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Siyamak Shahab, Liudmila Filippovich, Masoome Sheikhi, Rakesh Kumar, Evgenij Dikusar, Hooriye Yahyaei, Alexander Muravsky

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Graphical Abstract

Polarization, Excited States, Trans–Cis $(E\rightarrow Z)$ Isomerization Properties and Anisotropy of Thermal and Electrical Conductivity of the 4-(phenyldiazenyl)aniline in the presence of polyvinyl alcohol (PVA) matrix were studied. DFT, UV/Vis, IR-Spectroscopies and Indicator Method were used for Determination of Thermal Conductivity of polymer films. The molecular HOMO-LUMO, excitation energies and oscillator strengths for *E* and *Z* isomers of the 4-(phenyldiazenyl)aniline have also been calculated and presented. Optical Properties of the PVAfilms containing 4-(phenyldiazenyl)aniline have been also investigated.

NH₂ ·NH₂ (E)-4-(phenyldiazenyl)aniline (Z)-4-(phenyldiazenyl)aniline

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Siyamak Shahab

Institute of Physical Organic Chemistry National Academy of Sciences of Belarus, 13 Surganov Str., Minsk 220072 E-mail: siyamak.shahab@yahoo.com

Liudmila Filippovich

Institute of Physical Organic Chemistry National Academy of Sciences of Belarus, 13 Surganov Str., Minsk 220072 E-mail: <u>luda1977@list.ru</u>

Masoome Sheikhi

Department of Chemistry, Gorgan Branch, Islamic Azad University, Gorgan, Iran E-mail: Masoome <u>Sheikhi2@gmail.com</u>

Rakesh Kumar Department of Chemistry,DAV University , Jalandhar -144012 (Punjab) India E-mail: <u>rakesh_nitj@yahoo.co.in</u>

Dikusar Evgenij Anatol'evich Institute of Physical Organic Chemistry National Academy of Sciences of Belarus, 13 Surganov Str., Minsk 220072 E-mail: <u>dikusar@ifoch.bas-net.by</u>

Hooriye Yahyaei Department of Chemistry, Zanjan Branch, Islamic Azad University, Zanjan, Iran Email id : <u>hoorie_yahyaei@yahoo.com</u>

Alexander Muravsky Institute of Chemistry of New Materials, National Academy of Sciences of Belarus, 36 Skarina Str., Minsk 22014 E-mail: <u>alexander.muravsky@ichnm.basnet.by</u>

Polarization, Excited States, Trans-Cis Properties and Anisotropy of Thermal and Electrical Conductivity of the 4-(phenyldiazenyl)aniline in PVA Matrix

Siyamak Shahab^{a,b}, Liudmila Filippovich^{a,b}, Masoome Sheikhi^c, Rakesh Kumar^d, Evgenij Dikusar^a, Hooriye Yahyaei^e, Alexander Muravsky^b

^aInstitute of Physical Organic Chemistry, National Academy of Sciences of Belarus, 13 Surganov Str, Minsk 220072 ^bInstitute of Chemistry of New /Materials, National Academy of Sciences of Belarus, 36 Skarina Str., Minsk 220141 ^cDepartment of Chemistry, Gorgan Branch, Islamic Azad University, Gorgan, Iran

^dDepartment of Chemistry, DAV University, Jalandhar - 144012 (Punjab) India

^eDepartment of Chemistry, Zanjan Branch, Islamic Azad University, Zanjan, Iran

ABSTRACT

In the present work, Polarization, Excited States, Trans–Cis $(E \rightarrow Z)$ Isomerization Properties and Anisotropy of Thermal and Electrical Conductivity of the 4-(phenyldiazenyl)aniline in the presence of polyvinyl alcohol (PVA) matrix were studied. DFT, UV/Vis, IR-Spectroscopies and Indicator Method were used for Determination of Thermal Conductivity of polymer films. The absorption spectra of the 4-(phenyldiazenyl)aniline in dimethylformamide (DMF) solvent and in aqueous medium were calculated. The nature of absorption peaks of the 4-(phenyldiazenyl)aniline in the UV/Vis spectral regions were interpreted. The solvent effect on the absorption spectrum of the 4-(phenyldiazenyl)aniline has established. The molecular HOMO-LUMO, excitation energies and oscillator strengths for *E* and *Z* isomers of the 4-(phenyldiazenyl)aniline have also been calculated and presented. Optical Properties of the PVAfilms containing 4-(phenyldiazenyl)aniline have been also investigated. Polarizing Efficiency (PE) of obtained PVA-film is 98-99 % at Stretching Degree (R_s) 3.5. Anisotropy of thermal and electrical conductivity of PVA-films containing *E* and *Z* isomers of the 4-(phenyldiazenyl)aniline was also measured and discussed.

Keywords: Polarization, excited state, trans-cis isomerization, anisotropy of thermal conductivity, PVA matrix Corresponding authors: <u>m.sheikhi2@gmail.com</u> (M. Sheikhi); <u>rakesh nitj@yahoo.co.in</u> (R. Kumar)

1. Introduction

Organic compounds induce electro-optic effects and produces large nonlinear optical responses due to the large delocalization of π electrons compared to the more traditional inorganic compounds [1]. For the production of organic nonlinear optical (NLO) compounds donor and/or acceptor substituents such as azo-, amino-, nitro-, cyano-, halo-, hydroxyl are used. Azo compounds contain nitrogen as the azo (-N=N-) group that are one of the important synthetic organic dyes [2]. They are used as colorants in the textile, paper, cosmetics, drugs, foods coloring, and other consumer goods. They are promising systems for dyestuffs, pH indicators [3-6] and optical applications such as holographic and digital storage, polarizing films, lasers [7-12] liquid crystal command surfaces and nonlinear optical devices [13]. 4-(phenyldiazenyl)aniline is an aromatic amine and an intermediate in the production of diazo dyes. The single crystals of 4-(phenyldiazenyl)aniline were reported by Eazhilarasi and coworkers [14]. In recent years, computational chemistry has become an important tool for chemists and a well-accepted partner for experimental chemistry [15-17]. Density functional theory (DFT) method has become a major tool in the methodological arsenal of computational organic chemists. The trans-cis $(E \rightarrow Z)$ isometization is observed for azobenzene and its derivatives, which has recently considered in optical materials [4,18], media storage materials [19], light-triggered nanomachines [6,20], etc. The *trans-cis* $(E \rightarrow Z)$ isomerization can readily occur at room temperature and can be promoted by visible light irradiation. The DFT and CASSCF calculations were performed to optimize the 4-(phenyldiazenyl)aniline and scan the potential energy surfaces (PES) of the transition state structures $S_0(n \rightarrow \pi^*)$ and $S_1(\pi \rightarrow \pi^*)$ [21]. The initial development of photoinduced anisotropy in highly photosensitive monolayers of an aminoazobenzene molecule (a derivative of o-methyl red) that are initially randomized using circularly polarized light is found to be significantly slower than in monolayers randomized by thermal relaxation. Youngwoo Yi and coworkers [22] propose that this is a direct consequence of the slow thermal relaxation of isomers from the cis to the trans state and suggest that such considerations are important in designing even more sensitive photoactive monolayers and in understanding their photodynamics. The absorption spectra of three azoaminobenzene dyes and two its derivatives have been computed with TD-DFT approach using four hybrid functional, different basis sets and four salvation model such as PCM, I-PCM, SCI-PCM and IEF-PCM [23,24]. The aim of the current work is to study polarization, excited states, *trans-cis* $(E \rightarrow Z)$ isomerization properties and anisotropy of thermal conductivity in colored by 4-(phenyldiazenyl)aniline PVA-films by DFT, UV/Vis, IR-Spectroscopies and Indicator Method for Determination of Thermal Conductivity of polymer films.

2. Experimental

2.1 Reagent and Apparatus

All chemical used in this study were of analytical reagent grade. Used PVA «Mowiol 28-99» manufactured by the Hoëchst Aktiengesllschaft Co., Germany. The (E)-4-(phenyldiazenyl)aniline was purchased from Sigma-Aldrich Co. and used without further purification. Experimental UV/Vis spectrum of the compound was recorded on UV-Visible Spectrophotometer Cary 300 (Varian, USA). Experimental IR-spectrum of films was recorded in the frequency region 400-4000 cm⁻¹ on a Spectrophotometer of Protégé 460 (Nicolet, US). *Trans-cis* $(E \rightarrow Z)$ isomerization of films was studied using unfiltered radiation of high-pressure Hg-lamp DRSH-1000 (Belarus). The intensity of light falling perpendicular to the surface of the sample was 0.009 W/cm². At exposure temperature of sample was 20-22 °C. The absorption spectra of the films were measured before and after UV radiation. Thermal and electrical conductivity of PVA-films was measured on the complex equipment LC - 201 (Alfa Laval Group, Sweden).

2.2 Preparation of PVA-films containing the (E)-4-(phenyldiazenyl)aniline

The PVA-films were prepared from (wt. %) 10 PVA solution containing 0.01-0.03 of the (*E*)-4-(phenyldiazenyl)aniline (0.10-0.30 in colored dried PVA-film), 0.01 boric acid (H₃BO₃), 6.0 ethyl alcohol (C₂H₅OH), 0.5 dimethylformamide (DMF) and water. An initial composition was prepared by dissolving PVA in distilled water and ethyl alcohol. The composition was mixed at temperature 80-85 °C. (*E*)-4-(phenyldiazenyl)aniline and additives were added after 3 h. after starting of heating PVA solution at intervals 20 minutes. (*E*)-4-(phenyldiazenyl)aniline was dissolved in dimethylformamide previously. The mixture was heated for 3.5 h. The hot solution was filtered through two layers of technical nylon. Deaeration was occurred during 10 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 35 minutes at temperature 60-63 °C. The value of Stretching Degree (R_s) 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 60 to 65 µm. The film thickness was measured with a micrometer with an accuracy of $\pm 5\mu$ m (GS SSSR 6507-90).

3. Optical properties

3.1 Polarization Properties of PVA-films containing the (*E*)-4-(phenyldiazenyl)aniline

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. (1,2) [12,24]:

 $PE = (T_{max} - T_{min}) / (T_{max} + T_{min}) * 100$ $R_d = D_{max} / D_{min}$

(1)(2)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. Polarizing Efficiency (PE) of colored oriented PVA-films depends on the concentration of injected (E)-4-(phenyldiazenyl)aniline and Stretching Degree ($R_s = 3.5$) of the films, therefore the optimum concentration of the (E)-4-(phenyldiazenyl)aniline in PVA-film was obtained (Fig. 1).



Fig. 1 Transmission spectra $(1 - T_{\parallel}, 2 - T_{\perp})$ and polarizing efficiency (3 - PE) of polarizing PVA-films containing 0.30 wt. % of the (E)-4-(phenyldiazenyl)aniline.

Changes in concentration of the (E)-4-(phenyldiazenyl)aniline from 0.10 to 0.30 wt. % in the colored oriented PVA-film show that with increasing concentration of the (E)-4-(phenyldiazenyl)aniline, maximum light transmission in parallel and perpendicular direction are reduced. At [(E)-4-(phenyldiazenyl)aniline] = 0.30 wt. % $T_{max} = 45.3$ %, $T_{min} = 0.25$ % (photo of the polarizing PVA-film containing 0.30 wt. % of the (E)-4-(phenyldiazenyl)aniline in parallel and perpendicular directions of stretching is presented in Fig. 2 a,b). PVA-film effectively

polarizes the light from UV (353 nm) to Visible region (466 nm) of spectrum with PE = 98-99%.



Fig. 2 PVA-films containing the 0.30 wt. % of the (*E*)-4-(phenyldiazenyl)aniline in parallel (a) and perpendicular (b) directions of stretching

The best optical parameters has PVA-film containing 0.30 wt. % of the (*E*)-4-(phenyldiazenyl)aniline ($T_{max} = 45.3$ %, $T_{min} = 0.25$ %, $D_{max} = 2.70$, and $D_{min} = 0.34$, $R_d = 7.94$, EP = 99 %).

4. Computational details

4.1 Geometric Structure of (E)-4-(phenyldiazenyl)aniline

The structural energy minimization calculation was carried out using the program HyperChem 08 by molecular mechanics (MM^+). The obtained structure was fully optimized by DFT calculations with a hybrid functional B3LYP (Becke's three parameter hybrid functional using LYP correlation functional) and PBE1PBE (Perdew, Burke and Enzerhof GGA exchange-correlation functional) at 6-31G, 6-31G*, 6-31⁺⁺G* basis sets (Fig. 3). To account



Fig. 3 Optimized molecular structure of the (E)-4-(phenyldiazenyl)aniline calculated by B3LYP/6-31G method.

solvent 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 [25]. All density functional calculations were performed with the Gaussian 09W software package and Gauss view 05 visualization programs [26].

4.2 Electronic Structure and Excited States of (*E*)-4-(phenyldiazenyl)aniline

Theoretical absorption spectra of the title molecule optimized in solvents (DMF and Water) were calculated using TDB3LYP/6-31G, TDB3LYP/6-31G*, TDB3LYP/6-31⁺⁺G*, TDPBE1PBE/6-31G, TDPBE1PBE/6-31G*, TDPBE1PBE/6-31⁺⁺G*, TDPBE1PBE/6-31G*, TDPBE1PBE/6-31⁺⁺G* methods. To account solvent effect Polarized Continuum Model (PCM) was used.



Fig. 4 Calculated (\mathbf{a} – in DMF, \mathbf{b} – in Water) and \mathbf{c} – experimental (in DMF) UV/Vis spectrum of the (*E*)-4-(phenyldiazenyl)aniline

The theoretical UV/Vis spectra (in DMF and Water) show that the title molecule is not very sensitive to solvents (Fig. 4 a,b,c). 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 (Table 1). Experimental UV/Vis spectrum of the (*E*)-4-(phenyldiazenyl)aniline in DMF at concentration $3.5 \cdot 10^{-4}$ M/l and temperature 21 °C is presented in Fig. 4 c.

Table 1Electronic absorption spectrum of the (E)-4-(phenyldiazenyl)aniline calculated by TDB3LYP/6-31Gmethod

Excited	Wavelength	Excitation	Configurations Composition	Oscillator
State	(nm)	Energy (eV)	(corresponding transition orbitals)	Strength (f)
S_1	501	2.48	0.71(H-1→L)	0.00
S_2	402	3.08	0.71(H→L)	1.05
S ₃	297	4.17	$0.57(H-3\rightarrow L) + 0.35(H-2\rightarrow L) - 0.10(H\rightarrow L+1) + 0.17(H\rightarrow L+2)$	0.01
S_4	293	4.24	$\begin{array}{c} 0.63(\text{H-4}{\rightarrow}\text{L}) - 0.13(\text{H-2}{\rightarrow}\text{L}) \\ - 0.24(\text{H}{\rightarrow}\text{L}{+1}) - 0.12(\text{H}{\rightarrow}\text{L}{+2}) \end{array}$	0.00
S ₅	279	4.45	$0.16(\text{H-4}\rightarrow\text{L}) - 0.32(\text{H-3}\rightarrow\text{L}) + 0.57(\text{H-2}\rightarrow\text{L}) + 0.19(\text{H}\rightarrow\text{L+3})$	0.06
S ₆	259	4.79	$0.27(H-4\rightarrow L) + 0.56(H\rightarrow L+1) + 0.30(H\rightarrow L+2)$	0.13
S ₇	254	4.89	$-0.2(H-3\rightarrow L) - 0.31(H\rightarrow L+1) + 0.59(H\rightarrow L+2)$	0.06
S ₈	249	4.98	0.71(H→L)	0.00
S ₉	248	5.00	$+ 0.17(H-1 \rightarrow L+2)$	0.00
S ₁₀	230	5.40	$+ 0.17(H-1 \rightarrow L+3)$	0.00
S ₁₁	223	5.56	$0.15(\text{H-}5\rightarrow\text{L}) + 0.11(\text{H-}4\rightarrow\text{L+}1) - 0.14(\text{H-}2\rightarrow\text{L}) + 0.64(\text{H}\rightarrow\text{L+}3)$	0.00
S ₁₂	211	5.87	$0.64(H-5\rightarrow L) - 0.16(H\rightarrow L+3) - 0.20(H\rightarrow L+4)$	0.04
S ₁₃	204	6.09	$- 0.24(H-3 \rightarrow L+2) - 0.32 (H-3 \rightarrow L+3) - 0.32(H-2 \rightarrow L+1) + 0.42(H-2 \rightarrow L+2) - 0.11(H-2 \rightarrow L+3)$	0.02
S ₁₄	201	6.18	$0.10(\text{H-8}\rightarrow\text{L}) + 0.12(\text{H-7}\rightarrow\text{L}) + 0.66(\text{H-6}\rightarrow\text{L}) \\ - 0.14(\text{H-1}\rightarrow\text{L+4})$	0.00
S ₁₅	199	6.24	$-0.28(H-7\rightarrow L) + 0.17(H-6\rightarrow L) + 0.62(H-1\rightarrow L+4)$	0.00
S ₁₆	198	6.26	$-0.22(H-3\rightarrow L+1) + 0.55(H-2\rightarrow L+1) + 0.34(H-2\rightarrow L+2) - 0.13(H\rightarrow L+4)$	0.00
S ₁₇	196	6.34	$0.15(H-5\rightarrow L) + 0.19(H-4\rightarrow L+1) - 0.12(H-3\rightarrow L+2) + 0.11(H-2\rightarrow L+1) - 0.61(H\rightarrow L+4)$	0.00
S ₁₈	195	6.36	$0.63(H-7\rightarrow L) + 0.30(H-1\rightarrow L+4)$	0.00
S ₁₉	191	6.47	$\begin{array}{c} 0.60(\text{H-3} \rightarrow \text{L+1}) + 0.26(\text{H-3} \rightarrow \text{L+2}) - 0.11(\overline{\text{H-3}} \rightarrow \text{L+3}) + \\ 0.13(\text{H-2} \rightarrow \text{L+1}) + 0.18(\text{H-2} \rightarrow \text{L+2}) \end{array}$	0.01
S ₂₀	188	6.59	- 0.36(H-4→L+1) - 0.60(H-4→L+2)	0.00

*H-HOMO, L-LUMO

The experimental absorption spectrum of the title compound (Fig. 4 c) has a wide absorption at about 350-485 nm which characterized by maximum at 399 nm and calculated spectrum in DMF

(Fig. 4 a) shows the highest oscillation in 402 nm at f = 1.05. The strong peak at 402 nm is due to the Charge-Transfer (CT) excited state. The other peaks are local excited states corresponding to electrons going into anti-bonding orbitals associated with the benzene rings. Excitation of one electron at 402 nm belonged to the transition into the excited singlet state S_2 ($S_0 \rightarrow S_2$) and describes by a wave function corresponding to configuration for one-electron excitation (52 (HOMO) \rightarrow 53(LUMO)) (Fig. 5). The other excited states have very small intensity ($f \approx 0$): these transitions are nearly forbidden by orbital symmetry considerations (Table 1).



Fig. 5 Form of the MO involved in formation of absorption spectrum of the (*E*)-4-(phenyldiazenyl)aniline at $\lambda_{max} = 402$ nm.

The results of calculations of electronic spectrum of the (*E*)-4-(phenyldiazenyl)aniline in DMF and Water with different methods and basis sets (using TDB3LYP/6-31G, TDB3LYP/6-31G*, TDB3LYP/6-31+G* and TDB3LYP/6-31++G*, TDPBE1PBE/6-31G, TDPBE1PBE/6-31G*, TDPBE1PBE/6-31+G*, TDPBE1PBE/6-31++G*) show that TDB3LYP/6-31G method is better than the other methods that predicts changes in the absorption spectrum of the title molecule (Fig. 4 a,c). In the work are presented results of calculations of geometry optimization and absorption spectrum calculated by B3LYP/6-31G and TDB3LYP/6-31G. We found that addition of diffusion and polarization functions increases electron density of small atoms and distorts electron spectrum of the (*E*)-4-(phenyldiazenyl)aniline [10,11].

4.3 $(E \rightarrow Z)$ isomerization of the (E)-4-(phenyldiazenyl)aniline

In order to study $(E \rightarrow Z)$ isomerization of the (E)-4-(phenyldiazenyl)aniline, experimental UV/Vis spectrum of solution of the (E)-4-(phenyldiazenyl)aniline in DMF after 1 h. UV radiation was recorded (Fig. 6). As seen from Fig. 6 after 1 h. UV radiation character of the curve (2) did not change. *E* and *Z* isomers of the 4-(phenyldiazenyl)aniline absorb light at $\lambda_{max} =$ 399 nm. Optical density decreases from 2.0 (curve 1) to 1.8 (curve 2).



Fig. 6 Experimental UV/Vis spectrum of solution containing the 4-(phenyldiazenyl)aniline in DMF: (1) - E isomer before UV radiation, (2) - Z isomer after 1 h. UV radiation

Then for investigation of $(E \rightarrow Z)$ isomerization (Fig. 7) in PVA matrix PVA-film containing (E)-4-(phenyldiazenyl)aniline was prepared according to 2.1.



Fig. 7 ($E \rightarrow Z$) isomerization of the (E)-4-(phenyldiazenyl)aniline

The absorption spectrum of the sample was recorded after 0.5; 1.0; 2.5 and 4.0 h. after beginning of UV radiation. During the exposure, the distance between the light source and the sample was 25 cm, while the temperature of the sample was 20-22 °C. As seen from Fig. 8 the peaks of absorption do not change ($\lambda_{max} = 399$ nm). Over time (curves 2,3,4,5) the optical density of the sample begins to decrease (for curve 3: D = 0.90, for curve 4: D = 0.68 and for curve 5 D = 0.44). It is indicated that initial PVA-film containing (*E*)-4-(phenyldiazenyl)aniline (curve 1) transfers to (*Z*)-4-(phenyldiazenyl)aniline (curve 5) after four h. UV radiation (Fig. 8).



Fig. 8 Experimental UV/Vis spectrum of film containing (*E*)-4-(phenyldiazenyl)aniline (1) – Initial film before UV radiation, (2) – after 0.5 h., (3) – after 1 h., (4) – after 2.5 h. and (5) – after 4.0 h. UV radiation.

In order to confirm the correctness of our findings IR-spectroscopy was used. IR-spectra of PVA-film were recorded before and after 2.5 h. and 4 h. UV radiation (Fig. S1a,S1b,S1c). Comparison of the IR-spectra of the (*E*)-4-(phenyldiazenyl)aniline and (*Z*)-4-(phenyldiazenyl)aniline has shown a small change in the absorption in region 3000-3500 cm⁻¹. IR-spectrum of PVA-film before UV radiation has absorption at 3322.59 cm⁻¹ (Fig. S1a) but in PVA-film after 2.5 h. (Fig. S1b) and 4 h. (Fig. S1c) UV radiation has absorption at 3307.03 cm⁻¹ and 3291.13 cm⁻¹ respectively. The change of absorption related to v_{C-H} in (*E*)-4-(phenyldiazenyl)aniline and (*Z*)-4-(phenyldiazenyl)aniline respectively.

4.4 Anisotropy of thermal conductivity of PVA-films containing the (E,Z)-4-(phenyldiazenyl)aniline

During $(E \rightarrow Z)$ isomerization many properties of the system changes like refractive index, solubility, viscosity and thermal and electrical conductivity [27]. In the present study, we have studied thermal conductivity of the PVA-(E) isomer and PVA-(Z) isomer systems. This method was described in [27]. Thermo-physical properties of films was determined by thermal

conductivity of samples in parallel $(\lambda_{\|})$ and perpendicular (λ_{\bot}) directions of stretching axis. During this work, it was established that the oriented PVA-film has the phenomenon of anisotropy of thermal conductivity ($\lambda_{\parallel} / \lambda_{\perp}$). Thermal conductivity in a direction of orientation (λ_{\parallel}) is higher than in a direction perpendicular orientations (λ_{\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) whereas in stretched PVA-film anisotropy of thermal conductivity is observed clearly (Table 2).

	λ, W/ m.°C				
R _s	λ _{ll} , W/ m.°C	λ_{\perp} , W/ m.°C	λ_{\parallel} / λ_{\perp}		
1.0	0.875	0.872	1.00		
1.5	0.876	0.764	1.15		
2.0	0.878	0.636	1.38		
2.5	0.880	0.549	1.60		
3.0	0.881	0.503	1.75		
4.0	0.882	0.475	1.86		

Table 2 Dependence of thermal conductivity on stretching degree in pure PVA-films

When we inject the dye in PVA-film there is change in its thermal conductivity (Table 3). 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 (E,Z)-4-(phenyldiazenyl)aniline depending on stretching degree are presented in Table 3.

wt.%				
		λ, W/ m.°C		
4-(phenyldiazenyl)aniline	R _s	$\lambda_{\parallel}, W/m.^{o}C$	$\lambda_{\perp}, W/m.^{\circ}C$	λ_{\parallel} / λ_{\perp}
	2.0	0.862	0.340	2.54
(E) isomer	3.0	0.849	0.311	2.73
	4.0	0.842	0.248	3.40
Y	5.0	0.841	0.194	4.36
	2.0	0.865	0.236	3.67
(Z) isomer	3.0	0.853	0.189	4.51
	4.0	0.846	0.132	6.41
	5.0	0.835	0.102	8.19

Table 3 Thermal conductivity of PVA-films containing the (E,Z)-4-(phenyldiazenyl)aniline at concentration 0.3

The obtained data suggest that in the PVA-(*Z*) isomer system, anisotropy of thermal conductivity is stronger than in the PVA-(*E*) isomer system. We found that at $(E \rightarrow Z)$ isomerization the *Z*isomer which is less stable (has a larger energy system) has a greater anisotropy of thermal conductivity as compared with the more stable *E*-isomer. Theoretical calculation of the full energies of the (*E*,*Z*)-4-(phenyldiazenyl)aniline by DFT/B3LYP/6-31G level of theory leads to the following values: $HF_{(E \text{ isomer})} = -627.9655682$ Hartree and $HF_{(Z \text{ isomer})} = -627.9425978$ Hartree.

4.5 Anisotropy of electrical conductivity of PVA-films containing the (E,Z)-4-(phenyldiazenyl)aniline

In the present section, we have studied electrical conductivity of the PVA-(*E*) isomer and PVA-(*Z*) isomer systems. Electrical conductivity of PVA-films was measured on the complex equipment LC – 201(Alfa Laval Group, Sweden). The PVA-films were placed on the surface of the thin sheet (electrode) from SnO₂ (thickness 70 µm). And then the films were coated with an aluminum electrode (S = 2.5 cm²). The thickness of the PVA samples was 65 µm. The electrical conductivity of PVA-films was measured in parallel (δ_{\parallel}) and perpendicular (δ_{\perp}) directions of stretching axis. In unstretched PVA-film anisotropy of electrical conductivity is not observed (δ_{\parallel} = 1.1·10⁵ S.cm⁻¹; δ_{\perp} = 1.1·10⁵ S.cm⁻¹) whereas in stretched PVA-film anisotropy of electrical conductivity is observed very clearly (Table 4).

	δ, S.cm ⁻¹				
R _s	$\delta_{\parallel}, \text{ S.cm}^{-1}$	δ_{\perp} , S.cm ⁻¹	$\delta_{\parallel} / \delta_{\perp}$		
1.0	$1.1 \cdot 10^{5}$	$1.1 \cdot 10^5$	1.10^{0}		
1.5	$4.6 \cdot 10^5$	$8.4 \cdot 10^4$	$0.5 \cdot 10^{1}$		
2.0	$9.8 \cdot 10^5$	$1.7 \cdot 10^4$	$5.7 \cdot 10^{1}$		
2.5	$3.6 \cdot 10^6$	$2.2 \cdot 10^3$	$1.6 \cdot 10^3$		
3.0	$7.8 \cdot 10^7$	$5.7 \cdot 10^2$	$1.3 \cdot 10^5$		
4.0	$6.5 \cdot 10^8$	$6.1 \cdot 10^{1}$	$1.1 \cdot 10^{7}$		

 Table 4
 Dependence of electrical conductivity on stretching degree in pure PVA-films

After injecting the dye in PVA-film there is change in its electrical conductivity (Table 5). It has been found that along an axis of orientation, it has increased, and in perpendicular axis it is reduced. Anisotropy of electrical conductivity of PVA-films was defined as $\delta_{\parallel} / \delta_{\perp}$ and is presented in Table 5.

		δ, S.cm ⁻¹		
4-(phenyldiazenyl)aniline	R _s	$\delta_{\parallel}, \text{ S.cm}^{-1}$	δ_{\perp} , S.cm ⁻¹	δ_{\parallel} / δ_{\perp}
	2.0	$3.2 \cdot 10^5$	$5.6 \cdot 10^4$	$5.7 \cdot 10^{0}$
(E) isomer	3.0	$6.1 \cdot 10^7$	$6.9 \cdot 10^2$	$0.9 \cdot 10^5$
	4.0	$9.8 \cdot 10^7$	$5.5 \cdot 10^{1}$	$1.8 \cdot 10^{6}$
	5.0	$4.6 \cdot 10^8$	$1.2 \cdot 10^{1}$	$3.8 \cdot 10^{7}$
	2.0	$6.6 \cdot 10^5$	$3.0 \cdot 10^4$	$2.2 \cdot 10^{1}$
(Z) isomer	3.0	$7.8 \cdot 10^7$	$3.4 \cdot 10^2$	$2.3 \cdot 10^5$
	4.0	$5.6 \cdot 10^8$	$4.9 \cdot 10^{1}$	$1.1 \cdot 10^{7}$
	5.0	$3.1 \cdot 10^9$	$5.2 \cdot 10^{0}$	$0.6 \cdot 10^9$

Table 5 Electrical conductivity of PVA-films containing the (E,Z)-4-(phenyldiazenyl)aniline at concentration 0.3 wt.%

The obtained data suggest that in the PVA-(Z) isomer system, anisotropy of electrical conductivity is stronger than in the PVA-(E) isomer system. At $(E \rightarrow Z)$ isomerization we found that the isomer which is less stable (has a larger energy system) has a greater anisotropy of electrical conductivity as compared with the more stable isomer.

5. Conclusions

In the present work electronic structure, trans-cis isomerization, polarization properties of 4-(phenyldiazenyl)aniline in PVA-matrix via theoretical and experimental investigations were studied. On the basis of PVA and (E)-4-(phenyldiazenyl)aniline PVA-polarizer for UV and Vis regions of spectrum was created. In spectral range 353-466 nm PE is 90 %. In the region 386-447 nm PE = 98-99 %. The results of calculations of electronic spectrum of the (E)-4-(phenyldiazenyl)aniline in DMF with different methods and basis sets (using TDB3LYP/6-31G, TDB3LYP/6-31G*, TDB3LYP/6-31+G* and TDB3LYP/6-31⁺⁺G*, TDPBE1PBE/6-31G, TDPBE1PBE/6-31⁺⁺G*) TDPBE1PBE/6-31G*, TDPBE1PBE/6-31+G*, show that TDB3LYP/6-31G method is better than the other methods that predicts changes in the absorption spectrum of the title molecule. PVA-film before and after UV radiation has the same absorption spectra. The peaks of absorption do not change ($\lambda_{max} = 399$ nm). In the PVA-(Z) isomer system, anisotropy of electrical and thermal conductivity is stronger than in the PVA-(*E*) isomer system. PVA-(Z) isomer which is less stable ($HF_{(Z \text{ isomer})} = -627.9425978$ Hartree) has a greater anisotropy of electrical and thermal conductivity as compared with the more stable PVA-(E)isomer ($HF_{(E \text{ isomer})} = -627.9655682$ Hartree). There is relationship between optical and electrical anisotropy and anisotropy of thermal conductivity of PVA-films. Anisotropy of optical, electrical and thermal conductivity occurs only in stretched PVA-films.

References

- 1. A. Natansohn, P. Rochon, Can. J. Chem. 79 (2001) 1093-1100.
- H. Zollinger, Color chemistry: Synthesis, properties, and applications of organic dyes and pigments. 2nd ed. VCH, Weinheim (1991)
- A. Dirksen, E. Zuidema, R.M. Williams, L. De Cola L, *Macromolecules* 35 (2002) 2743-2747.
- 4. X.G. Wang, J. Kumar, S.K. Tripathy, L. Li, J. I. Chen, S. Marturunkakul, *Macromolecules* 30 (1997) 219-225
- 5. T. Ikeda, O. Tsutsumi, *Science* 268 (1995) 1873-1875.
- T. Hugel, N.B. Holland, A. Cattani, L. Moroder, M. Seitz, H.E. Gaub, *Science* 296 (2002) 1103-1106.
- 7. V.A. Loiko, A.A.Miskevich, A.V. Konkolovich, *Phys Rev E* 74 (2006) 031704-031707.
- 8. P.G. Lisinetskaya, A.A. Konkolovich, V.A. Loiko, Appl Opt 48 (2009) 3144-3153.
- P.J. Colling. Liquid crystals: nature's delicate phase of matter. 2nd ed. Princeton, NJ: Princeton University Press (2002).
- H. Almodarresiyeh, S. Shahab, V. Zelenkovsky, N. Ariko, L. Filippovich, V. Agabekov. J. Appl. Spectrosc. 81 (2014) 31-36.
- H. Almodarresiyeh, S. Shahab, V. Zelenkovsky, V. Agabekov. J. Appl. Spectrosc. 81 (2014) 161-163.
- 12. S. Shahab, R. Kumar, M. Darroudi, M. Y. Borzehandani, J. Mol. Struc. 1083 (2015) 198-203.
- D.S. Chemla, J. Zyss (Eds.), Nonlinear Optical Properties of Organic Molecules and Crystals, Academic Press, New York (1987).
- G. Eazhilarasi, R. Nagalakshmi, V. Krishnakumar, Spectrochimica Acta Part A 71 (2008) 502-507.
- (a) D. Avci, Y. Atalay, Struct. Chem., 20 (2009)185-201. (b) R. B. Nazarski, J. Phys. Org. Chem., 22 (2009) 834-844.
- S. M. Shoaei, A. R. Kazemizadeh, A. Ramazani, *Chin. J. Struct. Chem.*, 30 (2011) 568-574.
- 17. H. Hopfl, B. Gomez, R. Martinez-Palou, J. Mex. Chem. Soc. 49 (2005) 307-311.

- X.G. Wang, J.I. Chen, S. Marturunkakul, L. Li, J. Kumar, S.K. Tripathy, *Chem. Mater.* 9 (1997) 45-50.
- 19. T. Ikeda, O. Tsutsumi, Science 268 (1995) 1873-1875.
- 20. Y.L. Yu, M. Nakano, T. Ikeda, Nature 425 (2003) 145-148.
- 21. L. Wang, J. Xu, H. Zhou, C. Yi, W. Xu, *Journal of Photochemistry and Photobiology A: Chemistry* 205 (2009) 104-108.
- Y. Yi, Guanjiu Fang, J. E. Maclennan, N. A. Clark, J. Dahdah, T. E. Furtak, K. Kim, M. J. Farrow, E. Korblova, D. M. Walba, *J. Appl. Phys.* 109 (2011) 103521.
- A. Mahmood, S. Ud-Din Khan, F. ur Rehman, Journal of Saudi Chemical Society 19 (2015) 436-441.
- S. Shahab, F. Haji Hajikolaee, L. Filippovich, M. Darroudi, V. Aleksandrovich Loiko, R. Kumar, M. Yousefzadeh Borzehandani, *Dyes and Pigments* 129 (2016) 9-17.
- 25. B. Mennucci, E. Cancés, J. Tomasi. J. Phys. Chem. B 101 (1997) 10506-10517.
- M. J. Frisch, G. W. Trucks, H. B. Schlegal, G. E. Scuseria, M. A. Robb, et al., Gaussian 09, Revision A.02, Gaussian Inc., Wallingford, CT, 2009.
- H. A. Almodarresiyeh, S. Shahab, L. N. Filippovich, N. G. Ariko, A. P. Lugovsky, V. E. Agabekov. RSC Advances 6 (2016) 42062-42068.

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Highlights

- ✓ Polarization, Excited States, Trans–Cis $(E \rightarrow Z)$ Isomerization Properties of 4-(phenyldiazenyl)aniline
- ✓ DFT, UV/Vis, IR-Spectroscopic Determination of 4-(phenyldiazenyl)aniline
- \checkmark Solvent effect on the absorption spectrum
- ✓ HOMO-LUMO, excitation energies and oscillator strengths for *E* and *Z* isomers of the 4-(phenyldiazenyl)aniline
- ✓ Optical Properties of the PVA-films containing 4-(phenyldiazenyl)aniline