer, are due to electrons’ delocalization. Designed compounds Q3D1–Q3D3, Q4D1, Q4D2, and Q5D1 exhibit strong redshift absorption compared to Q3–Q5. The decreasing order of softness among all the investigated molecules is Q3D2 > Q3D3 > Q4D2 > Q4D1 > Q5D1 > Q3D1 > Q4 > Q3 > Q5. The same order exists for bandgaps and there is an inverse pattern for hardness. The designed compounds of Q4 with \(-\text{C}_8\text{H}_{17}\) and Q5 with \(-\text{C}_{10}\text{H}_{21}\) moieties exhibited a more promising NLO response than Q3 with \(-\text{CH}_3\). This difference in NLO efficacy results from the alkyl chain length difference and diverse acceptors. Moreover, the dipole polarizability magnitudes of all designed compounds (Q3D1–Q3D3), (Q4D1, Q4D2), and (Q5D1) exceed the dipole polarizabilities of corresponding reference compounds (Q3, Q4, and Q5). The second-order polarizability (\( \beta_{\text{tot}} \)) magnitudes of Q3D1, Q3D2, and Q3D3 exceed 2.38, 4.99, and 3.99 times that of Q3. The \( \beta_{\text{tot}} \) for Q4D1 and Q4D2 were 17.55 and 18.10 times that of Q4, while \( \beta_{\text{tot}} \) for (Q5D1) was 16.16 times that of Q5. Among the all investigated compounds, the highest value of \( \beta_{\text{tot}} \), 59,316.4 (a.u), belongs to Q4D2. In short, this data disclosed that entitled compounds might become promising materials in the NLO field. Further, high-performance NLO active entitled compounds could become interesting in synthetic chemistry for lab researchers.

Supplementary Materials: The following are available online. Table S1. Cartesian coordinates of Q3; Table S2. Cartesian coordinates of Q3D1; Table S3: Cartesian coordinates of Q3D2; Table S4: Cartesian coordinates of Q3D3; Table S5: Cartesian coordinates of Q4; Table S6: Cartesian coordinates of Q4D1; Table S7: Cartesian coordinates of Q4D2; Table S8: Cartesian coordinates of Q5; Table S9: Cartesian coordinates of Q5D1; Table S10: Second order Perturbation theory analysis of Fock matrix in Q3; Table S11: Second order Perturbation theory analysis of Fock matrix in Q4; Table S12: Second order Perturbation theory analysis of Fock matrix in Q5; Table S13: Second order Perturbation theory analysis of Fock matrix in Q3D1; Table S14: Second order Perturbation theory analysis of Fock matrix in Q3D2; Table S15: Second order Perturbation theory analysis of Fock matrix in Q3D3; Table S16: Second order Perturbation theory analysis of Fock matrix in NBO Q4D1; Table S17: Second order Perturbation theory analysis of Fock matrix in Q4D2; Table S18: Second order Perturbation theory analysis of Fock matrix in Q5D1; Table S19: Wave length, excitation energy and oscillator strength of investigated compound Q3; Table S20: Wave length, excitation energy and oscillator strength of investigated compound Q4; Table S21: Wave length, excitation energy and oscillator strength of investigated compound Q5; Table S22: Wave length, excitation energy and oscillator strength of...
investigated compound Q3D2; Table S25: Wave length, excitation energy and oscillator strength of investigated compound Q3D3; Table S26: Wave length, excitation energy and oscillator strength of investigated compound Q4D1; Table S27: Wave length, excitation energy and oscillator strength of investigated compound Q4D2; Table S28: Wave length, excitation energy and oscillator strength of investigated compound Q5D1; Figure S1: Graph of investigated compound Q3; Figure S2: Graph of of investigated compound Q4; Figure S3: Graph of of investigated compound Q5. Figure S4: Graph of investigated compound Q3D1; Figure S5: Graph of investigated compound Q3D2; Figure S6: Graph of investigated compound Q3D3; Figure S7: Graph of investigated compound Q4D1; Figure S8: Graph of investigated compound Q4D2; Figure S9: Graph of investigated compound Q5D1.

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