Rational Design of Bay-Annulated Indigo (BAI)-Based Oligomers for Bulk Heterojunction Organic Solar Cells: A Density Functional Theory (DFT) Study
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ABSTRACT: In this paper, we have designed a series of oligomers based on the donor−acceptor concept. Here, acceptor bay-annulated indigo (BAI) dye and donor N-methyl-4,5-diazacarbazole (DAC) are joined by a thiophene linkage. We have substituted the 5th and 5′th positions of the acceptor unit and the 2nd position of the donor unit with various electron-withdrawing and electron-donating groups to study various structural and electronic properties of the compounds. In this regard, we have calculated the dihedral angle, distortion energy, bond length alteration (BLA) parameters, bang gap (ΔH−L) values, partial density of states (PDOS), electrostatic potential (ESP) surface analysis, reorganization energy, charge transfer rates, hopping mobility values, and absorption spectra of the compounds. The ESP plots of the compounds indicate significant charge separation in the studied compounds. Our study manifests that the designed compounds are prone to facile charge transport.

INTRODUCTION
Organic π-conjugated semiconducting oligomers have attracted much interest of the researchers due to the major role played by them in the charge transfer process of organic solar cells (OSCs), organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), etc. Although the efficiency of organic materials lags behind the inorganic materials, they are still promising due to their abundant availability, low cost, easy fabrication, and flexibility.1−4 Suitable band gaps between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and the widespread spectrum to increase the overlap are essential features for an efficient semiconductor.5 Exploring the electronic properties of the organic oligomers is very crucial, and the charge transport properties of the oligomers are key factors governing the performance of the optoelectronic devices.6 The research of establishing a relationship between the structural properties and charge carrier mobility is immensely important.6,7

Generally, in the π-conjugated semiconducting materials, the semiconducting behavior is achieved by the overlapping of π molecular orbitals along the conjugation chain length.2 Owing to the large band gap and controlled charge carrier density compared to the inorganic molecules, their performance in optoelectronic devices is diminished.2,3 Up to now, many research studies have widely been carried out to modify the organic semiconducting materials to decrease the band gap and increase the charge carrier mobility. Proper designing of the molecular structure is proven as an effective way to enhance the intermolecular interaction and to increase the charge carrier mobility of the semiconducting materials.6 The donor (D)—acceptor (A)-based architecture where an alternating electron-rich donor (D) and electron-deficient acceptor (A) are incorporated along the conjugated polymer backbone leads to the development of efficient organic semiconductors.8−12

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The low-lying HOMO of the donor moiety and the high-lying LUMO of the acceptor moiety result into a much narrower band gap compared to the individual parent compound.\textsuperscript{2,11} This type of architecture can promote efficient intramolecular charge transfer from the donor moiety to its acceptor units through its $\pi$-conjugated spacer.\textsuperscript{13} Along the lines of materials discovery, for better control of the optoelectronic devices, the search for appropriate pairs of electron donor and acceptor units becomes one of the most crucial steps.\textsuperscript{14,15}

The band gap of the D−A-based systems can be tuned by considering a proper choice of the donor and acceptor moiety.\textsuperscript{16} The ionization potential of the donor moiety and the electron affinity of the acceptor moiety determine the band gap of the donor−acceptor-based systems. This popular and trendy strategy allows us to rationally design and study D−A-based organic oligomers that can absorb light in the infrared and visible region of the electromagnetic spectrum. Such materials would be very useful for the fabrication of optoelectronic devices, particularly the solar cells.\textsuperscript{2}

Formerly, the fullerene derivatives (e.g., PC$_{61}$BM ([6,6]-phenyl-C$_{61}$-butyric acid methyl ester), PC$_{71}$BM ([6,6]-phenyl-C$_{71}$-butyric acid methyl ester), ICBA (indenec-C$_{60}$ bisadduct), etc.) were used as the principal electron acceptors in the D−A-based systems due to their high electron affinity and exceptional electron transporting property.\textsuperscript{17} However, these materials have several disadvantages, viz., difficulty to synthesize and purify, weak absorption in the solar spectrum, difficulty in tuning the energy levels, etc. To overcome these

Figure 1. Sketches of the studied monomer units.
issues, rapid progress in the development of nonfullerene acceptors has shown the wider edge for the molecular design in OSCs.18

As a nonfullerene acceptor, naturally occurring dyes and pigments are deserving demand from thousands of years. At present, many dyes and pigments have been drawing the interest of researchers in the flourishing field of organic electronic research. Decades of research have proven that indigo and its derivatives are among the best electron-accepting species for the preparation of electroactive materials for organic electronics. It is well known that indig-based material bay-annelated indigo (BAI) has conquered the world of polymer-based solar cells with its outstanding electron-accepting capacity.12,19 Formerly, various electron acceptors like benzothiodiazole (BTD), benzoazole, isoindigo, diketopyrrolopyrrole (DPP), etc. have been copolymerized with various electron donors to design polymers with tunable electronic properties.5,20 The presence of a coplanar diketopiperidine core makes BAI as the most promising electron acceptor unit with a deeper LUMO energy level compared to some well known dye-based acceptors such as isoindigo and DPP.14,21

A simple strategy to enhance the device performance is to modify any of the π-bridge, donor, and acceptor moieties. Previously, we reported an isoindigo- and diithiophene derivate-based donor–acceptor system linked by a thiophene linkage.1 In this work, we have designed D–A-type oligomers based on a bay-annelated indigo (BAI) acceptor unit and N-methyl-4,5-diazacarbazole (DAC) as the donor unit flanked by a thiophene π-bridge. Here, we have introduced various electron-withdrawing groups, viz., −NO2, −CF3, −CN, and electron-donating groups such as −CH3, −OH, −NH2, −OCH3 at the 5th and 5′th positions of the acceptor BAI (compounds 2–8). Since the −NO2-substituted monomer possesses the lowest value of \( \Delta H_{\text{LUMO-HOMO}} \) (the difference in energy between the HOMO and LUMO energy level), we have substituted the 5th and 5′th positions of the acceptor BAI by −NO2 groups. On the other hand, the 2nd position of the donor DAC (compounds 9–15) has been substituted with −CF3, −CN, −CH3, −OH, −NH2, −OCH3 groups. The sketches of all the studied compounds are presented in Figure 1. We have computed various electronic properties, viz., ionization potential (IP), electron affinity (EA), dipole moment (\( \mu \)), reorganization energy (\( \lambda \)), charge transfer rate (\( k_{\text{CT}} \)), hopping mobility (\( \mu_{\text{hop}} \)), absorption properties, etc.12 To keep the computational cost under control, we have performed our calculations up to trimers (n = 3). The coordinates of the studied monomers have been provided in Table S1 (in the Supporting Information).

## THEORETICAL METHODOLOGY

It is well known that the performance of a device is affected by the energy barrier for the charge injection process. Ionization potential (IP), electron affinity (EA), and reorganization energy (\( \lambda \)) are the key parameters that determine the energy barrier for the charge injection process of organic polymers. We have presented the IP and EA in two different ways, (1) vertical (v) and (2) adiabatic (a). Vertical and adiabatic IP and EA can be calculated using the following equations:22,23

\[
\text{vIP} = E^+(M^0) - E^+(M^0)
\]

\[
\text{aIP} = E^+(M^+) - E^+(M^+)
\]

where \( E^0, E^+, \) and \( E^- \) are the energies of the molecules in the neutral, cationic, and anionic states, respectively, and \( M^0, M^+, \) and \( M^- \) represent the neutral, cationic, and anionic geometry of the molecules, respectively. The potential energy of the molecules has been graphically represented in Figure 2.

\[
v_{\text{EA}} = E^0(M^0) - E^-(M^0)
\]

\[
a_{\text{EA}} = E^0(M^0) - E^-(M^-)
\]

Figure 2. Representation of potential energy curves for the neutral and charged species.

Usually, the reorganization energy has the contribution from the outer sphere and inner sphere. The outer-sphere part arises from the polarization of the surrounding medium or the relaxation of electrons/nucleus. On the other hand, the inner-sphere part arises from the relaxation process of the associated geometry when a charge is accepted or released by the molecule.23 In this work, we have taken into account only the inner-sphere part of the reorganization energy. The reorganization energy values for holes (\( \lambda_h \)) and electrons (\( \lambda_e \)) can be calculated using eqs 5 and 6.23–26

\[
\lambda_h = \lambda_1 + \lambda_2
\]

\[
\lambda_e = \lambda_3 + \lambda_4
\]

The charge transfer rate (\( k_{\text{CT}} \)) between two adjacent molecules can be calculated with the help of Marcus’ theory. The relevant expression of \( k_{\text{CT}} \) when there exists no barrier can be given by the following equation:25,24,27–31

\[
\lambda_h = \lambda_1 + \lambda_2 + \frac{1}{2} \left[ (E^+(M^0) - E^+(M^0)) + (E^-(M^0) - E^-(M^0)) \right]
\]

\[
\lambda_e = \lambda_3 + \lambda_4 + \frac{1}{2} \left[ (E^-(M^-) - E^-(M^-)) + (E^+(M^+) - E^+(M^+)) \right]
\]

\[
E^0(M) - E^+(M^+) = v_{\text{IP}} - E^+(M^+) - E^+(M^+)
\]

\[
E^0(M) - E^-(M^-) = a_{\text{IP}} - E^+(M^+) - E^+(M^+)
\]
\[ k_{CT} = \left( \frac{\pi}{\lambda k_B T} \right)^{1/2} V^2 \frac{\exp\left(-\frac{\lambda}{\lambda k_B T}\right)}{\hbar} \]  

where \( T \) is the temperature at the absolute scale, \( k_B \) is the Boltzmann constant, \( V \) is the electronic coupling matrix element between two molecules, and \( \hbar \) is the reduced Planck’s constant. \( k_{CT} \) mainly depends on the charge transfer integral (\( V \)) and reorganization energy (\( \lambda \)).

The values of the electronic coupling matrix element for holes (\( V_h \)) and electrons (\( V_e \)) between two species are calculated as follows (eq 8).

\[ V_{\pm}(\omega) = \frac{E_{H(l+1)} - E_{H(l-1)}}{2} \]  

where \( E_{H(l)} \), \( E_{H(l+1)} \), \( E_{H(l-1)} \), and \( E_{L(l+1)} \) represent the energies of HOMO, HOMO−1, LUMO, and LUMO+1, respectively, of the closed-shell configuration of the neutral state of the oligomers. The value of the electronic coupling matrix element depends on the orbital overlap between the two species and needs to be larger for efficient charge mobility along the conjugated chain.23,29 The pictorial representation of the dihedral angle in a dimer is provided in Figure S1 (in the Supporting Information). We can estimate the value of hopping mobility (\( \mu_{hop} \)) using Einstein’s equation (eq 9).

\[ \mu_{hop} = \frac{eD}{k_B T} \]  

where \( e \) denotes the charge. In a one-dimensional system, \( D \) and \( k_{CT} \) are related as \( D = k_{CT}I^2/2 \) where \( I \) represents the space distance between two interacting molecules.

### RESULTS AND DISCUSSION

#### Geometrical and Structural Properties. Dihedral Angle. The dihedral angle is the most prominent parameter that will affect the planarity of the molecules.24,32 The representation of the dihedral angle in a dimer is provided in Figure S1 (in the Supporting Information). The values of dihedral angles of the studied dimers in both gas and solvent phases have been reported in Table 1. From this table, it is clearly seen that the dihedral angle values are changed upon attachment of the substituents at various positions. Among the studied compounds, dimer 7 with the −CN group at the 5th and 14th positions possesses the lowest value of dihedral angle.

| compounds | gas (°) | solvent (°) |
|-----------|--------|-------------|
| 1         | −49.34 | −50.71      |
| 2         | −45.46 | −47.26      |
| 3         | −49.07 | −50.33      |
| 4         | −49.36 | 48.92       |
| 5         | 46.08  | 48.28       |
| 6         | 46.12  | 47.98       |
| 7         | −45.25 | −47.11      |
| 8         | −45.46 | −47.25      |
| 9         | −49.45 | −51.03      |
| 10        | −49.12 | −50.92      |
| 11        | −48.36 | −50.79      |
| 12        | −48.93 | −50.61      |
| 13        | 45.58  | 49.83       |
| 14        | 49.08  | 50.31       |
| 15        | 48.89  | 50.00       |

This manifests that dimer 7 will have a comparatively planar structure among the studied compounds. Hence, substitution by the −CN group was supposed to increase the extent of conjugation of the oligomeric backbone. Conversely, dimer 9 having −NO2 groups at the acceptor and −COCH3 groups at the donor part possesses the highest value of dihedral angle in both phases. As a result, the extent of conjugation in compound 9 is supposed to be less.

#### Average Inter-ring Bridge Bond Distance (\( l \)). The average inter-ring bridge bond distance (\( l \)) (represented in Figure S1 in the Supporting Information) for all the monomers are calculated and reported in Table 2. It is observed from Table 2 that \( l \) values are shorter than the C−C single-bond distance (1.54 Å) and longer than the C=C double-bond distance (1.33 Å). The \( l \) values of compounds 4, 6, 7, 8, 11, 12, and 13 are shorter in comparison to the \( l \) value of the unsubstituted compound 1. This observation manifests an increase in the extent of conjugation in the compounds upon attachment of the substituents. Conversely, in compounds 2, 3, 5, 9, 10, 14, and 15, the \( l \) values increased, which in turn reflects a decrease in the extent of conjugation. Among all the studied compounds, compound 11 possesses the lowest \( l \) value. Hence, this compound is supposed to exhibit maximum conjugation.

#### Inter-ring Torsional Angle (\( \phi \)). The pictorial representation of inter-ring torsional angles (\( \phi_1 \) and \( \phi_2 \)) of the monomers has been provided in Figure S1 (in the Supporting Information) and the calculated values are reported in Table 3. From this table, it has been observed that among all the studied compounds, compound 11 possesses the lowest value of inter-ring torsional angle. Moreover, among compounds 2−9 where only the acceptor unit is substituted with different substituents, compound 6 (having −NO2 as a substituent) possesses the lowest value of \( \phi_1 \) and \( \phi_2 \). These values reveal that substitution by −NO2 groups at the acceptor unit is favorable.

#### Distortion Energy (\( \Delta E_{dis} \)). The distortion energy (\( \Delta E_{dis} \)) has been calculated to derive a relationship between the geometric structure and the electronic properties of the oligomers. The \( \Delta E_{dis} \) can be defined as the amount of energy required to planarize the molecules. To calculate the \( \Delta E_{dis} \) the dihedral angles of the molecules have been adjusted to zero to planarize the molecules, and then, single-point energy calculations have been performed at the planarized geometries. The energy difference between the planarized and the neutral geometry yields the distortion energy.33 The calculated \( \Delta E_{dis} \) values of the studied monomers have been reported in Table 4. From this table, it is observed that among the studied compounds, compound 11 possesses the lowest value of \( \Delta E_{dis} \). This is also in accordance with the lowest value of the interunit dihedral angle of this compound. Among compounds 2−9 where only the acceptor unit is substituted, compound 6 having −NO2 groups at the acceptor unit possesses the lowest value of \( \Delta E_{dis} \). This value also agrees with its low value of interunit dihedral angle. These observations manifest that substitution by electron-withdrawing −NO2 groups at the acceptor unit is favorable. It can also be concluded that −NO2 substitution at the acceptor unit and −OH substitution at the donor unit in compound 11 lead to a low value of interunit dihedral angle and hence account for its low \( \Delta E_{dis} \) values.

#### Bond Length Alteration (BLA) Parameter (\( \Delta r \)). BLA has been considered as a key geometrical parameter for π-conjugated polymers. It is related to the HOMO−LUMO

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gap, transport properties, photon absorption characteristics, linear–nonlinear polarizabilities of the molecules, etc. Here, we have calculated the average BLA parameters of the rings of the monomers to measure the extent of conjugation present in the molecules. This evaluation helps us to establish the geometric structure–property relationship. BLA is calculated as the average difference between the length of the single and adjacent double or triple bonds along the π-conjugated backbone. The calculated average BLA parameters of the studied monomers have been presented in Figure 3. All the studied compounds show BLA parameter values smaller than 0.05 Å, which is an indication of high electron delocalization along the π-conjugated backbone. Among the studied compounds, compound 11 possesses the lowest value of Δr. This may be attributed to the formation of a greater amount of conjugation by the O and N atom of the −OH and −NO2 group attached at the donor and the acceptor part of the molecule, respectively. Conversely, compound 15 possesses the highest value of Δr. This high value of Δr may be due to the greater size of the −CF3 group at the donor part, which in turn results into reduction of conjugation in this compound.

**Frontier Molecular Orbital Analysis.** The energies of the frontier molecular orbitals (FMOs) are one of the most prominent factors that influence the charge transport in OSCs.

### Table 3. Inter-ring Torsional Angles of the Studied Monomers

| compounds | ϕ1 (°) | ϕ2 (°) |
|-----------|-------|-------|
| 1         | 29.03 | −29.58 |
| 2         | −28.80 | −29.52 |
| 3         | 26.29 | 29.25 |
| 4         | 29.36 | 29.88 |
| 5         | 26.88 | 29.17 |
| 6         | 25.02 | 27.66 |
| 7         | 29.15 | −29.08 |
| 8         | −29.17 | −29.17 |
| 9         | −50.80 | 30.36 |
| 10        | −42.64 | 29.08 |
| 11        | −23.40 | 27.63 |
| 12        | −36.87 | 27.69 |
| 13        | −25.93 | 27.73 |
| 14        | −38.85 | 29.81 |
| 15        | −48.28 | 30.20 |

### Table 4. ΔE_{dis} Values of the Studied Monomers

| compounds | ΔE_{dis} (kcal mol⁻¹) |
|-----------|----------------------|
| 1         | 12.24                |
| 2         | 12.37                |
| 3         | 13.07                |
| 4         | 13.10                |
| 5         | 11.09                |
| 6         | 10.99                |
| 7         | 12.11                |
| 8         | 11.87                |
| 9         | 41.25                |
| 10        | 19.58                |
| 11        | 10.79                |
| 12        | 18.39                |
| 13        | 11.10                |
| 14        | 15.80                |
| 15        | 29.64                |
The energies of HOMO and LUMO and $\Delta_{H-L}$ values (difference between the energies of HOMO and LUMO) can be correlated with the electronic properties of the compounds. Based on the ground state calculations, the HOMO and LUMO energies and the $\Delta_{H-L}$ values of all the studied oligomers are reported in Table 5 for the gas phase and in Table 6 for the solvent phase. From Tables 5 and 6, it is observed that for both the gas and solvent phase, compound 12 possesses the lowest value of $\Delta_{H-L}$ for all the three oligomers. The highest destabilization of the HOMO energy level for compound 12 (in all the three oligomers) leads to the observed lowest $\Delta_{H-L}$ value (in the three oligomers). Conversely, compound 3 possesses the highest value of $\Delta_{H-L}$ for all the three oligomers. This happens due to the highest destabilization of LUMO energy levels for this compound for all the three oligomers in both phases.

It is also observed from Tables 5 and 6 that the $\Delta_{H-L}$ values of the compounds are dependent on the positions of the substituents. Among compounds 2–8 where substituents are present only at the 5th and 5’th positions of the acceptor unit, compound 6 having $\text{NO}_2$ as a substituent possesses the lowest $\Delta_{H-L}$ value for all the three oligomers. It is also observed that when electron-withdrawing groups are attached at the acceptor unit (in compounds 6, 7, and 8) the $\Delta_{H-L}$ values get reduced. Conversely, when electron-donating groups are attached at the acceptor unit (in compounds 2, 3, 4, and 5), the $\Delta_{H-L}$ values get increased for all the three oligomers. Moreover, compounds 9–15 (where the acceptor unit contains $\text{NO}_2$ as a substituent and the 2nd position of the donor unit contains other substituents) exhibit low $\Delta_{H-L}$ values in comparison to compounds 1–8 (where only the donor unit is unsubstituted). These results can be explained by the fact that proper substitution at the donor and acceptor unit by electron-donating and electron-withdrawing groups respectively leads to an increase in the electron density of the molecular backbone. This in turn reflects the increase in the extent of conjugation along the molecular backbone, which results into the lowering of the $\Delta_{H-L}$ values. This observation can be supported by the plot of frontier molecular orbitals (FMOs) of compounds 1, 3, 6, and 12 provided in Figure 4. From this figure, it is observed that substitution at the donor unit by $\text{NH}_2$ groups in compound 12 increases the electron density of the HOMO. Conversely, in the same compound, substitution at the acceptor unit by $\text{NO}_2$ groups increases the electron density of the LUMO.

Solvent effects also dictate the $\Delta_{H-L}$ values. From Table 6, it is observed that the $\Delta_{H-L}$ values of the compounds are larger in the solvent phase than in the gas phase. This can be

### Table 5. Energies of HOMO and LUMO and $\Delta_{H-L}$ Values of All the Studied Oligomers in the Gas Phase

| compound | type | HOMO (eV) | LUMO (eV) | $\Delta_{H-L}$ (eV) | compound | type | HOMO (eV) | LUMO (eV) | $\Delta_{H-L}$ (eV) |
|----------|------|-----------|-----------|---------------------|----------|------|-----------|-----------|---------------------|
| 1        | M    | −5.28     | −3.00     | 2.28                | 9        | M    | −5.68     | −3.65     | 2.03                |
|          | D    | −5.20     | −3.12     | 2.08                |          | D    | −5.71     | −3.82     | 1.89                |
|          | T    | −5.18     | −3.17     | 2.01                |          | T    | −5.71     | −3.91     | 1.80                |
| 2        | M    | −5.21     | −2.93     | 2.28                | 10       | M    | −5.75     | −3.75     | 2.00                |
|          | D    | −5.12     | −3.03     | 2.09                |          | D    | −5.69     | −3.86     | 1.83                |
|          | T    | −5.10     | −3.08     | 2.02                |          | T    | −5.68     | −3.91     | 1.78                |
| 3        | M    | −5.00     | −2.61     | 2.39                | 11       | M    | −5.58     | −3.69     | 1.89                |
|          | D    | −4.93     | −2.73     | 2.20                |          | D    | −5.53     | −3.82     | 1.71                |
|          | T    | −4.90     | −2.77     | 2.13                |          | T    | −5.61     | −3.96     | 1.65                |
| 4        | M    | −5.26     | −3.00     | 2.26                | 12       | M    | −5.46     | −3.73     | 1.73                |
|          | D    | −5.09     | −2.95     | 2.14                |          | D    | −5.42     | −3.84     | 1.58                |
|          | T    | −5.12     | −3.05     | 2.07                |          | T    | −5.42     | −3.89     | 1.53                |
| 5        | M    | −5.16     | −2.89     | 2.27                | 13       | M    | −5.54     | −3.67     | 1.87                |
|          | D    | −5.08     | −2.93     | 2.15                |          | D    | −5.48     | −3.80     | 1.68                |
|          | T    | −5.02     | −2.93     | 2.09                |          | T    | −5.47     | −3.86     | 1.61                |
| 6        | M    | −5.74     | −3.76     | 1.98                | 14       | M    | −5.92     | −3.82     | 2.10                |
|          | D    | −5.67     | −3.88     | 1.79                |          | D    | −5.93     | −4.02     | 1.91                |
|          | T    | −5.67     | −3.94     | 1.73                |          | T    | −5.95     | −4.08     | 1.97                |
| 7        | M    | −5.71     | −3.58     | 2.13                | 15       | M    | −5.87     | −3.77     | 2.10                |
|          | D    | −5.63     | −3.77     | 1.89                |          | D    | −5.86     | −3.93     | 1.93                |
|          | T    | −5.62     | −3.84     | 1.78                |          | T    | −5.90     | −4.00     | 1.90                |
| 8        | M    | −5.55     | −3.37     | 2.18                |          |      |           |           |                    |
|          | D    | −5.47     | −3.52     | 1.95                |          |      |           |           |                    |
|          | T    | −5.46     | −3.58     | 1.88                |          |      |           |           |                    |
explained by the fact that in the solvent phase, the stabilization of the HOMO energy level is higher than the LUMO energy level compared to the gas phase. However, in both phases, trends in $\Delta_{H-L}$ values are similar. These observations led us to conclude that substitution by electron-withdrawing groups at the acceptor unit and electron-donating groups at the donor unit is favorable.

From the plot of frontier molecular orbitals (FMOs) presented in Figure 4, it is clear that the molecular orbitals are of $\pi$-character. The HOMOs of the compounds are delocalized over the whole molecule, and the LUMOs are concentrated on the BAI acceptor unit. From this figure, it is also evident that the FMOs of the compounds in both phases are almost similar.

**Density of States Calculation.** For a detail correlation of the electronic structure with the FMOs, the partial density of states (PDOS) of the compounds has been calculated and the respective spectral data have been provided in Table S3 (in the Supporting Information). From Table S3, it is observed that the BAI acceptor unit offers maximum contribution to the frontier orbitals in all the investigated compounds except compounds 12 and 13. In compounds 12 and 13, the BAI acceptor offers maximum contribution to the LUMOs, and the donor part offers maximum contribution to the HOMOs. In compound 1, it is observed that the contribution of the acceptor to the HOMO is 56% and to the LUMO is 85%, and the contribution of the donor to the HOMO is 16% and to the LUMO is 4%.

In compounds 14 and 15 where the donor unit is substituted with electron-withdrawing $\text{NO}_2$ and $\text{CF}_3$ groups and the acceptor unit is substituted with $\text{NH}_2$, a dominant contribution of the acceptor unit toward the HOMO is observed. Moreover, the acceptor unit has maximum contribution (88%) toward the LUMOs in compounds 9, 14, and 15. In compounds 12 and 13 where the acceptor part is substituted with $\text{NO}_2$ groups and the donor part is substituted with $\text{NH}_2$ and $\text{OCH}_3$ groups, the donor unit offers a contribution of 67% and 38%, respectively, toward the HOMOs. Thus, it can be concluded that attachment of electron-withdrawing $\text{NO}_2$ groups at the acceptor unit increases the contribution of the acceptor unit toward the LUMO. Similarly, attachment of electron-donating groups at the donor unit increases the contribution of the donor unit to the HOMO energy level. Therefore, these observed facts reveal that the PDOS spectra give a clear vision of the nature of HOMO and LUMO energy levels. The PDOS spectra of compounds 1, 6, 12, and 13 have been provided in Figure S5, and the same spectra for the other compounds have been provided in Figure S2 (in the Supporting Information).

**Ionization Potential (IP) and Electron Affinity (EA).** Ionization potential (IP) and electron affinity (EA) of organic compounds are the key factors that determine the charge injection process.\(^{23}\) For an organic material to act as a p-type

![Table 6. Energies of HOMO and LUMO and $\Delta_{H-L}$ Values of All the Studied Oligomers in the Solvent Phase](http://pubs.acs.org/journal/acsodf)

| compound | type | HOMO (eV) | LUMO (eV) | $\Delta_{H-L}$ (eV) |
|----------|------|-----------|-----------|---------------------|
| 1        | M    | -5.38     | -3.03     | 2.35                |
|          | D    | -5.30     | -3.12     | 2.18                |
|          | T    | -5.27     | -3.16     | 2.11                |
| 2        | M    | -5.35     | -2.99     | 2.36                |
|          | D    | -5.13     | -3.07     | 2.18                |
|          | T    | -5.22     | -3.10     | 2.12                |
| 3        | M    | -5.20     | -2.74     | 2.46                |
|          | D    | -4.93     | -2.84     | 2.29                |
|          | T    | -5.11     | -2.88     | 2.23                |
| 4        | M    | -5.34     | -3.01     | 2.33                |
|          | D    | -5.23     | -3.00     | 2.27                |
|          | T    | -5.13     | -3.05     | 2.08                |
| 5        | M    | -5.33     | -2.98     | 2.35                |
|          | D    | -5.24     | -3.00     | 2.24                |
|          | T    | -5.20     | -3.02     | 2.18                |
| 6        | M    | -5.39     | -3.57     | 2.02                |
|          | D    | -5.48     | -3.64     | 1.84                |
|          | T    | -5.46     | -3.67     | 1.79                |
| 7        | M    | -5.36     | -3.23     | 2.27                |
|          | D    | -5.45     | -3.50     | 1.95                |
|          | T    | -5.43     | -3.53     | 1.90                |
| 8        | M    | -5.30     | -3.23     | 2.27                |
|          | D    | -5.40     | -3.36     | 2.04                |
|          | T    | -5.37     | -3.39     | 1.98                |

Table 6. Energies of HOMO and LUMO and $\Delta_{H-L}$ Values of All the Studied Oligomers in the Solvent Phase

![Figure 4. Plot of FMOs of compounds 1, 3, 6, and 12 in both gas and solvent phase.](http://pubs.acs.org/journal/acsodf)
semiconductor, the value of IP should be low so that injection of holes into the HOMO becomes easier. On the other hand, high electron affinity is desired to inject electrons into the LUMO for a material to act as an n-type semiconductor. The calculated vertical ionization potential (vIP), adiabatic ionization potential (aIP), vertical electron affinity (vEA), and adiabatic electron affinity (aEA) of the studied monomers have been presented in Table 7. From this table, it is observed that for compounds 1–5, both vIP and aIP values are low, which signifies that holes can be easily injected to the HOMOs of these compounds. In compounds 6–15, vIP and aIP values and vEA and aEA values are high, which in turn reflects that electron injection to the LUMOs of these compounds becomes favorable.

Table 7. Energies of HOMO and LUMO, IPs and EAs, of the Studied Monomers in the Gas Phase

| monomers | IP (eV) | EA (eV) |
|----------|---------|---------|
|          | vertical | adiabatic | vertical | adiabatic |
| 1        | 6.36     | 6.23     | 1.85     | 2.01      |
| 2        | 6.29     | 6.16     | 1.81     | 1.96      |
| 3        | 6.07     | 5.31     | 1.50     | 1.72      |
| 4        | 6.34     | 6.21     | 1.86     | 2.03      |
| 5        | 6.23     | 6.09     | 1.77     | 1.95      |
| 6        | 6.78     | 6.63     | 2.67     | 2.80      |
| 7        | 6.75     | 6.61     | 2.47     | 2.61      |
| 8        | 6.61     | 6.54     | 2.47     | 2.39      |
| 9        | 6.74     | 6.60     | 2.34     | 2.72      |
| 10       | 6.79     | 6.65     | 2.55     | 2.78      |
| 11       | 6.63     | 6.50     | 2.65     | 2.74      |
| 12       | 6.53     | 6.38     | 2.66     | 2.77      |
| 13       | 6.56     | 6.49     | 2.61     | 2.73      |
| 14       | 6.98     | 6.86     | 2.73     | 2.87      |
| 15       | 6.94     | 6.80     | 2.67     | 2.81      |

Molecular Electrostatic Potential (ESP) Surface of the Compounds. The molecular electrostatic potential (ESP) plots are evaluated to gain a qualitative indication of the nature of charge transfer from the donor to the acceptor.31 The evaluated molecular ESP surfaces of the compounds 1, 6, and 13 have been presented in Figure 6 and the same for the other compounds have been presented in Figure S3 (in the Supporting Information). The ESP plots for the compounds have been evaluated from the total SCF density [isovalie = 0.001 a.u.; (mapped with ESP)]. The positive potential increases in the color order red < orange < yellow < green < blue. The blue color represents the electron-deficient region and the red color represents the electron-rich region. From Figure 6, it is observed that in all the compounds, a significant charge separation is observed. Thus, from the above implications, we can conclude that the studied compounds have significant charge transfer characteristics.
The evolution of transition dipole moment for the vertical transition ground state to the first excited state \((S_0 \rightarrow S_1)\) as a function of the number of repeating units is provided in Figure 7. For the materials to absorb more photons, large transition dipole moments are required. The transition dipole moment is dependent on the length of the oligomer chain and hence increases upon going from the monomer to trimer. From this figure, it is observed that compound 14 exhibits the highest transition dipole moment.

**Charge Transport Properties.** Both the structural and electronic effects are dominant factors in determining the reorganization energy values for both holes \(\lambda_h\) and electrons \(\lambda_e\). For efficient charge transportation, the reorganization energy \(\lambda_h\) or \(\lambda_e\) of the molecule needs to be small. The lower the value of \(\lambda_h\), the more will be the hole transporting capacity of the molecule. Conversely, a lower value of \(\lambda_e\) indicates that the molecule will have electron transporting capacity. It is well known that the length of the conjugation chain determines the amount of reorganization energy. The longer the conjugation chain length along the backbone, the smaller will be the amount of reorganization energy for both holes and electrons. Besides, the rigidity of the molecular backbone and the nonbonding character of the frontier molecular orbitals also dictate the low values of reorganization energies. The calculated \(\lambda_h\) and \(\lambda_e\) values of the monomers are reported in Table 8.

From Table 8, it is observed that among the studied compounds, for the compounds 6, 10, 11, and 13, \(\lambda_h\) values are smaller than \(\lambda_h\) values. Hence, the ease of electron transportation for these compounds will be high. However, for compounds, 1–5, 7–9, 14, and 15, the \(\lambda_h\) values are smaller than the \(\lambda_e\) values. Therefore, these compounds will demand less energy for hole transportation. To gauge the electronic coupling matrix element \((V)\), we have considered \(\pi\)-stacking arrangement of the compounds, and the corresponding \(V\) values are presented in Table 8. The \(\pi\)-stacking arrangement of the compounds has been represented in Figure S4 (in the Supporting Information). Using the \(V\) values obtained from the \(\pi\)-stacking arrangement, we have calculated the charge transfer rates for holes \((k_{CT}^+\)\) and electrons \((k_{CT}^-)\) and the same have been reported in Table 8. From this table, it is observed that for compounds 1–5, 7–8, 14, and 15, the \(k_{CT}^+\) values are higher than the \(k_{CT}^-\) values. Therefore, these compounds will act as a hole-transporting material. On the other hand, for compounds 6 and 9–13, the \(k_{CT}^-\) values are higher than the \(k_{CT}^+\) values. Therefore, these compounds will act as an electron-transporting material. The hopping mobility \((\mu_{hop})\) values are an important parameter in the determination of conducting capacity of the organic oligomers. A high \(\mu_{hop}\) value indicates a greater electronic coupling between the adjacent molecules, which is an indication of a better conducting capacity of the oligomers. The \(\mu_{hop}\) values for holes and electrons have been calculated and are presented in Table 8. From this table, it is evident that compounds 11 possesses the highest value of \(\mu_{hop}\) and compound 13 possesses the highest value of \(\mu_{hop}\). These values are in accordance with the observed \(k_{CT}^-\) and \(k_{CT}^+\) values of these compounds, respectively. Thus, we can conclude that our designed compounds can act as potential candidates for the application in optoelectronic devices.

**Spectral Absorption Properties.** It is noteworthy to mention that the short circuit current density \((J_{sc})\) of the device depends on the spectral range and intensity of the solar

![Figure 7: Plot of transition dipole moment of the compounds.](https://dx.doi.org/10.1021/acsomega.0c00784)

Table 8. \(\lambda_h\), \(V\), \(k_{CT}^+\), and \(\mu_{hop}\) Values of the Studied Monomers

| compounds | \(\lambda_h\) (eV) | \(\lambda_e\) (eV) | \(V\) | \(V\) | \(k_{CT}^+ \times 10^{15}\) (s\(^{-1}\)) | \(k_{CT}^- \times 10^{15}\) (s\(^{-1}\)) | \(l\) (Å) | \(\mu_{hop}^+\) \((× 10^{-2} \text{cm}^2 \text{V}^{-1} \text{s}^{-1})\) | \(\mu_{hop}^-\) \((× 10^{-2} \text{cm}^2 \text{V}^{-1} \text{s}^{-1})\) |
|-----------|----------------|----------------|-----|-----|-----------------|-----------------|-----|----------------|----------------|
| 1         | 0.2631         | 0.2988         | 0.0881 | 0.0291 | 1.96           | 1.42            | 3.5 | 6.98           | 7.01           |
| 2         | 0.2574         | 0.2998         | 0.0888 | 0.0637 | 2.13           | 0.67            | 3.6 | 3.13           | 3.50           |
| 3         | 0.3575         | 0.3844         | 0.0438 | 0.0133 | 0.17           | 0.01            | 4.0 | 0.90           | 0.65           |
| 4         | 0.2596         | 0.3144         | 0.1020 | 0.0484 | 2.74           | 0.33            | 3.5 | 13.53          | 1.63           |
| 5         | 0.2522         | 0.3150         | 0.0819 | 0.0753 | 1.93           | 0.79            | 3.7 | 10.65          | 4.36           |
| 6         | 0.2516         | 0.2404         | 0.0601 | 0.1369 | 1.04           | 6.18            | 3.6 | 5.43           | 3.23           |
| 7         | 0.2624         | 0.2676         | 0.0800 | 0.0389 | 1.63           | 0.36            | 3.5 | 8.05           | 1.78           |
| 8         | 0.2764         | 0.3001         | 0.0553 | 0.0514 | 0.66           | 0.44            | 3.8 | 3.84           | 2.86           |
| 9         | 0.2740         | 0.3072         | 0.0672 | 0.0859 | 1.01           | 4.49            | 3.8 | 5.88           | 26.14          |
| 10        | 0.2681         | 0.2442         | 0.0906 | 0.0935 | 1.96           | 1.12            | 3.7 | 10.82          | 6.18           |
| 11        | 0.2344         | 0.2317         | 0.1061 | 0.1169 | 3.98           | 4.99            | 3.8 | 23.17          | 29.05          |
| 12        | 0.3058         | 0.2353         | 0.0537 | 0.1045 | 0.45           | 3.83            | 3.6 | 2.35           | 26.08          |
| 13        | 0.2383         | 0.2303         | 0.1093 | 0.1614 | 2.88           | 7.45            | 3.7 | 15.90          | 41.12          |
| 14        | 0.2398         | 0.2865         | 0.0694 | 0.0652 | 1.60           | 0.82            | 3.7 | 8.83           | 4.52           |
| 15        | 0.2688         | 0.2791         | 0.0710 | 0.0488 | 1.19           | 0.50            | 3.6 | 6.22           | 2.61           |
absorption. $J_{sc}$ is a function of external quantum efficiency ($\eta_{EQE}$) of the device and the photon number $S(\lambda)$ over the whole frequency region. $J_{sc}$ can be defined as

$$J_{sc} = q \int \eta_{EQE}(\lambda) S(\lambda) d\lambda$$

where $\eta_{EQE}$ is the product of exciton diffusion efficiency ($\eta_{EDA}$), light harvesting efficiency ($\eta_{LH}$), charge collection efficiency ($\eta_{CC}$), and charge transfer efficiency ($\eta_{CT}$).34 It is clear from the above equation that the absorption capacity of materials is the vital factor for increased efficiency of the solar cells. The light harvesting efficiency ($\eta_{LH}$) of a molecule correlates with the oscillator strength ($f_{osc}$) of a particular wavelength as follows:25,34

$$\eta_{LH} = 1 - 10^{-f_{osc}}$$

For better understanding of the electronic properties of the BAI-based compounds, the vertical excitation properties have been obtained for 15 excited states with the TD-DFT method employing the CAM-B3LYP functional, and the dominant electronic transitions are labeled in Table 9 for the gas phase and in Table S4 (in the Supporting Information) for the solvent (DCM) phase. The maximum wavelength ($\lambda_{max}$), excitation energy ($E_g$), oscillator strength ($f_{osc}$), and light harvesting efficiency ($\eta_{LH}$) have been presented in the table for the respective phases. It has been found from Table 9 that among the calculated singlet–singlet transitions, the maximum $f_{osc}$ of the compounds is attributed to the HOMO $\rightarrow$ LUMO transition. Among the compounds (2–8) where only the acceptor unit is substituted with different substituents), compound 6 possesses the highest $\lambda_{max}$ value. Among all the studied compounds, dimer 13 possesses the highest $\lambda_{max}$ value. The presence of $-\text{NO}_2$ groups at the acceptor and $-\text{OCH}_3$ groups at the donor part causes a maximum redshift in this compound. We have already observed that compound 13 possesses the lowest $\Delta H_{\text{L} - \text{L}}$ value. The presence of $-\text{NO}_2$ groups at the acceptor part and $-\text{OCH}_3$ groups at the donor part increases the electron density of this compound, which results into the maximum redshift of this compound. However, compound 3 possesses the lowest value of $\lambda_{max}$ among all the studied compounds, which is again in accordance with the observed highest $\Delta H_{\text{L} - \text{L}}$ value.

From Table 9, it is observed that in dimers 2, 3, 4, and 5 (where we have substituted the acceptor unit with electron-donating substituents), the $\lambda_{max}$ values undergo a blueshift compared to the $\lambda_{max}$ value of the unsubstituted dimer 1. Meanwhile, in other compounds, the $\lambda_{max}$ values have shifted to the longer region. The above results reveal that substitution by electron-withdrawing groups at the acceptor unit and electron-donating groups at the donor unit shifts the absorption wavelength toward the longer region.

Comparing Table 9 with Table S4, we have found that a correlation exists between the $E_g$ (optical band gap) and $\Delta H_{\text{L} - \text{L}}$ values. Here, $E_g$ values follow the same trend as that of the $\Delta H_{\text{L} - \text{L}}$ values. It is already observed that compound 3 possesses the highest value of $\Delta H_{\text{L} - \text{L}}$, and consequently, the $E_g$ value for this compound is also maximum. Similarly, the $E_g$...
value of compound 13 is observed to be minimum due to its observed lowest $\Delta_{H-L}$ value.

To increase the power conversion efficiency (PCE) of the organic photovoltaics, it is necessary to have effective photon absorption in the visible region of light. Therefore, energy calculation of the $S_0 \rightarrow S_1$ transition state is important. From Table 9, it is observed that for all the D–A systems, the oscillator strength values are considerable for the low-lying excited state. Among the D–A systems, compound 13 possesses the lowest $E_{g}$ and maximum $f_{OSC}$ value. Conversely, compound 3 possesses the highest value of $E_{g}$ and as a result, it exhibits the lowest $\lambda_{max}$ value. The plots of the absorption spectra of compounds 1, 3, 6, and 13 have been provided in Figure 8.

![Figure 8. Plot of the absorption spectra of dimers 1, 3, 6, and 13.](Image)

We have also calculated the absorption spectra of the dimers using the functionals M06-2X-D3 and B3LYP-D3. We have observed that the results follow the similar trend with the results obtained using the CAM-B3LYP functional. The absorption spectra of the compounds obtained using the functionals M06-2X-D3 and B3LYP-D3 have been provided in Figures S5 and S6, respectively (in the Supporting Information).

Natural Transition Orbital (NTO) Analysis. To find the population of the dominant electronic transitions, we have performed natural transition orbital (NTO) analysis. The calculated largest NTO eigenvalues for the crucial transitions obtained by employing the TD-DFT method have been provided in Table 9. The visualization of the hole and particle NTOs of compounds 1, 3, 12, and 13 has been provided in Figure 9. It is observed from the hole and particle NTOs presented in Figure 9 that electron density is transferred from the donor to the acceptor unit after electronic transitions.

![Figure 9. Plot of NTOs 1, 3, 11, and 12.](Image)

**CONCLUSIONS**

In this paper, we have performed DFT and TD-DFT calculations on a series of BAI-based D–A-type oligomers. In order to investigate the structural and electronic properties, we have attached various electron-withdrawing and electron-donating substituents at the 5th and 5′th positions of the BAI acceptor unit and the 2nd position of the donor unit. From the study of structural and electronic properties, we have observed that substitution by various units at different positions affects these properties in a varied manner. From the observed $\Delta_{H-L}$ values, it can be inferred that substitution by $-\text{NO}_2$ groups at the acceptor unit and electron-donating groups at the donor has a profound effect. The plot of the ESP surface of the compounds indicates that all the compounds have significant charge transport properties. We have calculated the values of $\lambda_{H}, \lambda_{L}, V_+, V_-$ to calculate the values of $k_{CT}^+ \text{and} k_{CT}^-$. The charge transport study reveals the hole transporting nature of compounds 1–5, 7, 8, 14, and 15. On the other hand, compounds 6 and 9–13 will act as an electron-transporting material. We have investigated the absorption properties of the compounds using the TD-DFT method. The absorption studies manifest that compound 13 possesses the highest value of $\lambda_{max}$, lowest value of $E_g$, and highest value of $f_{OSC}$. Moreover, it is observed that attachment of $-\text{NO}_2$ groups at the acceptor unit and electron-donating groups at the donor unit causes a redshift of the absorption wavelength.

Thus, we can conclude that attachment of electron-withdrawing $-\text{NO}_2$ groups at the acceptor unit and electron-donating groups at the donor unit is more favorable for better tuning of the optoelectronic properties. Our study presents effective guidelines for designing efficient oligomers for the purpose of organic solar cell applications.

**VALIDATION OF THE APPLIED METHODOLOGY**

It is essential to choose an appropriate methodology for better accuracy of calculated results. An extensive study has been carried out to validate the methodology used for the calculations. A test calculation has been performed with the
The dye P2 reported in the literature for which experimental results are available.\textsuperscript{36} We have performed the test calculations using seven different computational models, viz., B3LYP/6-31G(d,p), B3LYP-D3/6-31G(d,p), CAM-B3LYP/6-31G(d,p), PBE0PBE/6-31G(d,p), HSEH1PBE/6-31G(d,p), ωB97XD/6-31G(d,p), and M06-2X-D3/6-31G(d,p), applying the DFT method. We have correlated the calculated energies of the HOMO and LUMO, ΔH − L, and absorption wavelength (λ_{\text{max}}) values with the experimental results. The obtained results using different levels of theory have been presented in Table S2 (in the Supporting Information). From this table, it is observed that the functionals HSEH1PBE/6-31G(d,p) and B3LYP-D3/6-31G(d,p) agree well with the experimental results obtained at the ground state. However, in the excited-state calculations, M06-2X-D3 and CAM-B3LYP functionals correlate well with the experimental results. However, to keep the computational cost under control, we have used the B3LYP-D3/6-31G(d,p) and CAM-B3LYP/6-31G(d,p) level of theory for the ground- and excited-state calculations, respectively.

**COMPUTATIONAL DETAILS**

All the calculations have been carried out by employing electronic structure program package Gaussian09.\textsuperscript{37} Geometry optimization of the oligomers has been carried out using the density functional theory (DFT) method. Solvent phase calculations have been carried out using dichloromethane (DCM) solvent because photochemical reactions are prevented in this condition. For the solvent phase calculations, the conductor-like polarizable continuum model (CPCM) has been used.\textsuperscript{38} All the ground-state calculations have been carried out by the dispersion-corrected density functional theoretical method (B3LYP-D3 functional) with the 6-31G(d) basis set.\textsuperscript{1,23,25,32,38,42} The vibrational frequencies of the compounds have also been calculated for the optimized geometries to confirm that each of the geometries belongs to a minimum in the potential energy surface. The vertical and adiabatic ionization potential (IP(v) and IP(a)) and electron affinity (EA(v) and EA(a)) have also been computed for all the monomers at the same level of theory. The reorganization energy (ξ) and charge transfer rate (κ_{CT}) have been computed for the dimers using the same methodology. Excited-state calculations have been carried out using the time-dependent density functional theory (TD-DFT) method employing the long-range-corrected CAM-B3LYP functional along with the 6-31G(d) basis set.\textsuperscript{1,13,24,26,32,38,42–45}

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c00784.

XYZ coordinates of the studied compounds; energies of HOMO and LUMO, ΔH − L values, and λ_{\text{max}} values of the reference dye P2; representation of dihedral angle, inter-ring torsional angle, and inter-ring bridge bond length; spectral data obtained from the PDOS spectra; PDOS spectra of the studied compounds; ESP plot of the studied monomers; representative structure of two-stacked monomers along with the distance (l); absorption properties of the studied dimers in the solvent phase; absorption spectra of the dimers studied at the M06-2X-D3 and B3LYP-D3 level of theory (PDF).

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**Notes**

The authors declare no competing financial interest.

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