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Quantum Chemical Modeling of New Derivatives of (*E*,*E*)-Azomethines: Synthesis, Spectroscopic (FT-IR, UV/Vis, Polarization) and Thermophysical Investigations

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# Highlights

- Modeling and Synthesis of new azomethine dyes.
- Investigation of electronic properties and NBO analysis.
- Preparation of polarizing PVA-films.
- Anisotropy of thermal conductivity of PVA-films contains new dyes.
- Recording experimental and calculated UV-Vis spectra of new dyes.

# **Title Page Information**

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# Quantum Chemical Modeling of New Derivatives of (E,E)-Azomethines: Synthesis, Spectroscopic (FT-IR, UV/Vis, Polarization) and Thermophysical Investigations

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#### Abstract

In the present work, the molecular structures of three new azomethine dyes:

*N-benzylidene-4-((E)-phenyldiazenyl)aniline* (PAZB-1), 2-methoxy-4-(((4-((E)phenyldiazenyl)phenyl)imino)methyl)phenol (PAZB-2) and 2-methoxy-5-((E)-((4-((E)phenyldiazenyl)phenyl)imino)methyl)phenol (PAZB-8) have been predicted and investigated using Density Functional Theory (DFT) in dimethylformamide (DMF). The geometries of the azomethine dyes were optimized by PBE0/6-31+G\* level of theory. The electronic spectra of these azomethine dyes in a DMF solution was carried out by TDPBE0/6-31+G\* method. After quantum-chemical calculations three new azomethine dyes for optoelectronic applications were synthesized. FT-IR spectra of the title compounds are recorded and discussed. The computed absorption spectral data of the azomethine dyes are in good agreement with the experimental data, thus allowing an assignment of the UV/Vis spectra. On the basis of polyvinyl alcohol (PVA) and the new senthesized azomethine dyes polarizing films for Visible region of spectrum were developed. The main optical parameters of polarizing PVA-films (Transmittance, Polarization Efficiency and Dichroic Ratio) have been measured and discussed. Anisotropy of thermal conductivity of the PVA-films has been studied.

#### Keywords

Azomethine dye; DFT calculation; UV/Vis spectrum; Polarizing film; Anisotropy of thermal conductivity

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#### 1. Introduction

Azomethines with phenyl rings isolated by an azo (-N=N-) bond, serves as the guardian molecule for a wide class of aromatic compounds. These chromophores are adaptable atoms, and have obtained much consideration in both fundamental and applied research. Azo groups are moderately strong and chemically stable, has provoked broad investigation of azomethines based structures as dyes and colorants [1,2]. Azomethines have flexible relevance in different areas running from complexes [3], photoluminescence materials [4] to advanced applications such as optical materials and devices [5,6], organic light-emitting diodes [7], photovoltaic cells [8] and polarizing films [1,2,5]. Azomethines also possess interesting properties like cis-trans photoisomerization about the azo p-bond when heated or irradiated in UV [9]. They are the most widely used classes of dyes for photonic applications like lasers, spectroscopic analysis, liquid crystal devices and optoelectronic systems [1-6]. Conventionally, polarizing films are manufactured from uniaxially oriented polymer sheet containing dichroic material such as azomethines. These structures are beneficial for achieving higher dichroism due to their linear structure and anisotropic transition moment. Theoretical quantum chemistry methods based on HF and DFT are widely used for the calculation of optimized geometry, absorption spectrum, UV, IR and NMR spectra of organic molecules [4-5,7-15]. According to the authors [9,10] DFT method fully describes the geometry of molecules, vibration spectra and excited states of platinum-Olefin complexes and benznidazole. Electronic transitions of benznidazole were also obtained after DFT calculations. Molecular geometry optimizations and absorption peaks were also obtained within the DFT and TD-DFT methods and it has been found that there is excellent agreement between theory and experiment [11,12]. It has been claimed that the *ab initio* method

provides more accurate results than thesemi-empirical calculation of the intensity in the IR spectra of compounds. Researchers have also presented the results of TD-DFT calculations of the oxazine dyes [13,14]. The gas-phase optimized geometries of the dyes were used as the basis for the single point excited state calculations. From the literature survey it has been observed that the *ab initio* Hartree-Fock-Roothaan with different choices of basis sets compared to other *ab initio* quantum chemistry methods fully describes the features of the electronic structure of molecules containing the biphenyl fragment [4-5]. In this study we predicted and modeled geometrical parameters, UV/Vis and IR spectra of new synthesized azomethines by PBE0 method with 6-31+G\* basis set. On the basis of PVA, the new synthesized dichroic structures polarizing films absorbing in Visible region of spectrum with high anisotropy of thermal conductivity were developed.

#### 2. Experimental details

#### 2.1 Reagent and apparatus

All chemicals used were of analytical reagent grade. PVA used in this work «Mowiol 28-99» was purchased from Hoëchst Akiengesllschaft Co. (Germany). The experimental UV absorption spectra of the title molecules were recorded on UV-Visible Spectrophotometer Cary300 (Varian, USA). The optical transmission spectra were measured in polarized light with UV-NIR Spectrophotometer HR4000 (Ocean optics, USA). Experimental IR-spectra of films was recorded in the frequency region 400-4000 cm<sup>-1</sup> on a Spectrophotometer of Protégé 460 (Nicolet, US). Thermal conductivity of films was measured on the complex equipment LC–201 (Alfa Laval Group, Sweden) using indicator method of determining the thermal conductivity of polymer materials and thin films.

#### 2.2 Preparation of polarizing PVA-films

The PVA-films were prepared from (wt. %) 10 PVA solution containing 0.01-0.03 **PAZB-1**, **PAZB-2**, **PAZB-8** (0.10-0.30 in film), 0.01 boric acid (H<sub>3</sub>BO<sub>3</sub>), 6.0 ethyl alcohol (C<sub>2</sub>H<sub>5</sub>OH) and water. An initial composition was prepared by dissolving PVA indistilled water and ethyl alcohol. The composition was mixed at temperature 85-90 °C. The compounds **PAZB-1**, **PAZB-2**, **PAZB-8** and additives were added after 3 hours after starting of heating PVA solution at intervals 20 min. The mixture was heated for 3 h. The hot solution was filtered through two layers of technical nylon. Deaeration was occurred during 12-15 h. The composition was cast on the polished glasses and dried in the closed box at temperature 20-22 °C. Uniaxial orientation was done in the 4 % boric acid solution at temperature 42-45 °C. The washed film was dried for 30 min. at temperature 60-63 °C. The value of Stretching Degree (R<sub>s</sub>) was determined as the ratio between length of the films after and before ( $l_{aft} / l_{bef}$ ) uniaxial orientation. The thickness of the resulting films was between 50 to 55 µm [1,2]. The film thickness was measured with amicrometer with an accuracy of ±5 µm (GS SSSR6507-90).

Accuracy of measurements in this research limits the accuracy of the results:

- Sample of the starting composition for preparation of solutions and films for casting taken on an analytical balance accurate to 0.0005 g;

- Temperature measurement error was:

 $\pm 2.0$  °C in the preparation of polymer solutions with additives,

 $\pm 1.0$  °C in the chemical treatment of the films,

 $\pm 3.0$  °C at thermal fixation and drying films;

- Relative error of spectrophotometric analysis did not exceed 1.0 % and thermal conductivity 0.1 %.

The standard deviation of parallel measurements determined by the formula [12-15]:

$$S(d) = \sqrt{\sum_{i} (d_i - d)^2 / n - 1}$$
(1)

Whered<sub>i</sub> -the result of a single measurement,

d- Arithmetic mean

n- Number of measurements.

#### 2.3 Computational methods

In this work, we have carried out quantum theoretical calculations and have optimized structures of the title compounds using the Density Functional Theory (DFT) method with 6-31+G\* basis set by the Gaussian 09W program package [16] in a solvent DMF. The optimized molecular structures, HOMO and LUMO surfaces were visualized using GaussView 05 program. The obtained structures were fully optimized by functional PBE0 (One-parameter hybrid PBE functional incorporating 25% HF exchange) at 6-31+G\* basis set. Inaddition to optimization, the Time Dependent Density Functional Theory (TD-DFT) was also used for computing the electronic transitions. To account solvent effect Polarized Continuum Model (PCM) was used [15]. Theoretical absorption spectrum of all the molecules in a solvent DMF was calculated using TDPBE0/6-31+G\* method. Also the theoretical IR spectra of optimized structures was calculated using PBE0/6-31+G\* method. The electronic properties such as E<sub>HOMO</sub>, E<sub>LUMO</sub>, HOMO-LUMO energy gap (Eg) and natural charges were calculated [6]. Also the electronic structure of the title compound were studied using Natural Bond Orbital (NBO) analysis [17] at the PBE0/6-31+G\* level of energy in order to understand hyperconjugative interactions and charge delocalization.

#### 2.3.1 Optimized structure of the compounds PAZB-1, PAZB-2, PAZB-8

DFT calculations were performed for the three new compounds PAZB-1, PAZB-2, PAZB-8 and their optimized molecular structures are shown in Fig. 1. The entire quantum chemical calculations were performed using the Gaussian 09 software package and Gauss view 05 visualization programs [16] on a Pentium IV/4.02 GHz personal computer. The theoretical molecular structure of the title compounds in the ground state was optimized by DFT/PBE0/6-31+G\* level of theory. To account solvent (DMF) effect the IEFPCM (Integral Equation Formalism PCM) method coupled to UAKS radii was used. The Integral Equation Formalism PCM, by Cances, Mennucci and Tomasi is the most popular PCM version. It employs a molecule shaped cavity composed of spheres centered on the nuclei, while the reaction field is modeled by placing charges on the cavity surface.









Fig. 1. Optimized molecular structures of compounds PAZB-1, PAZB-2, PAZB-8 calculated by PBE0/6-31+G\* method.

**2.3.2 Electronic Structure and Excited States of the compounds PAZB-1, PAZB-2, PAZB-8** Theoretical absorption spectra of the title compounds optimized in DMF were calculated using TDPBE0/6-31+G\* method. The equations were solved for 20 excited states, where the computational studies were performed using the IEFPCM (Integral Equation Formalism PCM)

method coupled to UAKS radii. The TDDFT method is able to detect accurate absorption wavelength at a relatively small computing time, which corresponds to electronic transitions computed on the ground state geometry.

**PAZB-1)** The broad absorption band at  $\lambda_{max} = 369$  nm and the oscillator strength f = 1.45 refers to the transition of the molecule to excited singlet state  $S_3$  (Table 1). The strong peak at 369 nm is due to the Charge-Transfer (CT) excited singlet state. Excitation of one electron at 369 nm belonged to the transition into the excited singlet state  $S_3$  and describes by a wave function corresponding to configuration for one-electron excitation from (HOMO) $\rightarrow$ (LUMO). According to Fig. 2, the electron density of HOMO is mainly focused on azo group (-N=N-) and LUMO is mainly focused on double bonds (-C=C-) of three aryl rings and azo group (-N=N-). Therefore the electronic transitions from the HOMO to LUMO are due to the contribution of pi ( $\pi$ ) bonds. The other excited states have very small intensity ( $f \approx 0$ ): these transitions are nearly forbidden by orbital symmetry considerations (Table 1).

#### Table 1

Electronic absorption	spectrum of the com	oound PAZB-1 calcu	lated by TDPBE0/6	-31+G* method.
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Excited	Wavelength	Excitation	Configurations Composition	Oscillator	
State	(nm)	Energy (eV)	(corresponding transition orbitals)	Strength (f)	
<b>S</b> <sub>1</sub>	545	2.28	$-0.12(H-2\rightarrow L) + 0.67(H-1\rightarrow L) + 0.16(H-1\rightarrow L+1)$	0.00	
S <sub>2</sub>	440	2.82	$0.12(H-2\rightarrow L) - 0.20(H-2\rightarrow L+1) + 0.12(H-1\rightarrow L)$	0.00	
S <sub>3</sub>	369	3.36	0.71(H→L)	1.45	
S <sub>4</sub>	324	3.82	$0.54(H-4\rightarrow L) + 0.40(H-3\rightarrow L) - 0.12(H\rightarrow L+1)$	0.00	
Se	320	3.88	$0.49(H-6\rightarrow L) - 0.17(H-5\rightarrow L) + 0.33(H-4\rightarrow L)$	0.11	
	520 5.00		$-0.30(H-3\rightarrow L) + 0.12(H\rightarrow L+2)$	0.11	
S	319	3 89	$0.36(H-6\rightarrow L) - 0.17(H-5\rightarrow L) - 0.25(H-4\rightarrow L)$	0.00	
56	36 319	5.07	$+ 0.37(H-3\rightarrow L) - 0.36(H\rightarrow L+1)$	0.00	
<b>S</b> <sub>7</sub>	317	3.91	$0.26(H-6\rightarrow L) + 0.64(H-5\rightarrow L)$	0.03	
$S_8$	311	3.99	$0.21(H-2\rightarrow L) + 0.59(H-2\rightarrow L+1) + 0.32(H-1\rightarrow L+1)$	0.00	
<b>S</b> <sub>9</sub>	308	4.02	$-0.33(H-2\rightarrow L+1) - 0.16(H-1\rightarrow L) + 0.60(H-1\rightarrow L+1)$	0.00	
$S_{10}$	292	4.25	$0.18(H-6\rightarrow L) + 0.33(H-3\rightarrow L) + 0.59(H\rightarrow L+1)$	0.18	
<b>S</b> <sub>11</sub>	264	4.68	$0.68(H-7\rightarrow L) + 0.14(H\rightarrow L+5)$	0.01	
			$0.12(H-5\rightarrow L) + 0.56(H-5\rightarrow L+1) - 0.10(H-4\rightarrow L+1)$		
S <sub>12</sub>	252	252 4.91	$+ 0.12(H-3\rightarrow L+1) - 0.10(H-3\rightarrow L+2) + 0.30(H\rightarrow L+2)$	0.00	
			- 0.12(H→L+4)		
S <sub>13</sub>	249	4.98	$0.48(H-6\rightarrow L+1) + 0.13(H-5\rightarrow L+1) - 0.44(H-3\rightarrow L+1) - 0.19(H\rightarrow L+4)$	0.09	

$S_{14}$	243	5.10	$- 0.12(\text{H-}4\rightarrow\text{L}) + 0.56(\text{H-}4\rightarrow\text{L+}1) + 0.21(\text{H-}3\rightarrow\text{L+}1) - 0.29(\text{H}\rightarrow\text{L+}3)$	0.00
S <sub>15</sub>	241	5.13	$0.45(\text{H-6}\rightarrow\text{L+1}) - 0.17(\text{H-4}\rightarrow\text{L+1}) + 0.45(\text{H-3}\rightarrow\text{L+1}) - 0.17(\text{H}\rightarrow\text{L+5})$	0.08
S <sub>16</sub>	240	5.15	$0.55(H-1\rightarrow L+2) - 0.10(H-\rightarrow L+3) + 0.42(H-1\rightarrow L+4)$	0.00
S <sub>17</sub>	239	5.16	$-0.13(H-2\rightarrow L+3) + 0.67(H-1\rightarrow L+3) + 0.16(H-1\rightarrow L+4)$	0.08
S <sub>18</sub>	238	5.21	$ - 0.13(H-6\rightarrow L) + 0.13(H-6\rightarrow L+1) - 0.12(H-6\rightarrow L+5) - 0.18(H-5\rightarrow L+1) + 0.55(H\rightarrow L+2) + 0.29(H\rightarrow L+4) $	0.00
S <sub>19</sub>	231	5.36	$0.62(H-2\rightarrow L+2) + 0.31(H-2\rightarrow L+4)$	0.12
S <sub>20</sub>	229	5.42	$0.33(H-4\rightarrow L+1) + 0.59(H\rightarrow L+3)$	0.06

\*H-HOMO, L-LUMO



Fig. 2. Form of the MO involved in formation of absorption spectrum of the compound PAZB-1 at  $\lambda_{max} = 369$  nm. Experimental UV/Vis spectrum of the compound PAZB-1 in DMF at concentration  $4.0 \cdot 10^{-4}$ M and calculated spectrum in DMF is presented in Fig. 3a,b. The experimental absorption spectrum of the title compound (Fig. 3b) has a wide absorption at 367 nm with D = 1.282.





**Fig. 3.** UV/Vis spectrum of the PAZB-1 in DMF: a) calculated by TDPBE0/6-31+G\* method and b) experimental at concentration of dye:  $4.0 \cdot 10^{-4}$ M.

**PAZB-2)** According to Table 2, the highest oscillation observed in  $\lambda_{max} = 380$  nm at f = 1.08. Calculations show excitation of one electron from (HOMO) $\rightarrow$ (LUMO) gives the main contribution to the formation of the absorption band at 380 nm that belonged to the transition into the excited singlet state  $S_2$ . According to Fig. 4, the electron density of HOMO is mainly focused on azo group (-N=N-) and LUMO is mainly focused on double bonds (-C=C-) of three aryl rings and azo group (-N=N-). Therefore the electronic transitions from the HOMO to LUMO are due to the contribution of pi ( $\pi$ ) bonds. The other excited states have very small intensity (f  $\approx$  0): these transitions are nearly forbidden by orbital symmetry considerations (Table 2).

Table 2

Electronic absorption spectrum of the compound PAZB-2 calculated by TDPBE0/6-31+G\*.

Excited	Wavelength	Excitation	Configurations Composition	Oscillator
State	(nm)	Energy (eV)	(corresponding transition orbitals)	Strength (f)
$S_1$	515	2.41	$0.68(H-1\rightarrow L) + 0.14(H-1\rightarrow L+1)$	0.00
$S_2$	380	3.26	0.70(H→L)	1.08
S <sub>3</sub>	371	3.34	$0.65(H-2\rightarrow L) - 0.22(H\rightarrow L+1)$	0.08
S <sub>4</sub>	352	3.52	$-0.36(H-3\rightarrow L) + 0.21(H-2\rightarrow L) + 0.11(H-2\rightarrow L+1) + 0.51(H\rightarrow L+1)$	0.02

S <sub>5</sub>	305	4.06	$0.65(H-4\rightarrow L) + 0.19(H-3\rightarrow L)$	0.01
S <sub>6</sub>	301	4.11	$-0.33(H-6\rightarrow L) + 0.58(H-5\rightarrow L) + 0.16(H\rightarrow L+2)$	0.00
$S_7$	299	4.14	$- 0.16(H-4\rightarrow L) + 0.56(H-3\rightarrow L) + 0.12(H-2\rightarrow L) + 0.16(H-2\rightarrow L+1) + 0.32(H\rightarrow L+1)$	0.00
$S_8$	294	4.21	$- 0.14(H-8\rightarrow L) + 0.57(H-6\rightarrow L) + 0.31(H-5\rightarrow L) - 0.15(H\rightarrow L+1)$	0.00
S <sub>9</sub>	289	4.29	$-0.14(H-1\rightarrow L) + 0.68(H-1\rightarrow L+1)$	0.03
S <sub>10</sub>	283	4.37	$\begin{array}{c} -0.11(\text{H-8}\rightarrow\text{L}) - 0.10(\text{H-5}\rightarrow\text{L}+1) - 0.11(\text{H-3}\rightarrow\text{L}) \\ -0.14(\text{H-3}\rightarrow\text{L}+1) + 0.59(\text{H-2}\rightarrow\text{L}+1) - 0.19(\text{H}\rightarrow\text{L}+1) \\ + 0.12(\text{H}\rightarrow\text{L}+3) \end{array}$	0.07
S <sub>11</sub>	263	4.71	$\begin{array}{c} - 0.13(\text{H-}7\rightarrow\text{L}) - 0.12(\text{H-}6\rightarrow\text{L+}1) - 0.15(\text{H-}5\rightarrow\text{L+}1) + \\ 0.11(\text{H-}3\rightarrow\text{L}) + 0.50(\text{H-}3\rightarrow\text{L+}1) + 0.13(\text{H-}2\rightarrow\text{L+}3) \\ - 0.32(\text{H}\rightarrow\text{L+}3) \end{array}$	0.06
S <sub>12</sub>	259	4.78	$\begin{array}{c} 0.55(\text{H-8}{\rightarrow}\text{L}) + 0.26(\text{H-7}{\rightarrow}\text{L}) - 0.12(\text{H-6}{\rightarrow}\text{L}) + \\ 0.19(\text{H-2}{\rightarrow}\text{L}{+1}) - 0.15(\text{H}{\rightarrow}\text{L}{+5}) \end{array}$	0.10
S <sub>13</sub>	255	4.86	$-0.29(H-8\rightarrow L) + 0.61 (H-7\rightarrow L) - 0.14(H-7\rightarrow L+1) + 0.12(H-3\rightarrow L+1)$	0.00
S <sub>14</sub>	250	4.95	$0.19(H-6\rightarrow L+1) - 0.11(H-5\rightarrow L) - 0.41(H-5\rightarrow L+1) + 0.47(H\rightarrow L+2)$	0.01
S <sub>15</sub>	249	4.96	$\begin{array}{c} -0.19(\text{H-8} \rightarrow \text{L}) - 0.18(\text{H-8} \rightarrow \text{L} + 1) + 0.35(\text{H-6} \rightarrow \text{L} + 1) + \\ 0.35(\text{H-5} \rightarrow \text{L} + 1) + 0.17(\text{H-4} \rightarrow \text{L} + 1) + 0.13(\text{H-3} \rightarrow \text{L} + 1) \\ + 0.18(\text{H-2} \rightarrow \text{L} + 1) + 0.24(\text{H} \rightarrow \text{L} + 2) \end{array}$	0.00
S <sub>16</sub>	246	5.04	$\begin{array}{c} 0.15(\text{H-6}{\rightarrow}\text{L+1}) + 0.13(\text{H-4}{\rightarrow}\text{L}) - 0.31(\text{H-4}{\rightarrow}\text{L+1}) + \\ 0.11(\text{H-2}{\rightarrow}\text{L+4}) - 0.20(\text{H}{\rightarrow}\text{L+2}) + 0.15(\text{H}{\rightarrow}\text{L+3}) + \\ 0.51(\text{H}{\rightarrow}\text{L+4}) \end{array}$	0.06
S <sub>17</sub>	244	5.08	$\begin{array}{c} 0.44(\text{H-6}{\rightarrow}\text{L+1}) - 0.29(\text{H-5}{\rightarrow}\text{L+1}) + 0.19(\text{H-1}{\rightarrow}\text{L+2}) \\ - 0.31(\text{H}{\rightarrow}\text{L+2}) - 0.18(\text{H}{\rightarrow}\text{L+4}) \end{array}$	0.00
S <sub>18</sub>	241	5.14	$-0.13(H-6\rightarrow L+1) + 0.67(H-1\rightarrow L+2) + 0.12(H\rightarrow L+2)$	0.06
S <sub>19</sub>	241	5.15	$0.36(H-3\rightarrow L+1) + 0.54(H\rightarrow L+3) - 0.17(H\rightarrow L+4)$	0.00
S <sub>20</sub>	237	5.22	$0.18(H-1\rightarrow L+3) + 0.67(H-1\rightarrow L+4)$	0.01

\*H-HOMO, L-LUMO



Fig. 4. Form of the MO involved in formation of absorption spectrum of the compound PAZB-2 at  $\lambda_{max} = 380$  nm. The experimental absorption spectrum of the compound PAZB-2 (Fig. 5b) has a wide absorption at 383 nm with D = 2.575. Comparison of calculated and experimental absorption spectra of the compound PAZB-2 shows high accuracy of the constructed model calculations (Fig. 5a,b).



**Fig. 5.** UV/Vis spectrum of the PAZB-2 in DMF: a) calculated by TDPBE0/6-31+G\* method and b) experimental at concentration of dye:  $3.6 \cdot 10^{-4}$ M.

**PAZB-8)** As seen in Table 3, intense absorption band with the highest oscillation are observed in  $\lambda_{max} = 378$  nm at f = 1.12. Calculations show that the excited state at 378 nm described by a wave function corresponding to the imposition of the three configurations for single-electron excitations [(H-2 $\rightarrow$ L+1), (H-1 $\rightarrow$ L) and (H $\rightarrow$ L+1)]. Excitation of an electron from (H-1 $\rightarrow$ L) gives the main contribution to the formation of the absorption band at 378 nm (Table 3). According to Fig. 6, the electron density of HOMO-1 is mainly focused on imin group (-C=N-) and aryl ring with substituents hydroxyl and methoxy, whereas LUMO is mainly focused on

double bonds (-C=C-) of two aryl rings and azo group (-N=N). Therefore the electronic transitions from the HOMO-1 to LUMO are due to the contribution of pi ( $\pi$ ) bonds. Molecular orbitals involved in formation of absorption spectrum of the PAZB-8 are demonstrated in Fig. 6.

#### Table 3

Excited	Wavelength	Excitation	Configurations Composition	Oscillator
State	(nm) 528	Energy (ev)	(corresponding transition orbitals)	Strength (I)
$S_1$	328	2.55	$-0.10(\Pi - 3 \rightarrow L) + 0.24(\Pi - 2 \rightarrow L) + 0.04(\Pi \rightarrow L)$	0.00
$\mathbf{S}_2$	376	3.24	$0.20(H-2\rightarrow L) = 0.15(H-2\rightarrow L+1) = 0.51(H-1\rightarrow L)$ 0.16(H \rightarrow L) + 0.52(H \rightarrow L+1)	0.04
C C	278	2 27	$-0.10(H \rightarrow L) + 0.52(H \rightarrow L+1)$ 0.11(H 2 J+1) + 0.58(H 1 J) + 0.27(H J+1)	1.12
	578	5.57	$-0.11(H_4 \to L) + 0.55(H_2 \to L) + 0.24(H_1 \to L)$	1.12
$S_4$	361	3.43	$-0.20(H \rightarrow L) - 0.20(H \rightarrow L+1)$	0.07
S5	311	3.98	$-0.14(H-5\rightarrow L) + 0.52(H-4\rightarrow L) - 0.38(H-3\rightarrow L)$	0.01
~ 5			$-0.13(H-2\rightarrow L) - 0.15(H\rightarrow L+2)$	
S <sub>6</sub>	303	4.09	$0.10(H-6\rightarrow L) - 0.30(H-5\rightarrow L) + 0.15(H-3\rightarrow L)$	0.07
~0			$-0.12(H-3 \rightarrow L+1) - 0.13(H-2 \rightarrow L) + 0.55(H-1 \rightarrow L+1)$	
S <sub>7</sub>	299	4.14	$0.53(H-5\rightarrow L) + 0.26(H-4\rightarrow L) + 0.17(H-3\rightarrow L) +$	0.01
,			$0.24(H-1\to L+1) - 0.13(H\to L+2)$	
S <sub>8</sub>	298	4.16	$0.24(H-6\rightarrow L) - 0.11(H-5\rightarrow L) + 0.30(H-4\rightarrow L) + 0.47(H-2\rightarrow L) - 0.27(H-1\rightarrow L+1) + 0.11(H-L+2)$	0.01
			$\frac{0.4/(H-3\to L)-0.2/(H-1\to L+1)+0.11(H\to L+2)}{0.12(H(L+1)+0.20(H-L+1)+0.20(H-L+1))}$	
$S_9$	296	4.19	$-0.12(H-0\rightarrow L) + 0.62(H-2\rightarrow L+) + 0.20(H\rightarrow L+1)$	0.05
			$-0.15(H \rightarrow L+2)$	
$S_{10}$	288	4.30	$0.1/(H-0\rightarrow L) + 0.24(H-0\rightarrow L) - 0.32(H-0\rightarrow L) + 0.32(H-0\rightarrow L) + 0.32(H-0\rightarrow L+1) + 0.42(H\rightarrow L+2) + 0.11(H\rightarrow L+3)$	0.01
			$- 0.35(H-5\rightarrow L) + 0.16(H-4\rightarrow L) - 0.12(H-2\rightarrow L+1)$	
S <sub>11</sub>	274	4.51	$+ 0.52(H \rightarrow L+2) - 0.18(H \rightarrow L+3)$	0.09
~			$-0.10(H-6\rightarrow L) + 0.59(H-3\rightarrow L+1) + 0.17(H-1\rightarrow L+1)$	
S <sub>12</sub>	264	4.69	$-0.22(H-1\rightarrow L+2) - 0.15(H-1\rightarrow L+4)$	0.09
G	250	4.92	$-0.22(H-6\rightarrow L) + 0.61(H\rightarrow L+3) + 0.10(H\rightarrow L+4)$	0.02
<b>S</b> <sub>13</sub>	230	4.83	$+ 0.13(H \rightarrow L+5)$	0.03
c	252	4.00	$-0.24(H-6\rightarrow L+1) - 0.15(H-5\rightarrow L+1) + 0.56(H-4\rightarrow L+1)$	0.00
<b>S</b> <sub>14</sub>	233	4.90	- $0.12(H-3\rightarrow L+1)-0.23(H-1\rightarrow L+2)-0.15(H\rightarrow L+4)$	0.00
c	240	4.07	$0.16(H-4\rightarrow L+1) + 0.13(H-3\rightarrow L+1) + 0.60(H-1\rightarrow L+2)$	0.00
<b>S</b> <sub>15</sub>	249	4.97	- 0.10(H-1→L+4) - 0.24(H→L+4)	0.00
S	245	5.06	$0.18(H-4\rightarrow L+1) - 0.18(H-2\rightarrow L+2) + 0.13(H-1\rightarrow L+2)$	0.05
<b>S</b> <sub>16</sub>	243	5.00	$+ 0.58(H \rightarrow L+4) - 0.15(H \rightarrow L+5)$	0.03
S <sub>17</sub>	241	5.14	$0.10(H-5\rightarrow L+1) - 0.16(H\rightarrow L+3) + 0.62(H\rightarrow L+5)$	0.00
S <sub>18</sub>	237	5.23	$0.19(H-6 \rightarrow L+1) + 0.61(H-5 \rightarrow L+1) + 0.23(H-4 \rightarrow L+1)$	0.04
S <sub>19</sub>	236	5.26	$0.65(H-2\rightarrow L+2) + 0.15(H\rightarrow L+4)$	0.01
S <sub>20</sub>	233	5.32	$-0.40(H-7\rightarrow L) + 0.53(H-1\rightarrow L+3) - 0.14(H-1\rightarrow L+4)$	0.01

Electronic absorption spectrum of the compound PAZB-8 calculated by TDPBE0/6-31+G\* method.

\*H-HOMO, L-LUMO



HOMO-1



LUMO



![](_page_16_Figure_6.jpeg)

![](_page_16_Figure_7.jpeg)

LUMO+1

![](_page_16_Figure_9.jpeg)

HOMO-6

.

![](_page_16_Figure_11.jpeg)

LUMO+2

![](_page_16_Picture_13.jpeg)

LUMO+4

![](_page_16_Figure_15.jpeg)

The experimental UV/Vis spectrum of the PAZB-8 in DMF (Fig. 7b) has a wide absorption at about 310-430 nm which characterized by maximum at 373 nm with D = 0.946 and calculated spectrum in DMF (Fig. 7a) shows the highest oscillation in 378 nm at f = 1.12.

![](_page_17_Figure_2.jpeg)

**Fig. 7.** UV/Vis spectrum of the PAZB-8 in DMF: a) calculated by TDPBE0/6-31+G\* method and b) experimental at concentration of dye: 3.6·10<sup>-4</sup>M.

#### 2.3.3 Frontier molecular orbital analysis of compounds PAZB-1, PAZB-2, PAZB-8

Quantum chemical methods are important for obtaining information about molecular structure and electrochemical behavior. The frontier molecular orbitals (FMO) analysis plays an important role in the electronic and optical properties, as well as in UV/Vis spectrum and chemical

reactions. The values of energy of the highest occupied molecular orbital ( $E_{HOMO}$ ) can act as an electron donor and the lowest unoccupied molecular orbital (E<sub>LUMO</sub>) can act as the electron acceptor. Also the HOMO-LUMO energy gap is a important parameter in determining molecular electrical transport properties. For the compound PAZB-1, LUMO energy is -5.85 eV and HOMO -2.44 eV. The energy gap of HOMO-LUMO (3.41 eV) explains the ultimate charge transfer interaction within the molecule (Table 4). The energy of HOMO is directly related to the ionization potential ( $I = -E_{HOMO}$ ), while the energy of LUMO is related to the electron affinity (A = -  $E_{LUMO}$ ). The global hardness ( $\eta = I - A/2$ ), electronegativity ( $\chi = I + A/2$ ), electronic chemical potential  $(\mu = -(I + A)/2)$  and electrophilicity  $(\omega = \mu^2/2\eta)$  [6], chemical softness  $(S=1/\eta)$  [10] are calculated. The global hardness (n) corresponds to the HOMO-LUMO energy gap. A molecule with a small energy gap has high chemical reactivity, low kinetic stability and is a soft molecule, while a hard molecule has a large energy gap [10]. Electronegativity ( $\chi$ ) is a measure of the power of an atom or a group of atoms to attract electrons and the chemical softness (S) describes the capacity of an atom or a group of atoms to receive electrons. These values for structures PAZB-1, PAZB-2, PAZB-8 are summarized inTable 4.

#### Table 4

Property	PAZB-1	PAZB-2	PAZB-8
E <sub>HOMO</sub> (eV)	-5.85	-5.59	-5.24
E <sub>LUMO</sub> (eV)	-2.44	-2.17	-1.66
Energy gap (eV)	3.41	3.42	3.58
Ionisation potential, <i>I</i> (eV)	5.85	5.59	5.24
Electron affinity, A (eV)	2.44	2.17	1.66
Electronegativity, $\chi(eV)$	4.14	3.88	3.45
Global hardness, $\eta(eV)$	1.70	1.71	1.79
Chemical potential, $\mu(eV)$	-4.14	-3.88	-3.45
Global electrophilicity, $\omega$ (eV)	5.04	4.40	3.32
Chemical softness, $S(eV^{-1})$	0.59	0.58	0.56
Dipole moment (Debye)	2.1967	4.4138	8.7451

The calculated electronic properties of the compounds PAZB-1, PAZB-2, PAZB-8.

Total electronic densities of states (DOSs) [10] of the compounds PAZB-1, PAZB-2, PAZB-8 were computed (Fig. 8). The DOS analysis indicates that the HOMO–LUMO energy gaps (Eg) of the compounds PAZB-1, PAZB-2, PAZB-8 are about 3.41 eV, 3.42 eV and 3.58 eV at the PBE0/6-31+G\*method, respectively. The energy gap of the compound PAZB-8 has the highest value (3.58 eV) therefore it is less reactive compared with structures PAZB-1 and PAZB-2. It implies that the electronic transfer in the molecules PAZB-1 and PAZB-2 is easier.

![](_page_19_Figure_2.jpeg)

Fig. 8. Calculated DOS plots of the compounds PAZB-1, PAZB-2, PAZB-8 by PBE0/6-31+G\* method.

#### 2.3.4 Natural charge analysis of the compounds PAZB-1, PAZB-2, PAZB-8

The atomic charges play an important role on molecular polarizability, dipole moment, electronic structure and lot of related properties of molecular systems. The charge distributions over the atoms suggest the formation of donor and acceptor pairs involving the charge transferring the molecule. We calculated the charge distributions for equilibrium geometry of the compound PAZB-1, PAZB-2, PAZB-8 by the NBO (natural charge) charges [6] using the PBE0/6-31+G\* level of energy. The Fig. 9 shows results of natural charges in graphical form (Atoms labeling is according to Fig. 1).

![](_page_20_Figure_2.jpeg)

![](_page_21_Figure_1.jpeg)

Fig. 9. Natural charges distribution of the compounds PAZB-1, PAZB-2, PAZB-8 calculated by PBE0/6-31+G\* method.

The total charge of the investigated compounds is equal to zero. The natural charge (NBO) analysis of the title compounds show that carbon atoms have both positive and negative charges magnitudes. According to results, all carbon atoms of the compound PAZB-1 have negative charge excepting C6, C11, C14 and C16 atoms due to attachment to nitrogen atoms. Also in the compounds PAZB-2 and PAZB-8, the positive carbons are observed for the carbons atoms attachment to the electron-withdrawing nitrogen and oxygen atoms (C6, C9, C12, C16, C20, C21 atoms for PAZB-2 and C6, C11, C14, C16, C21, C22 atoms for PAZB-8). The highest negative charge in the compounds PAZB-1, PAZB-2 and PAZB-2 and PAZB-3 is observed for N15 (-0.475e), O23 (-0.679e) and O23 (-0.693e) atoms, respectively. According to Natural charge's plot (Fig. 9) all hydrogen atoms have the positive charge (0.491e for PAZB-8 and 0.504e for PAZB-8) compared with other hydrogen atoms due to the electron-withdrawing nature of the O23, therefore it is more acidic.

#### 2.3.5 NBO analysis of the compounds PAZB-1, PAZB-2, PAZB-8

Natural bond orbital (NBO) analysis is important method for studying intra- and inter-molecular bonding and interaction between bonds [17]. Electron donor orbital, acceptor orbital and the interacting stabilization energy resulting from the second-order micro disturbance theory are reported in Table 5.

#### Table 5

Significant donor–acceptor interactions and second order perturbation energies of the compound PAZB-2 calculated using the PBE0/6-31+G\* level of energy.

Donor (i)	Occupancy	Acceptor (j)	Occupancy	E <sup>(2)a</sup>	E(j)-E(i) <sup>b</sup>	F(i,j) <sup>c</sup>
				kcal/mol	a.u.	a.u.
π(C1-C6)	1.61401	π*(C2-C3)	0.32682	19.36	0.28	0.067
× ,		$\pi^{*}(C4-C5)$	0.29037	19.17	0.28	0.067
		π*(N7-N8)	0.22149	20.09	0.23	0.063
$\pi$ (C2-C3)	1.65964	$\pi^{*}(C1-C6)$	0.37340	20.95	0.28	0.069
		$\pi^{*}(C4-C5)$	0.29037	18.44	0.29	0.066
$\pi$ (C4-C5)	1.67718	$\pi^{*}(C1-C6)$	0.37340	19.19	0.28	0.067
		$\pi^{*}(C2-C3)$	0.32682	20.58	0.28	0.068
π(N7-N8)	1.98696	$\pi^{*}(C1-C6)$	0.37340	10.73	0.39	0.062
		$\pi^{*}(C9-C10)$	0.38560	10.62	0.39	0.062
$\pi$ (C9-C10)	1.60982	$\pi^{*}(N7-N8)$	0.22149	21.23	0.23	0.065
		$\pi^{*}(C11-C12)$	0.38468	19.01	0.28	0.065
		$\pi^{*}(C13-C14)$	0.26588	18.78	0.29	0.068
$\pi$ (C11-C12)	1.62335	$\pi^{*}(C9-C10)$	0.38500	23.07	0.28	0.072
		$\pi^{*}(C13-C14)$	0.26588	15.81	0.29	0.062
$\pi^{*}(N7-N8)$	0.22149	$\pi^{*}(C1-C6)$	0.37340	26.69	0.05	0.059
		$\pi^{*}(C9-C10)$	0.38560	28.87	0.05	0.060
$\pi^{*}(C11-C12)$	0.38468	$\pi^{*}(C13-C14)$	0.26588	213.14	0.01	0.080
$\pi^{*}(C19-C20)$	0.39118	$\pi^*(C17-C18)$	0.39432	242.37	0.01	0.081
		$\pi^{*}(C21-C22)$	0.31198	157.21	0.02	0.081
σ(C1-C2)	1.97983	σ*(C1-C6)	0.02145	2.54	1.26	0.051
		σ*(C2-C3)	0.01557	2.51	1.27	0.051
		σ*(C6-N7)	0.02853	3.14	1.13	0.053
σ(C2-C3)	1.98124	σ*(C3-C4)	0.01600	2.35	1.26	0.049
σ(C3-C4)	1.98141	σ*(C2-C3)	0.01557	2.37	1.27	0.049
		σ*(C4-C5)	0.01430	2.45	1.28	0.051
σ(C4-C5)	1.97886	σ*(C6-N7)	0.02853	4.32	1.13	0.062
σ(C5-C6)	1.97926	σ*(C4-C5)	0.01430	2.47	1.28	0.050
		σ*(C6-N7)	0.02853	0.78	1.12	0.027
σ(C6-N7)	1.98020	σ*(C1-C2)	0.01391	1.87	1.34	0.045
σ(C9-C14)	1.97900	σ*(N8-C9)	0.02796	0.84	1.13	0.027
σ(N15-C16)	1.98712	σ*(C12-C13)	0.02500	2.08	1.43	0.049
σ(C20-C21)	1.97408	σ*(C19-C20)	0.02457	2.96	1.26	0.055
	·	σ*(C21-C22)	0.02315	2.87	1.30	0.055
		σ*(O24-C25)	0.00920	0.58	1.00	0.022
σ(C21-O24)	1.98983	σ*(C17-C22)	0.02032	1.55	1.44	0.042
		σ*(C19-C20)	0.02457	1.44	1.43	0.041
n1(N7)	1.95732	σ*(C1-C6)	0.02145	0.60	0.97	0.022
		σ*(C5-C6)	0.03143	8.21	0.96	0.080

		σ*(C9-C10)	0.02155	0.82	0.97	0.025
		σ*(C14-H34)	0.01536	0.66	0.88	0.022
n1(N8)	1.95649	σ*(C1-C6)	0.02145	0.82	0.97	0.025
		σ*(C5-H30)	0.01554	0.69	0.88	0.022
		σ*(C9-C10)	0.02155	0.65	0.97	0.22
		σ*(C9-C14)	0.03189	8.40	0.96	0.080
n1(N15)	1.87899	σ*(C12-C13)	0.02500	0.71	0.89	0.023
		σ*(C16-C17)	0.03141	2.83	0.83	0.044
		σ*(C16-H35)	0.04016	13.09	0.76	0.091
n1(O23)	1.97856	σ*(C19-C20)	0.02457	6.08	1.16	0.075
		σ*(C25-H41)	0.02034	0.67	1.06	0.024
n2(O23)	1.86455	$\pi^*(C19-C20)$	0.39118	29.22	0.35	0.097
n1(O24)	1.95038	σ*(C20-C21)	0.04487	6.87	1.02	0.075
		σ*(C21-C22)	0.02315	0.51	1.08	0.021
		$\pi^*(C21-C22)$	0.31198	2.26	0.53	0.033
n2(O24)	1.90766	σ*(C20-C21)	0.04487	2.44	0.87	0.042
		σ*(C21-C22)	0.02315	5.09	0.94	0.063
		$\pi^*(C21-C22)$	0.31198	9.16	0.38	0.056

<sup>a</sup>E<sup>(2)</sup>Energy of hyperconjucative interactions,

<sup>b</sup> Energy difference between donor and acceptor i and j NBO orbitals.

<sup>c</sup> F(i, j) is the Fock matrix element between i and j NBO orbitals.

The electron delocalization from filled NBOs (donors) to the empty NBOs (acceptors) describes a conjugative electron transfer process between them. For each donor (*i*) and acceptor (*j*), the stabilization energy  $E^{(2)}$  associated with the delocalization  $i \rightarrow j$  is estimated:

$$E^{(2)} = \Delta E_{ij} = q_i \frac{F(i,j)^2}{\varepsilon_j - \varepsilon_i}$$
(2)

where  $q_i$  is the donor orbital occupancy,  $\varepsilon_j$  and  $\varepsilon_i$  are diagonal elements and F(i,j) is the off diagonal NBO Fock matrix element. The resonance energy ( $E^{(2)}$ ) detected the quantity of participation of electrons in the resonance between atoms. The larger  $E^{(2)}$  value, the more intensive is the interaction between electron donors and acceptor, i.e. the more donation tendency from electron donors to electron acceptors and the greater the extent of conjugation of the whole system [18]. Delocalization of electron density between occupied Lewis-type (bond or lone pair) NBO orbitals and formally unoccupied (antibond or Rydgberg) non Lewis NBO orbitals correspond to a stabilization donor–acceptor interaction. NBO analysis has been performed for the title compound at the PBE0/6-31+G\* level of energy in order to elucidate the intramolecular,

rehybridization and delocalization of electron density within the compound PAZB-2. The strong, moderate and weak intramolecular hyperconjugative interactions of the title compound such as  $\pi \rightarrow \pi^*, \pi^* \rightarrow \pi^*, \sigma \rightarrow \sigma^*, n \rightarrow \sigma^*$  and  $n \rightarrow \pi^*$  transitions are presented in Table 5. According to NBO analysis, the  $\sigma(C4-C5)\rightarrow\sigma^*(C6-N7)$  transition has the highest resonance energy (4.32 kcal/mol) compared with other  $\sigma \rightarrow \sigma^*$  transitions of the title compound. The  $\sigma(C1-C2)$  orbital in phenyl ring participates as donor and the anti-bonding  $\sigma^*(C1-C6), \sigma^*(C2-C3)$  and  $\sigma^*(C6-N7)$  orbitals act as acceptor with resonance energies (E<sup>(2)</sup>) of is 2.54 kcal/mol, 2.51 kcal/mol and 3.14 kcal/mol, respectively. These values indicate  $\sigma(C1-C2)\rightarrow\sigma^*(C6-N7)$  transition has the highest resonance energy (3.14 kcal/mol) compared with  $\sigma(C1-C2)\rightarrow\sigma^*(C1-C6)$  and  $\sigma(C1-C2)\rightarrow\sigma^*(C2-C3)$ .

The intramolecular hyperconjugative interactions of the  $\pi \rightarrow \pi^*$  transitions in phenyl ring that lead to a strong delocalization are such as C9-C10 $\rightarrow$ N7-N8 and C11-C12 $\rightarrow$ C9-C10 with resonance energies (E<sup>(2)</sup>) 21.23 kcal/mol and 23.07 kcal/mol, respectively. The important intramolecular hyperconjugative interaction of the  $\pi \rightarrow \pi^*$  in phenyl ring is C20-C21 $\rightarrow$ C18-C19 transition that show the strong stabilization energy of 26.54 kcal/mol. The  $\pi^* \rightarrow \pi^*$  transitions have the highest resonance energies compared with other interactions of the title compound such as C11-C12 $\rightarrow$ C13-C14, C19-C20 $\rightarrow$ C17-C18 and C19-C20 $\rightarrow$ C21-C22 with resonance energies (E<sup>(2)</sup>) 213.14, 242.37 and 157.21 kcal/mol respectively, that lead to stability of the title compound. The strongest  $n \rightarrow \sigma^*$  interactions are due to  $n1(N15) \rightarrow \sigma^*(C16-H35)$ ,  $n2(O23) \rightarrow \pi^*(C19-C20)$  and  $n2(O24) \rightarrow \pi^*(C21-C22)$  interactions with stabilization energies of 13.09 kcal/mol, 29.22 kcal/mol and 9.16 kcal/mol, respectively.

The results of NBO analysis such as the occupation numbers with their energies for the interacting NBOs [interaction between natural bond orbital A and natural bond orbital B (A-B)]

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and the polarization coefficient amounts of atoms in title compound are presented using the  $PBE0/6-31+G^*$  method is summarized in Table 6 (Atoms labeling is according to Fig. 1).

#### Table 6

Calculated natural bond orbitals (NBO) and the polarization coefficient for each hybrid in selected bonds of the compound PAZB-2 using the PBE0/6-31+G\* level of energy.

Occupancy (a.u.)	Bond (A-B) <sup>a</sup>	Energy (a.u.)	ED <sub>A</sub> (%)	$ED_B(\%)$	NBO	S(%) (A)	S(%) (B)	P(%) (A)	P(%) (B)
1.97983	σ(C1-C2)	-0.68703	50.12	49.88	$0.7080 (sp^{1.81}) + 0.7063 (sp^{1.85})$	35.57	35.10	64.39	64.85
1.97671	σ(C1-C6)	-0.68300	49.37	50.63	0.7027 (sp <sup>1.89</sup> ) + 0.7115 (sp <sup>1.85</sup> )	34.59	35.06	65.36	64.90
1.61401	π(C1-C6)	-0.23932	48.25	51.75	$0.6946 (sp^{1.00}) + 0.7194 (sp^{1.00})$	0.00	0.00	99.96	99.98
1.98124	σ(C2-C3)	-0.72102	50.05	49.95	$0.7074 (sp^{1.84}) + 0.7068 (sp^{1.84})$	35.15	35.25	64.81	64.71
1.97926	σ(C5-C6)	-0.68418	49.37	50.63	0.7026 (sp <sup>1.95</sup> ) + 0.7116 (sp <sup>1.72</sup> )	33.83	36.75	66.13	63.22
1.98020	σ(C6-N7)	-0.75387	41.44	58.56	0.64.37 (sp <sup>2.56</sup> ) + 0.7653 (sp <sup>2.13</sup> )	28.06	31.89	71.84	68.03
1.98696	σ(N7-N8)	-0.93713	49.92	50.08	$0.7065 (sp^{2.30}) + 0.7077 (sp^{2.30})$	30.24	30.31	69.64	69.58
1.90724	π(N7-N8)	-0.35162	50.26	49.74	$0.7090 (sp^{1.00}) + 0.7052 (sp^{1.00})$	0.00	0.00	99.73	99.72
1.98035	σ(N8-C9)	-0.75993	58.63	41.37	0.7657 (sp <sup>2.09</sup> ) + 0.6432 (sp <sup>2.53</sup> )	32.30	28.33	67.62	71.57
1.97639	σ(C9-C10)	-0.68343	50.48	49.52	0.7105 (sp <sup>1.86</sup> ) + 0.7037 (sp <sup>1.88</sup> )	34.93	34.67	65.03	65.29
1.98123	σ(C12-N15)	-0.76729	41.02	58.98	0.6405 (sp <sup>2.48</sup> ) + 0.7680 (sp <sup>2.00</sup> )	28.73	33.25	71.21	66.60
1.98712	σ(N15-C16)	-0.86850	38.95	33.14	0.7716 (sp <sup>1.56</sup> ) + 0.6361 (sp <sup>2.02</sup> )	38.95	33.14	60.86	66.80
1.90455	π(N15-C16)	-0.32318	59.35	40.65	$0.7704 (sp^{99.99}) + 0.6376 (sp^{99.99})$	0.43	0.41	99.33	99.50
1.97570	σ(C17-C18)	-0.69320	50.86	49.14	$0.7131 (sp^{1.94}) + 0.7010 (sp^{1.83})$	33.96	35.28	66.01	99.98
1.99456	σ(C20-O23)	-0.92292	33.00	67.00	$0.5745 (sp^{3.04}) + 0.8185 (sp^{1.88})$	24.72	34.66	75.07	65.27
1.98983	σ(C21-O24)	-0.86920	33.62	66.38	0.5798 (sp <sup>2.90</sup> ) + 0.8248 (sp <sup>2.17</sup> )	25.59	31.56	74.22	68.36
1.98651	σ(C16-H35)	-0.53595	60.36	39.64	$0.7769 (sp^{2.19}) + 0.6296 (s)$	31.29	100	68.65	-
1.99739	σ(C25-H40)	-0.51755	60.46	39.54	$0.7776 (sp^{2.81}) + 0.6288 (s)$	26.26	100	73.67	-
1.98335	σ(C3-H28)	-0.51779	61.94	38.06	$0.7870 (sp^{2.37}) + 0.6170 (s)$	29.64	100	70.30	-
1.98854	σ(O23-H39)	-0.74729	74.80	25.20	$0.8649 (sp^{3.85}) + 0.5020 (s)$	20.61	100	79.29	-
1.95732	n1(N7)	-0.39311	-	-	sp <sup>1.62</sup>	38.10	-	61.84	-
1.95649	n1(N8)	-0.39247	-	-	sp <sup>1.66</sup>	37.62	-	62.33	-
1.87899	n1(N15)	-0.33363	-	-	sp <sup>2.66</sup>	27.31	-	72.55	-
1.97856	n1(O23)	-0.60742	-	-	sp <sup>1.24</sup>	44.69	-	55.25	-
1.86455	n2(O23)	-0.33102	-	-	sp <sup>1.00</sup>	0.00	-	99.88	-
1.95038	n1(O24)	-0.49408	-	-	sp <sup>2.02</sup>	33.07	-	66.86	-
1.90766	n2(O24)	-0.34871	-	-	${ m sp}^{10.00}$	9.08	-	90.84	-

<sup>a</sup> A-B is the bond between atom A and atom B. (A: natural bond orbital and the polarization coefficient of atom; A-B: natural bond orbital and the polarization coefficient of atom B).

The size of polarization coefficients shows the importance of the two hybrids in the formation of the bond. The differences in electronegativity of the atoms involved in the bond formation are

reflected in the larger differences in the polarization coefficients of the atoms (C-O, C-H C-N bonds). The calculated bonding orbital for the σ(C20-O23) bond is the  $\sigma = 0.5745(sp^{3.04}) + 0.8185(sp^{1.88})$  with high occupancy 1.99456 a.u. and low energy -0.92292 a.u. The polarization coefficients of C20=0.5745 and O23=0.8185 shows importance of O23 in forming  $\sigma$ (C20-O23) bond compared with C20 atom. The calculated bonding orbital for the  $\sigma(N7-N8)$  bond is  $\sigma=0.7065(sp^{2.30})+0.7077(sp^{2.30})$  with low energy -0.93713 a.u. and high occupancy 1.98696 a.u. The polarization coefficients of N7=0.7065 and N8=0.7077 shows low difference in polarization coefficients N7 and N8 atoms in N7-N8 bond and importance of two atoms in forming bond. According to NBO analysis, the natural hybrid orbital n2(O23) with low occupancy 1.86455 a.u. and high energy -0.33102 a.u. has p-character (99.88%), whereas n1(O23) occupy a lower energy orbital (-0.60742 a.u) with p-character (55.25%) and high occupation number (1.97856 a.u). The pure p-type lone pair orbital n2(O23) participates the electron donation to  $\pi^*(C19-c20)$  for  $n_2(O23) \rightarrow \pi^*(C19-C20)$  interaction with high resonance energies  $(E^{(2)})$  29.22 kcal/mol in the title compound. Also the natural hybrid orbital n1(N15) with occupancy 1.87899 a.u. has p-character (72.55%), whereas n1(N7) and n1(N8) have p-character (61.84%) and (62.33%). From Table 5, it is found that the p-type lone pair orbital n1(N15) participates the electron donation to  $\sigma^*(C16-H35)$  forn1(N15) $\rightarrow \sigma^*(C16-H35)$  interaction with high resonance energies ( $E^{(2)}$ ) 13.09 kcal/mol.

#### 2.4.1 Synthesis of the compounds PAZA-1, PAZB-2, PAZB-8

![](_page_27_Figure_1.jpeg)

Fig. 10. Scheme of synthesis of the compounds PAZB-1, PAZB-2 and PAZB-8.

**PAZB-1:** A mixture of 4-aminoazobenzne (1) (2 mmol) and aldehyde (2) (2 mmol) in 30 ml methanol was prepared. Then 2 drops of glacial acetic acid was added to the mixture and was refluxed for 1 h. The hot solution was filtered through a paper filter, cooled and left for 15 h. at 0-5°C. The solid was dissolved in cold methanol and washed with water and dried at 22-25 °C.

**PAZB-2:** A mixture of 4-aminoazobenzne (1) (2.4 mmol) and aldehyde (2.1) (2 mmol) in 33 ml methanol was prepared. Then 3 drops of glacial acetic acid was added to the mixture and was refluxed for 2 h. The hot solution was filtered through a paper filter, cooled and left for 10 h. at 0-5°C. The solid was dissolved in cold methanol and washed with water and dried at 22-25 °C.

**PAZB-8:** A mixture of 4-aminoazobenzne (1) (2.6 mmol) and aldehyde (2.3) (2 mmol) in 28 ml methanol was prepared. Then 4 drops of glacial acetic acid was added to the mixture and was refluxed for 4 h. The hot solution was filtered through a paper filter, cooled and left for 7 h. at 10

°C. The solid was dissolved in cold methanol and washed with water and dried at 22-25 °C (Fig.10).

#### 2.4.2 Vibrational frequencies of the compounds PAZB-1, PAZB-2, PAZB-8

In order to confirm the accuracy of our findings, IR spectroscopy was used. The theoretical IR spectra of optimized PAZB-1, PAZB-2, PAZB-8 was calculated using the PBE0/6-31+G\* method. The important calculated and experimental vibrational frequencies of PAZB-1, PAZB-2, PAZB-8 are summarized in Table 7, Table 8 and Table 9, respectively. The experimental and calculated spectra of the title compounds are found to be in good agreement with each other. The title compounds have the main vibrational modes:

**PAZB-1)** 1622 cm<sup>-1</sup> (C=N stretching vibration),1572 cm<sup>-1</sup> (N=N stretching vibration), 1285 cm<sup>-1</sup> (N stretching vibration), that indicates the presence of PAZB-1 (Table 7).

**PAZB-2)** 1620 cm<sup>-1</sup> (C=N stretching vibration), 1599 cm<sup>-1</sup> (N=N stretching vibrations), 1261 cm<sup>-1</sup> (C-N stretching vibration), 1571 cm<sup>-1</sup>(C-O stretching vibration), 1302 cm<sup>-1</sup>(O-H bending vibration), 3090 cm<sup>-1</sup> (asymmetric C-H stretching vibrations of CH<sub>3</sub>) that indicates the presence of PAZB-2 (Table 8).

**PAZB-8)** 1614 cm<sup>-1</sup> (C=N stretching vibration), 1578 cm<sup>-1</sup> (N=N stretching vibrations), 1221 cm<sup>-1</sup> (C-N stretching vibration), 1560 cm<sup>-1</sup>(C-O stretching vibration), 1278 cm<sup>-1</sup>(O-H bending vibration), 3075 cm<sup>-1</sup> (asymmetric C-H stretching vibrations of CH<sub>3</sub>) that indicates the presence of PAZB-8 (Table 9).

#### Table 7

Experimental and calculated vibrational frequencies and their assignment of PAZB-1 by using PBE0/6-31+G\* method.

$v_{exp}$ (cm <sup>-1</sup> )	$v_{cal.}$ (cm <sup>-1</sup> )	Assignment
562	580.99	C-H aromatic bending vibrations, out of plane
687	673.48	C-H aromatic bending vibrations, out of plane
760	769.95	C-H aromatic bending vibrations, out of plane

877	879.20	C-H aromatic bending vibrations, out of plane
970	974.84	C-H aromatic bending vibrations, out of plane
1001	1006.21	C-H aromatic bending vibrations, out of plane
1103	1106.2	C-H aromatic bending vibrations
1141	1136.16	C-H aromatic bending vibrations
1155	1154.61	C-N stretching vibrations, C-H aromatic bending vibrations
1186	1172.79	C-N stretching vibrations, C-H aromatic bending vibrations
1220	1229.06	C-N stretching vibrations, C-H aromatic bending vibrations
1285	1273.31	C-N stretching vibrations, C-H aromatic bending vibrations
1310	1317.33	C-H aromatic bending vibrations
1363	1351.55	C=C aromatic ring stretching vibrations, C-H aromatic bending vibrations
1448	1453.02	N=N stretching vibrations, C=C aromatic stretching vibrations
1493	1492.67	N=N stretching vibrations, C=C aromatic stretching vibrations
1572	1547.15	N=N stretching vibrations, C=C aromatic stretching vibrations
1585	1561.24	C-H bending vibrations of N=C-H
1622	1642.52	C=N stretching vibrations
3040	3044.32	C-H stretching vibrations of N=C-H
3059	3183.25	Asymmetric C-H aromatic stretching vibrations
3090	3185.25	Asymmetric C-H aromatic stretching vibrations

#### Table <mark>8</mark>

Experimental and calculated vibrational frequencies and their assignment of PAZB-2 by using PBE0/6-31+G\*

method.

$v_{exp.}$ (cm <sup>-1</sup> )	$v_{cal.}$ (cm <sup>-1</sup> )	Assignment
685	702.67	C-H aromatic bending vibrations, out of plane
766	791.43	C-H aromatic bending vibrations, out of plane
870	885.57	C-H aromatic bending vibrations, out of plane
920	915.16	C-H aromatic bending vibrations, out of plane
970	983.74	C-H aromatic bending vibrations, out of plane
1124	1133.30	C-H aromatic bending vibrations
1160	1167.00	C-N stretching vibrations, C-H aromatic bending vibrations
1177	1181.35	C-H aromatic bending vibrations
1210	1218.80	C-N stretching vibrations, C-H aromatic bending vibrations
1261	1270.20	C-N stretching vibrations, C-H aromatic bending vibrations
1284	1288.61	C-O stretching vibrations, O-H bending vibrations
1302	1302.28	C-H aromatic bending vibrations
1385	1392.11	C=C aromatic stretching vibrations, O-H bending vibrations
1427	1426.57	C-H bending vibrations of N=C-H
1463	1461.16	N=N stretching vibrations, C=C aromatic stretching vibrations
1515	1519.31	N=N stretching vibrations, C-H aromaticbending vibrations
1571	1559.79	C-O stretching vibrations, C=C aromatic stretching vibrations
1599	1610.83	N=N stretching vibrations, C=C aromatic stretching vibrations
1620	1637.33	C=N stretching vibrations
3001	3027.39	C-H stretching vibrations of N=C-H
3040	3037.34	Symmetric C-H stretching vibrations of CH <sub>3</sub>
3060	3113.84	Asymmetric C-H stretching vibrations of CH <sub>3</sub>
3085	3156.78	Asymmetric C-H stretching vibrations of CH <sub>3</sub>
3090	3167.82	Asymmetric C-H stretching vibrations of CH <sub>3</sub>

Experimental and calculated vibrational frequencies and their assignment of PAZB-8 by using PBE0/6-31+G\* method.

$v_{exp.}(cm^{-1})$	$v_{cal.}$ (cm <sup>-1</sup> )	Assignment
535	538.63	C-H aromatic bending vibrations, out of plane
809	811.25	C-H aromatic bending vibrations, out of plane
845	837.28	C-H aromatic bending vibrations, out of plane
870	859.77	C-H aromatic bending vibrations, out of plane
930	933.03	C-H aromatic bending vibrations, out of plane
971	973.27	C-H aromatic bending vibrations, out of plane
1132	1136.40	C-H aromatic bending vibrations, out of plane
1145	1152.58	C-N stretching vibrations, C-H aromatic bending vibrations
1200	1191.27	C-H aromatic bending vibrations
1221	1236.12	C-N stretching vibrations, C-H aromatic bending vibrations
1251	1251.27	C-O stretching vibrations, O-H bending vibrations
1278	1281.81	C-O stretching vibrations, O-H bending vibrations
1304	1320.07	C-O stretching vibrations, C=C aromatic stretching vibrations
1340	1340.89	C=C aromatic stretching vibrations, C-H aromatic stretching vibrations
1436	1456.30	C=C aromatic stretching vibrations
1491	1499.22	C-H bending vibrations of CH <sub>3</sub>
1512	1513.89	C=C aromatic stretching vibrations, C-Hbending vibrations of CH <sub>3</sub>
1560	1560.35	C-O stretching vibrations, C=C aromatic stretching vibrations
1578	1591.35	N=N stretching vibrations, C=C aromatic stretching vibrations
1614	1635.74	C=N stretching vibrations, C=C aromatic stretching vibrations
3005	3039.45	Symmetric C-H stretching vibrations of CH <sub>3</sub>
3030	3091.93	C-H stretching vibrations of N=C-H
3050	3104.10	Asymmetric C-H stretching vibrations of CH <sub>3</sub>
3075	3168.77	Asymmetric C-H stretching vibrations of CH <sub>3</sub>

# 2.5 Polarization properties of PVA-films containing the compounds PAZB-1, PAZB-2,

#### PAZB-8

The main optical properties of polarizing films such as Transmittance ( $T_{max}$ ,  $T_{min}$ ), Polarizing Efficiency (PE) and Dichroic Ratio ( $R_d$ ) were evaluated at the absorption maximum of the polarizing films according to Eqs. (3,4) [15]:

$$PE = (T_{max} - T_{min}) / (T_{max} + T_{min})^* 100$$
(3)  

$$R_d = D_{max} / D_{min}$$
(4)

Where,  $T_{max}$ ,  $T_{min}$ ,  $D_{max}$  and  $D_{min}$ - Absorbance and Transmittance for linearly polarized light parallel and perpendicular to direction of stretching of colored PVA-film. Multi-angle spectral photometric measurements were performed for all samples in the spectral range from 200-600 nm at incidence angles of 7°, 10°, 20°, 30°, and 40° for s- and p-polarized light. In all optical

characterization and reverse-engineering procedures throughout this study, we used measurement data taken in the spectral range from 300-500 nm only. Polarizing Efficiency (PE) of colored oriented PVA-films depends on the concentration of injected PAZB-1, PAZB-2 and PAZB-8 and Stretching Degree ( $R_s = 3.5$ ) of the films, therefore the optimum concentration of the PAZB-1, PAZB-2 and PAZB-8 in PVA-film was obtained (Fig. 11).

![](_page_31_Figure_2.jpeg)

(b)

![](_page_32_Figure_1.jpeg)

**Fig. 11.** Transmission spectra (1,2) and polarizing efficiency (3) of the film containing 0.3 wt. % of: a) PAZB-1, b) PAZB-2, c) PAZB-8 [Rs = 3.5; 1- T<sub>||</sub>, 2-T<sub>⊥</sub>, 3-PE]

#### Table 10

Main optical parameters of PVA-films containing PAZB-1, PAZB-2 and PAZB-8.

Dyes, λ <sub>max</sub> nm	D <sub>max</sub>	D <sub>min</sub>	T <sub>max</sub>	T <sub>min</sub>	РЕ	R <sub>d</sub>
PAZB-1,406	2.00	0.18	66.0	1.0	97	11.1
PAZB-2,408	1.60	0.15	71.0	2.5	93	10.7
PAZB-8,408	1.63	0.14	72.5	2.3	93	11.6

**PAZB-1:** Changes in concentration of the PAZB-1 from 0.10 to 0.30 wt. % in the colored oriented PVA-film show that with increasing concentration of the PAZB-1, maximum light transmission in parallel and perpendicular direction are reduced. At [PAZB-1] = 0.30 wt. %  $T_{max}$  = 66.0 %,  $T_{min}$  = 1.0 %. PVA-film effectively polarizes the light from UV (377 nm) to Visible region (433 nm) of spectrum with PE = 97-99 %.R<sub>d</sub>=D<sub>max</sub>/D<sub>min</sub>=2.0/0.18= 11.1 (Table 10).

Absorption peak of the PAZB-1 in PVA matrix has bathochromic shift at 39 nm (406 nm –367 nm) (Fig. 3b,11a).

**PAZB-2:** Changes in concentration of the PAZB-2 from 0.10 to 0.30 wt. % in the colored oriented PVA-film show that with increasing concentration of the PAZB-1, maximum light transmission in parallel and perpendicular direction are reduced. At [PAZB-2] = 0.30 wt. %  $T_{max}$  = 71.0 %,  $T_{min}$  = 2.5 %. PVA-film effectively polarizes the light from UV (388 nm) to Visible region (422 nm) of spectrum with PE = 93 %.R<sub>d</sub>=D<sub>max</sub>/D<sub>min</sub>=1.6/0.15=10.7 (Table 11). Absorption peak of the PAZB-2 in PVA matrix has bathochromic shiftat 25 nm (408 nm – 383 nm) (Fig. 5b,11b).

**PAZB-8:** Changes in concentration of the PAZB-8 from 0.10 to 0.30 wt. % in the colored oriented PVA-film show that with increasing concentration of the PAZB-8, maximum light transmission in parallel and perpendicular direction are reduced.At [PAZB-2] = 0.30 wt. %  $T_{max}$  = 72.5 %,  $T_{min}$  = 2.3 %. PVA-film effectively polarizes the light from UV (388 nm) to Visible region (427 nm) of spectrum with PE = 93 %.Rd=D<sub>max</sub>/D<sub>min</sub>=1.63/0.14=11.6 (Table 11). Absorption peak of the PAZB-2 in PVA matrix has bathochromic shift at 35 nm (408 nm – 373 nm) (Fig. 7b,11c).

# 2.6 Anisotropy of thermal conductivity of PVA-films containing the compounds PAZB-1, PAZB-2, PAZB-8

In the present study, we have studied thermal conductivity of the PVA systems containing new synthesized azomethines PAZB-1, PAZB-2 and PAZB-8. It is very important parameter for creation of thermostable polarizing films. In the earlier researches [13-14] we reported that special paints were used to sharply change the initial color at a critical temperature ( $T_{cr}$ ). The isothermal surface moves at a certain speed in the proportion to a local gradient of the

temperature field. Thermo-physical characteristics of material can be judged by the speed of isotherm movement and the form of flowed surface. Thermal indicators of Ciba Com. (Switzerland) with small sizes of T<sub>cr</sub> in order to avoid thermal destruction of polymer material were used. Thermal indicator is put on a film by a thin layer and at regular intervals by a drawplate. Then, after some drying period its unpainted surface is resulted on some time (30 sec.) in dense contact to a dot source of heat (it is heated up approximately to 55 °C metal needles). Thermo-physical properties of films was determined by thermal conductivity of samples in parallel ( $\lambda_{\parallel}$ ) and perpendicular ( $\lambda_{\perp}$ ) directions of stretching axis. In case of anisotropic materials the ellipse a ratio of which axes is proportional to thermal conductivity of a film lengthways and perpendicularly to axis of its stretching is drawn. During this work, it was established that the oriented PVA-films with new synthesized azomethines have the phenomenon of anisotropy of thermal conductivity ( $\lambda_{\parallel} / \lambda_{\perp}$ ). Thermal conductivity in a direction of orientation  $(\lambda_{\parallel})$  is higher than in a direction perpendicular orientations  $(\lambda_{\perp})$ . On resulting anisotropy at a known degree of extension it is possible to judge anisotropy of chain structure. It has been noticed that during thermal expansion and thermal conductivity geometric parameters of molecule, intermolecular forces play a significant role. In unstretched PVA-film anisotropy of thermal conductivity is not observed appreciably ( $\lambda_{\parallel}=0.875$ W/m.°C;  $\lambda_{\perp}=0.869$  W/m.°C;  $\lambda_{\parallel}$  /  $\lambda_1$ =1.00) whereas in stretched PVA-film anisotropy of thermal conductivity is observed (Table 11).

#### Table 11

Dependence of thermal conductivity on stretching degree in pure PVA-films.

	λ, W/m.°C					
R <sub>s</sub>	$\lambda_{\parallel}$	$\lambda_{\perp}$	$\lambda_{\parallel} / \lambda_{\perp}$			
1.5	0.876	0.764	1.15			
2	0.878	0.636	1.38			
2.5	0.880	0.549	1.60			

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3	0.881	0.503	1.75
4	0.882	0.475	1.86

When we inject the PAZB-1, PAZB-2, PAZB-3 in PVA-film there is change in its thermal conductivity (Table 12). It has been found that along an axis of orientation, it has increased, and in perpendicular axis it is reduced. Results of thermal conductivity measurements of PVA-films containing the PAZB-1, PAZB-2 and PAZB-8 depending on stretching degree are presented in Table 12.

#### Table 12

	λ, W/m.°C									
R <sub>s</sub>		PAZB-1			PAZB-2			PAZB-8		
	$\lambda_{\parallel}$	$\lambda_{\perp}$	$\lambda_{\parallel}$ / $\lambda_{\perp}$	$\lambda_{\parallel}$	$\lambda_{\perp}$	$\lambda_{\parallel}/\lambda_{\perp}$	$\lambda_{\parallel}$	$\lambda_{\perp}$	$\lambda_{\parallel}$ / $\lambda_{\perp}$	
2.0	0.865	0.259	3.34	0.864	0.257	3.36	0.862	0.253	3.41	
3.0	0.851	0.231	3.68	0.852	0.232	3.67	0.850	0.238	3.57	
4.0	0.846	0.194	4.36	0.848	0.191	4.44	0.842	0.186	4.53	
5.0	0.835	0.083	10.06	0.834	0.080	10.42	0.833	0.085	9.80	

Thermal conductivity of PVA-films containing the PAZB-1, PAZB-2, PAZB-8 at concentration 0.3wt.%.

The occurrence of anisotropy of thermal conductivity is connected that at orientation of PVAfilm occurs orientation of the amorphous part of polymer and also formation of additional number of intermolecular connections. Thermal conductivity of PVA-films changes after the injection of dyes (Table 12) and along an axis of orientation and in perpendicular axis decreases.

#### 3. Conclusion

Density functional theory (DFT/PBE0/6-31+G\*) were modeled 3 new azomethine dyes: *N*benzylidene-4-((*E*)-phenyldiazenyl)aniline (PAZB-1), 2-methoxy-4-(((4-((*E*)phenyldiazenyl)phenyl)imino)methyl)phenol (PAZB-2) and 2-methoxy-5-((*E*)-((4-((*E*)phenyldiazenyl)phenyl)imino)methyl)phenol (PAZB-8) absorbing in the ultraviolet region of spectrum. Their optimal geometries and absorption spectra in solvent DMF were calculated. There is a high degree of approximation between the calculated and experimental data was

established. These azomethine dyes were synthesized after spending quantum chemical studies. On the basis of PVA and the synthesized azomethine dyes were developed polarizing films operating at visible region of spectrum. Polarizing efficiency of colored oriented PVA-films depend on the concentration of injected dye and stretching degree of the films were found. Polarizing PVA-films containing the azomethine dyes: PAZB-1, PAZB-2 and PAZB-8 have PE  $\geq$  93 % at concentration 0.3 wt. % and R<sub>s</sub> = 3.5. Stretched colored PVA-films by new dichroic structures have phenomenon of anisotropy of thermal conductivity. Thermal conductivity in a direction of orientation ( $\lambda_{\parallel}$ ) is higher than in a direction perpendicular orientations ( $\lambda_{\perp}$ ). The manufactured polarizing PVA-films were used for optoelectronic applications and devices in Institute of Physical Organic Chemistry of the National Academy of Sciences of Belarus.

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