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New pyrene and fluorene-based π -conjugated Schiff bases: Theoretical and experimental investigation of optical properties

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Abstract: The new Schiff bases with D- π -A system were synthesized from the reaction of polycyclic aldehydes and substituted benzothiazoles. The structure of the synthesized Schiff bases (7a and 9a) was determined by FT-IR, ¹H NMR, ¹³C NMR, ESI-Mass and elemental analyses. The optical properties of the new compounds were investigated and the optical band gaps (E_g) were calculated by the Tauc method using the UV-Vis absorption spectra. Density Functional Theory (DFT/B3LYP/6-31 G (d, p)) calculations were conducted to get more insight on the structural and electronic properties of novel Schiff bases. The optimized molecular geometry, UV-Vis spectroscopic parameters and HOMO-LUMO energies were examined and the calculated results were compared with experimental data.

Keywords: imine; UV-visible; optical bandgap; Tauc method; DFT.

INTRODUCTION

Schiff bases are compounds that are formed by the nucleophilic addition reaction of aldehydes or ketones and amines, and contain the $-\text{CH}=\text{N}-$ group in their structure. Schiff base was firstly synthesized by the chemist Hugo Schiff in Germany in 1894.¹ They are stable in the presence of aryl groups attached to imine group of the Schiff base.² It is known that Schiff base complexes containing aromatic rings are used in many different fields today. Since the imine group has strong bonds, Schiff bases are effectively used in the development of chemosensors.³ At the same time, their complexes are versatile compounds used in qualitative and quantitative analysis, dyestuff, pharmaceutical and plastics industries, synthesis of bioactive compounds, cycloaddition reactions and nucleophilic addition with organometallic reagents.⁴⁻⁶ Schiff bases are used in

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pharmacological chemistry, pharmaceutical chemistry, and used the most especially in antibacterial,⁷ antifungal⁸ and antitumor⁹ activity applications. Schiff bases have been investigated in recent years as functional material interesting optoelectronic properties due to their easily prepared and purified π -conjugated organic compounds¹⁰. New conjugated organic compounds with favorable optoelectronic properties offer significant advantages over carbon analogs as they can be easily prepared, purified¹¹ and synthesized without expensive catalysts. In previous studies, Schiff bases were used as optically molecular switches,¹² luminescence, pH indicators,¹³ electrochromic and photochromic materials.¹⁴ Schiff bases, which are isoelectronic with their vinyl bond, are a π -conjugated organic semiconductor material and form a kind of hole-transporting material.¹⁵ The azomethine nitrogen of the Schiff base can be protonated with unshared electron pairs and organic and inorganic acids. In this way, the optical and electrooptical properties of azomethine compounds can be adjusted.¹⁶ Organic materials play very important role in the field of nonlinear optics due to their delocalized electronic structure, are usually formed by bonding electron-donating and withdrawing groups from a π -electronic bridge with a large D- π -A conjugated system. The electron push-pull system helps to improve the molecular polarity so that larger nonlinear optical (NLO) materials can be obtained.¹⁷ The electron-donating part in this system usually has been chosen as aromatic and heteroaromatic rings. These rings are great components for making tertiary NLO materials. In recent years, many studies have been conducted on the development of conjugated organic compounds.¹⁸ Among π -conjugated organic compounds, especially Schiff base derivatives have emerged as promising compounds for NLO materials due to the π -electron bridge in carbon-nitrogen double bonds.¹⁹ These compounds have very mobile clouds of π -electrons in the large molecular structures and can be easily polarized.²⁰

In this study, we synthesized two new Schiff bases and their structures have been elucidated by various techniques such as ¹H NMR, ¹³C NMR, ESI-Mass, and elemental analyses. The optical properties of these compounds have been investigated by UV-Visible spectroscopy. The band gap energies of the compounds have been determined by the UV-Visible absorption spectra using the Tauc method. Calculations of Density Functional Theory (DFT) were performed using the Gaussian 09 program to investigate the optical properties of the compounds, and compare them for experimental data. DFT has been employed in theoretical studies to determine the vibrational frequencies, geometrical shapes and electrochemical characteristics of the molecule. In Schiff bases, the basic functional set of B3LYP/6-31 G (d, p) was mostly preferred,^{21,22} to explore the nature and type of UV-Vis shifts, a modified computation study time-dependent DFT was done.²³

EXPERIMENTAL

Experimental and additional datas are given in Supplementary Material to this paper.

RESULTS AND DISCUSSION

Chemistry

In the FT-IR spectra of compounds **7a** and **9a**, peaks at 3400 cm^{-1} belonging to the amino group of 4-methyl-2-amino benzothiazole, and at 1720 cm^{-1} belonging to the C=O group of aldehyde have been not observed. The imine group of compound **7a** is marked at 1593 cm^{-1} . The other peaks have been observed at 3038 cm^{-1} (for aromatic C-H), $2965\text{--}2918\text{ cm}^{-1}$ (for aliphatic C-H), 1576 cm^{-1} , 1537 cm^{-1} and 1478 cm^{-1} (for C=C peaks). Aromatic C-H, aliphatic C-H, aromatic C=C peaks have been observed at 3038 cm^{-1} , $2965\text{--}2918\text{ cm}^{-1}$, 1576 cm^{-1} , 1537 cm^{-1} and 1478 cm^{-1} , respectively (Fig.S1). The FT-IR spectrum of compound **9a** was showed similar signals to the FT-IR spectrum of compound **7a** (Fig. S3).

According to ^1H NMR spectrum compound **7a**, signals of 3 non-identical protons of the benzothiazole ring and 9 protons of the pyrene ring have been observed in the range of 8.15-9.28 ppm. Since the π electrons in the pyrene ring of compound **7a** are conjugated with the imine group and are a donor group, the ring electrons are resonantly directed towards the benzothiazole ring (Fig. 1).

Therefore, considering the resonance structures of the compound **7a**, the protons in the pyrene ring have been observed in the low field compared to the protons in the benzothiazole ring, as expected. As seen in Fig. S2, since the electron density around the H17 and H10 protons decreases with resonance, these protons resonate in the lower field due to the distance to the imine group ($-\text{CH}=\text{N}-$) compared to the other protons of pyrene ring. One proton doublets at 9.28 ppm and 8.84 ppm have been observed as H17 and H10 protons, respectively. Other pyrene protons are marked as 8.44 ppm (m, 5H, H11, H16, H14, H15 and H9). One doublet at 8.28 ppm and one triplet at 8.15 ppm observed belonging to H13 and H12 protons, respectively. On the other hand, the H5 and H7 protons of the acceptor benzothiazole ring are labeled as doublet at 7.31 ppm. Generally, the Schiff base imine proton resonates at about 8-9 ppm, while the resonance delocalization of the π electrons from the pyrene ring increases the polarization of the imine bond, and therefore the imine signal resonates at 9.98 ppm. In the ^{13}C NMR of compound **7a**, 18 signals were observed instead of 23 signals of carbons in the aromatic region due to identical carbons in the pyrene ring. In the ^1H NMR spectrum of compound **9a**, it has been observed that the protons in the fluorene ring resonate in a higher field than substance **7a**, depending on the resonance structure (Fig. 2).

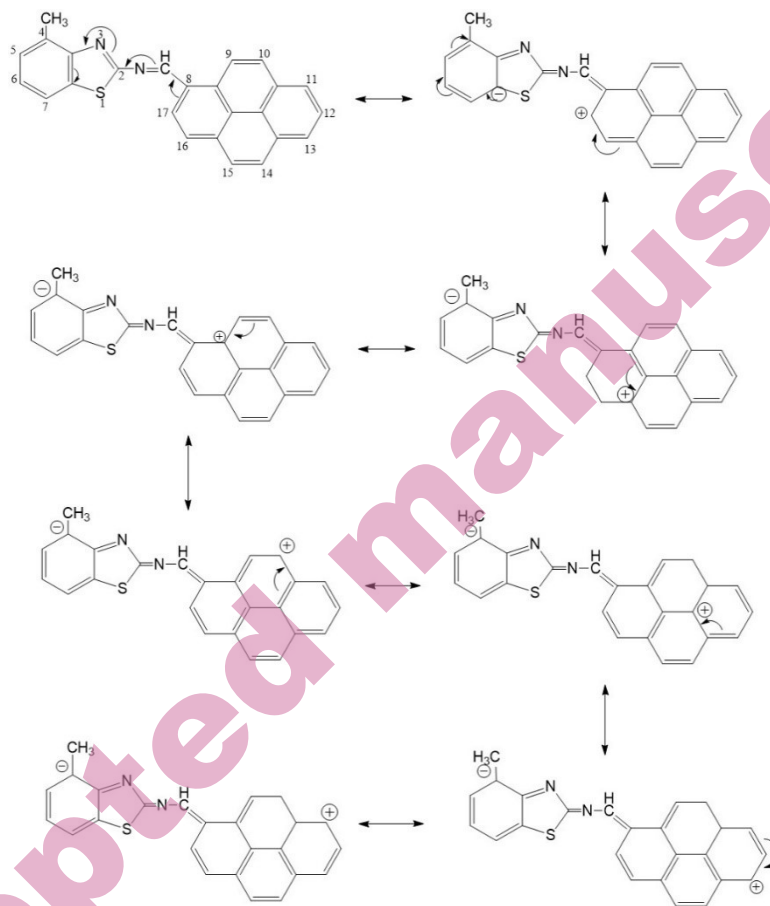
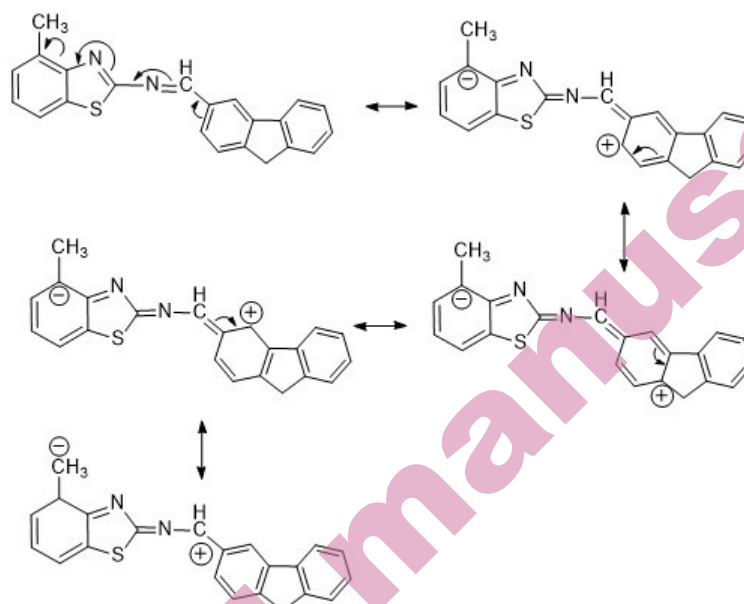


Fig. 1. Resonance forms of compounds **7a** .

Fig. 2. Resonance forms of compounds **9a**

The ^1H NMR of compound **9a** shows similar properties to compound **7a**. However, the increase in electron density around the protons in the fluorene ring of compound **9a** lead these protons to resonate in the higher field, so the fluorene protons in compound **9a** are resonated in higher field than the protons in the pyrene ring of compound **7a**. Therefore, the signal of the imine proton has been observed in the higher field as 9.14 ppm (Fig.S4).

In the ESI-MS spectrum of compound **7a**, the signal at 377.68 (M^+) is the peak of the molecular mass. 165.15 (m/z) and 245.48 (m/z) are the signals of molecular masses of 4-methyl-2-amino benzothiazole and pyrenecarbaldehyde, respectively. M^++1 , M^++2 peaks have been observed at 378.71 and 379.77. In the ESI-MS spectrum of **9a**, the main peak of the compound has been observed at 341.63 (M^+). The peaks at 342.63 and 343.65 were observed as belonging to M^++1 and M^++2 , respectively. The peaks of fluorene and benzothiazole ions have been observed at 209 and 165.1, respectively.

The UV-visible spectrum of material provides important structural information and a good way to study the properties of semiconductors, as it involves boosting an electron from the ground state from σ and π orbitals to the large energy state²⁴. It also gives information about the optical bandgap energy of the material. The forbidden energy gap of insulators is higher than 4 eV, whereas for semiconductors it is less than 3 eV²⁵. In this study, solutions of Schiff bases (**7a** and **9a**) in different solvents n-hexane, tetrahydrofuran THF, dichloromethane DCM, *N,N*-dimethylformamide DMF and dimethyl sulfoxide DMSO have been

prepared at 10^{-5} M concentrations and absorbance spectra has been recorded to clarify their optical properties. Two types of transitions, $n-\pi^*$ and $\pi-\pi^*$, belonging to the imine group ($-\text{CH}=\text{N}-$), have been observed to be expected in the UV-visible spectrum of Schiff bases **7a** and **9a** (Figure 3).

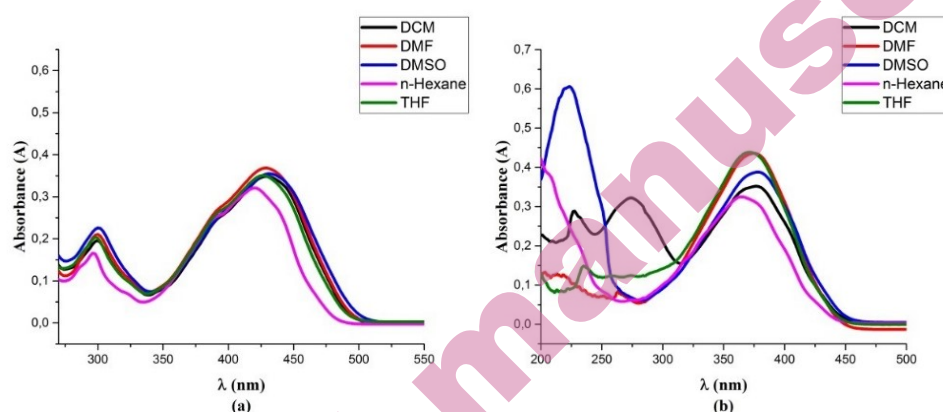


Fig. 3. (a):UV-visible spectrum of compounds **7a** in various solvents (1×10^{-5} M) , (b): UV-visible spectrum of compounds **9a** in various solvents (1×10^{-5} M).

The short wavelength band results from electron conjugation on the backbone molecule and is known as the $\pi-\pi^*$ electronic transition. Long wavelength transitions are known as $n-\pi^*$ transitions as shown in Table I. This transition occurs as a result of solute-solvent interaction via lone electron pair for compound **7a** and **9a** (Fig. S5 and S6).

TABLE I. The λ_{max} values of the $n-\pi^*$ and $\pi-\pi^*$ transitions of compounds **7a** and **9a** in different solvents

	Transition type	n-Hexane (λ_{max})	DCM (λ_{max})	THF (λ_{max})	DMF (λ_{max})	DMSO (λ_{max})
7a	$n-\pi^*$	420 nm	429 nm	426 nm	429 nm	431 nm
	$\pi-\pi^*$	297 nm	300 nm	299 nm	301 nm	302 nm
9a	$n-\pi^*$	363 nm	376 nm	371 nm	374 nm	379 nm
	$\pi-\pi^*$	209 nm	274 nm	234 nm	265 nm	225 nm

In the UV-Visible spectrum of compounds **7a** and **9a**, $\pi-\pi^*$ and $n-\pi^*$ transitions were observed to be red-shifted by solvent effect in five solvents with different polarities: n-hexane, THF, DCM, DMF and DMSO. This situation, as seen in Fig. 1 and 2, , it is explained due to the increased stability of the excited state by the conjugation effect. Due to the increase in the polarity of the solvent, the absorption band of the $\pi-\pi^*$ and $n-\pi^*$ transitions of compound **7a** was observed to be in the range of 297-302 nm and 420-431 nm, respectively. This situation is explained as, increased stability of the excited state due to conjugation, decreased of the energy of the excited state especially due to interaction with polar solvents,

and a red shift of the π - π^* transition and n - π^* transition absorption band since the ground state energy does not change. Similarly, π - π^* and n - π^* transitions of compound **9a** are observed at 209-274 nm and 363-379 nm, respectively. With increasing solvent polarity, the n - π^* transition of the imine of compound **9a** displays a red shift. However, a shift to a shorter wavelength has been observed due to decreasing conjugation in compound **9a** compared to compound **7a**. This red shift and high absorption in the UV visible regions is a desirable property in organic electronics.

Calculation of optical bandgap

Optical bandgaps which is synthesized materials were calculated by the Tauc method.²⁶ Tauc describes the absorption coefficient dependence on photon energy as given in Equation 1

$$(\alpha h\nu) \propto A(h\nu - E_g)^n \quad (1)$$

Here A is a constant, $h\nu$ is the photon energy, E_g is the optical bandgap. The value of n takes the value of 1/2 for direct transitions and 2 for indirect transitions. For direct transitions, the equation is given as Equation 2

$$(\alpha n_0 h\nu) \cong (h\nu - E_0)^{1/2} \quad (2)$$

This approach is valid for direct transitions. Here, $n = 1/2$ corresponds to the allowed direct transition. For indirect transitions, the equation is given as Equation 3

$$(\alpha n_0 h\nu) \cong (h\nu - E_0)^2 \quad (3)$$

approach is valid. Here, $n = 2$ corresponds to possible allowed indirect transitions. Indirect transitions are generally valid for amorphous structures. Photon energies belonging to the wavelengths corresponding to the linear part of the curve in the absorption spectrum were calculated with the help of the $E = h\nu$ equation, and using these values, $(\alpha h\nu)^2 \sim h\nu$ Tauc curves were drawn for each Schiff base separately for the direct allowed transition. The direct transition optical bandgaps of the Schiff bases is calculated from the value $(\alpha h\nu)^2 = 0$ of the line passing through the maximum number of points on the absorption edge of these curves. For a direct bandgap semiconductor, the optical bandgap is equal to the electronic bandgap. The graphs of $(\alpha h\nu)^2 \sim h\nu$ of novel benzothiazole derived Schiff bases (**7a** and **9a**) are given in Figure 4 and 5.

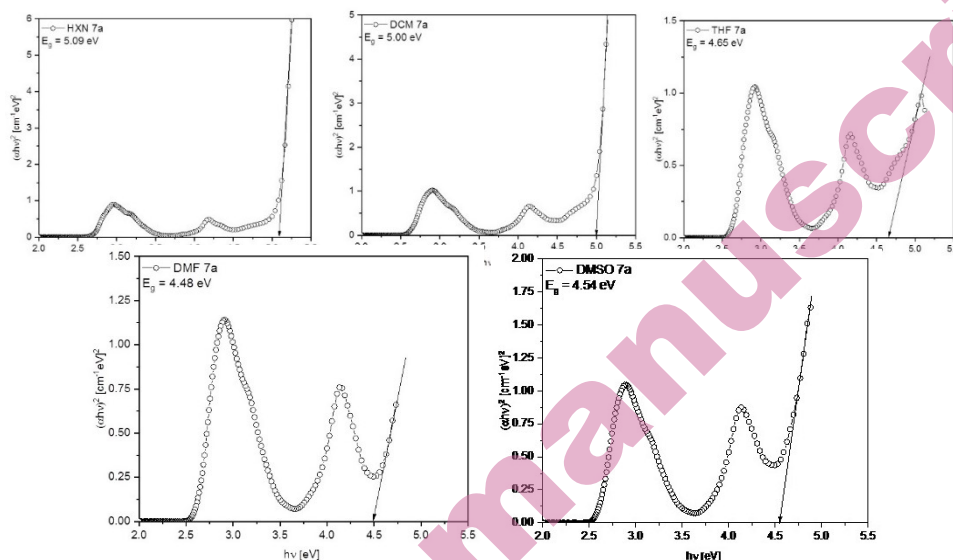


Fig. 4. Tauc curve and E_g values of compound **7a** in different solvents.

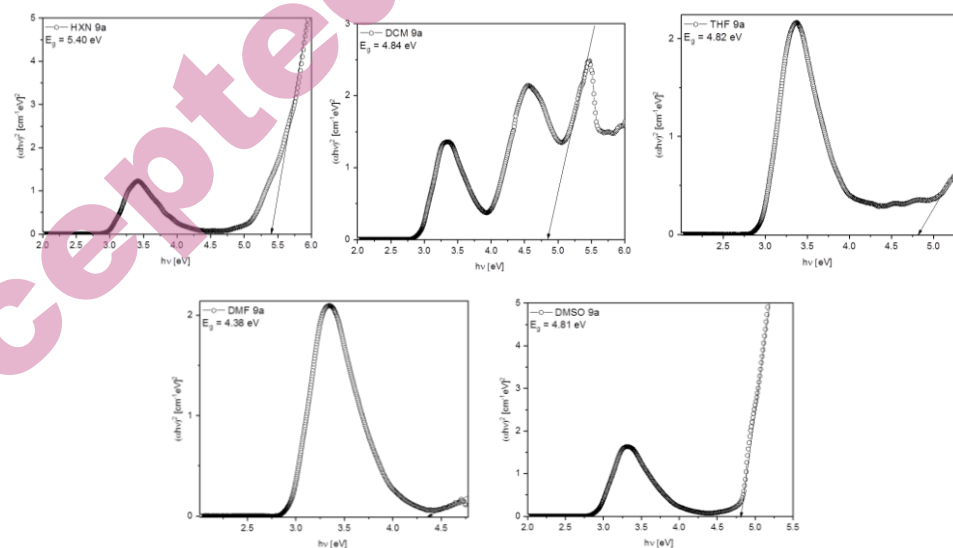


Fig.5. Tauc curve and E_g values of compound **9a** in different solvents.

The bandgap energy of organic π -conjugated semiconductors is related to the electronic structure of their molecules.^{21,22,27,28} The effect, which increases the conjugation of organic compounds and solvent polarity, decreases the energy

bandgap. Similarly, the difference in optical band gap E_g values of compounds **7a** and **9a** is due to their different resonance structures (Figure 1 and 2). Due to the conjugation of the pyrene ring in compound **7a**, the optical bandgap energy (E_g) is smaller than in compound **9a**. The high bandgap energy of compound **9a** is due to the fluorene ring. The E_g values of Schiff base **7a** and **9a** showed variable values in solvents of different polarity (Table II).

TABLE II. Optical Bandgap Energies (E_g) of compound **7a** and **9a**

	n-Hexane	DCM	THF	DMF	DMSO
7a	5.09 eV	5.00 eV	4.65 eV	4.48 eV	4.54 eV
9a	5.40 eV	4.84 eV	4.82 eV	4.38 eV	4.81 eV

The E_g of compound **7a** was decreased in polar solvents, particularly DMSO (4.54 eV) and DMF (4.48 eV) solvents. Although DMSO is more polar than DMF, the high E_g value was measured to be greater in the DMSO solvent. DMSO and DMF solvents are aprotic polar solvents, so there is no hydrogen bond interaction with compound **7a**. This increase in the optical bandgap energy E_g value was explained by the increase in the molecular mass of DMSO. Due to the trapping of electrons and holes, the bandgap energy between the valence band and conduction band increases as the particle size decreases. The optical bandgap energy E_g decreases gradually with chain length. Therefore, when the E_g values of **7a** and **9a** are compared, the decrease in the E_g values of **9a** is due to the smaller particle size.

Computational study

An extensive body of research supports the idea that DFT calculation shed light on the structural and electronic properties of conjugated molecules.^{21,22} In Schiff bases, the B3LYP/6-31 G (d, p) basis functional set was mostly preferred to investigate the nature and type of UV-Vis shifts, and a modified computational study of Time-Dependent DFT (TD-DFT) was conducted. This function, particularly adept at accurately calculating electron distribution and energy levels in conjugated systems, facilitates the reliable modeling of molecular structures and spectroscopic properties.²¹⁻²³ In this way, the ground state optimization of compound **7a** and **9a** were performed at the B3LYP/6-31 G (d,p) level in the gas phase and dimethyl sulfoxide (DMSO) without any symmetry constraints employing the Gaussian09 package program.^{29,30} Optimization was first performed by scanning the Potential Energy Surface (PES) and selecting the geometry around zero. Following the optimization with B3LYP, vibration frequency calculations were performed at the same level of theory and the minima of the calculated structures were verified by analyzing the harmonic vibrational frequencies using analytical second derivatives, which have NIMAG=0. The conductor-like polarizable continuum model (CPCM) was implemented to discern the solvent effect in DMSO.^{27,31} The construction of frontier molecular orbitals (FMO) was

completed using Gausview²⁸ while the dihedral angle between benzothiazole and the pyrene ring is 174° in compound **7a**, the dihedral angle between benzothiazole plane and fluorene is 180° in compound **9a**. The angles indicated that pyrene and fluorene rings are planar with the benzothiazole plane in **7a** and **9a**. The dihedral angles of the related atoms are given in detail in the supporting information.

To reach more insight into intramolecular charge transfer (ICT) characters of the compounds Frontier Molecular Orbitals (FMO) were calculated. The HOMOs were found to be, in both **7a** and **9a**, localized on benzothiazole, azomethine bonds, and the rings (pyrene in **7a**, fluorene in **9a**). Concerning the LUMOs, they were localized on the azomethine bonds, pyrene(**7a**) and fluorene (**9a**) rings spreading slightly over benzothiazole. As demonstrated in Figure 6, the azomethine bond is a π bridge between the benzothiazole and the rings in compound **7a** and **9a**. $\lambda_{\max}$ values and vertical excitation energies of the compounds were predicted by a time-dependent DFT (TD-DFT) method.

In order to receive absorption bands, N states of 50 for singlets were computed. The $\lambda_{\max}$ values of compounds **7a** and **9a** are predicted to be 431.8 and 388.56 nm in DMSO, which shows low energy transitions resulting from HOMO-LUMO (95-98%). The calculated excitation and absorption energies agree well with the experimental results.

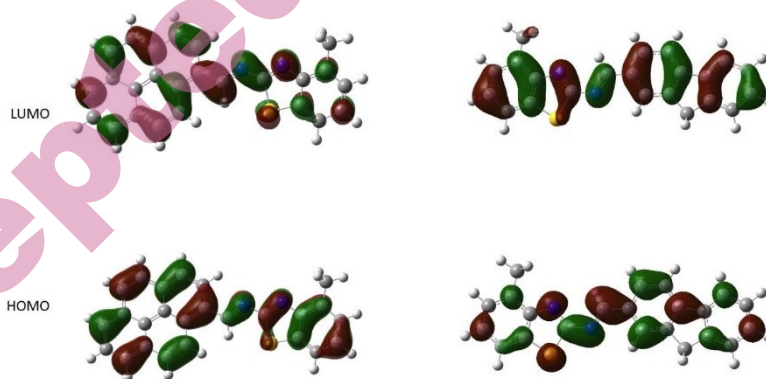


Fig. 6. HOMOs and LUMOs of **7a** (left) and **9a** (right) estimated at the B3LYP/6-31 G (d, p) level in the gas phase.

In parallel with all calculations performed, a dispersion component was added to the B3LYP 6-31 G (d,p) level of theory used in DFT calculations, and re-optimization and frequency calculations of the investigated **7a** and **9a** molecules were completed. First, there is no difference in the dihedral angles and therefore the geometry of the optimized structures by using the dispersion component.

Excited energy calculations were rerun with the freshly optimized geometries, and results were compared with previously obtained theoretical results. When the

HOMO-LUMO band gap energies of **7a** and **9a** were examined, narrower band gap energies were detected compared to the calculations conducted without using this dispersion component. The band gap energy values obtained both without and using the dispersion component tend to decrease or increase in the same way as the experimental study. However, it is seen that the band gap value obtained by adding the dispersion component deviates further from the experimental data. The results of the calculations with and without the dispersion component are given in supporting information.

CONCLUSION

In this study, we have synthesized and characterized two novel Schiff bases **7a** and **9a**. Optical properties have been investigated by UV visible spectra. The optical bandgap has been calculated by the Tauc method and DFT calculation. The optical band gap of compounds **7a** and **9a** in the DMF solvent is 4.48 eV, 4.38 eV, respectively. Experimental results showed that the optical band gap of compounds **7a** and **9a** decreases with increasing optical absorption, red-shift, π -electronic system, solvent polarity, and particle size. Finally, the increased optical absorption and reduced energy gap make the optimized samples suitable materials for solar applications.

Since pyrene contributes more to conjugation than fluorene, the experimental band gap energy of compound **7a** is expected to be less than that of compound **9a**. This difference was observed as 2.87 eV for **7a** and 3.19 eV for **9a** in calculated data conducted in DMSO by B3LYP 6-31 G (d, p). Considering the optical band gap energy obtained by the Tauc method from the experimental absorbance graphs recorded in DMSO (4.54 eV for **7a** and 4.81 eV for **9a**), the trends in the calculated band gap energies are in agreement with the experimental data. In addition, when the frontier molecular orbital is examined, it is clearly seen that the electrons are not located in only one region, but that these electrons are homogeneously distributed throughout the molecule. The fact that the charge transport in the molecule can continue unhindered throughout the molecule can be explained by the fact that compounds **7a** and **9a** have almost planar structures. For future studies, molecules with narrow band gap energies can be designed and synthesized by increasing the conjugated groups attached to compounds **7a** and **9a**.

SUPPLEMENTARY MATERIAL

Additional data are available electronically at the pages of journal website: <https://www.shd-pub.org.rs/index.php/JSCS/article/view/12546>, or from the corresponding author on request.

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ИЗВОД

НОВЕ, π -КОЊУГОВАНЕ ШИФОВЕ БАЗА ЗАСНОВАНЕ НА ПИРЕНУ И ФЛУОРЕНУ:
ТЕОРИЈСКО И ЕКСПЕРИМЕНТАЛНО ИСТРАЖИВАЊЕ ОПТИЧКИХ ОСОБИНАYUNUSCAN SIVRIKAYA¹, HANDAN CAN SAKARYA², GÖKHAN KILIÇ³, SULTAN FUNDA EKTİ⁴ AND MERVE
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У реакцији полициклических алдехида и супституисаних бензотиазола, синтетисане су нове Шифове базе са D- π -A системом. Структуре синтетисаних Шифових база (7a и 9a) одређене су помоћу FT-IR, ¹H NMR, ¹³C NMR, ESI-Масеном и елементалном анализом. Истражене су оптичке особине нових једињења и оптички јаз између трака (E_g) је израчунаван Тауковом методом користећи UV-Vis апсорпционе спектре. Да би се добио бољи увид у структурне и електронске особине нових база урађена су израчунавања Теоријом Функционала Густине (DFT/B3LYP/6-31 G (d, p)). Оптимизоване молекулске геометрије, UV-Vis спектроскопски параметри и HOMO-LUMO енергије су испитани и резултати израчунавања су упоређени са експерименталним подацима.

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