DFT/TD-DFT Study Of D–π–A Dyes Explore The NLO Properties

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Abstract— **The molecular structures and optical properties of six different N.dimethylphenylendiamino dyes were analyzed using a combination of DFT functions (B3LYP and CAM-B3LYP/6-311+G(p,d)). The six dyes are D1-D6. The various parameters of the solvated phase, such as the polarizabilities, hyperpolarizabilities, peak absorption wavelengths, and HOMO-LUMO energy gaps, were calculated and analyzed. The results of the study are in agreement with the results of the NLO activity order thiophene linker then pyrrole bridge. Compared to the dipyrrole versions, the designed dithiophene-linker dyes exhibit longer absorption wavelengths and smaller HOMO-LUMO gaps. The predicted first hyperpolarizability of dyes D1-D3 are higher than that of D4-D5. This is mainly due to its enhanced electron-withdraw ability and the long π-conjugating action of the thiophene moiety. Highly elevated total hyperpolarizability of the designed dyes, suggests its potential application in organic NLO devices, which is expected to be useful.**

Keywords— **D–π–A dyes, NLO properties, DFT,**

I. Introduction

Among the many applications for electro-optics, nonlinear optical materials (NLO) show promise in signal analysis, fiber optics, telecommunications, and information technology [1-3]. Current studies focus on NLO compounds made based on the organic texture due to their simple motivation chemistry, inexpensive cost of exploitation, and tolerance for structural amendments that enable a marvelous NLO characteristic. Intramolecular charge transfer (ICT), primarily from a donor unit (D) via a π-conjugated linker (π) to an acceptor unit (A) [4-6], is the foundation of these NLO properties of materials. Data from experiments and simulations indicate that the robust NLO response can result from the assembly of D and A groups on opposite ends of a π-linker. Delocalized π-electrons in a D-π-A configuration improve charge transfer transitions in compounds [7,8].

NLO compounds with π-conjugated linkers have been discovered to be a rich source of non-metal organic D-A complexes with enhanced electron transfer in an applied electric field. Many different chemical structures have been described in the literature that make use of ICT between the negative charge carrier donor and the withdrawal unit to construct neoteric donor-π-acceptor orders that able to control the transitions bandgap by employing a wide variety of acceptor or donor parts with high first hyperpolarizability worth (β_{total}) [9,10]. However, progress on some key features necessary for widespread adoption and effective industrial applications is hampered by current constraints. The need for quick skeleton modifications is one of these issues, along with dependable synthesis, low manufacturing costs, flexible substitutions, tunable absorption wavelength, and ease of use. We have interested with the utility of N.dimethylphenylendiamino (as Donor) dyes via enhanced bridges through double heteroaromatic rings.

In this manuscript, we show that modifying the bridge is a simple way to improve NLO response and create new NLO materials. Motivated by these discussed methods, the optoelectronic properties of a D-π-A have been the system of N.dimethylphenylendiamino is extended with the introduction of a π-conjugated system of dipyrrole [11] and dithiophene [12]. There are three different types of acceptors used: 2cyano acrylonitrile (2CA), cyano acrylic acid (CAA) and 2carboxy acrylic acid (2CAA). N.dimethylphenylendiamino (NDPD) is widely used in hole transport materials due to its donor unit status as an electron donor and charge transfer medium [13-15].

Six new D-π-A dyes D1-D6 have been modeled. This computational analysis is suitable for estimating the properties of NLO and to examining the impact of various π-conjugated linkers on NLO performance. The electronic properties, absorption spectrum, polarizability, and first hyperpolarizability values of the newly designed dyes were calculated using density functional theory (DFT). We hope that contemporary non-metal organic dyes that have superior NLO properties can be developed as a result of these studies.

II. COMPUTATIONAL PROCEDURE

The electronic and optical properties, electron transfer phenomena and NLO behavior of freshly projected D-π-A systems were investigated using density functional theory (DFT). Gaussian 09 [16] with the B3LYP functional and 6-311+G (d, p) basis set was used for all calculations. The entitled dyes (D1-D6) were optimized geometrically at the B3LYP/6-311+G (d, p) level. Newly discovered frontier molecular orbitals (FMOs). Time-dependent density functional theory (TD-DFT) was used to calculate the absorption spectra of these organic dyes using the aforementioned basis set. The calculations were performed at the Coulomb-Attenuated Method (CAM) with hybrid B3LYP functional. It can figure out the polarizability values and tensors of hyperpolarizability (β_{tot}) of the designed dyes with the help of Equations (1) and (2) [17].

$$\alpha = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3 \qquad (1)$$

And

$$\beta_{tot} = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{xyz})^2]^{1/2} \qquad (2)$$

For the x, y, and z directions, the Gaussian file produced ten hyperpolarizability tensors: β_{xxx}, β_{xyy}, β_{xzz}, β_{yyy}, β_{yzz}, β_{yxx}, β_{zzz}, β_{zxx} and β_{xyz}. In addition, the output results were interpreted using Gauss View 5.0 [18].

III. RESULTS AND DISCUSSION

In donor-π-acceptor type chromophores, screening of π-spacers is essential for achieving a promising NLO response. Using structural tailoring with different π-bridges, this work aims to candidate a new N.dimethylphenylendiamino-based NLO material for cutting-edge optoelectronic applications. In this case, a designed non-metal organic dye is used for the theoretical design. N.dimethylphenylendiamino (NDPD) serves as the donor moiety in our designed chromophores (D1-D6), the first and second π-spacers act as the bridge, and 2cyano acrylonitrile (2CA), cyano acrylic acid (CAA) and 2carboxy acrylic acid (2CAA) are the acceptor units. Six molecules are constructed with two π-conjugates (dipyrrole and dithiophene). Figure 1 show the components of all these new six dyes, D1-D6.

A. ELECTRONIC STRUCTURE

When looking into molecules chemical stability and optoelectronic properties, FMO analysis is a great method. Absorption spectra and mechanical modeling of compounds rely heavily on the FMOs, specifically the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital). The band gap (E_{LUMO}-E_{HOMO}) is the most important factor for judging the hardness of the designed compounds. Molecules with a large HOMO-LUMO distance are considered less reactive, more stable, and hard, while those with a small E_{LUMO}-E_{HOMO} energy gap are considered more reactive, less stable, soft and more

polarized competitor in offering the best NLO response. With these considerations in mind, we calculate the band gap between the orbitals of the D1-D6 chromophores and present the results in table 1.
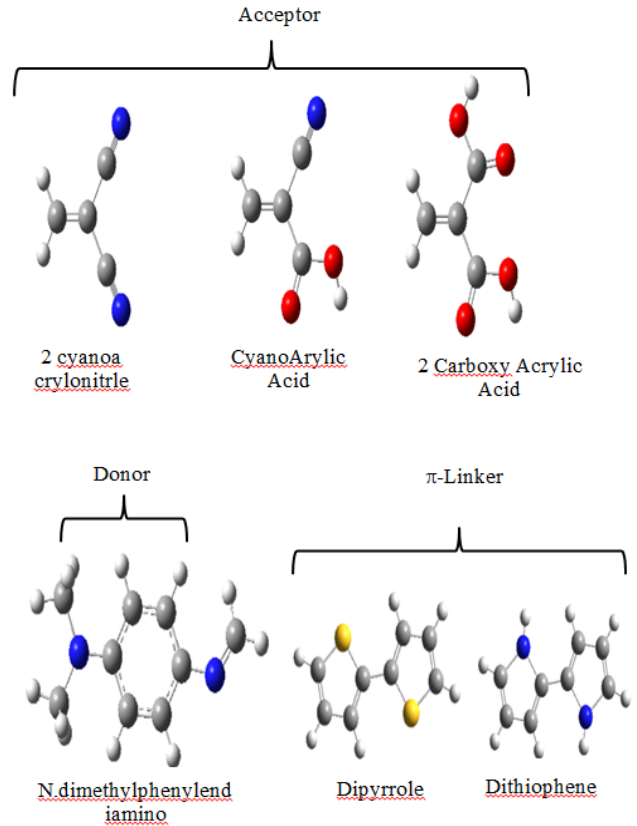

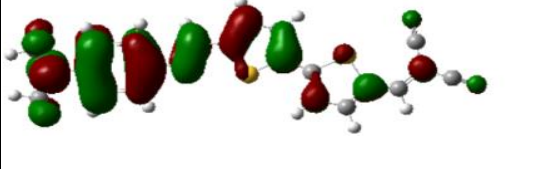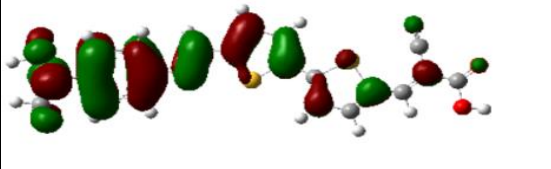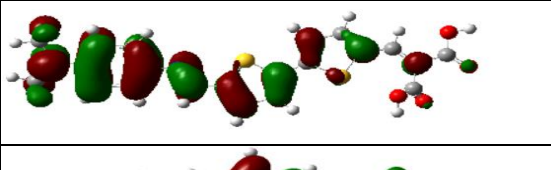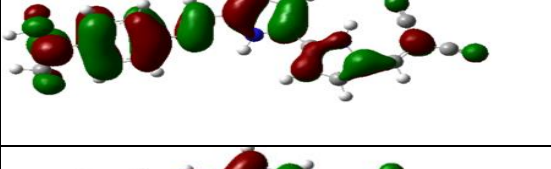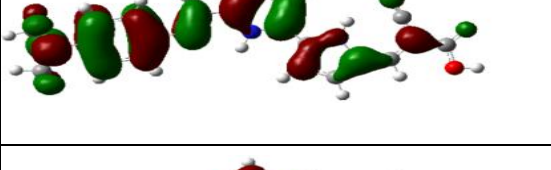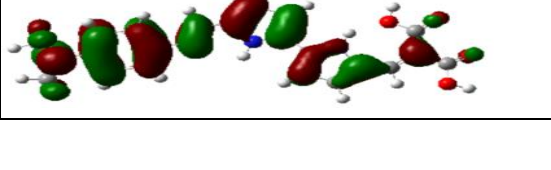Fig 1: Chemical structure of dyes components.

Table 1 shows that the lowest band gap was found in the thiophene family in the π-conjugated linker D1 with 2CA as the first acceptor (2.144 eV). A large energy gap is also observed in other dyes, such as D2, D3, D4, D5, and D6, which contain dithiophene and dipyrrole π-spacers, respectively (see table 1). The overall bandgap order of these dyes is obtained as follows: D6 > D5 > D4 > D3 > D2 > D1, demonstrating that 2CA yields the best results with a dithiophene spacer and narrowed the energy gap. Furthermore, a comparison of the energy gaps of the chromophores D1 to D6, all of which have 2CAA as their second π-linker, reveals that D6 has the largest gap at 2.524 eV. The following series of dyes can be arranged in decreasing order of energy gap: D6 > D5 > D4 > D3 > D2 > D1 (table 1). Dye compounds containing a dithiophene π-spacer is discovered that their band gaps are narrower than those of pyrrole compounds. Since dithiophene has twice as many Sulphur atoms, its basicity is increased by a factor of 100. This could improve the resonance stabilization in the aromatic ring, which in turn stabilizes the molecule by decreasing its band gap. Figure 2 depicts the results of an additional investigation into the charge densities on the orbital surfaces. The LUMO charge density is concentrated at the donor center of the valence shell and to a lesser extent
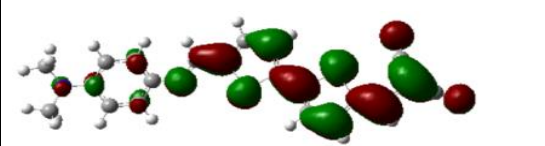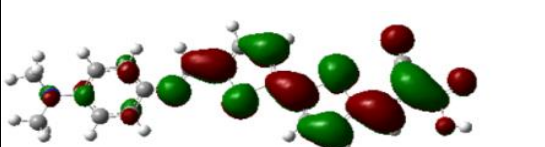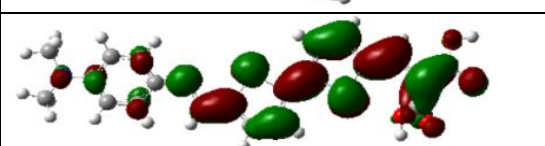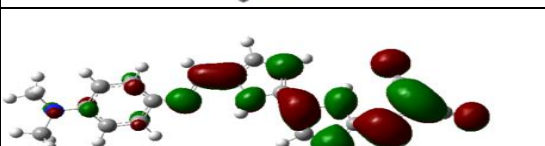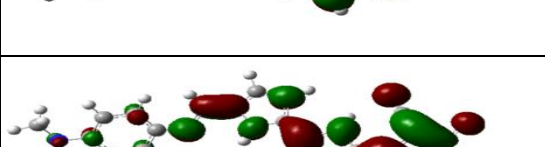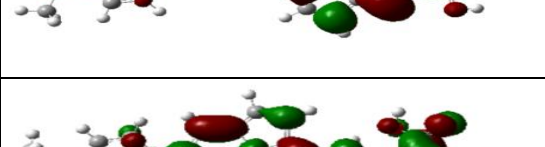
in the interstitial spaces, whereas the HOMO charge density is concentrated over the entire molecule.

TABLE 1: THE FRONTIER ORBITALS AND ENERGY GAP OF DYES.

Dye	HOMO (eV)	LUMO (eV)	Eg (eV)
D1	-5.139	-2.995	2.144
D2	-5.043	-2.804	2.239
D3	-4.80	-2.560	2.24
D4	-4.963	-2.530	2.433
D5	-4.616	-2.128	2.488
D6	-4.853	-2.329	2.524

TABLE 2: THE ELECTRON DENSITY OF FRONTIER ORBITALS.

DYE	HOMO
D1	
D2	
D3	
D4	
D5	
D6	

DYE	LUMO
D1	
D2	
D3	
D4	
D5	
D6	

B. ELECTRONIC STRUCTURE

There has been a marked increase in interest in organic NLO-based dyes over their inorganic counterparts over the past decade or more. Specifically, their superior manufacturing and quicker response times are to blame for drawing so much attention. NLO products find widespread application in fields as diverse as optoelectronics, optic memory systems, networking, and signal manipulation. In order to modulate highly valuable complexes, in-depth knowledge of NLO materials is required. To evaluate the effects of various π-conjugates and π-spacers on NLO characteristics of D1-D6, the linear polarizability and hyperpolarizability values of entitled compounds have been determined and tabulated in tables 2 and 3, respectively. In the first family, D1 with bithiophene as the π-linker has the highest value of linear polarizability (1230.42 a.u.), followed by D2, D3, D4, D5 and D6 with a bipyrrole π-linker. When ranked from highest to lowest, the values of dyes are found to be, in order: D1 > D2 > D3 > D4 > D5 > D6.

An decreased polarization indicates a larger HOMO-LUMO band gap and vice versa. It is also clear that greater hyperpolarizability is associated with a smaller band gap and a larger linear polarizability, thereby referring to a significant NLO response. Response of the first hyperpolarizability to NLO polarization is associated with charge transfer between molecules (ICT). From donor to acceptor, via π-linkers, we test for a successful charge transfer. Table 4 displays the results of an investigation into the NLO response of D1-D6 in relation to their respective second-order polarizability values.

TABLE 3: THE ELECTRON DENSITY OF FRONTIER ORBITALS.

Dye	α_{xx}	α_{yy}	α_{zz}	$<\alpha>$
D1	1189.35	432.93	162.80	1230.42
D2	1131.19	408.23	147.28	1211.58
D3	1065.05	393.60	160.60	1146.75
D4	1009.82	368.04	131.86	1082.85
D5	973.24	384.08	132.08	1054.59
D6	970.1	375.3	138.5	1049.34

TABLE 4: ELECTRON DENSITY OF FRONTIER ORBITALS.

Dye	β_{xx}	β_{yy}	β_{zz}	β_{tot}
D1	89242.78	-383.13	73.87	92242.88
D2	85929.15	-288.95	51.00	85929.65
D3	60802.22	328.60	-50.50	60803.13
D4	46119.26	267.11	56.76	46120.07
D5	42227.67	350.89	61.70	42229.17
D6	34146.97	-230.40	60.17	34147.80

C. UV-VISIBLE SPECTRUM ANALYSIS

The UV-visible spectral region is probed using TD-DFT calculations at CAM-B3LYP with a 6-311+ G (d, p) basis set. The six lowest energy singlet-singlet transitions were studied using time-dependent density-functional theory (TD-DFT) calculations. The spectra data of D1-D6 are shown in table 4, and the calculated transition energy (E_{ex}), oscillator strength (f), maximum absorption wavelength (λ_{max}) and nature of transitions. The absorbance spectrum of dye compounds was observed to span the visible to ultraviolet spectrum. The highest value of λ_{max} is analyzed for all compounds with dithiophene and dipyrrole π-spacers. This maximum absorption value changes depending on

the π-linker and acceptor. Using D6, the minimum value is 431 nm. Computational and reported values show good agreement, which raises the possibility that NLO results for the molecules D1-D6 under study will be significant. D1, D2, D3, D4, D5 and D6 are all chromophores in which the majority of electron transitions (HOMO to LUMO with 60%) occur from the donor to the acceptor. The all members of dyes exhibits a HOMO-1 to LUMO (about 30%) and HOMO to LUMO+1 (about 19%) transitions. Light harvesting efficiency (*LHE*) also plays a significant role in determining the chromophore's optical efficiency. Materials with a high *LHE* values exhibit the greatest photocurrent response.

The equation below is used to determine *LHE* of compounds:

$$LHE = 1-10^{-f} \qquad (3)$$

Compound oscillator strengths are represented by f in the equation (3). Table 5 shows the *LHE* values for the dyes D1-D6. D6 has the largest *LHE* value of any dye in the following series, at 0.987. The critical excited and ground state in a sum-over-state expression can be found in the work of Oudar and Chemla [19], where it is represented by the equation. This model is widely used in the literature to probe the NLO response. The model's push-pull architecture stems from an interaction between the charge transfer transition and second-order polarizability. According to the aforementioned implications, by tinkering with different types of π-bridges, we can gain a crucial concept for the modeling of novel D-π-A structures, yielding remarkable NLO results that can improve photoelectric and optical properties.

TABLE 5: OPTICAL PROPERTIES OF DYES.

Dye	E_{ex} (eV)	λ_{max} (nm)	f	*LHE*	Major contributions to the electronic transitions (%)
D1	2.48	499	1.74	0.982	*H-1 – L (30), H–L (60), H–L+1 (19)*
D2	2.55	486	1.73	0.982	*H-1 – L (30), H–L (60), H–L+1 (19)*
D3	2.69	461	1.78	0.984	*H-1 – L (29), H–L (60), H–L+1 (18)*
D4	2.72	454	1.75	0.982	*H-1 – L (30), H–L (60), H–L+1 (18)*
D5	2.77	447	1.75	0.982	*H-1 – L (30), H–L (60), H–L+1 (18)*
D6	2.87	431	1.90	0.987	*H-1 – L (27), H–L (60), H–L+1 (19)*

IV. CONCLUSIONS

Theoretical structural tailoring was used to explore the structure and properties of N.dimethylphenylendiamino-based promising NLO dyes, and the effect of different π-spacers on NLO properties was analyzed. The results show that the π-linker strongly tuned the electronic, photophysical, and NLO properties of the designed chromophores over the D-π-A architecture. The absorption spectra of all the compounds studied extended from 414 to 497 nm, and the largest *LHE*s had the lowest transitional energies (2.48–2.87 eV). Specifically, we looked into D1, which has the highest red shift ever measured (λ_{max} = 499 nm). Results from the FMO showed that HOMO is migrated partially on π-linkers or acceptors and entirely over donor. Contrarily, LUMOs are predominantly attached to acceptor and partially to π-conjugates. Furthermore, D1-D6, respectively, were investigated for their smallest band gap values of 2.144-2.524 eV.

Results from oscillator strength also showed that electrons can be efficiently transferred from donor to acceptor via the π-linker, resulting in the formation of a charge-transfer state. The linear polarizability (α = 1230.42 - 1049.34 a.u.) and nonlinear hyperpolarizability (β_{tot} = 92242.88 -34147.80 a.u.) response to electronic transitions from donor to acceptor moieties via π-conjugated linkers was enhanced. Due to its more basic nature than pyrrole, compounds with a thiophene spacer showed a lower band gap and greater NLO properties. All of the synthetic dyes tested positive for NLO response, with the highest polarizability and first hyperpolarizability values exhibited by D1. These D-π-A framework-based organic metal-free dyes play an important role in the field and shed light on experimental approaches to the development of high-performance NLO materials.

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