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# Synthesis, nonlinear optical analysis and DFT studies of D- $\pi$ -D and A- $\pi$ -A configured Schiff bases derived from bis-phenylenediamine†

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Herein, an integral approach has been made towards the exploration of electronic and structural parameters of four synthesized (DMA with an A- $\pi$ -A configuration and DMM, DAM, and DMD with a D- $\pi$ -D configuration) and one designed (DMB-D) novel Schiff base compounds. Bis phenylenediamine derivatives were prepared by condensation of 4,5-dimethyl-*o*-phenylenediamine (**1**) with various substituted benzaldehydes (**2a-d**). The structures of compounds were confirmed by spectroscopic techniques, *i.e.*, UV-visible, FT-IR, and NMR spectroscopy. The DFT-based analysis of entitled compounds was performed *via* density functional theory utilizing the M06-2X functional in conjugation with the 6-311G(d,p) basis set to acquire geometrical parameters, natural bonding orbital (NBO), the density of states (DOS), non-linear optical (NLO), molecular electrostatic potential (MESP), and natural population analyses. The smallest band gap of (5.446 eV) was noted for DMA *via* frontier molecular orbital (FMO) analysis. GRPs were obtained with the aid of  $E_{\text{gap}}$  values as DMA with the lowest band gap displayed a small magnitude of hardness (2.723 eV) and a large magnitude of softness (0.183 eV). The  $\beta_{\text{tot}}$  values of DMA, DMM, DMB-D, DAM, and DMD were 56.95, 0.43, 2.53, 8.98, and 68.47 times larger than urea ( $\beta_{\text{tot}} = 3.71 \times 10^{-31}$  e.s.u.), respectively. The observed fascinating NLO properties of these novel compounds might be helpful for further advancement in non-linear optics.

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## Introduction

Schiff bases are synthesized when a primary amine is treated with either a ketone or an aldehyde under certain circumstances. Schiff bases are also known as azomethine or an imine, due to the presence of the HC=N chromophore.<sup>1,2</sup> Schiff bases have been discovered in the biological sciences to have

antioxidant, antimalarial, antifungal, anticancer, antibacterial, anti-inflammatory, and antiviral properties, as well as catalyzing the reduction of thionyl chloride, polymerization reaction, aldol condensation reaction, reduction of ketones, hydrosilylation of ketones, Henry reaction, epoxidation of alkenes, production of bis(indolyl) methane and Diels Alder reaction.<sup>3</sup> A series of metal-based compounds are synthesized by using Schiff bases as ligands because they can form stable complexes with metal ions.<sup>4,5</sup> Schiff bases with a solvatochromic UV-vis spectrum (solvatochromicity) can serve as NLO active materials.<sup>6</sup> The ligands could be beneficial in solid phase extraction and the development of ion-selective electrodes for determining anions in analytical samples.<sup>7</sup>

The NLO compounds play an excellent part in electro-optics for signal processing, especially in fiber optics, telecommunications, and information technology.<sup>8-10</sup> They have simple chemistry, a low cost of creation, and a tendency to allow structural modifications to permit diverse NLO behaviors. NLO materials formed from the organic networks have become the focus of recent research.<sup>11-13</sup> The unique property of NLO materials is the transfer of intramolecular charge transfer (ICT) from electron donating to electron accepting moieties through conjugation links.<sup>14-16</sup> Experimental and computational data suggest that introducing strong donor (D) and acceptor (A) parts

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on paradoxical edges of the spacer, *i.e.*, D–A, D–D–A, and A–D–A, can result in a broad second-order NLO response.<sup>13</sup> Charge transfer is improved in compounds containing delocalized electrons in a D–A configuration.<sup>17,18</sup> In optoelectronics and photonics, the demand for the production of new NLO materials has expanded dramatically in recent years. The intriguing photo-physical behavior of NLO materials, when exposed to strong laser light, is responsible for their wide range of applicability.<sup>19,20</sup> The synthetic organic compounds have a lot of interest in developing fast response rate, higher laser impairment approach, greater photo-electric quantum, a small value of dielectric constant, fabrication adaptability, and an inexpensive development price.

## Experimental

### Chemistry

All the chemicals used in this research were in extra pure form and purchased from Sigma-Aldrich. A Bruker FT-IR IFS48 spectrophotometer was used to record the FT-IR spectrum (KBr discs). On the melting point device (Büchi 434), melting points were measured. A Bruker Avance 400 spectrometer was used to capture the NMR spectrum in DMSO-*d*<sub>6</sub>. The thin layer chromatographs were visualized under the influence of ultraviolet light to check the progress of reaction.

**General method for the synthesis of phenylenediamine derivatives.** 4,5-Dimethylbenzene-1,2-diamine (**1**) (5 mmol) was added to a stirred solution of suitable benzaldehyde (**2a–d**) (5 mmol) in 10 mL of methanol with the catalytic quantity (1–2 drops) of glacial acetic acid. The resulting mixture was allowed to cool at room temperature after being refluxed overnight and continuously monitored by the TLC. The resulting crystalline products (**DMA**, **DMM**, **DAM** and **DMD**) were filtered, cleaned with hot methanol, and allowed to air dry. The desired products with 75–90% yield were recrystallized from the methanol (Scheme 1).

The targeted compounds are characterized as follows:

(*1E,1'E*)-*N,N'*-(4,5-Dimethyl-1,2-phenylene)bis(1-(2-nitrophenyl) methanimine) (**DMA**). Yield 80%, mp. 156–158 °C; FT-IR (cm<sup>-1</sup>): 1586 cm<sup>-1</sup> (C=N), 3287 cm<sup>-1</sup> (N–H), 1450 cm<sup>-1</sup> (NO<sub>2</sub>); <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ-ppm; 2.28 (s, 3H, CH<sub>3</sub>), 7.06 (s, 1H), 7.73 (t, *J* =

7.6 Hz, 1H), 7.82 (t, *J* = 7.5 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 8.15 (d, *J* = 7.7 Hz, 1H), 8.76 (s, 1H, CH=N); <sup>13</sup>C-NMR (δ-ppm) 19.2, 122.0, 124.5, 129.7, 130.1, 131.9, 133.6, 135.7, 141.4, 149.3, 156.9; anal. calcd for C<sub>22</sub>H<sub>18</sub>N<sub>4</sub>O<sub>4</sub> (402.13): C = 65.66, H = 4.51, N = 13.92; found (%): C = 65.74, H = 4.36, N = 14.01.

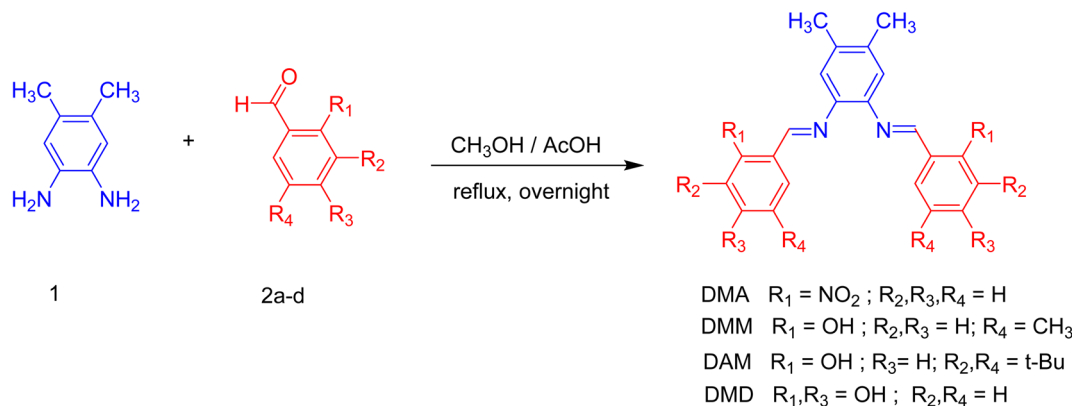
2,2'-((*1E,1'E*)-((4,5-Dimethyl-1,2-phenylene)bis(azaneylylidene)) bis(methaneylylidene))bis(4-methylphenol) (**DMM**). Yield 78%, mp. 157–159 °C. FT-IR (cm<sup>-1</sup>): 1586 cm<sup>-1</sup> (C=N), 3287 cm<sup>-1</sup> (N–H), 3050 cm<sup>-1</sup> (OH); <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>) δ-ppm; 2.26 (s, 3H, CH<sub>3</sub>), 2.29 (s, 3H, CH<sub>3</sub>), 6.85 (d, 2H, Ar-H, *J* = 8.4 Hz), 7.20 (s, 1H, Ar-H), 7.22 (dd, 2H, Ar-H, *J* = 8.4, 2 Hz), 7.43 (d, 2H, Ar-H, *J* = 2 Hz), 8.85 (s, 1H, CH=N), 12.81 (s, 1H, OH); <sup>13</sup>C-NMR (δ-ppm); 19.4, 20.3, 115.6, 128.9, 129.6, 130.6, 130.9, 136.2, 140.8, 154.3, 154.9, 163.0; anal. calcd for C<sub>24</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub> (372.18): C = 77.39, H = 6.50, N = 7.52; found (%): C = 77.51, H = 6.59, N = 7.67.

6,6'-((*1E,1'E*)-((4,5-Dimethyl-1,2-phenylene)bis(azaneylylidene)) bis(methaneylylidene))bis(2,4-di-*tert*-butylphenol) (**DAM**). Yield 90%, mp. 3.66–368 °C.; FT-IR (cm<sup>-1</sup>): 1586 cm<sup>-1</sup> (C=N), 3287 cm<sup>-1</sup> (N–H), 3570 cm<sup>-1</sup> (OH); <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>) δ-ppm; 1.29 (s, 9H, CH<sub>3</sub>), 1.39 (s, 9H, CH<sub>3</sub>), 2.31 (s, 3H, CH<sub>3</sub>), 7.35–7.38 (m, 2H, Ar-H), 7.48 (d, 1H, *J* = 8.0 Hz, Ar-H), 8.97 (s, 1H, CH=N), 13.8 (s, 1H, OH); <sup>13</sup>C-NMR (δ-ppm); 19.4, 20.3, 24.1, 115.6, 116.4, 117.3, 117.6, 128.9, 130.9, 132.5, 140.8, 154.8, 168.4; anal. calcd for C<sub>38</sub>H<sub>52</sub>N<sub>2</sub>O<sub>2</sub> (568.40): C = 80.24, H = 9.21, N = 4.92; found (%): C = 80.45, H = 9.05, N = 4.99.

4,4'-((*1E,1'E*)-((4,5-Dimethyl-1,2-phenylene)bis(azaneylylidene)) bis(methaneylylidene))bis(benzene-1,3-diol) (**DMD**). Yield 75%, mp. 315–317 °C; FT-IR (cm<sup>-1</sup>): 1586 cm<sup>-1</sup> (C=N), 3287 cm<sup>-1</sup> (N–H); <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>) δ-ppm; 2.28 (s, 3H, CH<sub>3</sub>), 6.28 (d, 1H, Ar-H, *J* = 2.2 Hz), 6.38 (dd, 1H, Ar-H, *J* = 2.2 Hz, 8.4 Hz), 7.20 (s, 1H, Ar-H), 7.42 (d, 1H, Ar-H, *J* = 8.4 Hz), 8.74 (s, 1H, CH=N), 12.25 (s, 1H, NH), 13.54 (s, 1H, OH); <sup>13</sup>C-NMR (δ-ppm) 19.5, 102.8, 108.1, 112.7, 120.6, 134.7, 135.7, 139.8, 162.4, 162.8, 163.8; anal. calcd for C<sub>22</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub> (376.14): C = 70.20, H = 5.36, N = 7.44; found (%): C = 70.45, H = 5.31, N = 7.59.

### Computational details

The DFT-based calculations of the studied compounds: **DMA**, **DMM**, **DMB-D**, **DAM**, and **DMD** were performed by using Gaussian 09 computational database package.<sup>21</sup> The obtained



Scheme 1 Synthesis of phenylenediamine derivatives.



output files were further analyzed by GaussView,<sup>22</sup> Avogadro,<sup>23</sup> Chemcraft <sup>24</sup>PyMOlyze 2.0,<sup>25</sup> Origin 8.0,<sup>26</sup> and Multiwfn 3.7,<sup>27</sup> programs. The analysis of NBO was done by NBO 3.1 program<sup>28</sup> at M06-2X/6-311G(d,p). Moreover, UV-vis spectrum were studied using the same level of theory to find out the maximum wavelength of light absorbed by the compounds. Moreover, NLO characteristics (dipole moment, 1<sup>st</sup> and 2<sup>nd</sup> hyperpolarizability) along with their tensor components in *x*, *y*, and *z* coordinates were computed at the abovementioned functional. NPA, DOS, and MEP were also computed at the same level. The FMO inspection was executed by using the same level of DFT and the energy difference between its orbitals was utilized to compute the global reactivity indices. The dipole moment ( $\mu$ ),<sup>29</sup> average linear polarizability ( $\langle\alpha\rangle$ ), first hyperpolarizability ( $\beta_{\text{tot}}$ ), and second hyperpolarizability  $\gamma_{\text{tot}}$  amplitudes were calculated by applying the given formulas<sup>27</sup> (eqn (1)–(4)).

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \quad (1)$$

$$\langle\alpha\rangle = (a_{xx} + a_{yy} + a_{zz})/3 \quad (2)$$

$$\beta_{\text{tot}} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad (3)$$

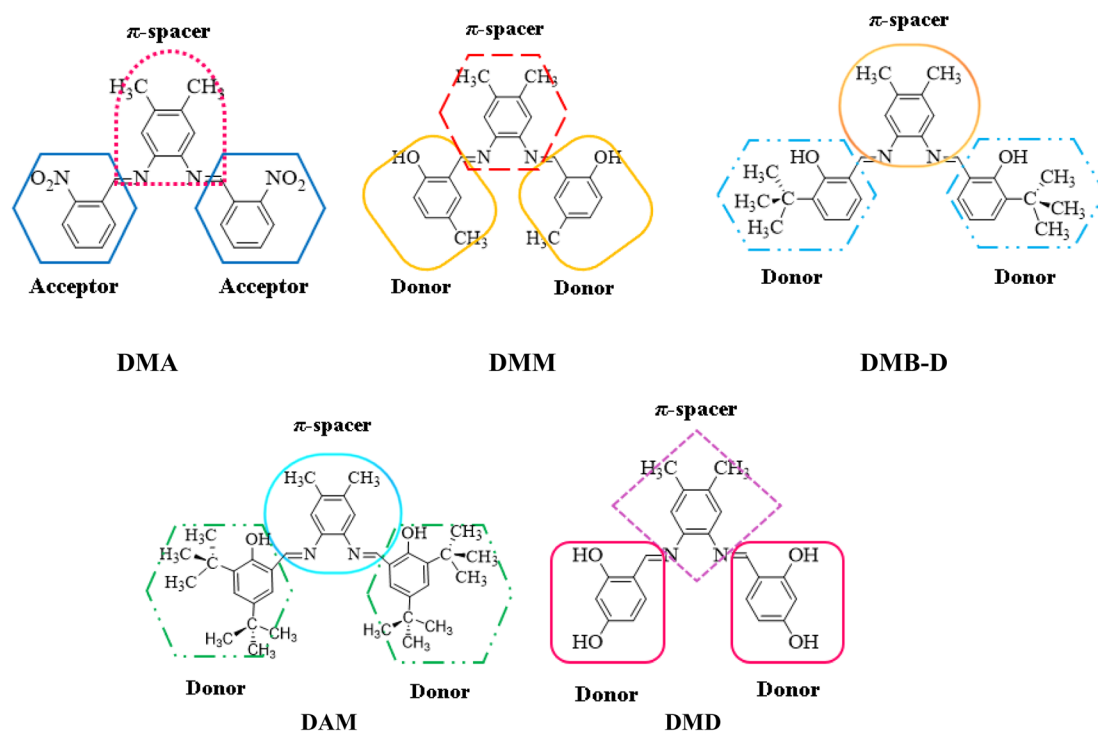
where  $\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$ ,  $\beta_y = \beta_{yxx} + \beta_{yyy} + \beta_{yzz}$  and  $\beta_z = \beta_{zxx} + \beta_{zyy} + \beta_{zzz}$ .

$$\gamma_{\text{tot}} = \sqrt{\gamma_x^2 + \gamma_y^2 + \gamma_z^2} \quad (4)$$

where  $\gamma_i = \frac{1}{15} \sum_j (\gamma_{iji} + \gamma_{ijj} + \gamma_{ijj}) \quad i, j = \{x, y, z\}$ .

## Results and discussion

The structures of the synthesized Schiff bases were determined by employing microanalysis (CHN) and spectral outcomes, *i.e.*, UV-vis, FT-IR, <sup>13</sup>C-NMR, <sup>1</sup>H-NMR spectroscopy. The C=N stretching band for different compounds in FT-IR was emerged in the range of 1484–1605 cm<sup>-1</sup>, whereas N–H stretching appeared in the range of 3152–3469 cm<sup>-1</sup>. In <sup>1</sup>H-NMR, the O–CH<sub>2</sub> signal appeared as a quartet at  $\delta$  4.04–4.07 ppm, and CH<sub>3</sub> attached to O–CH<sub>2</sub> appeared as a triplet due to the presence of neighboring CH<sub>2</sub> at  $\delta$  1.35 ppm, while the –CH=N– signal appeared as a singlet at  $\delta$  8.70–8.90 ppm. The spectral results of other aromatic and aliphatic protons were also in correspondence with the suggested structures of the molecules in the Tables S1, S4, S7 and S10.† In this work, DFT calculations were done to obtain the NLO parameters of four different synthesized compounds: **DMA**, **DMM**, **DAM**, and **DMD** and one designed compound **DMB-D**. **DMB-D** was designed from **DAM** in order to check the effect of single tertiary butyl group over the donor region. Compound **DMA** is an A– $\pi$ –A type, whereas the configuration of **DMM**, **DMB-D**, **DAM**, and **DMD** is D– $\pi$ –D (see Fig. S1†). The Chemdraw structures of compounds namely (*N1E,N2E*)-4,5-dimethyl-*N*<sup>1</sup>,*N*<sup>2</sup>-bis(2-nitrobenzylidene)benzene-1,2-diamine (**DMA**), 2,2'-((1*E*,1'*E*)-((4,5-dimethyl-1,2-phenylene)bis(azanylylidene))bis(methanylylidene))bis(4-methylphenol) (**DMM**), 6,6'-((1*E*,1'*E*)-((4,5-dimethyl-1,2-phenylene)bis(azanylylidene))bis(methanylylidene))bis(2-*tert*-butylphenol) (**DMB-D**), 6,6'-((1*E*,1'*E*)-((4,5-dimethyl-1,2-phenylene)bis(azanylylidene))bis(methanylylidene))bis(2,4-di-*tert*-butylphenol) (**DAM**), and 4,4'-((1*E*,1'*E*)-((4,5-dimethyl-1,2-phenylene)bis(azanylylidene))



Scheme 2 A sketch map of the entitled compounds.



bis(methanylylidene))bis(benzene-1,3-diol) (**DMD**) are displayed in Scheme 2. The core unit, *i.e.*, (4,5-dimethyl-*N*1,*N*2-dimethylenebenzene-1,2-diamine) is the same in all the explored compounds, which act as  $\pi$ -bridge. DFT calculations were accomplished to compute the UV-vis spectrum, FMO, NBO, linear polarizability ( $\alpha$ ), first hyperpolarizability ( $\beta_{\text{tot}}$ ), and second hyperpolarizability ( $\gamma_{\text{tot}}$ ). The energy gap had a great influence on the optical and NLO characteristics of the compounds. The consequences obtained from the computational analysis of the mentioned compounds show that these compounds are effective in non-linear optics. The chemical and optimized geometries of the investigated molecules are displayed in Fig. 1 and S13<sup>†</sup>, respectively.

### Frontier molecular orbital (FMO) investigation

The energy difference in the frontier molecular orbitals is utilized to evaluate the optical polarizability, chemical response, global hardness, and softness of the examined molecules.<sup>30,31</sup> The HOMO is termed as a donor orbital as it is filled with electrons, while the LUMO is a partially filled or vacant orbital, which is called as an acceptor orbital.<sup>32,33</sup> The pictographic representation is shown in Fig. 2, and Table 1 shows the band gap values between LUMO–HOMO of the studied compounds. The  $E_{\text{HOMO}} - E_{\text{LUMO}}$  gap is directly associated with the hardness ( $\eta$ ) and chemical potential ( $\mu$ ) of a compound and is inversely associated with the global softness ( $\sigma$ ) and reactivity.<sup>34</sup> The lesser the energy gap, the better will be

the electron transport from HOMO to LUMO, and the greater will be the polarizability of the molecules.<sup>30</sup>

It is shown in Table 1 that the minimum band gap value (5.446 eV) is observed in **DMA**, which illustrates good intra-molecular charge transfer. This excellent charge transfer in **DMA** may be found to occur due to the strong electron withdrawing effect of NO<sub>2</sub> attached at the acceptor site. While the maximum value of the energy gap is noted in **DMM** as 5.927 eV. The decreasing order of energy gap is **DMM** > **DMB-D** > **DMD** > **DAM** > **DMA**. Thus, **DMA** is an unstable and chemically reactive compound. It can be seen from Fig. 2 that electronic charge density is largely observed to be concentrated over the spacer region in HOMOs, whereas in the LUMO pictograph, it is found over terminal regions and partially over the spacer part, which indicates a significant charge transfer.

### Global reactivity descriptors (GRDs)

The LUMO–HOMO band gap is utilized to calculate the GRDs. The results of these indices, such as ionization potential ( $I$ ),<sup>35</sup> electron affinity (EA), global hardness ( $\eta$ ),<sup>36</sup> global electrophilicity ( $\omega$ ),<sup>37</sup> electronegativity ( $X$ ),<sup>38</sup> global softness ( $\sigma$ ), and chemical potential ( $\mu$ )<sup>39</sup> are estimated with the help of eqn (5)–(11), and their outcomes are tabulated in Table 2.

$$\text{IP} = -E_{\text{HOMO}} \quad (5)$$

$$\text{EA} = -E_{\text{LUMO}} \quad (6)$$

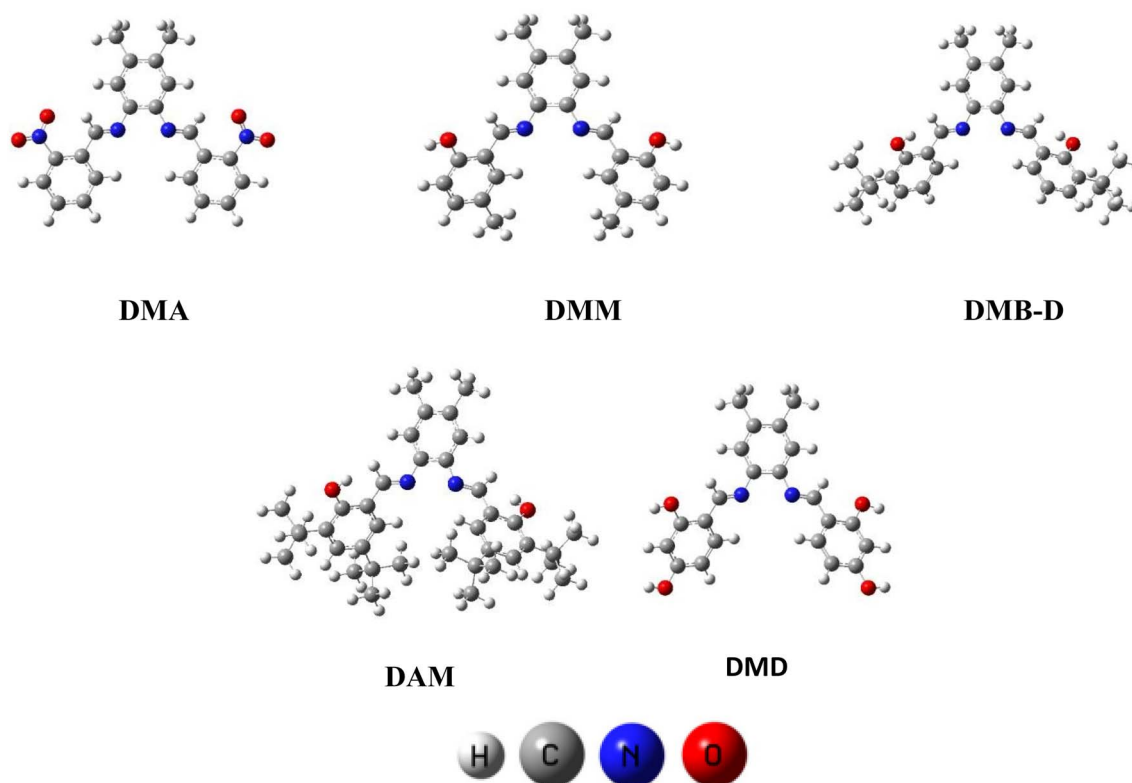


Fig. 1 Optimized geometries of the synthesized compounds.



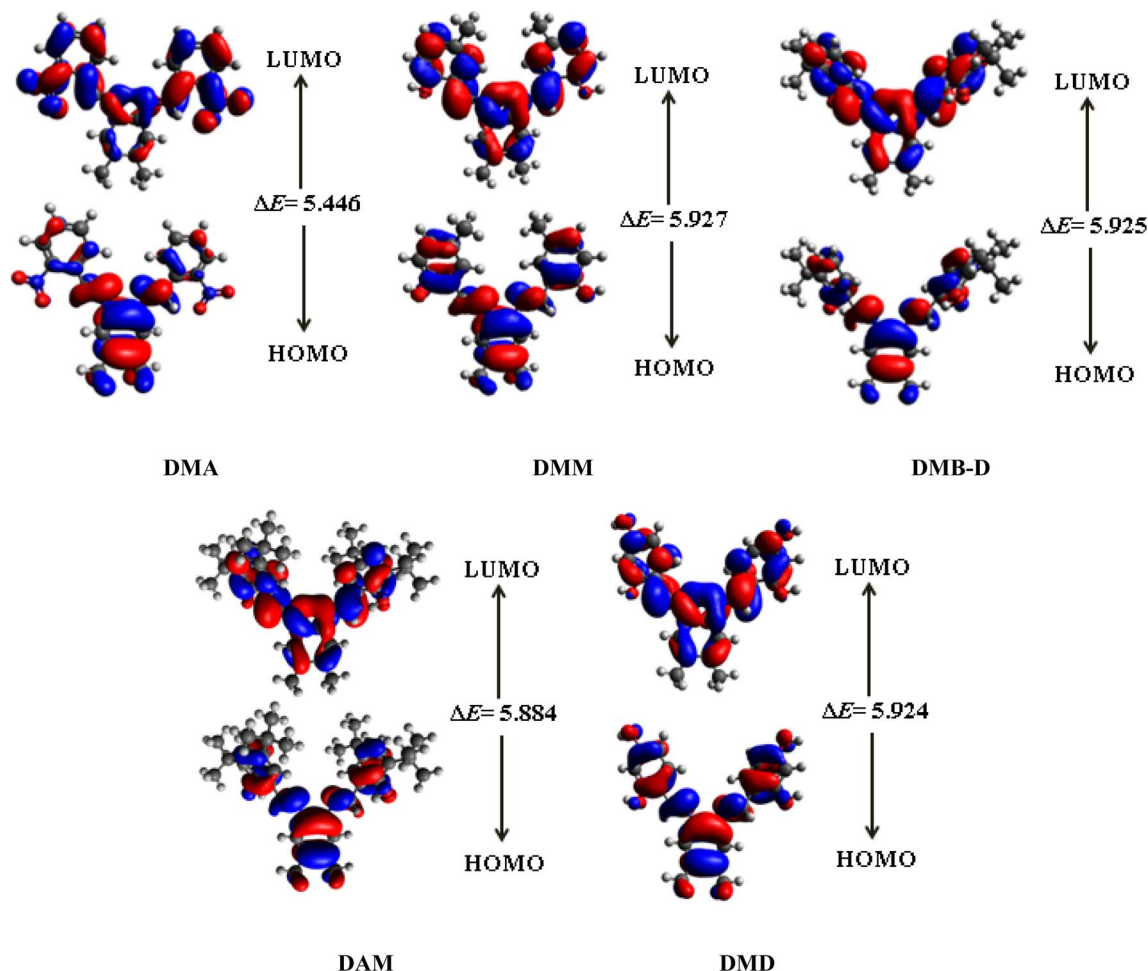


Fig. 2 Frontier molecular orbitals of the entitled compounds.

Table 1 HOMO/LUMO energies and band gaps of FMOs of the investigated structures<sup>a</sup>

Comp.	$E_{\text{HOMO}}$	$E_{\text{LUMO}}$	$\Delta E$ (eV)
<b>DMA</b>	-7.338	-1.892	5.446
<b>DMM</b>	-6.986	-1.059	5.927
<b>DMB-D</b>	-7.129	-1.204	5.925
<b>DAM</b>	-7.066	-1.182	5.884
<b>DMD</b>	-6.832	-0.908	5.924

<sup>a</sup> Units are in eV.

$$X = -\frac{[E_{\text{LUMO}} + E_{\text{HOMO}}]}{2} \quad (7)$$

$$\eta = -\frac{[E_{\text{LUMO}} - E_{\text{HOMO}}]}{2} \quad (8)$$

$$\mu = \frac{E_{\text{HOMO}} + E_{\text{LUMO}}}{2} \quad (9)$$

$$\sigma = \frac{1}{2\eta} \quad (10)$$

$$\omega = \frac{\mu^2}{2\eta} \quad (11)$$

The electron giving and gaining the capability of molecules is calculated from their EA and IP values, respectively.<sup>40</sup> The ionization potential values of **DMA**, **DMM**, **DMB-D**, **DAM**, and **DMD** are 7.338, 6.986, 7.129, 7.066, and 6.832 eV, respectively, while electron affinity (EA) values are 1.892, 1.059, 1.204, 1.182, and 0.908 eV, respectively. The EA values of the entitled compounds are smaller than IP, which indicates that the studied compounds have greater electron-donating capacity. The highest 0.183 eV softness is shown by compound **DMA**, and the lowest 0.168 eV global softness value is exhibited by compounds **DMM**, **DMB-D**, and **DMD**, respectively. The overall descending order of softness is as follows: **DMA** > **DAM** > **DMM** > **DMB-D** > **DMD**. The chemical potential of the investigated compounds in declining order is **DMA** > **DMB-D** > **DAM** > **DMM** > **DMD**. Among the studied compounds, **DMA** has the greatest amplitude of electrophilicity index (3.910 eV) and **DMD** has the smallest value (2.528 eV). The electronegativity ( $X$ ) values for **DMA** to **DMD** are found to be 4.615, 4.022, 4.166, 4.124 and 3.870 eV. These findings revealed that



Table 2 Global reactivity parameters of DMA, DMM, DMB-D, DAM, and DMD<sup>a</sup>

Comp.	IP	EA	$X$	$\eta$	$\mu$	$\omega$	$\sigma$
<b>DMA</b>	7.338	1.892	4.615	2.723	-4.615	3.910	0.183
<b>DMM</b>	6.986	1.059	4.022	2.963	-4.022	2.729	0.168
<b>DMB-D</b>	7.129	1.204	4.166	2.962	-4.166	2.929	0.168
<b>DAM</b>	7.066	1.182	4.124	2.942	-4.124	2.890	0.169
<b>DMD</b>	6.832	0.908	3.870	2.962	-3.870	2.528	0.168

<sup>a</sup> Units are in eV.

compound **DMA** has the highest softness value, which indicates that it is less stable, highly reactive and shows significant NLO response.

### Natural bonding orbital (NBO) analysis

The NBO approach is utilized to observe the electronic charge transference phenomenon from electron donating to electron accepting moieties, hyper conjugative and non-covalent interactions (inter and intra-molecular hydrogen bonding) in the molecule. The second-order perturbation energy is calculated by using eqn (12).

$$E^{(2)} = q_i \frac{F(i,j)^2}{\varepsilon_j - \varepsilon_i} \quad (12)$$

where,  $E^{(2)}$  represents stability energy,  $\varepsilon_j - \varepsilon_i$  indicates diagonal elements,  $q_i$  depicts orbital occupancy, and  $F(i,j)$  shows off-diagonal NBOs Fock matrix components.<sup>41</sup> The NBO analysis of the studied compounds is performed *via* using the above-mentioned functional and some of its outcomes are displayed in Table 3, while rest of the transitions are added in Tables S1–S4.†

Generally, four major kinds of electronic transitions are observed, *i.e.*,  $\sigma \rightarrow \sigma^*$ ,  $\pi \rightarrow \pi^*$ ,  $LP \rightarrow \sigma^*$ , and  $LP \rightarrow \pi^*$ .  $\pi \rightarrow \pi^*$  is found to be the most probable electronic transition. From these,  $\pi(C21-C22) \rightarrow \pi^*(C23-C24)$ ,  $\pi(C20-C21) \rightarrow \pi^*(C22-C23)$ ,  $\pi(C28-C29) \rightarrow \pi^*(C27-C32)$ ,  $\pi(C1-C6) \rightarrow \pi^*(C4-C5)$ , and  $\pi(C22-C23) \rightarrow \pi^*(C19-C24)$  have stabilization energy values of 34.52, 32.90, 30.73, 29.93, and 36.31 kcal mol<sup>-1</sup> in **DMA**, **DMM**, **DMB-D**, **DAM** and **DMD** respectively. The transitions like  $\pi(N46-O48) \rightarrow \pi^*(C28-C29)$ ,  $\pi(N17-C49) \rightarrow \pi^*(C19-C24)$ ,  $\pi(N17-C37) \rightarrow \pi^*(C19-C24)$ ,  $\pi(C19-C28) \rightarrow \pi^*(C19-C24)$ , and  $\pi(C17-C39) \rightarrow \pi^*(C19-C24)$  with energy values of 2.90, 8.23, 7.80, 7.93, and 7.97 kcal mol<sup>-1</sup> are observed in **DMA**, **DMM**, **DMB-D**, **DAM** and **DMD**, accordingly. These are the lowest stability energy amplitudes among all the  $\pi \rightarrow \pi^*$  transitions in the examined compounds. Likewise,  $\sigma(C19-C20) \rightarrow \sigma^*(C24-N43)$ ,  $\sigma(O47-H48) \rightarrow \sigma^*(C28-C33)$ ,  $\sigma(C20-H25) \rightarrow \sigma^*(C19-C24)$ ,  $\sigma(C20-H25) \rightarrow \sigma^*(C19-N24)$ , and  $\sigma(O37-H38) \rightarrow \sigma^*(C27-C32)$  transitions are observed with a maximum

Table 3 Natural bond orbital (NBO) analysis of the entitled compounds

Comp.	Donor ( $i$ )	Type	Acceptor ( $j$ )	Type	$E^{(2)}$ [kcal mol <sup>-1</sup> ]	$E(j) - E(i)$ (a.u.)	$F(i,j)$ (a.u.)
<b>DMA</b>	C19–C20	$\sigma$	C24–N43	$\sigma^*$	5.89	1.11	0.073
	C28–C33	$\sigma$	C28–N46	$\sigma^*$	0.53	1.14	0.022
	C21–C22	$\pi$	C23–C24	$\pi^*$	34.52	0.34	0.097
	N46–O48	$\pi$	C28–C29	$\pi^*$	2.90	0.59	0.041
	O44	LP(3)	N43–O45	$\pi^*$	214.63	0.22	0.197
	O47	LP(2)	C28–C29	$\sigma^*$	0.65	1	0.023
<b>DMM</b>	O47–H48	$\sigma$	C28–C33	$\sigma^*$	5.72	1.46	0.082
	C5–H8	$\sigma$	C4–N17	$\sigma^*$	0.53	1.1	0.022
	C20–C21	$\pi$	C22–C23	$\pi^*$	32.90	0.35	0.096
	N17–C49	$\pi$	C19–C24	$\pi^*$	8.23	0.45	0.060
	O45	LP(2)	C19–C24	$\pi^*$	33.66	0.46	0.120
	O45	LP(1)	C19–C24	$\sigma^*$	0.55	1.31	0.024
<b>DMB-D</b>	C20–H25	$\sigma$	C19–C24	$\sigma^*$	5.06	1.21	0.070
	C22–C23	$\sigma$	C43–C48	$\sigma^*$	0.51	1.21	0.022
	C28–C29	$\pi$	C27–C32	$\pi^*$	30.73	0.35	0.094
	N17–C37	$\pi$	C19–C24	$\pi^*$	7.80	0.45	0.058
	O35	LP(2)	C19–C24	$\pi^*$	29.12	0.46	0.112
	O36	LP(1)	C27–C28	$\sigma^*$	0.50	1.29	0.023
	C20–H25	$\sigma$	C19–C24	$\sigma^*$	5.03	1.21	0.070
	C22–C23	$\sigma$	C41–C42	$\sigma^*$	0.52	1.21	0.022
	C1–C6	$\pi$	C4–C5	$\pi^*$	29.93	0.34	0.091
<b>DAM</b>	C19–C28	$\pi$	C19–C24	$\pi^*$	7.93	0.46	0.059
	O35	LP(2)	C19–C24	$\pi^*$	29.10	0.46	0.112
	O36	LP(1)	C27–C28	$\sigma^*$	0.50	1.29	0.023
<b>DMD</b>	O37–H38	$\sigma$	C27–C32	$\sigma^*$	5.62	1.46	0.081
	C2–H7	$\sigma$	C3–N18	$\sigma^*$	0.52	1.1	0.021
	C22–C23	$\pi$	C19–C24	$\pi^*$	36.31	0.36	0.105
	C17–C39	$\pi$	C19–C24	$\pi^*$	7.97	0.37	0.012
	O45	LP(2)	C22–C23	$\pi^*$	38.03	0.45	0.125
	O45	LP(1)	C21–C22	$\sigma^*$	0.55	1.3	0.024



magnitude as 5.89, 5.72, 5.06, 5.03, and 5.62 kcal mol<sup>-1</sup> in **DMA**, **DMM**, **DMB-D**, **DAM** and **DMD**, respectively. Similarly,  $\sigma(\text{C28-C33}) \rightarrow \sigma^*(\text{C28-N46})$ ,  $\sigma(\text{C5-H8}) \rightarrow \sigma^*(\text{C4-N17})$ ,  $\sigma(\text{C22-C23}) \rightarrow \sigma^*(\text{C43-C48})$ ,  $\sigma(\text{C22-C23}) \rightarrow \sigma^*(\text{C41-N42})$ , and  $\sigma(\text{C2-H7}) \rightarrow \sigma^*(\text{C3-N18})$  transitions with the lowest energy values of 0.53, 0.53, 0.51, 0.52, and 0.52 kcal mol<sup>-1</sup> are detected in **DMA**, **DMM**, **DMB-D**, **DAM** and **DMD**, correspondingly.

Furthermore, the most prominent LP  $\rightarrow \pi^*$  transitions are LP3(O44)  $\rightarrow \pi^*(\text{N43-O45})$ , LP2(O45)  $\rightarrow \pi^*(\text{C19-C24})$ , LP2(O35)  $\rightarrow \pi^*(\text{C19-C24})$ , LP2(O35)  $\rightarrow \pi^*(\text{C19-C24})$ , and LP2(O45)  $\rightarrow \pi^*(\text{C22-C23})$  with 214.63, 33.66, 29.12, 29.10, and 38.03 kcal mol<sup>-1</sup> stabilization energy. Similarly, LP2(O47)  $\rightarrow \sigma^*(\text{C28-C29})$ , LP1(O45)  $\rightarrow \sigma^*(\text{C19-C24})$ , LP1(O36)  $\rightarrow \sigma^*(\text{C27-C28})$ , LP1(O36)  $\rightarrow \sigma^*(\text{C27-C28})$ , and LP1(O45)  $\rightarrow \sigma^*(\text{C21-C22})$  manifested minimum energy of 0.65, 0.55, 0.50, 0.50, and 0.55 kcal mol<sup>-1</sup>, correspondingly. Some other electronic transitions

are also observed, which are presented in the Tables S1–S4.† The NBO investigation disclosed the delocalization of electrons and hyper conjugative interactions, which in turn cause ICT, are the foremost reasons for the stability of the molecule and are crucial for good NLO response.

### Density of states (DOS)

The scattering of electronic clouds on different parts of the compound is studied with the help of DOS. To obtain the DOS graph, we made fragments of our compounds, *i.e.*, acceptor,  $\pi$ -spacer (linker) in **DMA** and donor,  $\pi$ -linker in **DMA**, **DMM**, **DMB-D**, and **DMD**. The PDOS (partial density of states) and TDOS (total density of states) graphs of the synthesized compounds are examined and presented in Fig. 3. In **DMA**, the contribution of 85.6% is made by the acceptor to LUMO, while it

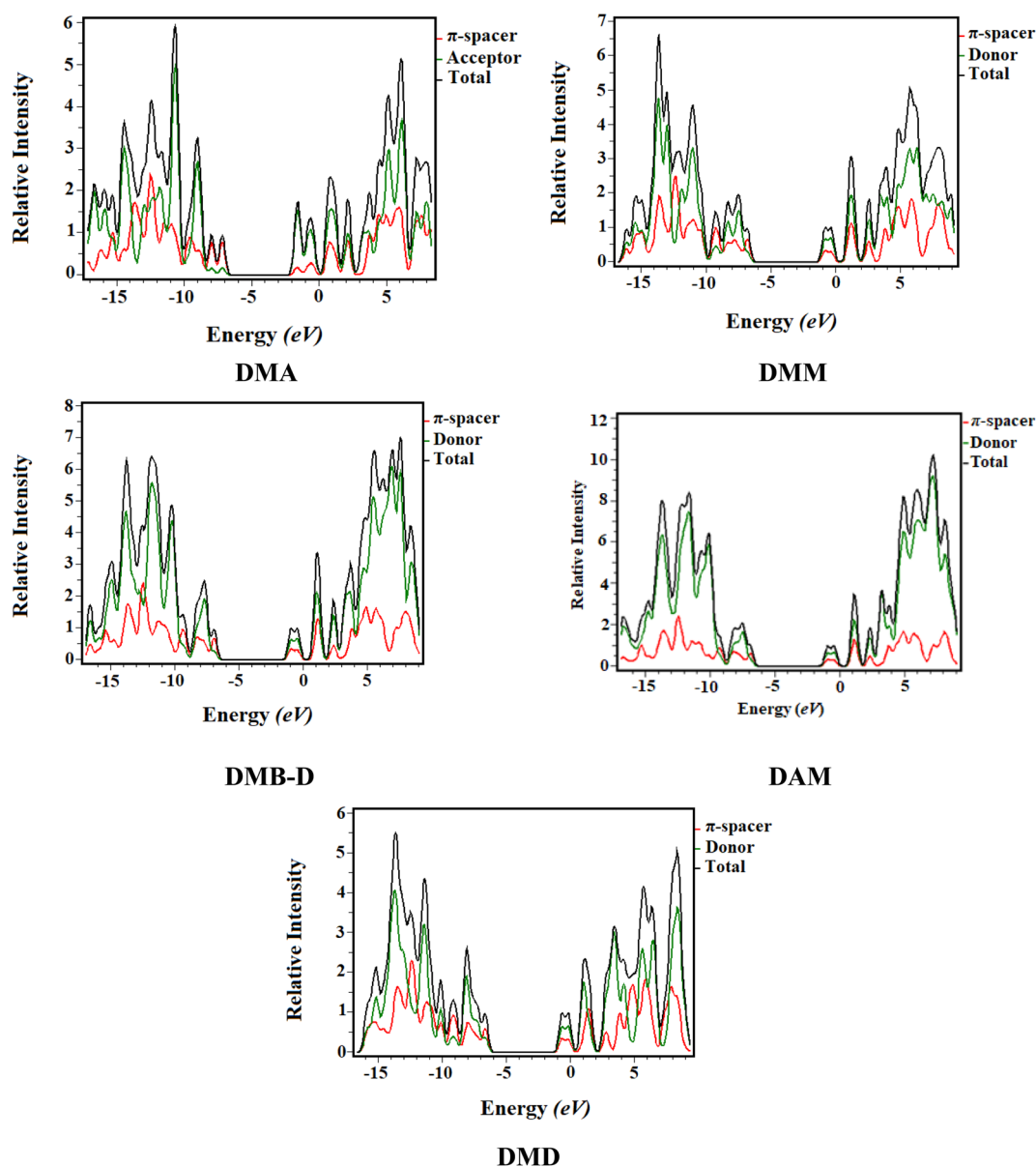


Fig. 3 Graphical representation of DOS for the entitled compounds.



contributes 18.2% to HOMO, whereas the  $\pi$ -spacer shows 14.4% of its involvement to LUMO and 81.8% to HOMO. In the cases of **DMM**, **DMB-D**, **DAM** and **DMD**, the donor contributes 66.6, 64.9, 65.2, and 64.9% to LUMO, while a contribution of 30.3, 28.5, 34.4 and 37.6%, respectively and is observed towards HOMO. The  $\pi$ -spacer depicts a 33.4, 35.1, 34.8, and 35.1% contribution pattern to LUMO, while 69.7, 71.5, 62.4, and 65.6% towards HOMO from **DMM**, **DMB-D**, **DAM** and **DMD**, correspondingly (Table S14<sup>†</sup>). In the synthesized molecule **DMA**, most of the electron density is present on the  $\pi$ -spacer in HOMO, whereas in LUMO it is more concentrated on the acceptor part. The other synthesized molecules have identical patterns of distribution of electron density as HOMO has electron density on  $\pi$ -linker (4,5-dimethyl-*N*<sup>1</sup>,*N*<sup>2</sup>-dimethylenebenzene-1,2-diamine), while LUMO has more density on the donor and a little bit is present on  $\pi$ -linker.

### UV-vis analysis

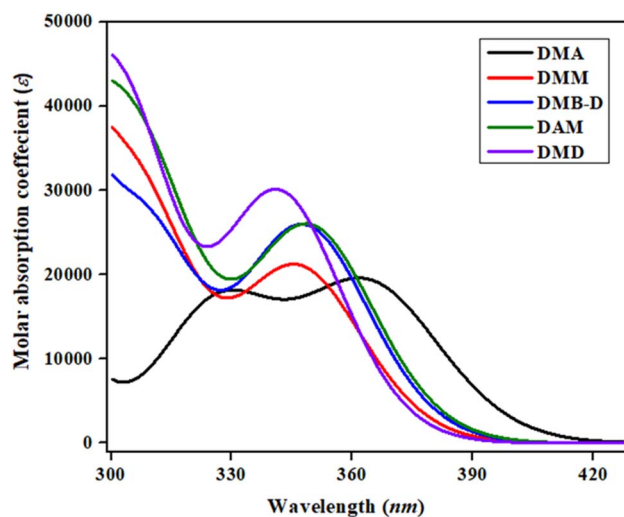
UV-vis analysis provides significant information regarding the charge transfer capability, nature of transitions, and phenomenon of absorption in the synthesized compounds (**DMA**, **DMM**, **DMB-D**, **DAM**, and **DMD**).<sup>42</sup> TD-DFT is employed to calculate the photophysical characteristics of **DMA**, **DMM**, **DMB-D**, **DAM**, and **DMD** using the dichloromethane (DCM) solvent. The maximum wavelength ( $\lambda_{\text{max}}$ ) of light absorbed, excitation energy ( $E$ ), molecular orbital (MO) contributions, and oscillator strength ( $f$ ) of the studied molecules are calculated by the same technique of TD-DFT and the outcomes are represented in Table 4, whereas, results of other molecular orbital contributions are displayed in Tables S5–S9.<sup>†</sup>

It is observed from the results that transition energy is inversely proportional to  $\lambda_{\text{max}}$  and directly related to oscillation strength. As the excitation energy value and oscillation strength increase, the wavelength of absorption maxima decreases. Therefore, the highest  $\lambda_{\text{max}}$  value of 364.068 nm was obtained in **DMA** with 3.405 eV excitation energy and 0.254 oscillation strength. Hence, it showed a bathochromic shift. Remarkably, the highest value of  $\lambda_{\text{max}}$  in **DMA** is due to the existence of strong electron withdrawing ( $-\text{NO}_2$ ) groups, which decrease the energy gap ( $E_{\text{HOMO}} - E_{\text{LUMO}}$ ). An appreciable decrease in the value of  $\lambda_{\text{max}}$  is observed in **DMB-D** (347.811 nm). The minimum value of  $\lambda_{\text{max}}$  value is 341.477 nm, as observed in **DMD**. The descending trend of  $\lambda_{\text{max}}$  of the investigated molecules is as follows: **DMA** > **DAM** > **DMB-D** > **DMM** > **DMD** (Fig. 4).

**Table 4** Excitation energy ( $E$ ), oscillator strength ( $f$ ), and wavelength ( $\lambda$ ) and of studied molecules<sup>a</sup>

Comp.	DFT $\lambda$ (nm)	$E$ (eV)	$f$	MO contributions
<b>DMA</b>	364.068	3.405	0.254	H $\rightarrow$ L(67%), H-1 $\rightarrow$ L+1(2%)
<b>DMM</b>	346.196	3.581	0.286	H $\rightarrow$ L(77%), H-1 $\rightarrow$ L+1(3%)
<b>DMB-D</b>	347.811	3.564	0.352	H $\rightarrow$ L(79%), H-1 $\rightarrow$ L+1(3%)
<b>DAM</b>	348.956	3.553	0.353	H $\rightarrow$ L(77%), H-1 $\rightarrow$ L+1(3%)
<b>DMD</b>	341.477	3.631	0.408	H $\rightarrow$ L(79%), H-1 $\rightarrow$ L+1(4%)

<sup>a</sup> MO = molecular orbital, H=HOMO, L = LUMO,  $f$  = oscillator strength.



**Fig. 4** Absorption spectrum of **DMA**, **DMM**, **DMB-D**, **DAM**, and **DMD**.

### Natural population analysis (NPA)

The electronic cloud distribution on an atom has a great impact on the chemical reactivity, dipole moment, and electrostatic interaction between the atoms and molecules, and many other properties of the chemical system. The effective calculation of the atomic charge of the titled compounds is essential for a better understanding of the conjugated system.<sup>43,44</sup> The Mulliken charges of **DMA**, **DMM**, **DMB-D**, **DAM** and **DMD** were calculated at the aforementioned level and are presented in Fig. 5.

The charge density distribution revealed that the nitrogen atoms associated with oxygen in **DMA** are positively charged, whereas those attached to carbon and hydrogen in all of the titled compounds are negatively charged. Moreover, all the hydrogen atoms are positively charged. The oxygen atoms linked with carbon and hydrogen atoms are negatively charged. All the nitrogen atoms present in the  $\pi$ -linker are negatively charged (see Fig. 5). The overall analysis of Mulliken charges revealed that the unequal distribution of charges on the entitled compounds is because of the nitrogen and oxygen atoms.

### Molecular electrostatic potential (MEP)

The MEP plot is widely used to predict electrostatic potential, chemical reactivity, electrophilic, and nucleophilic attacks on the reactive site in a molecular system. The MEP diagram is mapped over the optimized structure of the molecule to signify the overall electron density. The different colors are utilized to designate the electrostatic potential over the MEP surface, shown in Fig. 6. The enhancing trend of potential is: red < orange < yellow < green < blue.<sup>45,46</sup> The MEP plot displayed that most of the red color is on oxygen atoms, which showed the probability of electrophilic attack. Although most of the green and blue bands which elucidate positive potential are positioned on carbon and hydrogen atoms that are efficient for nucleophilic reactions.





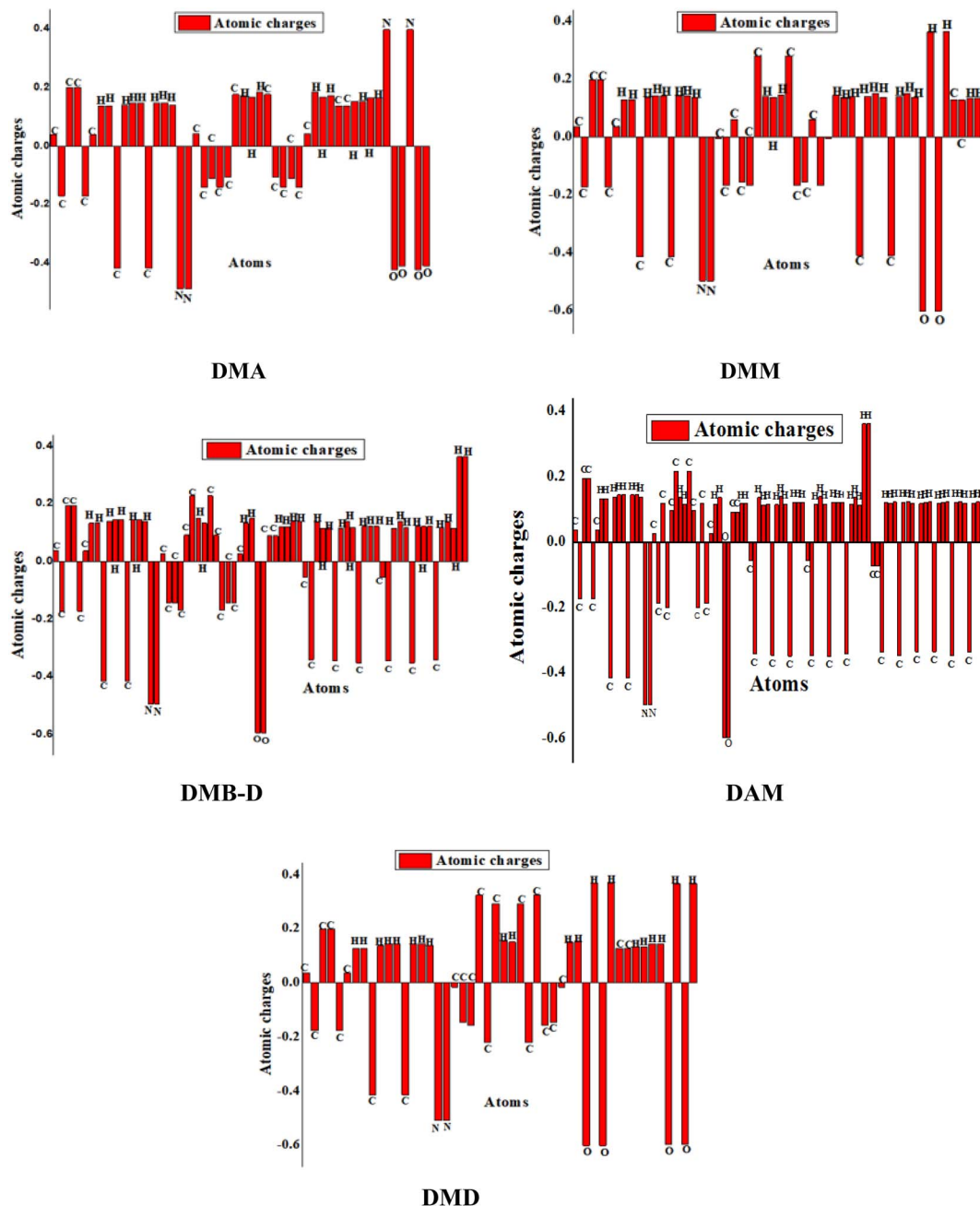


Fig. 5 Natural population analysis of DMA, DMM, DMB-D, DAM, and DMD.

### Non-linear optical (NLO) properties

The materials that display NLO properties have become an extensive research discipline because of their widespread applications in optoelectronics, telecommunication, and optical switches.<sup>47</sup> The dipole moment ( $\mu$ ) and hyperpolarizability ( $\beta_{\text{tot}}$  and  $\gamma_{\text{tot}}$ ) display the electronic communication in different fragments of the molecule.<sup>48</sup> The data computed for dipole moment ( $\mu$ ), average polarizability and hyper polarizabilities ( $\beta_{\text{tot}}$  and  $\gamma_{\text{tot}}$ ) are tabulated in Table 5 while the major contributing tensors are presented in Tables S10–S13.†

The utmost value of  $\mu_{\text{tot}}$  (2.385 D) is viewed in **DMA** while the least possible value (0.202 D) is noticed in **DMD**. For a better analysis of NLO behavior, the dipole moment and first hyperpolarizability of the studied compounds are compared with the urea molecule, which has been regarded as a standard molecule in the literature study. The dipole moment of **DMA** is greater than urea (1.3732 D),<sup>42</sup> while **DMM**, **DMB-D**, **DAM**, and **DMD** have smaller dipole moment values than urea.

The highest value of first-order polarizability ( $877.438 \times 10^{-25}$  e.s.u.) is noted for compound **DAM**, whereas the lowest value ( $549.863 \times 10^{-25}$  e.s.u.) is examined for compound **DMD** among the remaining synthesized compounds. The overall



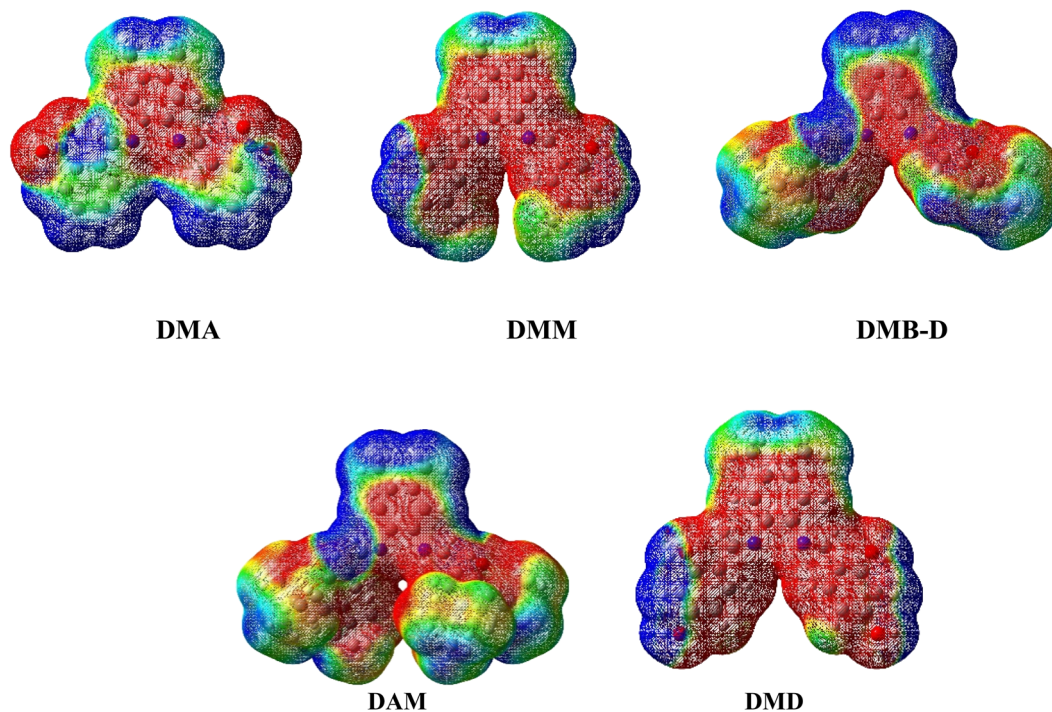


Fig. 6 MEP representation of the entitled compounds.

**Table 5** The, average polarizability, dipole moment, first hyperpolarizability, second hyperpolarizability results for investigated molecules<sup>a</sup>

Comp.	$\mu_{\text{tot}}$	$\langle\alpha\rangle \times 10^{-25}$	$\beta_{\text{tot}} \times 10^{-33}$	$\gamma_{\text{tot}} \times 10^{-35}$
<b>DMA</b>	2.385	561.702	21 129.545	20.761
<b>DMM</b>	0.705	566.066	161.594	17.170
<b>DMB-D</b>	0.882	700.910	942.348	19.320
<b>DAM</b>	0.659	877.438	3335.274	21.239
<b>DMD</b>	0.202	549.863	25 438.874	20.373

<sup>a</sup>  $\mu_{\text{tot}}$  has a unit in *D*, while  $\langle\alpha\rangle$ ,  $\beta_{\text{tot}}$  and  $\gamma_{\text{tot}}$  have units in e.s.u.

decreasing trend of  $\langle\alpha\rangle$  is in the following order: **DAM** > **DMB-D** > **DMM** > **DMA** > **DMD**. The  $\langle\alpha\rangle$  of the titled compounds is more dominant along the *y*-direction, which means that polarization predominantly takes place in the *y*-direction. The linear polarizability in  $\alpha_{xx}$ ,  $\alpha_{yy}$ , and  $\alpha_{zz}$  directions is 981.133, 983.541, and  $667.438 \times 10^{-25}$  e.s.u., correspondingly in **DAM**, which is the highest than the linear polarizability of other entitled compounds as shown in Table S11.† The lowest values of dipole polarizability in *x*, *y*, and *z*-direction are 675.571, 716.639, and  $257.399 \times 10^{-25}$  e.s.u., respectively, observed in **DMD**.

In first hyperpolarizability ( $\beta_{\text{tot}}$ ), the tensor  $\beta_{xxy}$  has the major contribution in  $\beta_{\text{tot}}$  value with  $12\,747.514 \times 10^{-33}$  e.s.u. amplitude in **DMA** while in **DMM**, **DMB-D**, **DAM**, and **DMD** the major involvement of  $\beta_{\text{tot}}$  is made by  $\beta_{yzz}$  (160.102, 6.038, 1176.196, and  $380.946 \times 10^{-33}$  e.s.u.), respectively. The declining trend  $\beta_{\text{tot}}$  values are: **DMD** > **DMA** > **DAM** > **DMB-D** > **DMM**. A comparative study of  $\beta_{\text{tot}}$  of the studied compounds with urea showed that the values of  $\beta_{\text{tot}}$  of **DMA**, **DMM**, **DMB-D**,

**DAM**, and **DMD** are 56.87, 0.43, 2.53, 8.98, and 68.47 times larger than urea ( $\beta_{\text{tot}} = 3.71 \times 10^{-31}$  e.s.u.),<sup>49</sup> correspondingly.

Moreover, compound **DAM** shows the largest  $21.239 \times 10^{-35}$  e.s.u. second hyperpolarizability ( $\gamma_{\text{tot}}$ ) value, and the smallest value of  $\gamma_{\text{tot}}$   $19.320 \times 10^{-35}$  e.s.u., is depicted by compound **DMM**. The  $\gamma_{\text{tot}}$  values of other synthesized compounds are in the following order: **DAM** > **DMA** > **DMD** > **DMB-D** > **DMM**. In the case of the second hyperpolarizability, the greatest involvement of tensor  $\gamma_y$  is observed for compound **DMM** with a value of  $9.181 \times 10^{-35}$  e.s.u. However, the tensor  $\gamma_z$  has a minor contribution in  $\gamma_{\text{tot}}$  value with an amplitude of  $0.228 \times 10^{-35}$  e.s.u. examined in compound **DMM**. From the above discussion, it is predicted that because of the higher values of dipole moment and first hyperpolarizability compound, **DAM** might act as an excellent NLO material.

## Conclusion

In the present work, 4,5-dimethyl-*o*-phenylenediamine based Schiff base compounds (**DMA**, **DMM**, **DMB-D**, **DAM**, and **DMD**) were synthesized and computationally analyzed to investigate their NLO characteristics. The highest bathochromic shift ( $\lambda_{\text{max}} = 364.068$  nm) was shown by **DMA** as compared to other compounds. The band gap was lowered from 5.927 to 5.446 eV and among all the compounds, the lowest  $E_{\text{gap}}$  was found in **DAM** (5.446 eV), which revealed a good transfer of charge within the molecule. However, in the case of NLO analysis, there was an enhancement in the  $\beta_{\text{tot}}$  value ( $25\,438.874 \times 10^{-33}$  e.s.u.) of **DMA** as compared to other molecules. The  $\sigma \rightarrow \sigma^*$  and  $\pi \rightarrow \pi^*$  interactions with 5.89 and 34.52 kcal mol<sup>-1</sup> stabilization energy in **DMA** observed are dominant over the rest of the studied



compounds, which was further supported by the results of global reactivity indices and uncovered the greatest chemical potential, electron donating and accepting competency of **DMA**. So, it is concluded that **DMA** and **DAM** exhibit excellent NLO material properties and might be the best candidates for future applications.

## Conflicts of interest

The authors declare no conflicts of interest.

## Acknowledgements

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