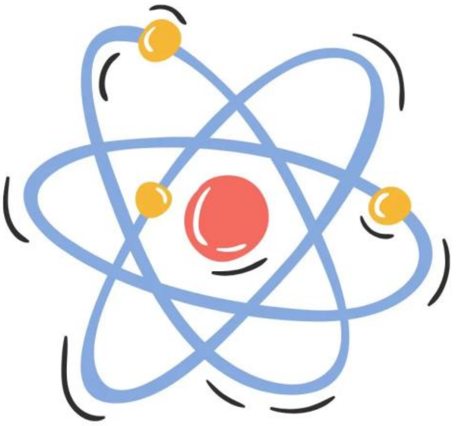


JOURNAL OF DYNAMICS AND CONTROL

VOLUME 8 ISSUE 12

EFFECT OF SUBSTITUENTS ON THE CHARGE TRANSFER PROPERTIES AND REORGANISATION ENERGIES OF TETRAPHENYL-1,4-PHENYLENEDIAMINE- A DFT COMPUTATIONAL APPROACH

Muhammad Niyas K.V.[1], Farhana Muhammad Ali[2], Karickal Raman Haridas[3]

[1,2]department of Chemistry, Government Brennen College Thalassery, Dharmadam, P.O. 670106, Kerala, India

[3]school Of Chemical Sciences, Kannur University, Payyanur Campus, Edat-P.O. 670327, Kerala, India

EFFECT OF SUBSTITUENTS ON THE CHARGE TRANSFER PROPERTIES AND REORGANISATION ENERGIES OF TETRAPHENYL-1,4-PHENYLENEDIAMINE- A DFT COMPUTATIONAL APPROACH

Muhammad Niyas K.V.[1], Farhana Muhammad Ali[2], Karickal Raman Haridas*[3]
[1,2]Department of Chemistry, Government Brennen College Thalassery, Dharmadam P.O. 670106, Kerala, India
(Affiliated to Kannur University, Kerala, India)
[3]School of Chemical Sciences, Kannur University, Payyanur Campus, Edat P.O. 670327, Kerala, India
[1]niyaskv@gmail.com, [2]farhana4212029@gmail.com, [3]haridaskr@kannuruniv.ac.in

***Corresponding Author**

Abstract: *This theoretical study explores the effect of substitution on the electronic properties and reorganisation energy of N,N,N,N-tetraphenyl-1,4-phenylenediamine derivatives (TPD), focussing on selected electron-donating groups (alkyl and alkoxy)substituted diagonally at the meta and para positions. Using computational methods, the energy levels (HOMO and LUMO), energy bandgap, ionisation potential and reorganisation energies were calculated to assess charge transfer properties. While alkyl substituents show minimal band gap variation with chain length, para-alkyl derivatives exhibit reduced reorganisation energy and improved hole mobility, with linear chains outperforming branched ones. For alkoxy derivatives, trends in reorganisation energy are less consistent, but increasing chain length enhances hole mobility and reduces electron mobility. This study emphasises the critical role of substitution patterns and side chain architecture in optimising TPD derivatives for charge transport applications*

Keywords: *N,N,N,N-tetraphenyl-1,4-phenylenediamine, Density Functional Calculations, Hole Transporting Materials, Substituent effects, Reorganisation energy.*

---

1. Introduction

Research on Dye-sensitised solid-state solar cells (DSSC) has been one of the most driven fields in recent decades[1–4]. It offers advantages such as flexibility, easy fabrication steps, cost-effectiveness, and minimal environmental impact[5,6]. A heterojunction formed by an electron donor-acceptor interface is known as dye-sensitised solar cell. According to the theory of DSSC, absorption of input photons, creation of an electron-hole pair, diffusion of the same, dissociation at the interface and migration of electrons are the primary processes for producing electricity[7]. Triphenylamine and phenylenediamine-based donor molecules have shown remarkable photovoltaic performance[8–10]. The area of performance-based solar cell studies includes nearly all of the characteristics of different substituents[11]. Nevertheless, there are fewer theoretical investigations on the electron withdrawing and electron donating natures of substituents [12,13]. Research on the correlations between the former effects of the substituents is not covered by the experimental relationships of phenylamine's structural properties.

In the current situation, computational studies are a novel and effective instrument that enables us to comprehend the theoretical context and provide an atomic level explanations of the reasons. These studies also help to understand the electrodics underlying the relationship between the nature of electron flow and the transport properties.

The theoretical investigation of the impact of different substituents on the charge transfer properties of tetraphenyl-1,4-phenylenediamine derivatives were presented in this paper. Two series of electron releasing groups, viz. alkyl and alkoxy groups, were studied. In first case, $-CH_3$, and $-OCH_3$ groups were substituted at the meta and para positions of tetraphenyl-1,4-phenylenediamine. Secondly. alkyl and alkoxy groups with different chain length were tried.

In our study of hole-transporting materials based on tetraphenyl-1,4-phenylenediamine for the DSSC application, we found that in certain cases, there is a correlation observed between the kind of substituents and the solar cells' efficiency. When the optimisation parameters of all other components remain unchanged, the efficiency of the solar cell depends mainly on the type of substituents on the phenylenediamine-based hole transporting materials. Hence, we are looking for the theoretical background for the correlation between the efficiency changes caused by the substituents on triphenylamine.

The solar cells' efficiency is dependent on the availability of electrons/holes on the hole transporting material and how quickly it renders to the semiconductor-dye system. We have compared the possibility of the performance of solar cells on a theoretical background by comparing unsubstituted N,N,N,N-Tetraphenyl-1,4-phenylenediamine with several alkyl, and alkoxy substituted derivatives of tetraphenyl-1,4-phenylenediamine at meta and para positions.

For the past few years, several researchers used Density Functional Theory (DFT) as an important tool to study the properties of the materials used in DSSC[14–16]. Charge carrier diffusion and light absorption are mainly influenced by a band gap, ionisation potential, and geometry. DFT calculations will lead to the possibility of finding out these properties of hole transporting materials and thereby acquire the possibility of using them in DSSC.

2. Computational Methods

In this study, all the structures were modeled using a web-based system called WebMo Version: 17.0.010e[17], from the Ohio Supercomputer Center (OSC) computational chemistry portal, and the graphical view was obtained from Gauss view 6.0[18]. The modeled structures were optimised without considering symmetry constraints using a Gaussian computational engine based on DFT[19]. Becke's three parameters hybrid functional with Lee-Yang-Parr correlation functional (B3LYP) and 6-31G(d) were the optimisation method and basis set used for the study[20]. The hole transport parameter and molecular orbital analysis were done using the DFT (B3LYP) 6-31G (d) technique. Several substituted tetraphenyl-1,4-phenylenediamine derivatives were studied theoretically to analyze the hole transporting property.

The charge transfer rate can be described by Marcus theory[21,22] via the following equation (1):

$$K= (V^2/h)(\pi/\lambda k_BT)^{1/2}\exp(-\lambda/4k_BT) \quad (1)$$

where, T is the temperature, k_B is the Boltzmann constant, λ represents the reorganization energy due to geometric relaxation accompanying charge transfer, and V is the electronic coupling matrix element (transfer integral) between the two adjacent species dictated largely by orbital overlap. For theoretical calculations along with other constants, the temperature was also made constant[23].

The energy values of the highest occupied molecular orbital (E_{HOMO}) and that of the lowest unoccupied molecular orbital (E_{LUMO}) are used to obtain the band gap (energy gap) of the molecules. Ionisation potential values were also calculated.

Reorganization energy is a domain factor in determining the hole-transport property. The importance of reorganisation energy (λ) is that it depends on the strength of vibration coupling energy of a hole localised on a single molecule. For better transport, this value should be as small as possible. The intramolecular reorganization energy is an intrinsic property[24].

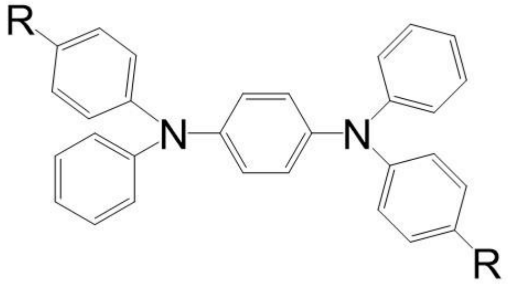
Reorganisation energy is calculated using the equation (2)

$$\lambda += (E_0^+ - E_+^+) + (E_+^0 - E_0^0) \quad (2)$$

where, E_0^+ is the energy of the cation calculated with the optimized structure of the neutral molecule, E_+^+ is the energy of the cation calculated with the optimized cation structure, E_+^0 is the energy of the neutral molecule calculated at the cationic state, and E_0^0 is the energy of the neutral molecule at the ground state. Similarly, the reorganization energy of an electron can also be calculated. The reorganization energy for the electron (k_e) and hole (k_h) of the molecules have been predicted from the single point energy at the B3LYP/6-31G (d) level based on the B3LYP/6-31G (d) optimized neutral, cationic, and anionic geometries[25,26].

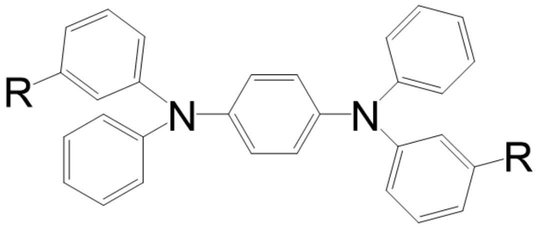
3. Results and discussions

The compound N,N,N,N-Tetraphenyl-1,4-phenylenediamine is di-substituted by alkyl and alkoxy groups at diagonally opposite para and meta positions to give corresponding para and meta derivatives (indicated as p-, and m-), to study the effect of substituent on energy levels, the shape of frontier molecular orbital, and hole transport properties. The primary structure of para substituted N,N,N,N-Tetraphenyl-1,4-phenylenediamine is shown in Figure 1 and that of meta substituted derivative is shown in Figure 2.



R= -H
-CH_3
-OCH_3

Figure 1. Para substituted derivatives of N,N,N,N-Tetraphenyl-1,4-phenylenediamine



R= -H
-CH_3
-OCH_3

Figure 2. Meta substituted derivatives of N,N,N,N-Tetraphenyl-1,4-phenylenediamine

3.1 Effect of electron donating substituents (CH_3, OCH_3) at meta and para positions.

The structures of unsubstituted, methyl substituted and methoxy substituted N,N,N,N-Tetraphenyl-1,4-phenylenediamine were optimized using the DFT-B3LYP (6-31G(d)) technique, and the optimized structures were shown in Figure. 3-5.

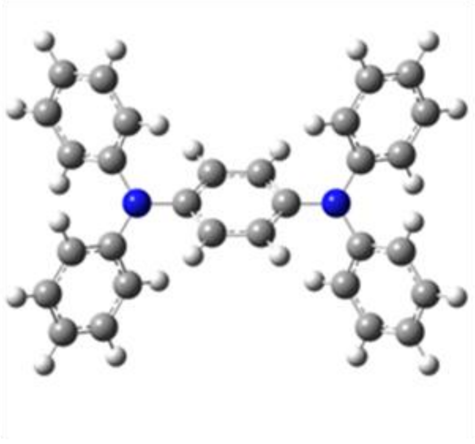


Figure 3. Optimised structure of N,N,N,N-Tetraphenyl-1,4-phenylenediamine

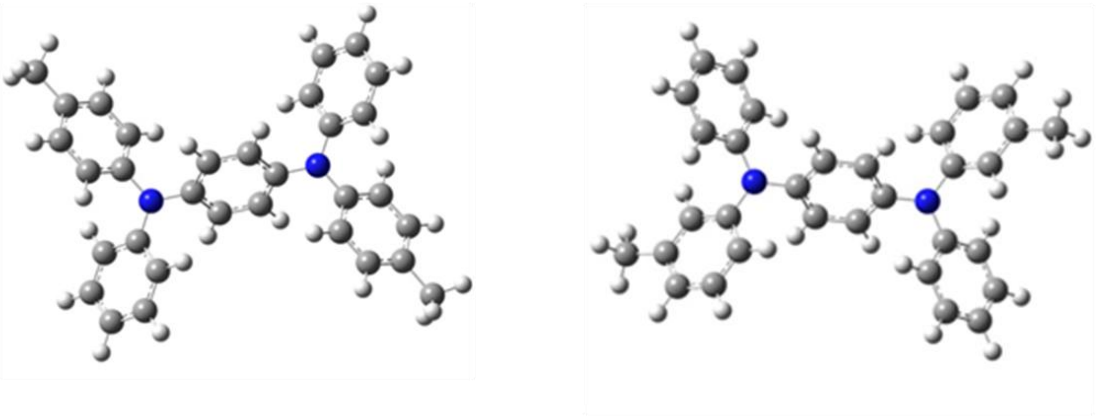


Figure 4. Optimised structures of p-methyl and m-methyl derivatives of N,N,N,N-Tetraphenyl-1,4-phenylenediamine

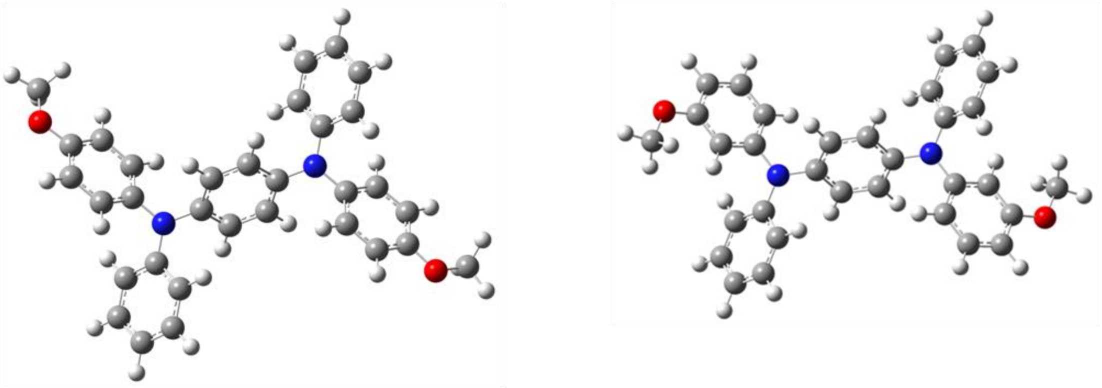


Figure 5. Optimised structures of p-methoxy and m-methoxy derivatives of N,N,N,N-Tetraphenyl-1,4-phenylenediamine

Figure 3-5 shows the molecular orbital diagram of unsubstituted, methyl, and methoxy substituted Tetraphenyl-1,4-phenylenediamine. The dipole moment of these structures was noted. Table 1. shows that, being almost symmetrical, Tetraphenyl-1,4-phenylenediamine possess almost zero (0.0002Debye) dipole moment and with substitution by $–CH_3$ and $-OCH_3$, a slight increase in dipole moment in meta-derivative, and a considerable increase in the para derivative. It is due to localized electron distribution in para and meta-substituted Tetraphenyl-1,4-phenylenediamine. The increase in dipole moment decreases the electron carrier mobility and thereby increases the hole mobility.

Table 1. Dipole moment, E_{HOMO}, E_{LUMO} and E_g of methyl and methoxy derivatives of N,N,N,N-Tetraphenyl-1,4-phenylenediamine

Tetraphenyl-1,4-phenylenediamine derivative	Dipole moment (Debye)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)
-H	0.0002	-4.6254	-0.4362	4.1892
p-CH_3	0.0585	-4.5299	-0.3864	4.1443
m-CH_3	0.0004	-4.5658	-0.3864	4.1794

p-OCH_3	2.3574	-4.4058	-0.3774	4.028
m-OCH_3	0.0012	-4.5919	-0.4196	4.1732

By analyzing the molecular orbital diagram, we can see that, the substitution at both para and meta position affects the HOMO and LUMO levels. Still, para-substituted raises the HOMO level much more significantly than LUMO, thereby decreasing the bandgap. The rise in HOMO level and LUMO level is significant in the p-OCH_3 derivative, and the bandgap is reduced considerably. A surge in HOMO level increases electron injection, and a rise in LUMO level decreases recombination rate. Meta substitution affected the LUMO level, and there is very little or no change in bandgap compared to the unsubstituted one (Table 1).

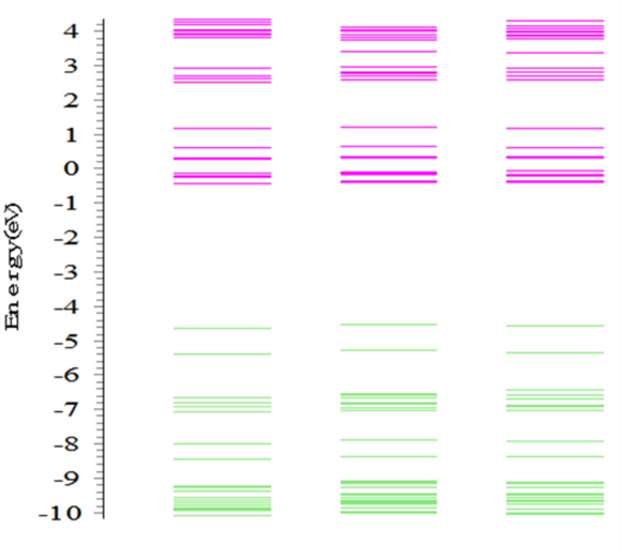


Figure 6. Molecular orbital diagram of unsubstituted, p-methyl and m-methyl derivatives of N,N,N,N-Tetraphenyl-1,4-phenylenediamine.

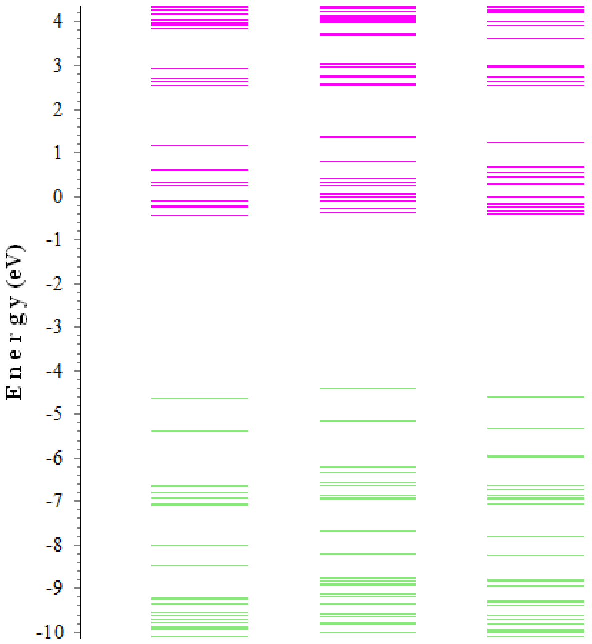


Figure 7. Molecular orbital diagram of unsubstituted, p-methoxy and m-methoxy derivatives of N,N,N,N-Tetraphenyl-1,4-phenylenediamine.

By studying dipole moment and energy levels of Tetraphenyl-1,4-phenylenediamine and its para and meta substituted derivatives, it is found that an increase in dipole moment and decrease in band gap by shifting the HOMO levels in para- Tetraphenyl-1,4-phenylenediamine favors the hole transport by decreasing the electron carrier mobility and increasing the electron extraction to occupy holes respectively.

The analysis of HOMO and LUMO of methyl derivative of Tetraphenyl-1,4-phenylenediamine (Figure 6) shows that the entire molecule contributes both the HOMO and LUMO, since $-CH_3$ is an electron-donating substituent and it transfers electron density to the phenyl ring; there is no significant difference in the HOMO and LUMO of para and meta-derivatives. However, the HOMO and LUMO of methoxy derivative of Tetraphenyl-1,4-phenylenediamine is quite different. Even the frontier molecular orbital of para and meta-derivatives ($-OCH_3$) differs significantly (Figure 8). Even though both the substituent under study is electron-donating, the contribution pattern to the ring is different (inductive and mesomeric effect), thereby differing in properties. So further studies are conducted by increasing the number of carbon in the alkyl/ alkoxy side chain.

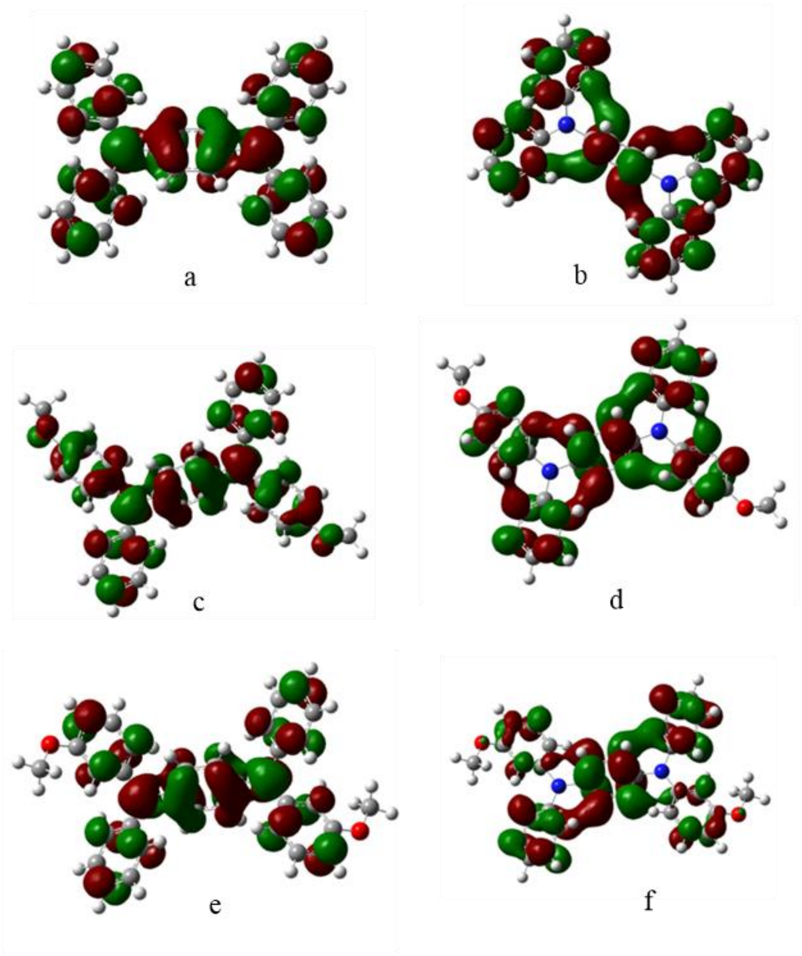


Figure 8. HOMO and LUMO of Tetraphenyl-1,4-phenylenediamine derivatives (a) and (b) -H, (c) and (d) p-OCH_3, (e) and (f) m-OCH_3.

3.2 Effect of Increasing Carbon Chain Length of Substituent on Energy Levels and Reorganisation Energy

Computational studies on the impact of increasing carbon chain length were conducted on Tetraphenyl-1,4-phenylenediamine core which is disubstituted at diagonally opposite para-position by methyl, ethyl, propyl, isopropyl, and butyl substituent. Similar studies were conducted with methoxy, ethoxy, propoxy, isopropoxy, and butoxy substituents.

3.2.1 Effect on Energy Levels

On molecular orbital calculation using DFT, the energy of HOMO, LUMO, and bandgap were obtained for all the structures under study (Table 2).

Table 2. Energies of HOMO, LUMO and band gap of para substituted derivatives of Tetraphenyl-1,4-phenylenediamine

Tetraphenyl-1,4-phenylenediamine	E_{HOMO}(eV)	E_{LUMO}(eV)	Eg(eV)
-p-CH_3	-4.5299	-0.3869	4.1430
-p-C_2H_5	-4.5380	-0.3921	4.1460
-p-C_3H_7	-4.5334	-0.3880	4.1454

-p-CH_3CHCH_3	-4.5386	-0.3910	4.1476
-p-C_4H_9	-4.5258	-0.3883	4.1438
-p-OCH_3	-4.4058	-0.3774	4.0284
-p-OC_2H_5	-4.3742	-0.3567	4.0175
-p-OC_3H_7	-4.3663	-0.3491	4.0172
-p-OCH_3CHCH_3	-4.3522	-0.3458	4.0063
-p-OC_4H_9	-4.3630	-0.3460	4.0170

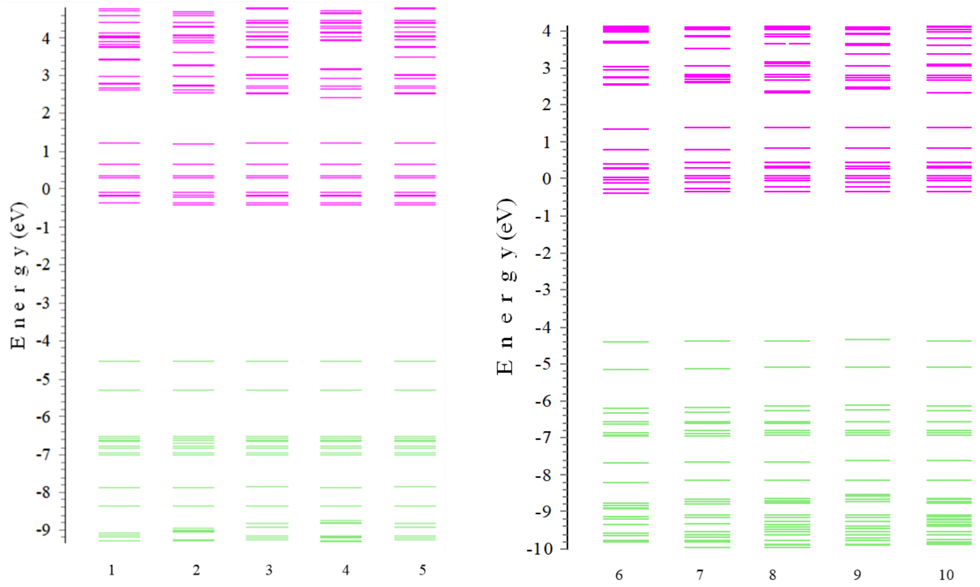


Figure 9. Molecular orbital diagram of p-derivatives of Tetraphenyl-1,4-phenylenediamine 1) p-CH_3, 2)p-C_2H_5, 3)p-C_3H_7, 4) p-CH_3CHCH_3, 5) p-C_4H_9, 6) p-OCH_3, 7) p-OC_2H_5, 8) p-OC_3H_7, 9) p-OCH_3CHCH_3,10) p-OC_4H_9

On analysis of the result, there is no significant change in bandgap when the carbon chain length of the methyl/methoxy substituent is increased. When the alkyl/alkoxy side chain, number of carbon (n)>2, the LUMO level is slightly lower in energy than methyl derivative, the LUMO level is somewhat raised in energy than methoxy derivative. However, there is no significant change in the bandgap except the isopropoxy (branched) derivative. This shows that electronic property depends on the functional group rather than the number of carbon atoms on the functional group.

3.2.1 Effect on Reorganization Energy

The reorganization energy of hole was calculated using DFT (B3LYP) technique for alkyl and alkoxy derivatives of Tetraphenyl-1,4-phenylenediamine under study.

Table 3. Ionization potential (Ip) and Reorganization energy of hole (λ+) of para-alkyl substituted derivatives of Tetraphenyl-1,4-phenylenediamine

Tetraphenyl-1,4-phenylenediamine derivatives	Ionization potential (Ip) (eV)	Reorganization energy of hole (λ+) eV
-p-CH_3	0.2087	0.3287
-p-C_2H_5	0.2085	0.3281
-p-C_3H_7	0.2081	0.3260
-p-CH_3CHCH_3	0.2082	0.3282
-p-C_4H_9	0.2076	0.3251

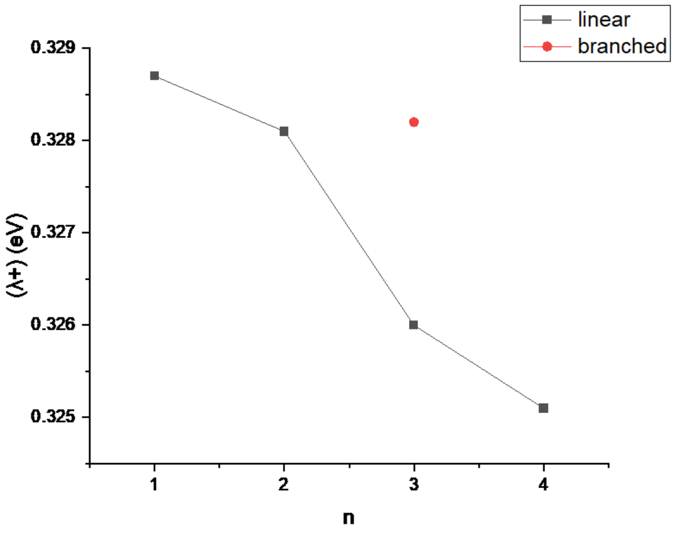


Figure 10. Reorganization energy with increase in number of carbon chain (n) of para-alkyl substituted tetraphenyl-1,4-phenylenediamine derivatives.

When para substituted alkyl derivatives of Tetraphenyl-1,4-phenylenediamine (p-) was studied, the reorganization energy decreases with increase in the number of carbons in the alkyl side chain (Table 3). Hole mobility increases up to n=4, in the linear chain (where, n= number of carbons in side chain), however with the same number of carbons, n=3, the branched side chain has higher reorganization energy than that of corresponding linear side chain. Figure 10 shows the relationship between the reorganization energy of hole with number of carbons in side chain. Figure 11 shows the comparison of effect of reorganization energy of para and meta-alkyl derivatives of Tetraphenyl-1,4-phenylenediamine. A decrease in reorganization energy is obtained up to n=3, here also, branching leads to increase in reorganization energy. However, comparing para and meta-derivatives, meta-alkyl derivatives of Tetraphenyl-1,4-phenylenediamine has higher reorganization energy than corresponding para derivatives, which favors p-alkyl substituted derivatives in hole transporting material.

Ionization potential and the HOMO level are the main factors of hole injection. Table 3 shows that as "n" increases, the ionization potential decreases and figure 9 shows that there is no significant dependence of HOMO level with "n". Similarly, the branching cause increase in ionic potential. Therefore, it is observed that increase in "n" in para substituted Tetraphenyl-1,4-phenylenediamine favors hole transport mobility and hole injection, whereas branching hinders the hole transport mobility and hole injection.

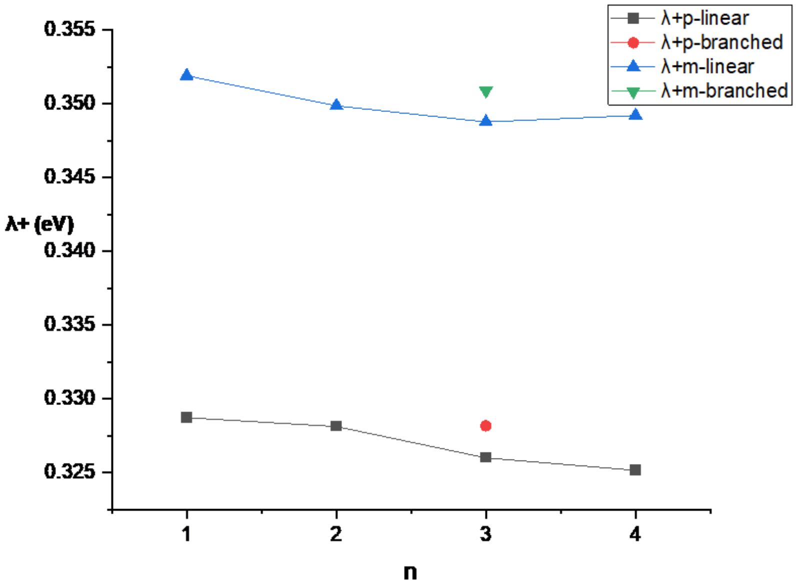


Figure 11. Reorganization energy with increase in number of carbon chain (n) of meta- and para-alkyl substituted tetraphenyl-1,4-phenylenediamine derivatives.

When para substituted alkoxy derivatives of Tetraphenyl-1,4-phenylenediamine (p-) were studied, no gradual decrease or increase of reorganization energy with an increase in "n" obtained. p–OCH_3 derivatives of Tetraphenyl-1,4-phenylenediamine under study have shown lower λ - than that of λ +, which enhance electron mobility. To study if any dependence of hole transport rate with electron transport rate, both the reorganization energies are compared. For (λ +), the order is of the form $-p-OC_2H_5 < -p-OC_3H_7 < -p-OCH_3 < -p-OC_4H_9 < -p-OCH_3CHCH_3$, which is not an exact reverse order for (λ -), i.e., $-p-OCH_3 < -p-OCH_3CHCH_3 < -p-OC_3H_7 < -p-OC_2H_5 < -p-OC_4H_9$ (Table 4). This indicates electron transport rate doesn't depend on hole transport rate and vice-versa.

Table 4. Electron affinity and Reorganisation Energy of para-alkoxy substituted derivatives of Tetraphenyl-1,4-phenylenediamine.

Tetraphenyl-1,4-phenylenediamine derivatives	Electron affinity (eV)	Reorganization energy of hole (λ +) eV	Reorganization energy of electron (λ -) eV
$-p-OCH_3$	0.0272	0.32537	0.1822
$-p-OC_2H_5$	0.0276	0.32482	0.2016
$-p-OC_3H_7$	0.0277	0.32529	0.2012
$-p-OCH_3CHCH_3$	0.0276	0.32752	0.1906
$-p-OC_4H_9$	0.0278	0.32618	0.2022

It has seen from table 4, branching increases electron mobility and decreases hole mobility with the corresponding linear chain. An increase in carbon number on the alkoxy side chain can increase hole mobility and reduce electron mobility to an extent and not linearly (Figure 12). Electron affinity and LUMO level are also significant factors in electron injection. The lower the electron affinity and LUMO level, the higher will be the electron injection.

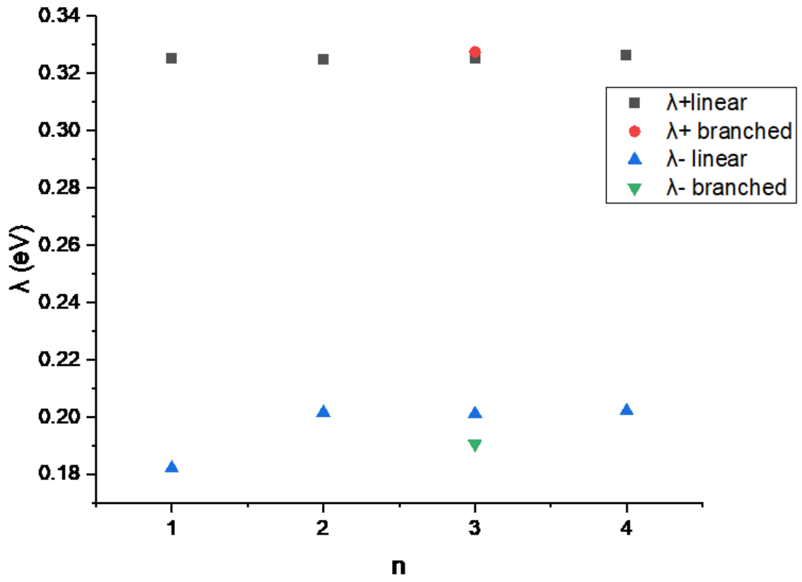


Figure 12. Reorganization energy with increase in number of carbons of para-alkoxy derivatives of tetraphenyl-1,4-phenylenediamine.

The reorganization energy of m- derivatives were also studied. Figure 13 shows the comparison of reorganization energy when alkoxy substituent is substituted at diagonally opposite meta-position of Tetraphenyl-1,4-phenylenediamine. In contrast to all the above cases, here, λ+ is slightly increases when "n" is increased, which is entirely opposite to the corresponding para derivatives. Figure 14 shows that λ- of meta-derivative decreases with "n" up to n=4. So, Alkoxy substituted at diagonally opposite meta Tetraphenyl-1,4-phenylenediamine has similar effect of reorganization energy with "n" (figure 15) as that of corresponding alkyl derivatives in para position. In all the above cases λ- is found to be decreased when branching occurs compared to the corresponding linear chain, but Figure 14 shows branching increases the λ- in meta alkoxy Tetraphenyl-1,4-phenylenediamine, when n=3. This is quite different behavior and further studies are needed. From the above discussion, it is seen, all the meta-derivatives have higher reorganization energy compared to para derivatives, in both λ + and λ-. There is no significant change in band gap when substitute at diagonally opposite meta position compared to the unsubstituted, whereas HOMO level is raised when substituted at diagonally opposite para position, which helps in electron injection.

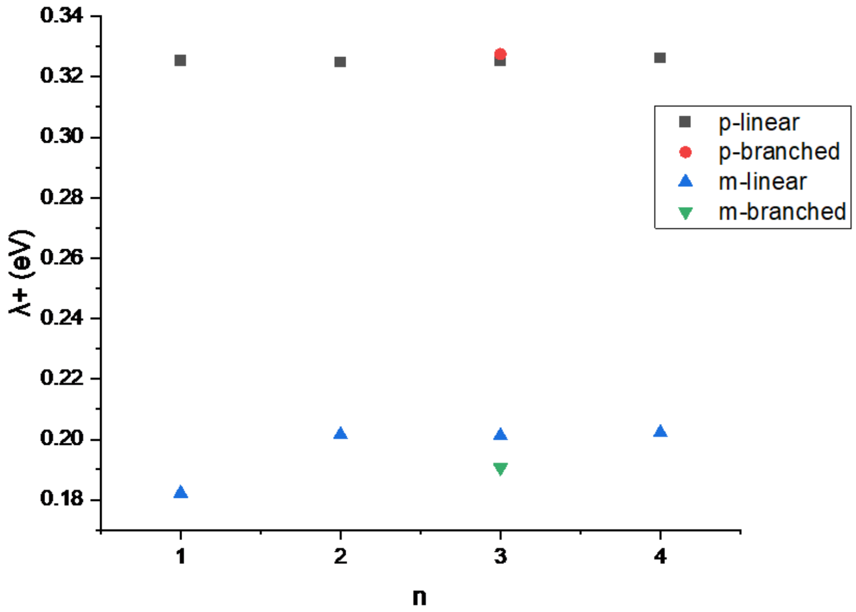


Figure 13. Reorganization energy (hole) of meta-alkoxy derivatives and para-alkoxy derivatives of tetraphenyl-1,4-phenylenediamine with increase in number of carbons.

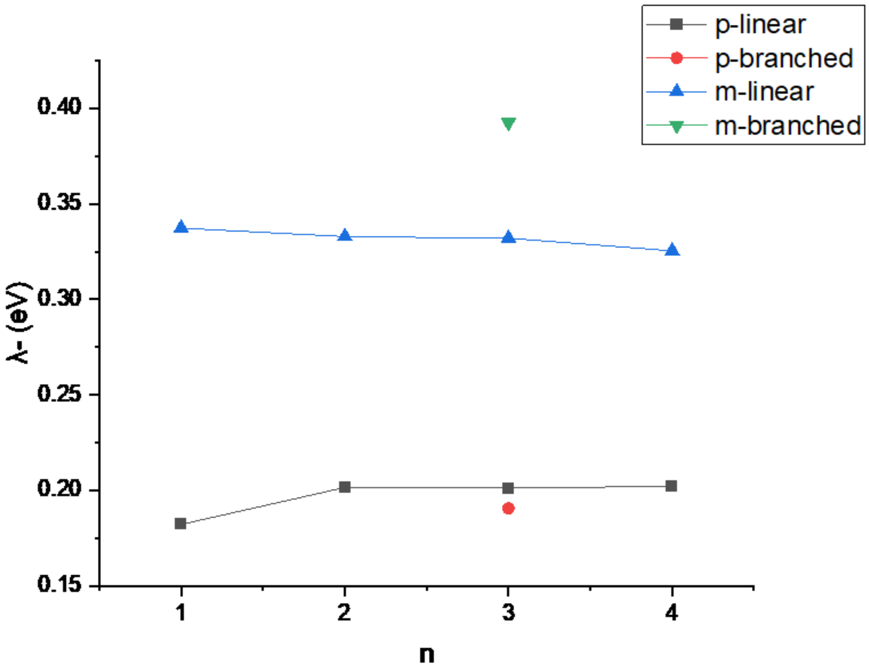


Figure 14. Reorganization energy (electron) of meta-alkoxy derivatives and para-alkoxy derivatives of tetraphenyl-1,4-phenylenediamine with increase in number of carbons.

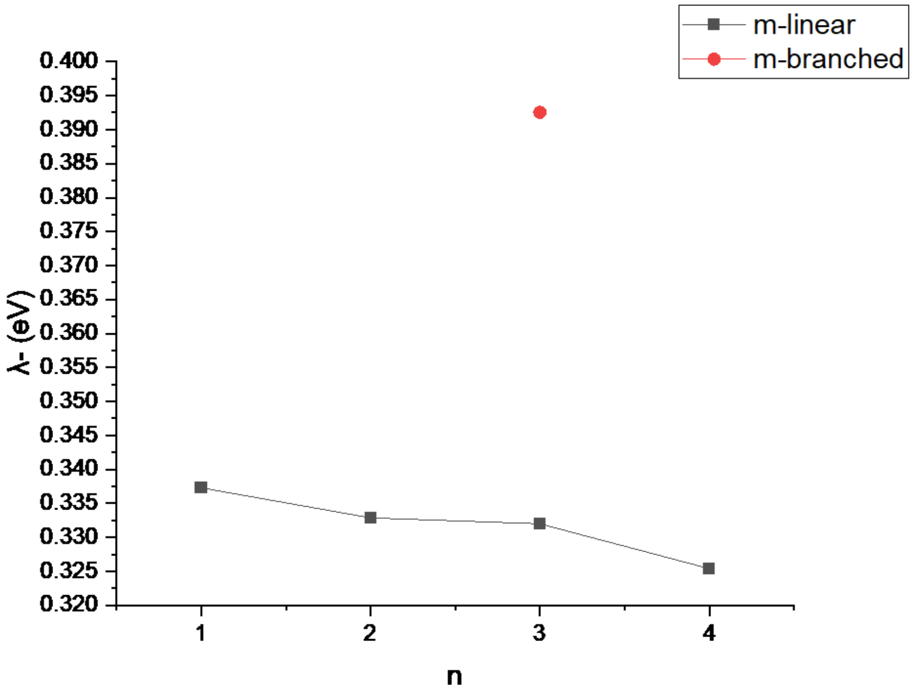


Figure 15. Reorganization energy (electron) of meta-alkoxy derivatives of tetraphenyl-1,4-phenylenediamine with increase in number of carbons.

4. Conclusion

The effect of substitution on the energy levels and reorganisation energy of N,N,N,N-Tetraphenyl-1,4-phenylenediamine with selected electron-donating groups was theoretically studied. The electron-donating group such as alkyl and alkoxy groups were di-substituted diagonally at meta and para positions of tetraphenyl-1,4-phenylenediamine. Computational calculations of HOMO, LUMO values, band gap, ionisation potential, and reorganisation energies were done. Detailed studies on the charge transfer properties, variations of reorganization energy of hole and electron with different alkyl and alkoxy groups were carried out.

The study of dipole moments and energy levels of Tetraphenyl-1,4-phenylenediamine and its para and meta-substituted derivatives reveals that an increase in dipole moment and a decrease in the band gap, particularly in para-substituted derivatives, enhances hole transport. This is achieved by shifting the HOMO levels, which reduces electron carrier mobility and facilitates electron extraction to fill holes, making para-substitution more favorable for efficient charge transport.

The analysis also reveals that while both –CH_3 and –OCH_3 are electron-donating substituents, their differing contributions to the phenyl ring (via inductive and mesomeric effects) significantly influence the HOMO and LUMO characteristics of Tetraphenyl-1,4-phenylenediamine derivatives. Unlike –CH_3, which shows minimal variation between para and meta derivatives, –OCH_3 exhibits notable differences in frontier molecular orbitals between these positions. This distinction underscores the importance of substituent effects on electronic properties, warranting further investigation into derivatives with extended alkyl or alkoxy chains to explore these trends in greater detail.

In order to analyse the effect of carbon chain length, on the energy levels and reorganisation energy, alkyl groups such as methyl, ethyl, propyl, isopropyl, butyl substituents and alkoxy groups such as methoxy, ethoxy, propoxy, isopropoxy, butoxy substituents were used. The study indicates that, the electronic properties of Tetraphenyl-1,4-phenylenediamine derivatives are primarily influenced by the nature of the functional group rather than the length of the carbon chain. While increasing the number of carbons in alkyl/methoxy substituents causes slight shifts in the LUMO energy levels, the bandgap remains largely unchanged, except for the isopropoxy (branched) derivative. This highlights the dominance of the functional group's intrinsic characteristics in determining the molecule's electronic behavior.

On the other hand, the para-substituted alkyl derivatives exhibit a decrease in reorganization energy with an increase in the number of carbons in the side chain up to n=4. This reduction enhances hole mobility, with linear side chains showing better performance than their branched counterparts, as branching increases reorganization energy. Comparing para and meta derivatives, the meta-alkyl derivatives consistently exhibit higher reorganization energy, making para-alkyl-substituted derivatives more favorable as hole-transporting materials.

The analysis of para-substituted alkoxy derivatives of Tetraphenyl-1,4-phenylenediamine shows no consistent trend in reorganization energy with an increase in the number of carbons in the alkoxy side chain. However, increasing carbon chain length can enhance hole mobility and reduce electron mobility to some extent, though not in a linear manner. Additionally, electron affinity and LUMO levels play crucial roles in electron injection, with lower electron affinity and LUMO levels favoring higher electron injection. These findings highlight the importance of substitution patterns and side chain architecture in optimizing electronic properties.

References

[1] T. V. Arjunan, T.S. Senthil, Review: "Dye sensitised solar cells", Materials Technology 28 (2013) 9–14.

[2] H. Khir, A.K. Pandey, R. Saidur, M. Shakeel Ahmad, N. Abd Rahim, M. Dewika, M. Samykano, "Recent advancements and challenges in flexible low temperature dye sensitised solar cells", Sustainable Energy Technologies and Assessments 53 (2022) 102745.

[3] M. Grätzel, "Dye-sensitized solar cells, Journal of Photochemistry and Photobiology", Photochemistry Reviews 4 (2003) 145–153.

[4] B. O'Regan, M. Grätzel, "A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO2 films", Nature 1991 353:6346 353 (1991) 737–740.

[5] W. Cao, J.Xue. "Science undefined 2014, Recent progress in organic photovoltaics: device architecture and optical design", Energy & Environmental Science, (2014).

[6] K. Mazzio, CK Luscombe, "The future of organic photovoltaics", Chemical Society Reviews, (2013) 1–3.

[7] M. Bavarian, S. Nejati, K.K.S. Lau, D. Lee, M. Soroush, "Theoretical and experimental study of a dye-sensitized solar cell", Ind Eng Chem Res 53 (2014) 5234–5247.

[8] N. Naeem, R.A. Shehzad, M. Ans, M.S. Akhter, J. Iqbal, "Dopant Free Triphenylamine-Based Hole Transport Materials with Excellent Photovoltaic Properties for High-Performance Perovskite Solar Cells", Energy Technology 10 (2022).

[9] K.R. Haridas, J. Ostrauskaite, M. Thelakkat, M. Heim, R. Bilke, D. Haarer, "Synthesis of low melting hole conductor systems based on triarylamines and application in dye sensitized solar cells", Synth Met 121 (2001) 1573–1574.

[10] S.J. Yeh, C.Y. Tsai, C.Y. Huang, G.S. Liou, S.H. Cheng, "Electrochemical characterization of small organic hole-transport molecules based on the triphenylamine unit", Electrochem Commun 5 (2003) 373–377.

[11] D. Alberga, G.F. Mangiatordi, F. Labat, I. Ciofini, O. Nicolotti, G. Lattanzi, C. Adamo, "Theoretical investigation of hole transporter materials for energy devices", Journal of Physical Chemistry C 119 (2015) 23890–23898.

[12] M.H. Tahir, T. Mubashir, T.U.H. Shah, A. Mahmood, "Impact of electron-withdrawing and electron-donating substituents on the electrochemical and charge transport properties of indacenodithiophene-based small molecule acceptors for organic solar cells", J Phys Org Chem 32 (2019).

[13] H. Tian, X. Yang, J. Cong, R. Chen, C. Teng, J. Liu, Y. Hao, L. Wang, L. Sun, "Effect of different electron donating groups on the performance of dye-sensitized solar cells, Dyes and Pigments 84 (2010) 62–68.

[14] S.S. Nishat, M.J. Hossain, F.E. Mullick, A. Kabir, S. Chowdhury, S. Islam, M. Hossain, "Performance Analysis of Perovskite Solar Cells Using DFT-Extracted Parameters of Metal-Doped TiO_2 Electron Transport Layer, "Journal of Physical Chemistry C 125 (2021) 13158–13166.

[15] A.D. Boese, "Density Functional Theory and Hydrogen Bonds: Are We There Yet?", ChemPhysChem 16 (2015) 978–985.

[16] *M.J. Saumya, K.R. Raghi, D.R. Sherin, K.R. Haridas, T.K. Manojkumar, "Butterfly Methanes: Designing a Novel Class of anti-van't Hoff Carbons", ChemPhysChem 21 (2020) 2272–2278.*

[17] *W.F. Polik, J.R. Schmidt, "WebMO: Web-based computational chemistry calculations in education and research", Wiley Interdiscip Rev Comput Mol Sci 12 (2022) 1–22.*

[18] *R. Dennington, T.A. Keith, J.M. Millam, "GaussView, version 6.0. 16", Semichem Inc Shawnee Mission KS (2016).*

[19] *A.D. Becke, "Density functional thermochemistry. I. The effect of the exchange-only gradient correction", Journal of Chemical Physics 96 (1992) 2155–2160.*

[20] *C. Lee, W. Yang, R.G. Parr, "Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density", Phys Rev B 37 (1988) 785–789.*

[21] *R. A Marcus, "Chemical and electrochemical electron-transfer theory", Annu. Rev. Phys. Chem. 15 (1964) 155.*

[22] *R.A. Marcus, "Electron transfer reactions in chemistry. Theory" Exp Rev Mod Phys 65: 599–610, (1993).*

[23] *F. Sun, R. Jin, "DFT and TD-DFT study on the optical and electronic properties of derivatives of 1,4-bis(2-substituted-1,3,4-oxadiazole)benzene", Arabian Journal of Chemistry 10 (2017) S2988–S2993.*

[24] *Y.H. Park, Y.H. Kim, S.K. Kwon, I.S. Koo, K. Yang, "Theoretical studies on dicyanoanthracenes as organic semiconductor materials: Reorganization energy", Bull Korean Chem Soc 31 (2010) 1649–1656.*

[25] *D. Moia, V. Vaissier, I. López-Duarte, T. Torres, M.K. Nazeeruddin, B.C. O'Regan, J. Nelson, P.R.F. Barnes, "The reorganization energy of intermolecular hole hopping between dyes anchored to surfaces", Chem Sci 5 (2014) 281–290.*

[26] *U. Daswani, U. Singh, P. Sharma, A. Kumar, "From Molecules to Devices: A DFT/TD-DFT Study of Dipole Moment and Internal Reorganization Energies in Optoelectronically Active Aryl Azo Chromophores", Journal of Physical Chemistry C 122 (2018) 14390–14401.*