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One- and two-photon-induced isomerization of styryl compounds possessing $A-\pi$ -A' structure



PIGMENTS

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ABSTRACT

Two styryl compounds with A- π -A' structure that feature a fixed pyridine ring as an electron acceptor (A) and pyridine or 5,6,7,8-tetrahydroisoquinoline cation as the other acceptor (A') have been synthesized. Their structures were elucidated by means of NMR and IR spectroscopy. One-photon fluorescence, fluorescence quantum yields and lifetimes were investigated. It was found that both visible (408 nm) and near-infrared (800 nm) light promotes the conversion of the E-isomer of the studied compounds to the Z-isomer. Under the UV irradiation (310 nm) the obtained Z-isomer reverts to the initial form in tens of minutes. The observed inter-conversion was found to be fast and efficient. The *trans*-to-*cis* isomerization was followed by decomposition of the compound upon longer than 100 s exposure to light as indicated from mass spectra.

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1. Introduction

Processes of photoisomerization of olefins and polyenes have been a subject of intense research for a long time since they serve as examples of unimolecular reactions in condensed phase [1].

Polymethine dyes are a large class of compounds, which have been extensively used in a wide range of applications from lasers [2] and photography [3] to diagnostics by fluorescent detection of analytes [4,5] and sensitizers for photodynamic therapy [6,7]. The basic structure of these dyes is characterized by a conjugated (polymethine) chain terminated at each end by a heterocyclic moiety. In general, polymethine dyes have a poor resistance to light compared with other chromophores such as azo and quinone dyes, but many structural modifications improving light-fastness and resistance can be made [8]. When the two end groups are different, the molecules possess a permanent electric dipole moment and show second-order nonlinear optical behavior [9].

Polymethine dyes are usually highly fluorescent and they absorb and emit light mostly in the visible region of the optical spectrum.

* Corresponding author. E-mail address: beata@utp.edu.pl (B. Jędrzejewska). Their spectral properties depend on the chain length and the terminating moieties. It is known that, at first, elongation of the polymethine chain increases the fluorescence quantum yields, but, as it grows further, it causes a decrease of the efficiency [10].

One example of the class of $A-\pi$ -A' compounds are styryl dyes. These dyes incorporate the univalent group C_6H_5 -CH=CH-that is derived from styrene. Thus, classical styryl dyes consist of aromatic and heterocyclic rings on opposite sides of the vinylene bond. There are many nitrogen-heterocyclic rings, which may be present in their structure, e.g. quinoline, pyridine, indole, benzothiazole, benzoxazole, benzoselenazole and others. In most cases styryl dyes bearing azaaromatic moieties are salts because they contain a quaternized heterocyclic nitrogen, although there are examples of neutral dyes in which the heterocyclic nitrogen is not quaternized. Moreover, a variety of substituents can be added to the two terminal moieties, allowing further diversification of the dye structure.

Because of the flexibility of the styryl dyes, several distinct isomers can be formed by rotation around the bonds of the styryl unit. The "all-trans" isomer conformation is generally more stable at room temperature and can be partially converted to the *cis*-form by applying light. This leads to an equilibrium state between the populations of *trans* and *cis* isomers. The *cis*-form can be reverted to



the *trans* isomer when the light of a corresponding wavelength is used to promote this reaction. Isomers formed by photoexcitation may remain stable at low temperatures [11-13]. These isomers present, in general, slightly shifted absorption spectra and weaker intensity bands [14,15].

Good photostability is main pre-requisite in laser-induced fluorescence, dye laser technology and all application involving fluorescence when either high sensitivity or a high signal rate is required [5]. A few hemicyanines present sufficient chemical stability in solution for practical use. For longer polymethine chains, the stability is improved with "rigidified" structures in which the possible rotation around the chain bonds is blocked by appropriate substituents [16,17]. On the other hand, photodegradation plays an important role in environmental applications. The rate constants for photodegradation may be influenced by a fast photoisomerization that, depending on molecular parameters and irradiation conditions, determines the rate of light absorption by the isomer mixture [18]. For this reason, it is important to investigate whether the tested compounds can be photoisomerized (or photodegraded) and under which conditions.

In this respect, two compounds of styryl derivatives (Chart 1) were designed and their photochromic properties evaluated. The kinetics of the photoisomerization process was investigated by measuring ¹H NMR and UV–Vis spectra. The interconversion was induced by absorption of either one or two photons by a molecule.

2. Experimental

2.1. Measurements

All reagents and solvents were purchased from Aldrich Chemical Co. and used without further purification. For thin layer chromatography, aluminum oxide IB-F flexible sheets (thickness 0.2 mm) were purchased from J.T. Baker Chemical Co., Germany.

HPLC analyses were done by an HPLC system equipped with UV–Vis detector (detection wavelength was 360 nm or 400 nm), Binary HPLC Pump and a Symmetry C18 column (3.5 μ m, 4.6 \times 75 mm). Separation was conducted under isocratic conditions with 1.0 mL/min flow rate, r.t., 20 μ L injection volume and HPLC grade THF or acetonitrile containing trifluoroacetic acid (0.05%) as a mobile phase.

The ¹H (200 MHz or 400 MHz) and ¹³C (50 MHz or 100 MHz) NMR spectra were recorded with the use of a Varian Gemini 200 or a Bruker AscendTM 400 NMR spectrometer, respectively. Perdeuterated dimethylsulfoxide (DMSO- d_6) was used as the solvent and tetramethylsilane (TMS) as internal standard.

The IR spectra of the synthesized salts were recorded using a Bruker Vector 22 FT-IR spectrophotometer (Germany) in the range $400-4500 \text{ cm}^{-1}$, by KBr pellet technique.

The elemental analysis was made with a Vario EL III (Elementar



Analysesysteme GmbH, Germany) operating with the VARIOEL software (version 5.14.4.22).

Melting points (uncorrected) were determined on the Boëthius apparatus (type PHMK 05, Germany).

Absorption (the concentration of the dye 1.0×10^{-5} M) and emission spectra (the concentration of the dye 3.0×10^{-6} M) in dimethylsulfoxide (DMSO), acetonitrile (MeCN), tetrahydrofuran (THF), dichloromethane (CH₂Cl₂) and 1,4-dioxane (1,4-Dx) were recorded at room temperature using a Shimadzu UV–vis Multispec-1501 spectrophotometer (Japan) and a Hitachi F-4500 spectrofluorimeter (Japan), respectively.

The fluorescence quantum yields of the studied dyes (φ_{dye}) were calculated using the Eq. (1):

$$\varphi_{dye} = \varphi_{ref} \frac{I_{dye} A_{ref}}{I_{ref} A_{dye}} \cdot \frac{n_{dye}^2}{n_{ref}^2}, \tag{1}$$

where:

 φ_{ref} is the fluorescence quantum yield of reference (Coumarine 1) in ethanol ($\varphi_{ref} = 0.64$ [19]), A_{dye} and A_{ref} are the absorbances of the dye and reference samples at the excitation wavelengths ($A \approx 0.1$ at 404 nm), I_{dye} and I_{ref} are the integrated intensities (areas) of dye and standard spectra, respectively, n_{dye} and n_{ref} are the refractive indices of the solvents used for the dyes and the reference, respectively.

For fluorescence lifetime measurements a time-correlated single-photon counting (TCSPC) system was used. It contains a cooled fast microchannel plate photodetector and is accessorized with a monochromator at the observation. As the excitation source a 375 nm laser diode was used. This laser has a pulse width of 58 ps and maximal average power of 5 mW. The fluorescence decays were fitted using double-exponential deconvolution model, where IRF(t) is the instrument response function at time t, α_i is the amplitude of the decay of the i-th component at time t and τ_i is the lifetime of the i-th component. Based on the data the average lifetime, τ_{av} was calculated as $\tau_{av} = (\Sigma_i \alpha_i \tau_i)/(\Sigma_i \alpha_i)$, The radiative (k_r) and the total non-radiative (k_{nr}) rate constants for the singletexcited state of the studied compounds were estimated from the fluorescence quantum yield (φ_{dye}) and the average lifetime (τ_{av}) values using the following equations

$$k_r = \frac{\varphi_{dye}}{\tau_{av}},\tag{2}$$

$$k_{nr} = \frac{\left(1 - \varphi_{dye}\right)}{\tau_{av}}.$$
(3)

Nonlinear optical absorption properties of the compounds **2** and **3** were characterized at 800 nm using the recently developed f-scan technique [20], which is a modification of the Z-scan technique used in our previous contributions (e.g. [21–27]). The difference between the techniques is that while in the Z-scan the sample is moved along the laser beam (in z direction), in f-scan its position is fixed but instead the focal length (f) of the lens is changed. We have used here an electrically focus-tunable lens (Optotune EL-10–30 series) capable of rapid changes of f. The advantage of f-scan over Z-scan is thus a much shorter time of a single scan, which minimizes the exposure time of organic compounds that are potentially unstable to the high-power pulsed laser radiation, e.g. show photochromic changes as in the present case. The investigated samples were placed in 1 mm path length, stoppered glasses cuvettes. The 800 nm laser pulses (~130 fs) at the repetition rate of 1 kHz were

supplied by a Quantronix Integra-C regenerative amplifier followed by a Quantronix-Palitra-FS optical parametric amplifier. The required wavelength was separated from the Palitra output using polarizing wavelength separators and color glass filters. The measurement was repeated three times for each dye in order to provide an error bar.

Mass spectrometry analysis was performed on a O-Exactive mass spectrometer (Thermo Scientific). Samples of all examined compounds were dissolved in methanol to give a final concentration of 10 μ M and were introduced into the mass spectrometer by use of electrospray source. Data acquisition and analysis were conducted using the Xcalibur (Thermo Scientific) software.

2.1.1. One-photon-induced isomerization

The photochemical process was studied in a guartz cuvette with dimensions $4 \times 1 \times 1$ cm. In order to ensure complete absorption of light, the cuvette was placed in a horizontal position and irradiated with diode pumped solid state (DPSS) laser light ($\lambda_{FM} = 408 \text{ nm}$) (or xenon lamp equipped with monochromator, $\lambda_{EM} = 310$ nm) through the bottom wall (the optical path length = 4 cm). The laser beam power was 20 mW. The solution was stirred during irradiation. After each period of irradiation the electronic absorption spectra were recorded on a Shimadzu UV-vis Multispec-1501 spectrophotometer (Japan).

The photobleaching quantum yield (φ_{bl}) was determined using the following formula:

$$\varphi_{bl} = \frac{N_A \cdot c \cdot h \cdot V \cdot \Delta A}{\lambda \cdot c \cdot t \cdot P \cdot l} \tag{4}$$

where N_A is the Avogadro's number, c is velocity of light in vacuum, *h* is Planck's constant, *V* is the reaction volume, ΔA is the difference between absorbances at the peak wavelength (λ) prior and post irradiation, t is the irradiation time, ε is the molar absorption coefficient of the dye, P is the power of absorbed light and l is the length of solution that the light passes through (the optical path length).

2.1.2. Two-photon-induced isomerization

The process was studied in either a 50 µL or 4 mL quartz cuvette. The cuvette was placed in a vertical position (the optical path length = 1 cm) and irradiated with 800 nm pulses from the Quantronix Integra amplifier (1.0 mJ/pulse, 130 fs pulse length, 1 kHz repetition rate). After each period of irradiation the electronic absorption spectra were recorded on a JASCO V-670 spectrophotometer.

In the case of monitoring the isomerization process by ¹H NMR measurements, the sample was irradiated in NMR tubes for 2–60 min. The samples were diluted to 7.5 mM with DMSO- d_6 before the ¹H NMR spectra were recorded on a Bruker AscendTM 400 NMR spectrometer. The initial concentration was 14.5 mM and the volume 150 μ L. For studies of the dependence of the initial reaction rate on laser power, samples were irradiated in NMR tubes for 6 min to give a low conversion for which the initial rate conditions are applicable.

2.2. Synthetic procedure

2.2.1. Synthesis of 2-[2-(4-formylphenyl)ethenyl]pyridine (1) [28]

2-[2-(4-formylphenyl)ethenyl]pyridine (1) was synthesized based on the condensation of 3.4 g (25.3 mmol) of terephthalaldehyde and 4.8 g (53.2 mmol) of α -picoline in 3 mL of acetic acid and 5 mL of acetic anhydride. The reaction mixture was refluxed for 12 h at 135 °C, cooled down to room temperature and placed in 100 mL of aqueous 6 M HCl. The resulting precipitate (the unreacted aldehyde) was collected and subsequently washed repeatedly with copious water. The filtrate was neutralized with 3 M NaOH. The crude product was collected by filtration and air-dried. Then it was dissolved in hot ethyl acetate, and the insoluble materials were removed by filtration. The formyl compound (1) obtained after evaporation of the solvent (5.4 g) was recrystallized from CHCl₃/ acetone to yield 4.1 g (57%) of pale-yellow powder.

C₁₄H₁₁NO; 209.24 g/mol; mp. 85.5–86.7 °C (lit. mp. 84–86 °C

[28]). ¹H NMR (DMSO- d_6) δ (ppm): 7.316 (m, 1H, Ar), 7.519–7.559 (d, ${}^{3}J_{H,H} = 16.0$ Hz, 1H, -CH=), 7.599–7.619 (d, ${}^{3}J_{H,H} = 8.0$ Hz, 1H, Ar), 7.754–7.794 (d, ${}^{3}J_{H,H}$ = 16.0 Hz, 1H, –CH=), 7.840 (m, 1H, Ar), 7.932 (m, 4H, Ar), 8.621 (m, 1H, Ar), 10.013 (s, 1H, CHO).

¹³C NMR (DMSO- d_6) δ (ppm): 123.48, 123.60, 128.08, 130.48, 131.19, 131.86, 137.45, 150.14, 192.93 (CH), 136.02, 142.79, 154.82 (C). IR (KBr): 2925, 1694, 1600, 1470, 1431, 1214, 1169, 975, 820, 533.

2.2.2. General procedure for synthesis of styryl dyes [29–31]

Quaternary salt (10 mmol), 2-[2-(4-formylphenyl)ethenyl]pyridine (10 mmol) and 25 mL ethanol were placed in a 100 mL onenecked flack with a stirrer and a condenser. Then three drops of piperidine were added as a catalyst and the resultant mixture was refluxed for 12 h. Upon cooling, microcrystals of the iodide salt were collected by filtration under reduced pressure and recrystallised from ethanol.

2.2.2.1. trans,trans-4-{4-[(2-(pyridine-2-yl)ethenyl]-styryl}-N-meth*vlpvridine iodide (2).* The compound **2** was prepared according to the general procedure using 1.4-dimethylpyridinium iodide (2.35 g. 10 mmol) and 2-[2-(4-formylphenyl)ethenyl]pyridine (2.09 g, 10 mmol). The dark yellow solid was crystallized from ethanol: C₂₁H₁₉N₂I; 426.29 g/mol; 3.15 g (73.8% yield); mp 284.4 °C. The purity of the dye was checked by TLC (methanol, aluminum oxide IB-F, $R_f = 0.29$).

¹H NMR (DMSO- d_6) δ (ppm): 4.246 (s, 3H, N⁺CH₃), 7.267 (m, 1H, Ar), 7.439–7.399 (d, ${}^{3}J_{H,H} = 16.0$ Hz, 1H, -CH=), 7.559–7.519 (d, ${}^{3}J_{H,H} = 16.0$ Hz, 1H, -CH=), 7.577-7.557 (d, ${}^{3}J_{H,H} = 8.0$ Hz, 1H, Ar), 7.706–7.666 (d, ${}^{3}J_{H,H} =$ 16.0 Hz, 1H, –CH=), 7.756 (m, 5H, Ar), 8.028–7.988 (d, ${}^{3}J_{H,H}$ = 16.0 Hz, 1H, -CH=), 8.231–8.214 (d, ${}^{3}J_{H,H} = 6.8$ Hz, 2H, Ar), 8.579 (m, 1H, Ar), 8.865–8.848 (d, ${}^{3}J_{H,H} = 6.8$ Hz, 2H, Ar).

¹³C NMR (DMSO-*d*₆) δ (ppm): 46.905 (N⁺CH₃), 122.565, 122.707, 123.144, 123.395, 127.612, 128.530, 129.404, 131.010, 136.790, 139.882, 144.897, 149.464 (CH), 134.889, 138.243, 152.239, 154.544 (C).

IR (KBr): 3004, 1644, 1621, 1520, 1431, 1336, 1190, 1050, 972, 839, 810, 767, 743, 620, 545.

Elemental analysis: calc. 59.2%C, 4.5%H, 6.6%N, 29.8%I, measured 59.13%C, 4.54%H, 6.54%N.

2.2.2.2. trans, trans-4-{4-[(2-(pyridine-2-yl)ethenyl]-styryl}-Nmethyl-5,6,7,8-tetrahydroisoquinolinium iodide (3). The compound 3 was prepared according to the general procedure using Nmethyl-5,6,7,8-tetrahydroisoquinolinium iodide (2.75 g, 10 mmol) and 2-[2-(4-formylphenyl)ethenyl]pyridine (2.09 g, 10 mmol). The yellow solid was crystallized from ethanol: C₂₄H₂₃N₂I; 466.36 g/ mol; 3.99 g (85.5% yield); mp 257.8–259.6 °C. The purity of the dye was checked by TLC (methanol, aluminum oxide IB-F, $R_f = 0.18$).

¹H NMR (DMSO- d_6) δ (ppm): 1.811 (m, 2H, $-CH_2-$), 2.890 (m, 4H, -CH₂-), 4.239 (s, 3H, N⁺CH₃), 7.276 (m, 1H, Ar), 7.388-7.428 (d, ${}^{3}J_{H,H} = 16.0$ Hz, 1H, -CH=), 7.569 (s, 1H, -CH=), 7.602–7.622 (d, ${}^{JH,H}_{JH,H} = 16.0$ Hz, 1H, -CH=), J050 (c, 1H, -CH=), ${}^{J}_{JH,H} = 8.0$ Hz, 2H, Ar), ${}^{7.687-7.727}$ (d, ${}^{3}_{JH,H} = 16.0$ Hz, 1H, -CH=), ${}^{7.751-7.771}$ (d, ${}^{3}_{JH,H} = 8.0$ Hz, 2H, Ar), ${}^{7.819}$ (m, 2H, Ar), ${}^{8.500-8.517}$ (d, ${}^{3}_{J} = 6.8$ Hz, 1H, Ar), ${}^{8.584}$ (m, 1H, Ar), ${}^{8.698-8.715}$ $(d, {}^{3}J_{H,H} = 6.8 \text{ Hz}, 1\text{H}, \text{Ar}), 8.807 (s, 1\text{H}, \text{Ar}).$

¹³C NMR (DMSO-*d*₆) δ (ppm): 21.023, 26.496, 26.955 (-CH₂-), 46.610 (N⁺CH₃), 121.352, 122.499, 122.576, 127.044, 129.077, 130.672, 131.098, 134.070, 136.757, 141.488, 144.394, 149.431 (CH), 131.611, 135.468, 136.003, 136.604, 150.873, 154.599 (C).

IR (KBr): 3030, 2931, 1640, 1603, 1587, 1472, 1322, 1233, 1162, 1055, 1014, 985, 960, 845, 822, 766, 746, 549.

Elemental analysis: calc. 61.8%C, 5.0%H, 6.0%N, 27.2%I, measured 61.61%C, 5.15%H, 5.94%N.

3. Results and discussion

3.1. Synthesis

The terephthalaldehyde was found to be reasonably reactive in cyanine condensations. Thus, the compound reacts with α -picoline in acetic anhydride to provide 2-[2-(4-formylphenyl)ethenyl]pyridine in a good yield. The reaction of the obtained 2-[2-(4-formylphenyl)ethenyl]pyridine with quaternary salt using piperidine as catalyst leads to long conjugated organic compounds **2–3** (Scheme 1). Synthesis of the compounds is based on the method reported by us and other authors [28–31]. We characterized the intermediate and objective compounds using standard spectroscopic methods and obtained satisfactory analysis of data corresponding to their molecular structure.

3.2. Spectral properties

Normalized and scaled between wavelength and wavenumber representation [32,33] UV–visible absorption and fluorescence spectra (excited at 404 nm) of compounds **2** and **3** in organic solvents of different polarity are shown in Fig. 1.

The styryl compounds **2** and **3** show intense long-wavelength (LW) absorption band ascribed to $\pi \rightarrow \pi^*$ transition with maximum located between 383 and 397 nm. The LW band of 2 is shifted to longer wavelength by about 200 cm^{-1} in comparison to **3**. The molar absorption coefficient of the LW band of the studied compounds ranges from 4.4×10^4 (**3**) to 5.6×10^4 M⁻¹ cm⁻¹ (**2**). The results suggest that the bonding of the methine group to the pyridine ring leads to a decrease in $\pi \to \pi^*$ transitions. The fluorescence maxima are located at ca. 536 nm and 530 nm for compounds 2 and 3, respectively. Rigidity of the methine group causes the blue shift of the fluorescence band probably because of poorer π electron conjugation caused by twisting of the alkyl bridge (disturbed planarity of the compound in the ground state). The large Stokes shifts ($\sim 6500-7300 \text{ cm}^{-1}$) suggest that the geometry of the compounds changes after excitation. The spectral properties of compounds 2 and 3 are listed in Table 1.

In order to obtain more insight into the photophysics of **2** and **3**, we determined their quantum yields in different solvents with Coumarine 1 in ethanol as the reference and their fluorescence lifetimes using time correlated single photon-counting technique



Fig. 1. Normalized and scaled [32,33] electronic absorption (solid line) and fluorescence (dash line) spectra of 2 and 3 in DMSO and THF at room temperature; $\lambda_{EX} = 404$ nm.

(TCSPC). Analyzing the data collected in Table 1, it follows that, for compound **2**, the fluorescence quantum yield clearly increases with increasing solvent polarity from 13% in THF to 20% in DMSO, whereas for **3**, the fluorescence quantum yield is found to be very low (below 1%) and almost independent of the microenvironment. The high value of fluorescence quantum yield in DMSO results from the increased viscosity of the solvent.

The low fluorescence quantum yield of compound **3** might be connected with some interactions between the excited solute molecule and solvent molecules, which modifies the excited-state configuration and the fluorescence spectrum intensity, e.g. proximity effect and conformational changes [35–38]. In a partially stiffened molecule, twisting of the alkyl bridge probably disturbs planarity of the compound. Thus, especially in non-polar solvents, the emitting polar π - π^* state might be destabilized to experience perturbation by the proximity effect and vibronic coupling to an energetically close lying n- π^* state. This opens an effective nonradiative deactivation pathway for the excited singlet state, which may explain the observed reduction in the fluorescence intensity.

The fluorescence decay profiles were double-exponential. Analyzing the fluorescence decay data obtained for both studied molecules, it is found that the temporal profile exhibits a fast (τ_1) and a slower decay (τ_2) components. The presence of the broad long-wavelength steady-state fluorescence band and two decay components in the studied molecules dissolved in polar solvents, suggest that two emitting states exist for the investigated fluorophores in polar solvents: a non-relaxed intramolecular charge transfer state (ICT)_{NR} and a relaxed ICT state (ICT)_R.



Scheme 1. General route for the synthesis of the styryl compounds.

Table 1						
Photophysical	data ^a	for	compounds	2	and	3

	Compound	2				Compound	3			
	DMSO	MeCN	THF	CH ₂ Cl ₂	1,4-Dx	DMSO	MeCN	THF	CH ₂ Cl ₂	1,4-Dx
λ_{max}^{abs}	396	392	390	416	392	389	386	383	405	381
ε	50800	56000	_	48400	_	44400	46200	_	44300	_
λ_{max}^{fl}	538	536	536	538	511	527	530	532	537	474
Δv	6665	6853	6984	5451	5941	6732	7039	7313	6069	5150
φ _{fl}	19.74	18.39	13.40	11.52	4.20	0.69	0.66	0.59	0.27	0.57
$ au_1$	0.393	0.317	0.374	0.327	0.216	0.033	0.076	0.299	0.062	0.246
α_1	21.18	22.87	37.52	26.09	93.61	75.46	71.15	40.06	27,53	33.19
$ au_2$	0.958	0.695	0.952	0.700	1.352	1.067	1.302	1.02	0.631	1.155
α2	78.82	77.13	62.48	73.91	6.39	24.54	28.85	59.94	72,47	66.81
τ_{av}	0.838	0.609	0.735	0.603	0.289	0.287	0.430	0.731	0.474	0.853
χ^2	1.06	1.01	1.14	1.11	1.53	1.48	1.33	1.45	1.46	1.34
$av k_r$	2.36	3.02	1.82	1.91	1.46	0.24	0.15	0.08	0.06	0.07
$av k_{nr}$	0.96	1.34	1.18	1.47	3.32	3.46	2.31	1.36	2.10	1.17
k _{nr} /k _r	4.1	4.4	6.5	7.68	22.8	144.1	150.1	169.9	369.4	174.4
f_{os}	0.952	1.02	_	1.01	_	0.931	0.914	_	0.96	_
σ	1.9	2.1	_	1.8	_	1.7	1.8	_	1.7	_
μ ₁₂	8.91	9.16	_	9.39	-	8.72	8.59	_	9.06	_

^a Absorption (λ_{max}^{ab} ; *nm*), fluorescence (λ_{max}^{fl} ; *nm*) maxima, Stokes shift (Δv ; cm⁻¹), molar absorption coefficient (ε_{max} ; M⁻¹ cm⁻¹), fluorescence quantum yield (φ_{fl} ; %), fluorescence lifetime (τ ; ns), their amplitudes (α ; %) and correlation coefficients (χ^2), radiative (${}^{av}k_r$; 10⁸ s⁻¹) and nonradiative (${}^{av}k_{nr}$; 10⁹ s⁻¹) rate constants, f_{os} oscillator strength, one-photon absorption cross-section (σ ; \dot{A}^2) and μ_{12} in D calculated based on the oscillator strength and the energy of the ICT maximum according to B.J. Coe et al. [34].

Because both studied dyes show the multimode emission character, the average values of the fluorescence decay times have been calculated. The calculated average lifetime was in the subnanosecond range and changed from 838 ps (**2** in DMSO) to 287 ps (**3** in DMSO). Radiative and non-radiative rate constants calculated from quantum yields and fluorescence lifetimes show that the non-radiative rate constants are two orders of magnitude larger than the radiative decay for compound **3** and only four or six times larger for compound **2**.

Using the f-scan technique, the effective two-photon absorption cross-section ($\sigma_2^{\text{eff.}}$) in DMSO was measured to be 156 ± 12 GM and 119 ± 9 GM at 800 nm for compounds **2** and **3**, respectively.

These interesting electronic properties of the newly synthesized dyes have prompted an intensive investigation of the *trans-cis* photoisomerization processes in them.

3.3. Photochemical observations

One- and two-photon induced photochemistry of compounds **2** and **3** was studied using a combination of UV–Vis and ¹H NMR spectroscopy upon laser irradiation.

3.3.1. One-photon induced isomerization

As shown in Fig. S1, the visible light irradiation (CW, 408 nm) of the investigated compounds in acetonitrile solutions leads to a decrease of the long-wavelength (LW) absorption band at λ_{max} (ca. 48-55%). This behavior is accompanied by increase of the shortwavelength (SW) absorption band with the maximum localized at ~310 nm. After a few minutes of irradiation the photostationary state (PSS) is reached and no further change in the intensity of the absorption occurs up to ca. 100 s of irradiation. We suppose that the observed changes are due to the E-Z photoisomerization process. Thus, the photostationary-state mixture generated after irradiation with visible light (408 nm) contains the formed *cis*-isomer and the residual trans-isomer with no change in the trans:cis ratio, or an appearance of any new products. The well-defined isosbestic points (340 and 250 nm) support the conclusion that both trans-2 and trans-3 are converted into respective single photoproducts. The obtained Z-isomer is thermally stable under given conditions but the UV irradiation (310 nm) causes the return of the molecule to its

initial state. The observed changes in the electronic absorption spectra of compounds **2** and **3** under 408 nm irradiation are depicted in SI (Fig. S1).

Based on UV–Vis data, the kinetics of the *trans-cis* photochemical isomerization was studied by measuring the absorbance at a fixed wavelength as a function of time. The relative absorbance A(t) was calculated based on Eq. (5) [39]:

$$A(t) = \frac{A(trans, t)}{A(trans, t_0)},$$
(5)

where A(trans, t) and $A(trans, t_0)$ are absorbances at λ_{max} before and after different times of irradiation, respectively.

The kinetic data were found to fit well to a mono-exponential function defined by Eq. (6).

$$A(t) = A_{(trans,PSS)} + (A_{trans,t_0} - A_{trans,PSS})\exp(-k \cdot t),$$
(6)

where k is the observed rate constant and t is the time of irradiation [39–41].

The apparent rate constant, k, for isomerization is expressed by the sum of the forward, $k_{trans \rightarrow cis}$, and backward rate constant, $k_{trans \leftarrow cis}$ [39].

$$trans = \frac{k_{trans \to cs}(h\nu)}{k_{trans \leftarrow cis}(h\nu)} cis$$
(7)

$$k = k_{trans \to cis}(h\nu) + k_{trans \leftarrow cis}(h\nu)$$
(8)

Fig. 2 shows the plots of relative absorbance vs. time of irradiation (Eq. 6) during the *trans* \rightarrow *cis* isomerization of **2** and **3** in MeCN and DMSO, respectively. The observed rate constants (*k*) for *cis*-**2** and *cis*-**3** in DMSO and MeCN at room temperature are collected in Table 2.

For both compounds an exponential relationship is observed. As shown in Table 2, the k values in DMSO are lower than those in MeCN. This indicates that the *trans-cis* isomerization is dependent on the polarity and viscosity of the medium [39].

The obtained results allow also to calculate the photobleaching quantum yield (Table 2). The values observed for compound **2** are



Fig. 2. The kinetics of absorbance changes of **2** (red) and **3** (blue) obtained in MeCN (circles) and DMSO (triangles); the *trans* \rightarrow *cis* isomerization was induced with 408 nm irradiation (DPSS laser, 20 mW). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

higher than for compound **3**, however the differences are not very significant. This behavior is understandable because the *trans* form of **3** possesses one partly stiffened vinylic group and has better photostability, whereas the compound **2** with freely rotating vinylic groups is less stable. Moreover, the photobleaching quantum yield is higher in MeCN ($\eta = 0.341 \cdot 10^{-3}$ Pa s; $E_T^N = 0.46$) than in DMSO ($\eta = 1.996 \cdot 10^{-3}$ Pa s; $E_T^N = 0.444$). Lower polarity and higher viscosity of the solvent increases photostability of the studied compounds.

To confirm the *trans-cis* photoisomerization and to exclude other photoinduced processes an NMR analysis was performed. Fig. 3 shows the NMR spectra of parent sample (*trans-***2**), sample stored in the dark, heated in the dark at 70 °C and irradiated at 408 nm.

The *trans* and *cis* isomers of styryl derivatives can be distinguished by their distinctive ${}^{3}J_{HH}$ coupling constants [38]. The analysis of ¹H NMR spectra of **2** in DMSO-*d*₆ indicates that storing the solution in the dark and heating at 70 °C for 5 h did not cause any changes in signals positions. In the region 7–9 ppm, there are well-separated pairs of doublets for the vinylic protons. The coupling constant ${}^{3}J_{H,H} = 16.0$ Hz is characteristic for the *trans* configuration (see experimental part and SI). After irradiation, the formation of the *cis* isomer is accompanied by a change of the peak positions. Indeed, the intensity of the peaks corresponding to the vinylic protons, located at 8.03, 7.71, 7.56 and 7.44 ppm for *trans*-**2**, decreased, while new pairs of doublets with the coupling constant equal ca. 12.0 Hz appeared at 7.71, 7.39, 7.25 and 6.84 ppm for *cis*-**2**, respectively. The observed changes in chemical shifts and the coupling constants are in perfect agreement with *cis* arrangement

[42]. It should be noted that the ¹H NMR spectrum of compound **3** after 408 nm irradiation, also displays the same changes i.e. the disappearance of the *trans* isomer and the increase of the photoproduct.

As can be seen in Figs. S2 and S3, when the *trans* solution is irradiated for ca. 2 h, the signals specific to *trans*-compound, disappear while the peaks characteristic for the *cis* photoproduct become more intense. The analysis of the NMR spectra does not reveal any new peaks which might be attributed to other photoproducts for the given conditions. By integrating the *cis* isomer signals corresponding to the vinylic doublets and/or the methyl groups relative to the *trans* peaks, it was found that the *cis* integral gradually increased before reaching a plateau of 56% or 53% relative to the sum of the *trans* and *cis* isomers of **2** and **3**, respectively after ca. 2 h of 408 nm irradiation in DMSO- d_6 . Fig. 4 compares the kinetic behavior for the tested styryl derivatives.

3.3.2. Two-photon induced isomerization

Similarly to one-photon irradiation, upon 800 nm light absorption the intensity of the long-wavelength band corresponding to the $\pi \rightarrow \pi^*$ transition of *trans* form decreases and the short-wavelength band attributed to the *cis* form (centered at around 310 nm) increases for the two compounds (Fig. 5). The results indicate the transformation of the more stable E-isomer to the Z-isomer that absorbs at shorter wavelengths. An isosbestic point can be clearly seen between these two bands, which indicates the presence of a precursor-successor relationship between the two absorbing states. After 20 min of irradiation the photostationary state was achieved.

In order to confirm the two-photon induced process, Fig. 6 illustrates the relationship between the initial rate of photoisomerization and the incident laser power. The slope of the log–log plot should give the number of photons absorbed per absorption event [43]. The experimental data points are fitted with lines having slopes of 1.94 ± 0.1 and 1.91 ± 0.1 for compounds **2** and **3**, respectively, suggesting a two-photon excitation mechanism. The slight deviation of the slopes from the theoretical value of two is believed to be due to the saturation effects at higher photon flux [41,44].

The corresponding ¹H NMR spectra for the sample before and after infra-red irradiation to the photostationary state (PSS) are shown in Fig. 7. Each of the resonances is assigned to either the *trans* or the *cis* form of **3**. Prior to irradiation, the sample is exclusively in the *trans* form. The pure *trans*-**2** displays a large coupling constant (${}^{3}J_{H,H}$) between vinylic protons equal to 16.0 Hz, typical of the *trans*-stilbene isomer. As expected, the ¹H NMR spectrum for the photogenerated *cis* isomer contains a signal pattern similar to that of the *trans* form, but with different chemical shifts (the coupling constants between vinylic protons ${}^{3}J_{H,H} = 12$ Hz).

As the signals for the *trans* and *cis* forms are well separated, the *trans:cis* ratio was readily determined. Analysis of the data collected

Table 2	
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Results of probing the sample of 2 and 3 after one- and two-photon irradiation.^a

No		Ratio <i>cis/trans</i> form ^b	k ^b	$\varphi_{bl}^{\mathbf{b}}$	Ratio <i>cis/trans</i> form ^c	k ^c	φ_{bl} c	Ratio cis/trans form ^d	k ^d
		From UV–Vis						From ¹ H NMR	
2	1PI 2PI	0.55/0.45 0.55/0.45	$\begin{array}{c} 0.442 \\ 8.06 \times 10^{-3} \end{array}$	0.298	0.54/0.46 0.55/0.45	$\begin{array}{l} 0.159 \\ 3.65 \times 10^{-3} \end{array}$	0.135	0.56/0.44 0.56/0.44	$\begin{array}{c} 1.32 \times 10^{-4} \\ 3.93 \times 10^{-3} \end{array}$
3	1PI 2PI	0.49/0.51 0.50/0.50	$\begin{array}{l} 0.308 \\ 4.51 \times 10^{-3} \end{array}$	0.221	0.48/0.52 0.53/0.47	$\begin{array}{l} 0.272 \\ 3.24 \times 10^{-3} \end{array}$	0.133	0.53/0.47 0.53/0.47	$\begin{array}{l} \textbf{4.17}\times 10^{-4} \\ \textbf{3.43}\times 10^{-3} \end{array}$

^a Observed rate constants (k, s⁻¹); quantum yields (φ_{bl}) of photobleaching process.

^b In MeCN.

c In DMSO.

^d Ratio based on integration of the vinylic doublets ([*trans*]/[*trans*]+[*cis*]) in DMSO-*d*₆.



Fig. 3. ¹H NMR spectra of compound **2** in DMSO- d_6 (from bottom): *a*) parent sample (*trans* form), *b*) sample stored in a dark, c) sample heated at 70 °C, *d*) and after one-photon irradiation at 408 nm leading to the photostationary state.



Fig. 4. Kinetics of one-photon isomerization of compounds **2** (red circles) and **3** (blue triangles) upon irradiation at 408 nm (70 mW), as monitored by ¹H NMR spectroscopy. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

in Table 2 revealed that UV–Vis data and NMR spectroscopy led to similar conclusion about the *trans-cis* conversion (Fig. 8).

3.3.3. Photodegradation

The presented above results indicate that the tested styryl derivatives undergo photoisomerization upon both 408 nm and 800 nm light absorption. However, this is not the only process. Additional processes like photobleaching or photodegradation should be also considered. From the literature [45,46] it is well known that the photodegradation of the styryl dyes is promoted by oxygen. Since oxygen is a good electron acceptor the sequence of reactions leading to photodegradation of the styryl dyes is likely to be that illustrated below (Eqs. 9–11) [45,46]:

$$Dye + h\nu \rightarrow Dye^* \tag{9}$$

$$Dye^* + O_2 \rightarrow Dye^{\cdot +} + O_2^{\cdot -}$$
 (10)

$$Dye + O_2^{-} \rightarrow degradation$$
 (11)

As can be seen from the above equations the photodegradation might follow either zero or first order kinetics. In the first case the interaction of the excited dye with oxygen (Eq. (10)) becomes the rate determining process. For the first-order reaction the limiting step of the process is dye excitation (Eq. (9)) [45,46]. The photodegradation process was monitored in UV-Vis and MS spectra. Analysis of the electronic absorption spectra (Fig. 9) recorded after different irradiation time revealed that short exposure of the sample to light (up to 100 s) resulted in trans-cis isomerization and then the destruction of the compounds occurred. Although the difference between dye 2 and dye 3 is not very large, dye 3 with one partly stiffened vinylic group exhibits less photostability than dye 2 with two ethyl groups. After irradiation for 7 h, the dye 3 showed 80-82% photobleaching, but dye 2 showed only 62-64% decrease in maximal absorbance. This may suggest that the photo-oxidative fading of the dves 2 and 3 occurs as a result of an oxygen attack onto the vinylene group upon light exposure. However, these compounds have different photostabilities. Compound 2 has much better photostability than **3.** According to literature data [47], when the methine chain length is shorter, the photostability of cyanine dyes greatly increases. Thus, we expected that the compound 3, having one vinylene group stiffened, should reveal worse photobleaching behavior. The effect illustrated in Fig. 9 is inconsistent with this expectation but it might be related to the fluorescence quantum yields of compound **2** (18.39%) and compound **3** (0.66%) (see Table 1). We suppose that the excited molecule 2 is quenched quicker than 3 by intra-molecular electron transfer and goes back to the ground state, and thus the compound is protected from photobleaching. A similar effect was observed by Peng et al. for a series of heptamethine 5-sulfo-3H-indocyanine dyes [48]. Additionally, the increase of the solvent viscosity (from MeCN to DMSO)



Fig. 5. The dependence of UV–Vis absorption spectra of 2 (left) and 3 (right) in MeCN upon irradiation with Quantronix Integra femtosecond laser (800 nm, 1.0 mJ/pulse, 130 fs pulse length, 1 kHz, 64 GW/cm²). Arrows indicate the direction of changes with time of irradiation.



Fig. 6. The dependence of the initial rate of *cis* isomer formation on the average laser power at 800 nm, as monitored by UV–Vis spectroscopy. The solid line shows the best straight line fit to the data.

increases the photostability of the compounds which is also consistent with the increase of the fluorescence quantum yield in DMSO.

The photodegradation of dyes **2** and **3** was followed at absorption maximum of the pure *trans* form. In both cases, there was a linear relationship between absorbance and irradiation time in the time range from 100 s to 7 h, as shown in Fig. 9, which means that the photodegradation followed zero-order kinetics.

The photodegradation rate constants for the tested compounds were affected by the experimental conditions such as the presence or absence of oxygen. The kinetics curves shown in Fig. 10 represent the relationship between the relative absorbance of **2** and **3** and time in the acetonitrile solution saturated with oxygen, air or helium.

For saturated solutions of **2**, the photodegradation rate constants were calculated to be 1.6×10^{-5} , 1.5×10^{-5} and 1.4×10^{-5} s⁻¹ in O₂, air and He, respectively. Saturated solutions of **3** gave rate constants of 6.3×10^{-5} , 5.7×10^{-5} , and 5.4×10^{-5} s⁻¹ for O₂, air, and He, respectively. The data indicate that photobleaching rate constants are enhanced in the presence of oxygen in



Fig. 7. ¹H NMR spectra of compound **3** in DMSO-*d*₆: before and after 10 min of two-photon irradiation at 800 nm (64 GW/cm²) with Quantronix Integra Ti:sapphire femtosecond laser (stacked spectra from bottom).



Fig. 8. Kinetics of two-photon isomerization of compound **2** (red circles) and **3** (blue triangles, inset) upon irradiation at 800 nm (64 GW/cm^2), as monitored by ¹H NMR spectroscopy. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 9. Kinetics of photobleaching upon irradiation at 408 nm (20 mW), as monitored by UV–Vis spectroscopy.

the sample but in a small extent.

In order to confirm the degradation of the compounds upon

Table 3

The major ions (m/z) produced from photodegradation of **2**.

<i>m/z</i> (measured)	<i>m/z</i> (calculated)	Assignment	Mass error (ppm)
299.15428	299.1548	Product 2 , [C ₂₁ H ₁₉ N ₂] ⁺	1.73
285.13824	285.1392	[C ₂₀ H ₁₇ N ₂] ⁺	3.36
226.08591	226.0868	[C ₁₄ H ₁₂ NO ₂] ⁺	3.93
210.09109	210.0919	[C ₁₄ H ₁₂ NO] ⁺	3.85
152.07047	152.0711	[C ₈ H ₁₀ NO ₂] ⁺	4.14
138.05486	138.0555	[C ₇ H ₈ NO ₂] ⁺	4.63
124.03938	124.0398	$[C_6H_6 NO_2]^+$	3.38

Table 4	4
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The major ions (m/z) produced from photodegradation of **3**.

<i>m/z</i> (measured)	<i>m</i> / <i>z</i> (calculated)	Assignment	Mass error (ppm)
339.18518	339.1861	Product 3 , $[C_{24}H_{23} N_2]^+$	2.71
325.16949	325.1705	$[C_{23}H_{21}N_2]^+$	3.10
294.14844	294.1494	[C ₁₉ H ₂₀ NO ₂] ⁺	3.26
285.13837	285.1392	[C ₂₀ H ₁₇ N ₂] ⁺	2.91
277.13335	277.1341	[C ₁₈ H ₁₇ N ₂ O] ⁺	2.70
262.12231	262.1232	[C ₁₈ H ₁₆ NO] ⁺	3.39
224.10669	224.1075	[C ₁₅ H ₁₄ NO] ⁺	3.61
197.11972	197.1204	[C ₁₄ H ₁₅ N] ⁺	3.44

long-time irradiation the mass spectra were recorded. Due to difficulty in isolation of the principal products the measurements were performed for the parent sample, the sample irradiated to the photostationary state and fully bleached dye. Given the high mass accuracy of the HRMS mass spectrometry there can be no question as to the elemental composition or charge of the ions formed. The structures of the formed ions have been confirmed by the application of the collision induced dissociation (CID) tandem mass spectrometry method. The major fragmentation ions observed in the mass spectrum of the product mixture are listed in Tables 3 and 4. Figs. S9–S14 show the ESI(+) HRMS mass spectra of the dyes under mentioned above conditions.

We suspect that the degradation of the dyes begins with the rupture of the vinylene bond. Then the second -CH=CH- bond is attacked to produce the remaining products shown in Fig. 11 for dye **2**. However, it is necessary to emphasize that the products detected by MS might arise from both the photodegradation and thermal decomposition of the dyes as previously detected for cyanine and merocyanine dyes [45,46]. So, it is difficult to evaluate the mechanism leading to the detected products. However, the detected photofragmentation products are consistent with the involvement of oxygen [49,50].



Fig. 10. Comparison of the 2 (left) and 3 (right) photofading profiles. Irradiation source: DPSS laser, 408 nm, 70 mW.



Fig. 11. Proposed main products for the photodegradation of compound 2. (The ortho pyridine derivatives are also possible).

4. Conclusion

Two styryl dyes were prepared and characterized by UV-Vis absorption, fluorescence and NMR spectroscopy. It was observed that the rigidity of the methine group attached to the pyridine moiety changed their spectral properties leading to hypsochromic shift of the absorption band and decreasing fluorescence intensity. In photostability investigations, the compound **3** with stiffened methine group shows the strongest photofading behavior. It was found that the photoisomerization is mainly responsible for the observed hypochromic effect in the initial time of irradiation. This process occurs from the excited singlet state of *trans* isomer to the *cis* isomer following a *trans*- $S_0 \rightarrow S_1$ excitation and can be induced by both visible-light and infra-red irradiation, by one-photon and two-photon absorption processes, respectively. Heating of the solution, under given conditions, did not cause any changes in signals position. The nature of the photoproduct was unambiguously confirmed by NMR spectroscopy. Kinetics of the trans-to-cis isomerization in both cases is analogous. Longer exposure of the solution to visible light leads to degradation of the compounds. The possible main products formed after decomposition of the tested compounds were determined based on MS spectra.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://

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