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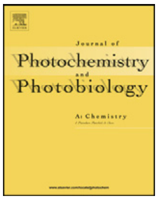

Polyenic spirobenzopyrans: Synthesis and study of photochromic properties

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ABSTRACT

Four new retinal analogs on basis of nitro-substituted indoline spiropyran were prepared and the spectral kinetic study of their photochromic properties was carried out. Specific influence of nature and length of polyenic substituents on spectral characteristics of spiropyran forms, efficiency of photochromic transformations and photodegradation was established.

1. Introduction

Among different classes of organic photochromic compounds, spiropyrans have been extensively investigated because of their remarkable properties and have spread in various applications. One of the most interesting directions is study of photodriving of biopolymers functional activity, such as photoswitching of protein activity by a spiropyran covalently bound to the protein. Significant attention is being paid to the possibility of development of neural net processing devices of optical signals on basis of photochromic compounds including those containing bacteriorhodopsin [1–15]. In this connection, the creation of new generation of hybrid photochromic compound, which would allow dual-frequency control of such photochromic systems, is of great interest. Toward this end, we began studies for design of new retinal analog structures on basis of thermally fast relaxing spiropyrans without nitro-substituent in the pyran heterocycle [10], and thermally irreversible diarylethenes [12].

The current article represents the development of study in this direction for the purpose of synthesis and investigation of photochromism of retinal analogs with nitro-substituent at 6-position of spiropyran molecule.

2. Experimental

The qualitative composition of the reaction mixtures and the homogeneity of the compounds were determined by TLC on Kieselgel 60 F_{254} precoated plates (Merck, Germany) in the following solvent mixture: dichloromethane/petroleum ether – 3:1 (v/v). The spots were visualized under UV- or Vis-light. Preparative adsorption column chromatography was done on Silicagel 60 (Merck, Germany) and aluminum oxide (Brockmann activity IV) (Reanal, Hungary).

^{1}H NMR spectra were recorded in deuterochloroform on Bruker DPX-300 spectrometer (Germany). Chemical shifts (δ) are given in ppm accurate to 0.01 ppm relatively internal standard of deuterochloroform (δ 7.25 ppm). Spin–spin coupling constant magnitudes were measured in Hz accurate to 0.1 Hz. IR-spectra were measured on Fourier spectrophotometer Bruker EQUINOX 55 (Germany) in KBr pellets. Mass spectra were performed on Cratos M-30 instrument (UK) by the direct pattern input and ionization by electron impact (EI 70 eV). Elemental analysis was carried out on automatic C, H, N-analyzer model Finnigan EA 1112 (Thermo, Italy).

When describing spectral data we used the following abbreviations: sh. – shoulder, s – singlet, d – doublet, t – triplet, q – quartet, dd – doublet doublets, val. – valence vibration, def. – deformation vibration, comb. – combinational band, asym. – asymmetrical, sym. – symmetrical.

Photochemical and kinetic investigations were carried out at identical experimental conditions at 25 °C. Electronic spectra were

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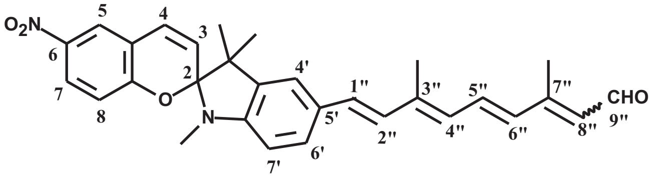
Table 1

^{1}H NMR data for compounds (**I**–**V**).

Compound structure | Data



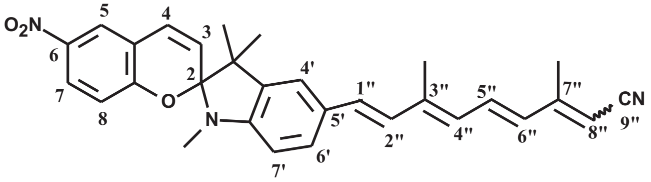
(I)

Polyenic chain

	1″-H	2″-H	3″-CH_3	4″-H	5″-H	6″-H	7″-CH_3	8″-H	9″-H
δ, ppm	6.41 d	6.35 d	2.09 s	6.15 d	7.15 dd	6.02 d	2.36 s	6.01 d	10.1 d
J, Hz	15.0	15.0	–	10.5	15.0/10.5	15.0	–	8.1	8.1
Integral	1H	1H	3H	1H	1H	1H	3H	1H	1H

Spiropyran part

	3-H	4-H	5-H	7-H	8-H	N–CH_3	3′a-CH_3	3b′-CH_3	4′-H	6′-H	7′-H
δ, ppm	5.84 d	6.95 d	8.01 d	8.02 dd	6.75 d	2.76 s	1.27 s	1.32 s	7.32 d	7.25 dd	6.53 d
J, Hz	10.3	10.3	2.8	8.7/2.8	8.7	–	–	–	1.9	8.2/1.9	8.2
Integral	1H	1H	1H	1H	1H	3H	3H	3H	1H	1H	1H



(V)

Polyenic chain

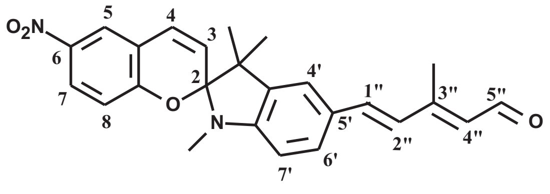
	1″-H	2″-H	3″-CH_3	4″-H	5″-H	6″-H	7″-CH_3	8″-H	9″-H
δ, ppm	6.77 d	6.70 d	2.07 s	6.25 d	6.97 d	6.31 d	2.21 s	5.18 s	–
J, Hz	16.0	16.0	–	11.5	15.0/11.5	15.0	–	–	–
Integral	1H	1H	3H	1H	1H	1H	3H	1H	–

Spiropyran part

	3-H	4-H	5-H	7-H	8-H	N–CH_3	3a′-CH_3	3′b-CH_3	4′-H	6′-H	7′-H
δ, ppm	5.84 d	6.94 d	7.98 d	8.15 dd	6.75 d	2.75 s	1.20 s	1.31 s	7.22 d	7.27 dd	6.51 d
J, Hz	10.3	10.3	2.8	8.6/2.8	8.6	–	–	–	1.6	8.1/1.6	8.1
Integral	1H	1H	1H	1H	1H	3H	3H	3H	1H	1H	1H

Table 1 (*Continued*)

Compound structure	Data



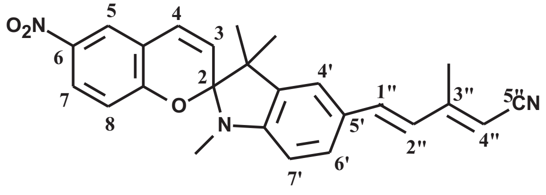
(IV)

Polyenic chain

	1″-H	2″-H	3″-CH_3	4″-H	5″-H	6″-H	7″-CH_3	8″-H	9″-H
δ, ppm	7.07 d	6.79 d	2.38 s	6.05 d	10.13 d				
J, Hz	16.0	16.0	–	8.2	8.2				
Integral	1H	1H	3H	1H	1H				

Spiropyran part

	3-H	4-H	5-H	7-H	8-H	N–CH_3	3′a-CH_3	3b′-CH_3	4′-H	6′-H	7′-H
δ, ppm	5.84 d	6.93 d	8.01 s	8.03 dd	6.77 d	2.78 s	1.21 s	1.33 s	7.27 d	7.34 dd	6.52 d
J, Hz	10.3	10.3	–	8.8/2.8	8.8	–	–	–	1.6	8.1/1.6	8.1
Integral	1H	1H	1H	1H	1H	3H	3H	3H	1H	1H	1H



(III)

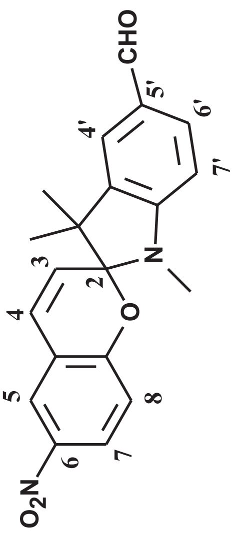
Polyenic chain

	1″-H	2″-H	3″-CH_3	4″-H	5″-H	6″-H	7″-CH_3	8″-H	9″-H
δ, ppm	6.89 d	6.71 d	2.26 s	5.25 s	–	–	–	–	–
J, Hz	16.0	16.0	–	–	–	–	–	–	–
Integral	1H	1H	3H	1H	–	–	–	–	–

Spiropyran part

	3-H	4-H	5-H	7-H	8-H	N–CH_3	3a′-CH_3	3′b-CH_3	4′-H	6′-H	7′-H
δ, ppm	5.84 d	6.93 d	8.01 s	8.03 dd	6.76 d	2.77 s	1.20 s	1.31 s	7.23 d	7.29 dd	6.53 d
J, Hz	10.3	10.3	–	9.1/2.7	9.1	–	–	–	1.6	8.1/1.6	8.1
Integral	1H	1H	1H	1H	1H	3H	3H	3H	1H	1H	1H

Table 1 (*Continued*)

Compound structure	Data												
 (II) DMSO-d_6	Spiropyran part												
		3-H	4-H	5-H	7-H	8-H	N–CH_3	3a′-CH_3	3′b-CH_3	4′-H	5′-CHO	6′-H	7′-H
	δ, ppm	6.04 d	7.28 d	8.25 d	8.02 dd	6.93 d	2.82 s	1.15 s	1.27 s	7.65 d	9.77 s	7.76 dd	6.81 d
	J, Hz	10.4	10.3	2.9	9.0/ 2.9	9.0	–	–	–	1.5	–	8.1/ 1.5	8.1
	Integral	1H	1H	1H	1H	1H	3H	3H	3H	1H	1H	1H	1H

measured in 10-mm quartz cuvettes on Shimadzu UV-2140PC (Japan) spectrophotometer.

The recording of electronic spectra, kinetic data for photocoloration and spontaneous decolouration processes were performed on fiber-optic spectrophotometric set – model HR-2000+ (Ocean Optics, USA) in quartz cell (10 mm) by means of irradiation by light of Hamamatsu model Lightincure – LC8 lamp (Hamamatsu, Japan) through the light filter UFS-2 with stirring of sample. The concentration of compounds in all experiments was C 10^{-5}–10^{-4} M. The photodegradation kinetics of photochromic compounds was examined by exposure to unfiltered light illumination of Hamamatsu LC8 lamp (light intensity 180 mW/cm^2).

All measurements were carried out in the same experimental conditions to allow comparative analysis of spectral-kinetic parameters. The magnitude of photoinduced optical density at absorption band maximum of photoinduced merocyanine form, located in visible spectrum, after achievement of photo-equilibrium between the initial and photoinduced forms of spiropyrans, was used in order to estimate the efficiency of photochromic spiropyran transformations. In order to obtain comparable values of photoinduced optical density we used the same values of optical density at maximum of absorption band of initial form. For this purpose we plotted the diagram “photoinduced density at maximum of absorption band of photoinduced form/optical density value at maximum of absorption band of initial form”. The value of photo-induced optical density (ΔD_{B}), as well as the rate constants for photobleaching (k_{BA}, s^{-1}) were calculated from these curves. The value of photodegradation was characterized by a decrease of photo-induced optical density for the photostationary state at the absorption maximum of the B form by one half ($t_{0.5}$, s). Solutions were stored in the darkness between measurements.

All manipulations with photosensitive compounds were carried out with covering the equipment from the visible light with aluminum foil. All operations with oxygen-sensitive reagents were carried out under argon atmosphere. All solvents were purified and dried according the standard procedures.

The reagents used were 1.5 M diisobutylaluminium hydride solution in toluene (DIBAH) (Aldrich, USA), salicylic aldehyde (Merck, Germany), the Fisher base (indolenine) (technical grade), (3-cyano-2-methyl-2-propenyl)diethylphosphonate (technical grade), 60% suspension of sodium hydride in mineral oil (Lancaster, USA). Reagents and solvents (reagent grade, analytical grade, and special purity grade) of domestic manufacture were also used.

5′-Formyl-6-nitro-1′,3′,3′-trimethylspiro[2H-1-benzopyran-2,2′-indoline] (**II**) was prepared according to the procedure developed earlier [16].

2.1. *5′-(4-Cyano-3-methylbuta-1,3-dienyl)-6-nitro-1′,3′,3′-trimethylspiro[2H-1-benzopyran-2,2′-indoline] (**III**) – a mixture (1″E,3″Z)- and all-E-isomers*

Sodium hydride (150 mg, 3.75 mmol, 60% suspension in mineral oil) was placed in the 100-ml three-necked reactor under argon and washed with anhydrous THF (2 × 5 ml). Then anhydrous THF (15 ml) was added, the mixture was cooled to 0 °C in the ice bath (3-cyano-2-methyl-2-propenyl)diethylphosphonate (**VI**) (C_5-phosphonate) (0.8 ml, 3.7 mmol) was added dropwise with a syringe at vigorous stirring, and the mixture was stirred for 1 h until the complete dissolution of sodium hydride. Then a solution of 5′-formyl-6-nitro-1′,3′,3′-trimethylspiro[2H-1-benzopyran-2,2′-indoline] (**II**) (1.0 g, 2.86 mmol) in THF (5 ml) was added dropwise at stirring. The mixture was stirred for 1 h; distilled water (8 ml) was added; and the pH value of the reaction mixture was brought to 6 with 0.1 M HCl. The product was extracted with dichloromethane (3 × 30 ml), the combined extract was dried over anhydrous sodium sulfate, and the solvent was removed in a vacuum. The target product was isolated by column chromatography on aluminum oxide. The residue was dried in a vacuum (0.2 mm Hg) for 1 h to yield 1,01 g (2.45 mmol) (85%) of compound (**III**); R_f 0.53 for (1″*E*, 3″*Z*)-isomer and R_f 0.51 for *all-E*-isomer. The (1″*E*, 3″*Z*)-/*all-E*- ratio was 1: 4 (according to the ^{1}H NMR spectral data). The analytical sample of pure *all-E*-isomer was isolated by additional chromatography on aluminum oxide and was finally purified by crystallization from alcohol; yellow crystals, mp 190–192 °C, R_f 0.51 (Kieselgel $60F_{254}$, spot detection-visible light exposure).

^{1}H NMR and UV–vis-spectral data are presented in Tables 1 and 2, respectively.

IR-spectrum (ν, cm^{-1}): 3100–2800 (C–H); 2212 (C≡N); 1800–1700 (overtone Ar,); 1652 (stretch, spiroC=C); 1608, 1580, 1480 (Ar); 1520 (N–O, asym); 1336 (N–O, sym); 1368, 1192, 1128, 1092 (Ar–N); 1276 (C–O–CAr, asym); 1020 (C–O–CAr, sym); 956 (Cspiro–O); 950 (C–H, bend, wag –CH=CH–); 816 (1,2,4-Ar, comb.).

Mass spectrum [*m/z*, I_{rel}]: 413 (M^+, 100).

Found, %: C 72.29, C H 5.78, N 9.72. Calculated for $C_{25}H_{23}N_3O_3$, %: C 72.62, H 5.61, N 10.16.

*2.2. 5′-(4-Formyl-3-methylbuta-1,3-dienyl)-6-nitro-1′,3′,3′-trimethylspiro[2H-1-benzopyran-2,2′-indoline] (**IV**)–a mixture (1″E,3″Z)- and all-E-isomers*

Compound (**III**) (500 mg, 1.21 mmol) as the mixture of isomers in freshly distilled dichloromethane (10 ml) was placed in the 100-ml three-necked reactor under argon at stirring. The reactor was cooled to −100 °C in the acetone – liquid nitrogen bath, DIBAH (1.2 ml of 1.5 M solution in toluene) was added dropwise with a syringe at stirring, and the temperature of the bath was slowly raised to 0 °C. The reaction mixture was quenched with 1 g of water in 5 g of aluminum oxide. The reaction mixture was filtered through a glass filter, the precipitate was washed with methanol (2 × 10 ml), and the solvent was removed in a vacuum. The target product was isolated by column chromatography on aluminum oxide. The resulting fractions were combined, the solvent was evaporated, and the residue was dried in a vacuum (0.2 mm Hg) for 1 h to give 250 mg (0.60 mmol) (50%). R_f 0.23 (Kieselgel $60F_{254}$, spot detection–visible light exposure). The ratio of isomers (1″*E*, 3″*Z*)-/*all-E*- ratio in reaction mixture was 1: 4. The starting nitrile (III) had the same ratio of (1″*E*, 3″*Z*)-/*all-E*- isomers (approved by ^{1}H NMR-data).

The analytical sample of pure *all-E*-isomer was isolated by additional chromatography on aluminum oxide and was finally purified by crystallization from alcohol.

^{1}H NMR and UV–vis-spectral data are presented in Tables 1 and 2, respectively.

IR-spectrum (ν, cm^{-1}): 3100–2800 (C–H); 1660 (C=O); 1652 (C=C); 1604, 1580, 1490 (Ar); 1520 (N–O, asym.); 1336 (N–O, sym.); 1364, 1192, 1120, 1092 (Ar–N); 1276 (C–O–CAr, asym.); 1020 (C–O–CAr, sym); 956 (C_{spiro}–O); 950 (C–H, band, wag –CH=CH–); 815 (1,2,4-Ar, comb.).

Mass spectrum [*m/z*, I_{rel}]: 416 (M^+, 100).

Found, %: C 71.85, H 6.23, N 6.34. Calculated for $C_{25}H_{24}N_2O_4$, %: C 72.10, H 5.81, N 6.73.

*2.3. 5′-(8-Cyano-3,7-dimethylocta-1,3,5,7-tetraenyl)-6-nitro-1′,3′,3′-trimethylspiro[2H-1-benzopyran-2,2′-indoline] (**V**)–a mixture (1″E,3″E,5″E,7″Z)- and all-E-isomers*

It was prepared similarly to compound (**III**) from (**IV**) (200 mg (0.48 mmol)) and the anion generated via treatment C_5-phosphonate (**VI**) (0.13 ml (0.6 mmol)) with sodium hydride (26 mg, 0.65 mmol, 60% suspension in mineral oil). The target compound was isolated by column chromatography on aluminum oxide to yield 185 mg (0.39 mmol, 80%) of compound (**V**); R_f 0.58 (Kieselgel $60F_{254}$, spot detection–visible light exposure).

The ratio of isomers (1″*E*, 3″*E*, 5″*E*, 7″*Z*)- and *all-E*- in reaction mixture was 1: 4 (according by ^{1}H NMR spectrum). The analytical sample of pure *all-E*-isomer (**V**) was isolated by additional chromatography on aluminum oxide.

^{1}H NMR and UV–vis-spectral data are presented in Tables 1 and 2, respectively.

Mass spectrum [*m/z*, I_{rel}]: 479 (M^+, 100).

Found, %: C 74.89, H 6.33, N 8.33. Calculated for $C_{30}H_{29}N_3O_3$, %: C 75.13, H 6.09, N 8.76.

*2.4. 5′-(3,7-Dimethyl-8-formylocta-1,3,5,7-tetraenyl)-6-nitro-1′,3′,3′-trimethylspiro[2H-1-benzopyran-2,2′-indoline] (**I**)–a mixture (1″E, 3″E, 5″E, 7″Z)- and all-E-isomers*

It was prepared similarly to (**IV**) by treatment the starting (**V**) (120 mg, 0.25 mmol) with DIBAH (0.3 ml of 1.5 M toluene solution) in dichloromethane. Yield: 55 mg (0.11 mmol) (46%). R_f 0.25 (Kieselgel $60F_{254}$, detection–visible light exposure). The ratio of isomers (1″*E*, 3″*E*, 5″*E*, 7″*Z*)-: *all-E*- 1: 4 (approved by ^{1}H NMR-spectrum). The analytical sample of pure *all-E*-isomer (**I**) was isolated by additional chromatography on aluminum oxide.

^{1}H NMR and UV–vis-spectral data are presented in Tables 1 and 2, respectively.

Mass spectrum [*m/z*, I_{rel}]: 482 (M^+, 100).

Found, %: C 74.21, H 6.74, N 5.43. Calculated for $C_{30}H_{30}N_2O_4$, %: C 74.67, H 6.27, N 5.80.

3. Results and discussion

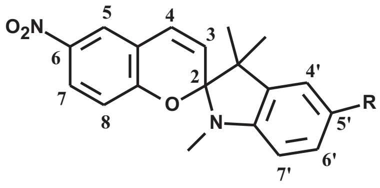
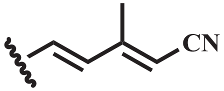
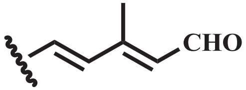
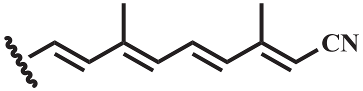
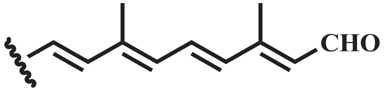
3.1. Synthesis

In the present work we used the synthetic procedure for creation of retinoid molecule and its analogs (Scheme 1), which was successfully implemented for synthesis of another retinal analogs earlier [8,10–14,17]. This procedure includes the Horner–Emmons olefination of carbonyl precursor (**II**) with anion of C_5–phosphonate reagent (**VI**), reduction of intermediate nitrile (**III**) into aldehyde (**IV**) by treatment with DIBAH, the subsequent olefination of aldehyde (**IV**) with reagent (**VI**) and reduction of resulting nitrile (**V**) into target aldehyde (**I**) (Scheme 1). C_5–phosphonate (**IV**) was used as a 60:40 mixture of *E*- and *Z*-isomers (according to ^{1}H NMR).

Nitrile (**III**) (Scheme 1) was obtained with yield of 85% as a mixture of 3″*E*- и 3″*Z*-isomers 4:1; newly formed bond had 1″*E*-configuration (approved by ^{1}H NMR data $J_{1\text{–}2''}$ 16.0 Hz). The following conditions were used for generation of the phosphonate anion, NaH/THF/0 °C and 1:1.3:1.35 aldehyde component–phosphonate–hydride ratio. The conversion of intermediate nitriles into aldehydes was carried out by reduction of nitrile group using DIBAH at −100 °C. The significant cooling of the reaction mixture was necessary to avoid the side reduction of the 3–4 double bond in the pyran ring. As a result, the intermediate polyenal (**IV**) was obtained with yield of 50% as a mixture of 3″*E*- и 3″*Z*-isomers, ratio 4:1.

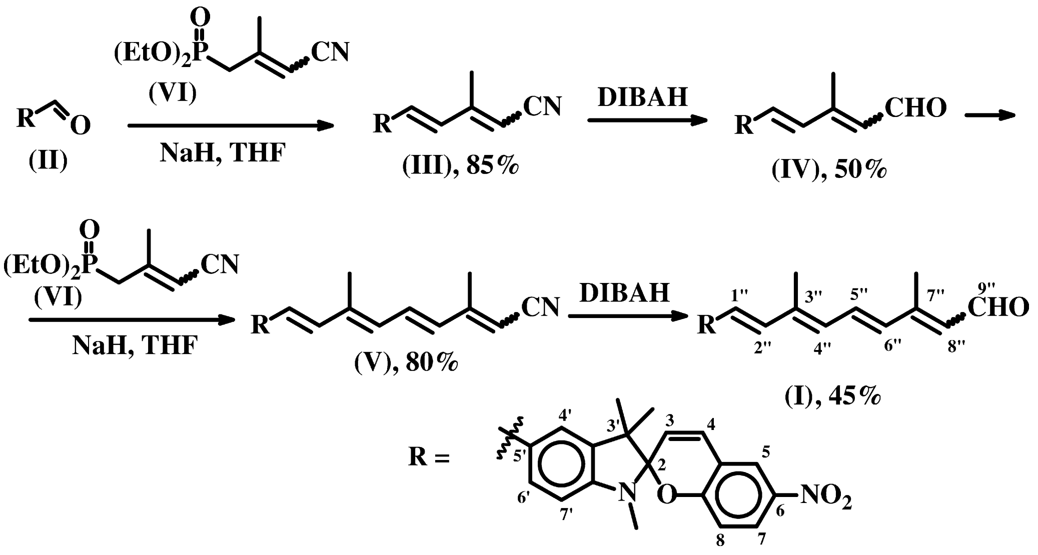
Target polyenal (**I**) was obtained by the repeated olefination reaction of aldehyde (**IV**) with C_5–phosphonate (**VI**) and the reduction of the resulting product with DIBAH. The newly formed double bond had mainly 5″*E*-configuration (with *J* 15.0 Hz) with ratio of 7″*E*- and 7″*Z*-isomers 4:1. The yields of the reactions during repetitive procedures of olefination and reduction are close to the yields of previous performed analogous reactions. Target and intermediate compounds were prepared in preparative amounts and their structures were confirmed by set of physicochemical methods of analysis.

Table 2
Spectral and kinetic characteristics of spiropyran derivatives **(I–V)** in toluene and ethanol.

Code	Compound	Toluene					Ethanol				
	 where R=	λ_{max}^{A}, nm	λ_{max}^{B}, nm	ΔD_B^{phot}	k_{BA}^{db}, s^{-1}	$t_{0.5}$, s	λ_{max}^{A}, nm	λ_{max}^{B}, nm	ΔD_B^{phot}	k_{BA}^{db}, s^{-1}	$t_{0.5}$, s
II		320	590 sh., 625	1.19	0.140	31	328	567	0.77	0.069	44
III		365	590 sh., 630	0.55	0.035	38	365	567	0.27	0.0065	[a]
IV		377	590 sh., 630	0.45	0.039	35	385	563	0.30	0.0036	[a]
V		407	590 sh., 630	0.16	0.033	70	405	567	0.099	0.0021	[a]
I		425	590 sh., 630	0.08	0.031	90	330, 433	563	0.104	0.0016	[a]

Note: λ_{max}^{A} и λ_{max}^{B} – absorption band maxima of the initial (spiro) and photoinduced (merocyanine) forms, respectively; ΔD_B^{phot} – is the maximal photoinduced change in absorbance at the absorption band maximum of the photoinduced form in the photoequilibrium state with the same value of absorbance (D 0.8) at the absorption band maximum of the initial form; k_{BA}^{db} – the rate constant of dark bleaching reaction; $t_{0.5}$ – is the time of the twofold decrease in the maximal photoinduced absorbance at the absorption band maximum of the photoinduced form upon continuous irradiation of the solutions with unfiltered light of a Hamamatsu LC8 lamp.

[a] Not observed over 10 min.



Scheme 1.

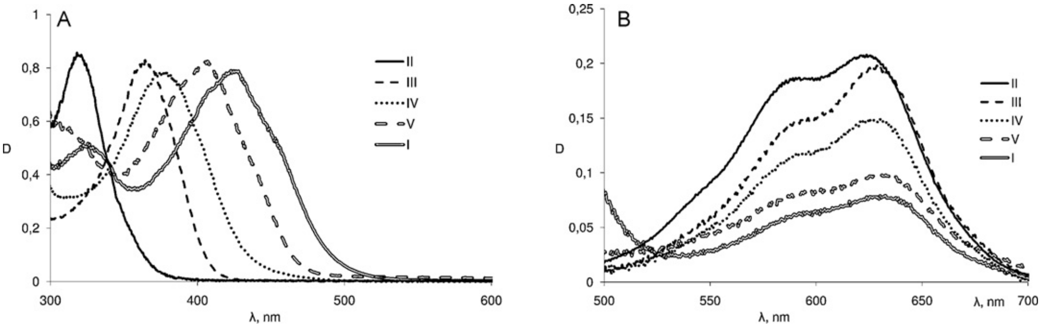


Fig. 1. Absorbtion spectra of spiropyrans (**II**–**V**, **I**) in toluene (C 10^{-5}–5×10^{-5} M) before (a) and after UV illumination (b).

3.2. Photochromic transformations study of prepared compounds

The results of spectral and kinetic study of photochromic transformations of synthesized compounds (**I**–**V**) in non-polar solvent (toluene) are shown in Table 2 and in Fig. 1.

According to data shown in Table 2 replacement of aldehyde group in (**II**) by polyenic substituents (**III**–**V**, **I**) causes bathochromic shift of absorption band of initial spiro form. As a result, spiropyrans with long polyene chains (**V** and **I**) are characterized by specific absorption band location in visible spectral region, that is unusual for initial spiro form (Fig. 1a). Such bathochromic shift of spiro form absorption band can be explained by conjugation of π–bonds of polyenic chains with π–electronic system of indoline fragment of the molecule. It is known that long-wavelength absorption band in nitro-substituted spiropyrans is attributed to two types of electron transitions ($\pi\pi^*$ и $n\pi^*$) occurring in pyran heterocycle [18]. The molecule takes more planar conformation and the absorption bands of spiropyran form, as well as in case of dithienylethenic analogs of carotenoids, shift to long-wavelength spectral region [19]. The value of observed spectral shift is determined by the number of conjugated double bonds and by the nature of terminal polar group.

There are two absorption bands in absorption spectrum of photoinduced form (Fig. 1b) in toluene solution. We assume that short-wavelength band is due to appearance of monomeric form, but the long-wavelength band is due to J-aggregated merocyanine form [20]. In contrast to closed form spectral characteristics, the maxima location of absorption bands of monomeric as well as aggregated photoinduced forms of photochromic retinoids weakly depends on nature of polyenic substituents (Table 2). This can be explained by lack of conjugation between polyenic chain and merocyanine form of spiropyran.

The efficiency of photochromic transformations estimated by value of photoinduced optical density at maximum of absorption band of photoinduced form in visible spectral region in photoequilibrium state decreases, if aldehyde group has been changed

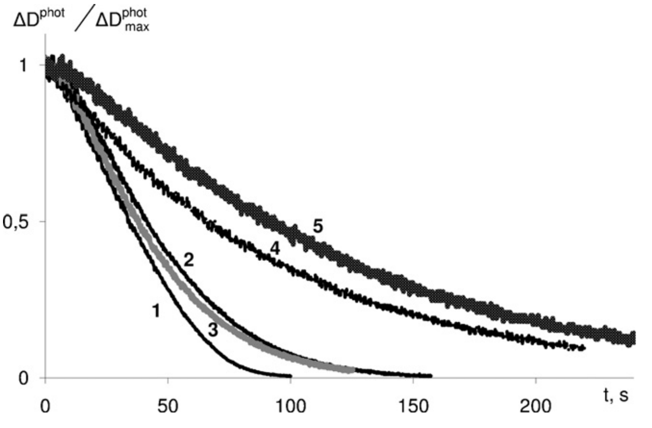


Fig. 2. Comparative photodegradation curves of spiropyrans (**II**–**V**, **I**) (1–5, respectively) in toluene (C 2×10^{-5} M) measured in maximum absorption band wavelength of photoinduced merocyanine form.

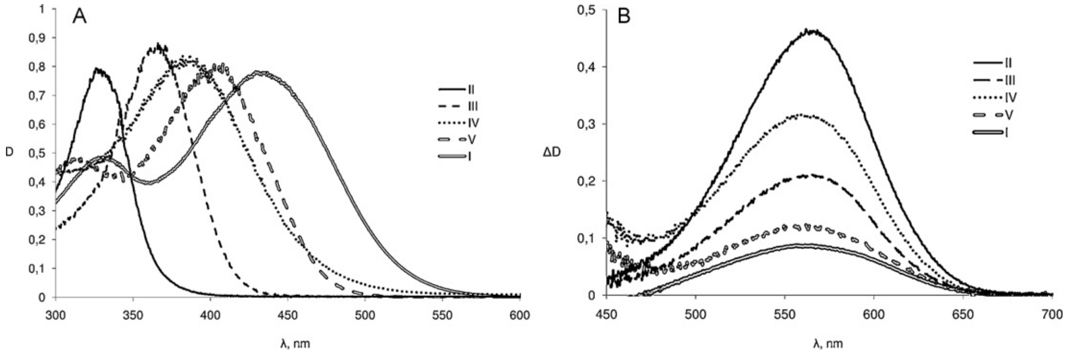


Fig. 3. Absorption spectra of spiropyrans (**II**–**V**, **I**) in ethanol (C 10^{-5}–5×10^{-5} M) before (a) and after UV illumination (b). For better readability graph (b) represents differential spectra between those of photoinduced open forms and those of closed ones.

by polyenic substituents (Table 2). At the same time, photocoloration efficiency decreases not only due to introduction of electron–acceptor substituents, but also because of the lengthening of the polyenic chain. The lifetime of the lowest excited singlet state $S_1{}^*$ of carotenoids is known to decrease with increasing chain length. Observed facts can be explained by life-time decline of excited singlet state $S_1{}^*$ of photochromic polyenes and by cis-trans isomerization of polyenic substituents competing with C–O–bond photodissociation in pyran fragment [19]. This phenomenon cannot be explained by lifetime decreasing of photoinduced merocyanine form of spiropyrans because the rate of spontaneous decolouration, when polyenic substituens were incorporated, is slowed down comparing to the rate of dark decolouration of aldehyde (**II**) (Table 2). It is interesting to note that dark decolouration rate constants of polyenic substituted spiropyrans depends very little on the substituent structure. As shown in Fig. 2, the efficiency of photodegradation slightly increases for spiropyrans with polyenic substituents comparing to aldehyde (**II**) (Table 2, Fig. 2).

The results of spectral and kinetic study of photochromic transformations of synthesized compounds (**I**–**V**) in polar solvent (ethanol) are shown in Table 2 and in Fig. 3.

Similarly to the case of photochromic spiropyran solutions in non-polar toluene, there is the bathochromic shift of long-wavelength absorption band of initial spiro form of synthesized compounds in polar solvent (ethanol), which is due to the length elongation of polyenic chain (Table 2, Fig. 3a). In contrast to spectral characteristics of closed form in toluene solution, there is only one short-wavelength absorption band in absorption spectra of photoinduced form in ethanol, which is specific for monomeric merocyanine form (Fig. 3b). The positions of the compound absorption maxima are approximately the same and are independent from the nature and length polyenic chain. Lack of the second long-wavelength band is the additional evidence of aggregates formation of merocyanine form in non-polar solvent [20].

Similarly to spiropyran spectral properties in toluene solutions, the efficiency of photocoloration process as well as thermal decoloration rate constants of spiropyrans in ethanol are decreasing with increase of polyenic chain length (Table 2). At the same time, rate constants in ethanol are lower than in toluene, which is probably due to formation of hydrogen bond between merocyanine form of spiropyran molecules and ethanol. Apparently, this is the reason of hypsochromic shift of monomeric absorption band, which is observed in spectra in ethanol, comparatively to corresponding absorption bands in toluene (compare data in Table 2).

For the comparative study of synthesized spiropyrans resistance to irreversible photochemical transformations in solution the method of express testing under no filtered irradiation of LC8 light source ("Hamamatsu", Japan) was used. This method provides simultaneous excitation of initial spiropyran and photoinduced merocyanine forms of spiropyrans by powerful irradiation (light intensity 180 mW/cm^2).

By comparison of data received for photochromic compounds solutions in ethanol and in toluene, it has been found that fatigue resistance of photochromic spiropyrans rises significantly when replacing of non-polar toluene to polar ethanol (Table 2). We attribute this fact to stabilization of photoinduced merocyanine form by the formation of hydrogen bonds between merocyanine form of molecules and solvent.

4. Conclusions

In result of spectral and kinetic phototransformations investigations of series of newly synthesized polyenic 6-nitrosubstituted indoline spiropyrans (**I**, **III**–**V**) we found out a number of specific features in spectral and photochromic properties which are different from initial spiropyran derivative (**II**). We demonstrated possibility of controlling the spiropyran spectral characteristics by varying the nature and length of polyenic substituents. Our results indicate that the differences in the spectral behaviour in depending on solvent polarity is attributed to the formation of photoinduced merocyanine forms aggregates in non-polar solvent.

It was found that decrease of photochromic transformations efficiency as well as decrease of decoloration reaction rate of photoinduced merocyanine depend on the length of polyenic substituent. At the same time, we could note that fatigue resistance of photochromic spiropyrans is increased in polar solvent as compared to toluene solution.

Acknowledgements

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