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# Synthesis and Photoisomerization of Mesogenic 4-Alkoxystyrylpyridines

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**Abstract**—Introduction of long-chain alkoxy substituents into molecules of styrylpyridines as potential ligands for photosensitive metal complexes endows them with liquid crystalline properties over a wide temperature range. *trans–cis* Photoisomerization of 4-alkoxystyrylpyridines in solution was revealed by NMR and electronic absorption spectroscopy, and the kinetics of transformations of their molecular forms after irradiation were estimated. Photoinduced *trans→cis* isomerization of 4-alkoxystyrylpyridines is characterized by a higher rate, and intramolecular cyclization of their *cis* isomers after irradiation is slower, as compared to unsubstituted analog.

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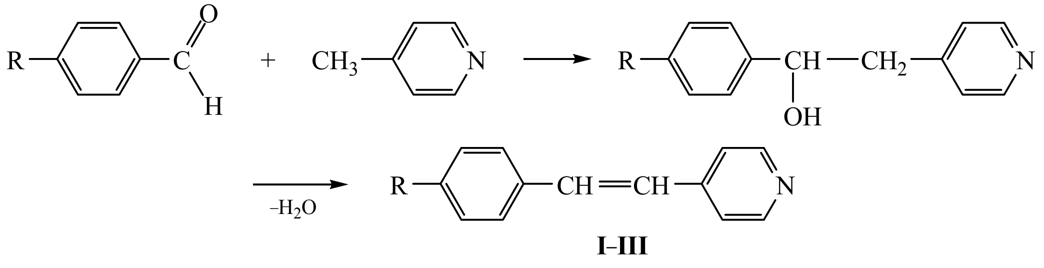
Photoprocesses, i.e. processes induced by irradiation in the visible and near-UV and near-IR regions, are widespread in nature and extensively used in technics [1]. Photochromic properties of many organic compounds are determined by *trans–cis* isomerization of their molecules. Such compounds are promising for the design of recordable and rewritable optical media and photoswitchable molecular devices [2–6].

4-Styrylpyridines are typical representatives of compounds possessing an active C=C bond, which is capable of changing molecular structure by the action of external factors [7–9]. Variation of a substituent in the 4-position could give rise to heteropolar molecules which attract interest as potential materials for nonlinear optics [10–12]. Such properties of 4-styrylpyridines make it possible to use them as photosensitive blocks in compounds possessing photoswitchable properties, in particular, magnetic parameters [13]. In this connection, of particular interest are 4-alkoxy-substituted styrylpyridines which are capable of forming liquid crystalline phase (mesophase) and acting as ligands in mesogenic spin-crossover metal complexes. Therefore, it was important to estimate differences in the kinetics of transformations of mesogenic and non-mesogenic 4-styrylpyridines both in the course of irradiation and after its termination.

In the present article we describe the synthesis of mesogenic alkoxy-substituted 4-styrylpyridines and their photoinduced isomerization. Unsubstituted 4-styrylpyridine (**I**) was synthesized according to the procedure described previously [14]. Its liquid crystalline derivatives **II** and **III** were obtained by



**I–III**

**I**, R = H; **II**, R = $C_8H_{17}O$; **III**, R = $C_{12}H_{25}O$.

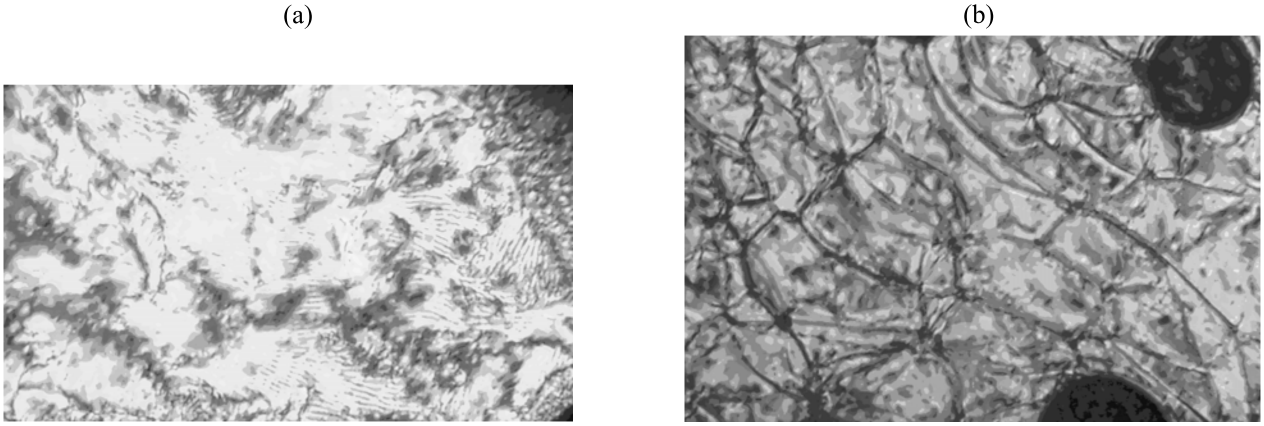


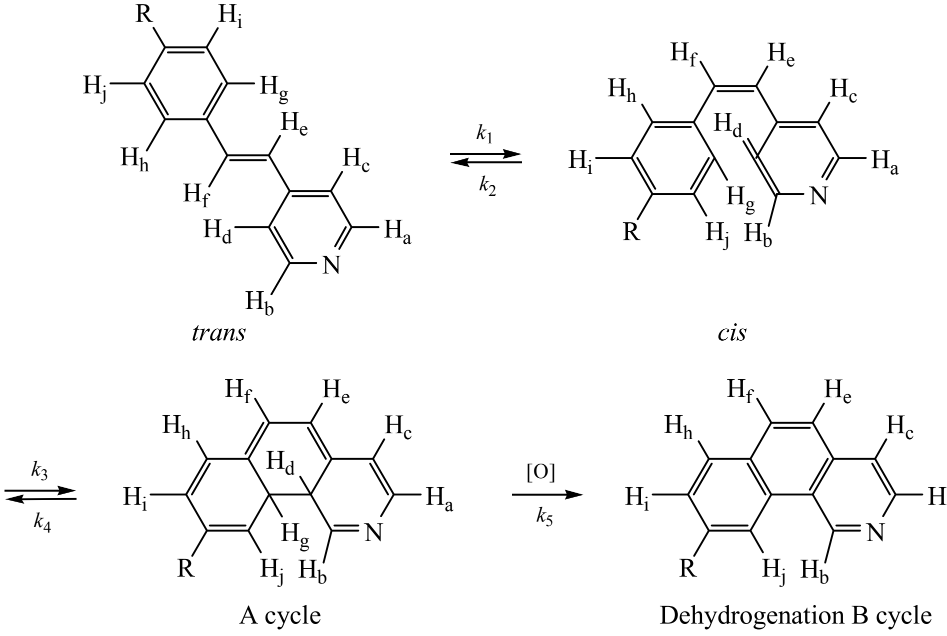
**Fig. 1.** Textures of mesophases formed by compound **III**: (a) smectic $S_E$ and (b) smectic $S_B$.

condensation of 4-methylpyridine with the corresponding 4-alkoxybenzaldehydes in acetic anhydride.

The structure of the newly synthesized compounds was confirmed by elemental analysis, $^1$H NMR and UV spectroscopy, and MALDI-TOF mass spectrometry. 4-Alkoxy-substituted styrylpyridines exhibited liquid crystalline properties over a wide temperature range. The type of mesophase was determined by examination of their characteristic textures, i.e., optical patterns observed with the aid of polarizing microscope in their thin films [15]. With rise in temperature crystalline compounds **II** and **III** produce smectic (E) mesophase ($S_E$) with characteristic striated texture, which is converted first into less structured smectic (B) mesophase ($S_B$) with Schlieren texture and almost parallel inverse sides (Fig. 1) and then into isotropic state. The phase transition temperatures and yields of compounds **I**–**III** are given in Table 1.

Irradiation of compounds **I**–**III** with UV light could induce not only their *trans–cis* isomerization but also subsequent intramolecular cyclization of the *cis* isomer, as well as dehydrogenation of the cyclization product in the presence of an oxidant ($I_2$, $FeCl_3$) or atmospheric oxygen [5]. The photocyclization process of stilbene was studied in most detail [16–22].

Figure 2 shows two regions of the $^1$H NMR spectra of compound **III**. The spectra recorded in 10 h and 30 min after irradiation coincide with each other. This means that a solution of **III** with a concentration of



$1.2\times10^{-3}$ M in 30 min reaches stationary state corresponding to the dihydro cyclic structure. Proton signals in the $^1$H NMR spectrum of **III** (Table 2) were assigned taking into account chemical shifts typical of particular groups of protons, spin–spin coupling constants, and signal intensities.

Before irradiation, the chemical shifts of $H_e$ and $H_f$ were as follows, δ ppm: 7.26 ($H_e$, *trans*), 7.71 ($H_e$, *cis*), 6.88 ($H_f$, *trans*), 6.33 ($H_f$, *cis*). The intensity ratio of these signals was 0.8 : 0.2 (*trans* : *cis*). Upon irradiation most part of molecules **III** is converted first into the *cis* isomer and then into the cyclic structure with covalent bond between the $C^g$ and $C^d$ atoms. Redistribution of electron density as a result of formation of the third ring leads to upfiedl shift of the $H_e$ and $H_f$ signals by $\Delta\delta \approx 0.50\pm0.05$ ppm for the *trans* isomer, $\Delta\delta \approx 0.20\pm0.10$ ppm for aromatic protons, and $\Delta\delta \le 0.05\pm0.01$ ppm from protons in the alkyl chain. Exceptions are signals from $H_e$ and $H_f$ of the *cis* isomer. The $H_e$ signal is displaced upfield by ~1 ppm, whereas the $H_f$ signal shifts downfield by ~0.05 ppm (Table 2).

The cyclization process continues when irradiation is terminated (Fig. 2). As follows from the signal intensity ratio (0.85 : 0.05 : 0.1), the fraction of the cyclic isomer of **III** reaches 85%, while the concentrations of the *trans* and *cis* isomers decrease to 5 and 10%, respectively. It should be emphasized that no dehydrogenation typical of stilbene [16–21] was observed in the examined system in the absence of oxidant ($k_5 = 0$) for at least several hours.

The $^1$H NMR spectra of compound **II** recorded both before and after irradiation were very similar to those of compound **III**, except for the intensity of the multiplet signal at δ 1.26 ppm belonging to methylene protons in the alkoxy group (8H instead of 16H).

Table 3 contains parameters of the $^1$H NMR spectra of compound **I**, recorded under the same conditions as the spectra of **III**. The spectrum of **I** before irradiation coincided with the spectrum of *trans*-**III** with an accuracy of 0.15 ppm (with account taken of the absence of alkoxy group in **I**). This means that compound **I** exists almost exclusively as *trans* isomer. After UV irradiation over a period of 5 min, signals in the $^1$H NMR spectra of **I** are also displaced upfield by approximately the same value Δδ as that found for **III**. However, the cyclization process is complete over the irradiation period, and no appreciable variation of the $^1$H NMR pattern of **I** was observed in several hours after irradiation.

**Table 1.** Phase transition temperatures and yields of 4-(4-alkoxystyryl)pyridines **I**–**III**

| Comp. no. | Phase transition temperatures, °C | Yield, % |
|---|---|---|
| **I** | 129 (Cr→I) | 42 |
| **II** | 97 ($Cr\to S_E$), 127 ($S_E\to S_B$), 165 ($S_B\to I$) | 20 |
| **III** | 94 ($Cr\to S_E$), 117 ($S_E\to S_B$), 161 ($S_B\to I$) | 27 |

The electronic absorption spectra of compounds **I**–**III** in the UV region contain several maxima (Fig. 3). Absorption maxima in the region λ 220–230 nm are obscured by the solvent (acetonitrile). The maxima at λ 305 and 322 nm correspond to the *trans* isomer of **III** (Fig. 3a), taking into account that before irradiation most part of 4-styrylpyridine molecules in solution exist as *trans* isomers [13, 22]. The UV spectrum of **II** was identical to the spectrum of **III**, while absorption maxima in the UV spectrum of **I** were observed at shorter wavelengths, λ 298 and 303 nm. The UV spectrum of **I** in acetonitrile is usually described as a characteristic absorption line at λ 299 nm [13]. The presence of an electron-donating alkoxy substituent in molecules **II** and **III** is responsible for electron density redistribution in their molecules and red shift of the absorption maxima belonging to the *trans* isomers of **II** and **III** as compared to compound **I** (Fig. 3). Variation of the number of methylene groups in the alkoxy substituent does not lead to appreciable variation of the position of absorption maxima in the UV spectra.

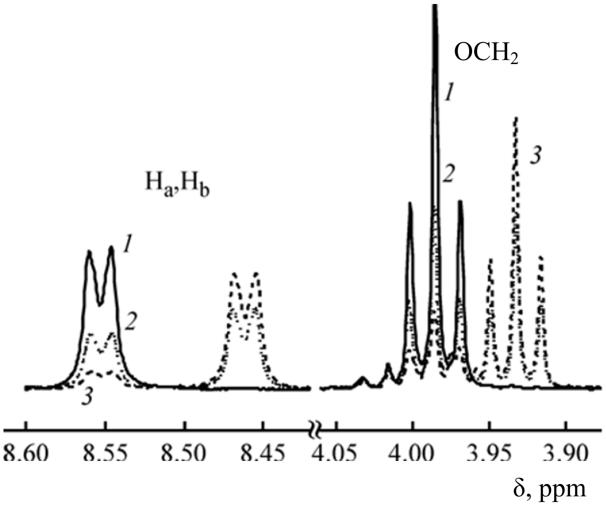


**Fig. 2.** Fragments of the $^1$H NMR spectra of compound **III** in CDCl$_3$ (*1*) before irradiation, (*2*) after UV irradiation over a period of 5 min, and (*3*) in 30 min after the end of irradiation.

**Table 2.** $^1$H NMR parameters (chemical shifts δ, ppm, and coupling constants *J*, Hz) of a solution of compound **III** in $CDCl_3$

| Proton | Before irradiation | After irradiation | |
|---|---|---|---|
| | | *cis*/*trans* | A |
| $H_a$, $H_b$ | 8.55 d (2H, *J* 5.8) | 8.55 d (0.3H, *J* 5.8) | 8.46 d (1.7H, *J* 5.8) |
| $H_c$, $H_d$ | 7.35 d (2H, *J* 6.0) | 7.36 d (0.3H, *J* 6.0) | 7.16 d (1.7H, *J* 6.0) |
| $H_e$ | 7.26 d (0.8H, *J* 16.8, *trans*)<br>7.71 d (0.2H, *J* 16.0, *cis*) | 7.26 d (0.05H, *J* 16.8, *trans*)<br>7.71 d (0.1H, *J* 16.0, *cis*) | 6.72 d (0.85H, *J* 12.4) |
| $H_f$ | 6.88 d (0.8H, *J* 16.8, *trans*)<br>6.34 d (0.2H, *J* 16.0, *cis*) | 6.88 d (0.05H, *J* 16.8, *trans*)<br>6.33 d (0.1H, *J* 16.0, *cis*) | 6.39 d (0.85H, *J* 12.4) |
| $H_g$, $H_h$ | 6.91 d (2H, *J* 8.8) | 6.91 d (0.3H, *J* 8.8) | 6.77 d (1.7H, *J* 8.8) |
| $H_i$, $H_j$ | 7.47 d (2H, *J* 8.8) | 7.47 d (0.3H, *J* 8.8) | 7.14 d (1.7H, *J* 8.8) |
| $OCH_2$ | 3.99 t (2H, *J* 6.7) | 3.99 t (0.3H, *J* 6.7) | 3.93 t (1.7H, *J* 6.7) |
| $OCH_2CH_2$ | 1.79 p (2H, *J* 6.7) | 1.77 p (2H, *J* 6.7) | |
| $OCH_2CH_2CH_2$ | 1.46 m (2H) | 1.44 m (2H) | |
| $CH_2$ | 1.26 m (16H) | 1.26 m (16H) | |
| $CH_3$ | 0.88 t (3H, *J* 6.7) | 0.88 t (3H, *J* 6.7) | |

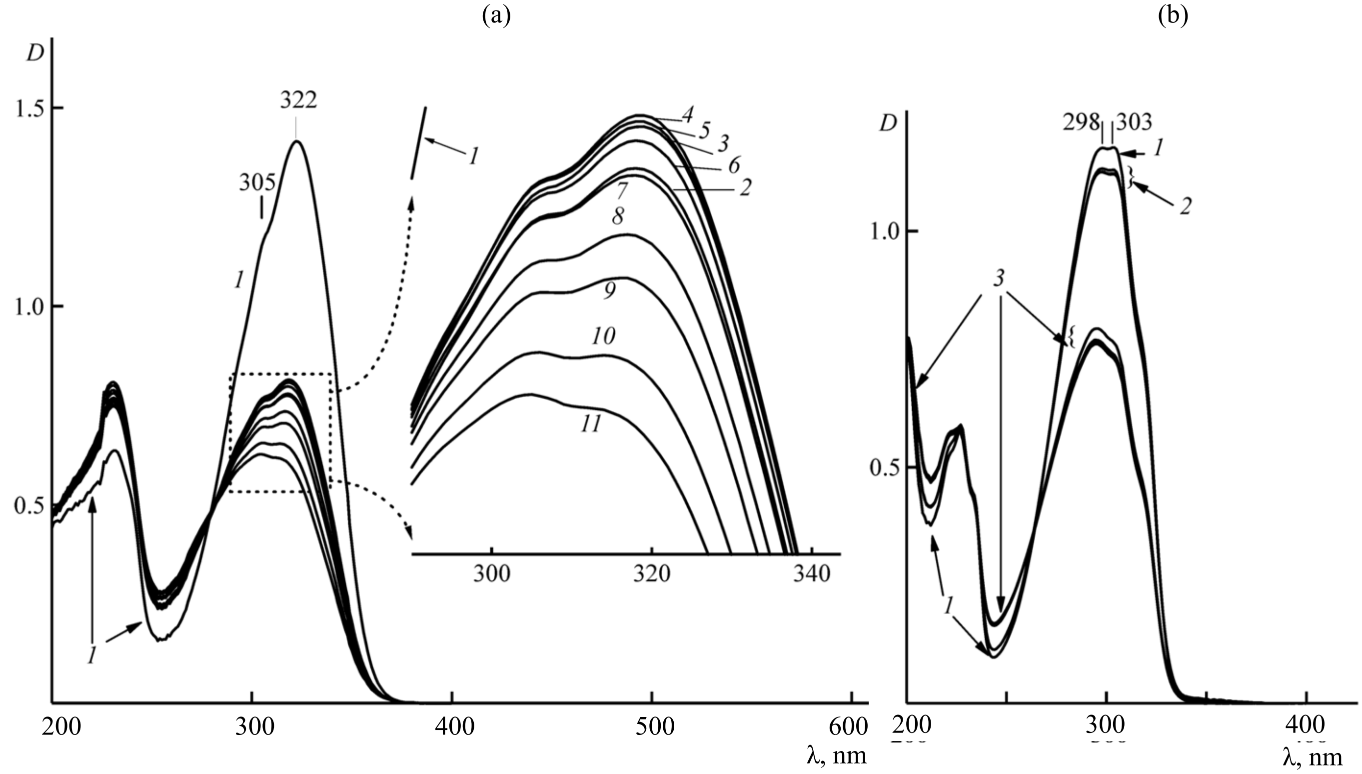


**Fig. 3.** (a) Electronic absorption spectra of a solution of compound **III** in acetonitrile (*1*) before irradiation and after irradiation with UV light (λ 365 nm) over a period of 5 s in (*2*) 10 s and (*3*), 2, (*4*) 4, (*5*) 6, (*6*) 9, (*7*) 15, (*8*) 26, (*9*) 37, (*10*) 53, and (*11*) 69 min. (b) Electronic absorption spectra of a solution of compound **I** in acetonitrile (*1*) before irradiation and after irradiation with UV light (λ 365 nm) over a period of (*2*) 5 and (*3*) 30 s in (*2*) 10 s and (*3*) 2, 4, 6, 8, 10, 15, 20, and 30 min.

Irradiation of 4-styrylpyridines in solution with UV light ($\lambda$ = 365 nm) over a period of 5 s induces photoisomerization, which is accompanied by characteristic variation of the spectral pattern, as shown in Fig. 3a for compound **III**. After irradiation over a period of 5 s, the absorption maxima typical of compound **III** sharply decrease in intensity. During the first ~5 min after irradiation, the absorption intensity slightly increases and then considerably decreases (Fig. 3a). Such kinetic pattern is not typical of systems where *trans–cis*–ring transformations occur [2, 22]; on the other hand, it is theoretically possible [23]: it may be described in terms of the scheme shown above provided that $k_2 > k_1$ and $k_4 = 0$. When the irradiation time is prolonged from 5 to 10, 30, and 60 s, the isomerization processes is complete during irradiation. Regardless of the irradiation time, the UV spectra of compound **III**, recorded after equilibration (cyclic structure **A** and some amount of *cis*-**III**), were similar.

A different pattern was observed for compound **I**. Figure 3b shows variations of the UV spectra of **I** after irradiation for 5 and 30 s, other conditions being equal. The intensities of all absorption maxima monotonically decreases after irradiation. However, the equilibrium state is determined by the irradiation time. The longer the irradiation period, the greater the fractions of the *cis* isomer and cyclization product **A** (Fig. 3b).

Thus introduction of an electron-donating alkoxy substituent into 4-styrylpyridine molecule accelerates *trans–cis* isomerization upon irradiation (in 10 s after 5-s irradiation the absorption intensities of compounds **I** and **III** drop down by 5 and 40%, respectively) and slows down the cyclization step after irradiation. The most probable reasons are different polarities of their molecules in the first case and different rates of thermodynamic equilibration in the system in the second.

These results are consistent with the NMR data which indicate predominant formation of cyclic product **A**. It should be taken into account that UV spectra recorded from solutions with a concentration lower by two orders of magnitude than in NMR experiments. Insofar as absorption bands in the UV spectra of compounds **I**–**III** are considerably overlapped, the first derivatives of the absorption curves were plotted in order to describe the kinetics of photoisomerization on a quantitative level. This is quite admissible, for the absorption line width is almost constant. Figure 4 shows the dependences of the amplitudes of the first derivatives upon time.

**Table 3.** $^1$H NMR parameters (chemical shifts $\delta$, ppm, and coupling constants *J*, Hz) of a solution of compound **I** in $CDCl_3$

| Proton | Before irradiation | After irradiation (A) |
|---|---|---|
| $H_a$, $H_b$ | 8.59 d (2H, *J* 6.0) | 8.48 d (2H, *J* 6.0) |
| $H_c$, $H_d$ | 7.44 d (2H, *J* 6.4) | 7.25 d (2H, *J* 6.4) |
| $H_e$ | 7.35 d (1H, *J* 16.4, *trans*) | 6.84 d (1H, *J* 16.4) |
| $H_f$ | 7.04 d (1H, *J* 16.4, *trans*) | 6.51 d (1H, *J* 16.4) |
| $H_g$, $H_h$ | 7.40 d (2H, *J* 7.6) | 7.24 d (2H, *J* 7.6) |
| $H_i$, $H_j$ | 7.56 d. t (2H, *J* 7.2, 1.6) | 7.26 d. t (2H, *J* 7.2, 1.6) |
| $H_R$ | 7.43 t (1H, *J* 1.6) | 7.23 t (1H, *J* 1.6) |

The kinetics of the above transformations were described with the aid of the following equation [23]: $A = l_1\exp\{-k_3\tau\} - l_2\exp\{-(k_2 - k_1)\tau\}$, where $k_3$, $k_2$, and $k_1$ are the rate constants for the corresponding transitions [21], and $l_1$ and $l_2$ are quantities determined by the initial isomer ratio and irradiation parameters. The results of fitting for compound **III** are represented by curves *1* and *2* in Fig. 4; $k_3 = (27\pm1)\times10^{-5}$ s$^{-1}$, $k_2 - k_1 = (7.6\pm2)\times10^{-3}$ s$^{-1}$ for $\lambda$ 322 nm; $k_3 = (57\pm1)\times10^{-5}$ s$^{-1}$, $k_2 - k_1 = (7.0\pm2)\times10^{-3}$ s$^{-1}$ for $\lambda$ 305 nm. The correlation coefficient for both dependences is $|R| > 0.97$.

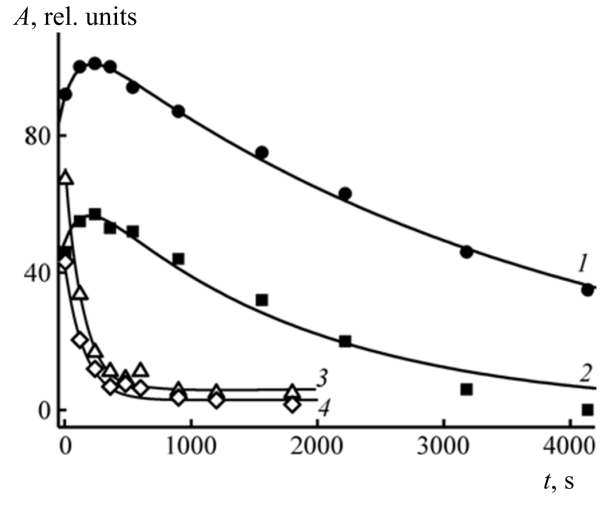


**Fig. 4.** Dependences of the amplitudes of two components of the first derivatives of the UV absorption curves of (*1*, *2*) compound **III** at (*1*) $\lambda$ 322 nm and (*2*) $\lambda$ 305 nm and (*3*, *4*) compound **I** at (*3*) $\lambda$ 298 and (*4*) $\lambda$ 303 nm upon time elapsed after irradiation.

The kinetics of transformations in the electronic spectra of compound **I** may be described by the simplified formula $A = l\exp\{-k\tau\}$ for both λ 298 nm, $k = (7.0\pm0.6)\times10^{-3}$ $s^{-1}$, and λ 303 nm, $k = (6.8\pm0.7)\times10^{-3}$ $s^{-1}$. The results of fitting for compound **I** are represented by curves *3* and *4* in Fig. 4. The correlation coefficient for these dependences is $|R| > 0.99$. The rate constant $k_3$ for compound **I** is higher by almost an order of magnitude than that for compound **III**, which confirms the above qualitative conclusions.

Presumably, the difference in the kinetics of photoisomerization of compounds **I**–**III**, as well as in the behavior of components with different absorption maxima, is determined to some extent by the existence of rotamers (i.e., conformers differing by the dihedral angle between the aromatic ring planes as a result of rotation about quasi-single CH–$C_{ring}$ bond) [24] and by the presence of some aggregated species in solution.

To conclude, introduction of a long-chain alkoxy substituent into styrylpyridine molecules gives structures capable of forming liquid crystalline mesophases (smectic E and B) over a wide temperature range. According to the $^1$H NMR and UV spectral data, 4-(4-alkoxystyryl)pyridines in solution undergo photoinduced *trans→cis* isomerization, and the kinetics of these transformations were estimated after irradiation. The rate of *trans→cis* isomerization in alkoxystyrylpyridines upon irradiation is considerably higher, while the rate of intramolecular cyclization of their *cis* isomer after irradiation is lower by an order of magnitude, as compared to the unsubstituted analog.

## EXPERIMENTAL

The $^1$H NMR spectra were recorded at room temperature (20°C) on a Bruker Avance 400 spectrometer [operating frequency 400 MHz; 90°-FID followed by Fourier transform; pulse duration 9.50 μs, delay 7.00 s, scan width 7 kHz (14.20 to –3.30 ppm), scan number 8, 32000 points per FID] from solutions in $CDCl_3$ with a concentration of $1.2\times10^{-3}$ M using 5-mm ampules.

Solutions of compounds **I**–**III** in organic solvents were irradiated with a Vilber Lourmat lamp (6 W) at λ 365 nm. The electronic absorption spectra were recorded at room temperature on a Varian Cary 100 spectrophotometer (cell path length $l = 10$ mm) in the range from 200 to 800 nm at a rate of 600 nm/min; slit width $d = 1.5$ nm. Samples were dissolved in acetonitrile to a concentration of $1.4\times10^{-5}$ M. The mass spectra (MALDI-TOF) were obtained on a Bruker Ultraflex III MALDI-TOF/TOF mass spectrometer.

The textures and phase transition temperatures were determined using a Boetius VEB Nagema polarizing microscope equipped with a temperature-control unit. The temperatures were measured with an accuracy of ±0.1°C.

4-Styrylpyridine (**I**) was synthesized according to the procedure described in [14]. Mass spectrum: *m*/*z* 181.24. Found, %: C 85.09, 85.33; H 6.04, 6.39; N 7.41, 7.66. $C_{13}H_{11}N$. Calculated, %: C 86.15; H 6.12; N 7.73.

**4-(4-Octyloxystyryl)pyridine (II).** A mixture of 4.42 ml of 4-methylpyridine and 11.3 g of 4-octyloxybenzaldehyde in 29 ml of acetic anhydride was heated for 40 h under reflux. After cooling, the precipitate was filtered off, recrystallized from hexane, and washed with acetone. The product was a light yellow crystalline powder. Mass spectrum: *m*/*z* 309. Found, %: C 81.55, 81.70; H 8.77, 8.87; N 4.49, 4.89. $C_{21}H_{27}NO$. Calculated, %: C 81.55; H 8.74; N 4.53.

**4-(4-Dodecyloxystyryl)pyridine (III)** was synthesized in a similar way. The light yellow precipitate was recrystallized from ethanol. Mass spectrum: *m*/*z* 365. Found, %: C 81.81, 82.10; H 9.97, 10.17; N 3.69, 3.89. $C_{25}H_{35}NO$. Calculated, %: C 82.19; H 9.59; N 3.84.

## ACKNOWLEDGMENTS

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