Spiropyrans and spirooxazines
1. Synthesis and photochromic properties of 9′-hydroxy- and 9′-alkoxy-substituted spironaphthooxazines

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A procedure was developed for phase-transfer catalyzed alkylation of 5-hydroxyindolenine and 9′-hydroxy-substituted spiro[indoline-2,3′-naphtho[2,1-*b*]oxazines] by alkyl halides. New 9′-hydroxy- and 9′-alkoxy-substituted spironaphthooxazines, spirooxazinyloxyacetic acids, and their esters containing substituents with different length of the carbon chain in the indoline moiety were synthesized. The influence of the substituents on the spectroscopic properties of the starting and colored forms and the kinetic characteristics of photochromic transformations of 9′-substituted spironaphthooxazines in solutions and polymeric films was investigated. The bipolar merocyanine forms of spirooxazines were found to produce H-aggregates.

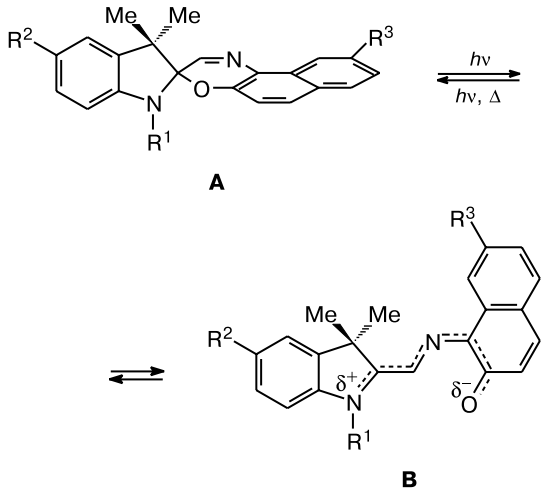
Key words: spironaphthooxazines, synthesis, photochromic properties, structure—property relationship, aggregates.

Reversible molecular rearrangements are of great interest because they are of fundamental importance in many chemical and biological processes used in modern technologies.[1—4] In recent years, photochromic organic molecules, including spiropyrans and spirooxazines, have attracted considerable attention because they can be used in optical systems for recording and display of information, sensors, opto- and optobioelectronics, transport systems, and catalysis.[1—6]

The mechanism of the photochromic transformation of spirooxazines (SPO) (Scheme 1, form **A**) as well as of spiropyrans involves the thermally and photochemically reversible process of the C_{spiro}—O bond cleavage in the excited state to form metastable merocyanine form **B**.[7]

In the synthesis of new spiropyrans and SPO, not only the direct condensation of the starting reagents containing the corresponding substituents (which are often difficult to prepare) but also the transformation of functional groups of spiro compounds, which are bound either directly or by a spacer to a spiropyran or spirooxazine molecule, finds wide use.[8—16] The synthesis and studies of new photochromic SPO have attract considerable recent interest because these compounds possess higher fatigue resistance compared to spiropyrans.[17a,18]

Scheme 1



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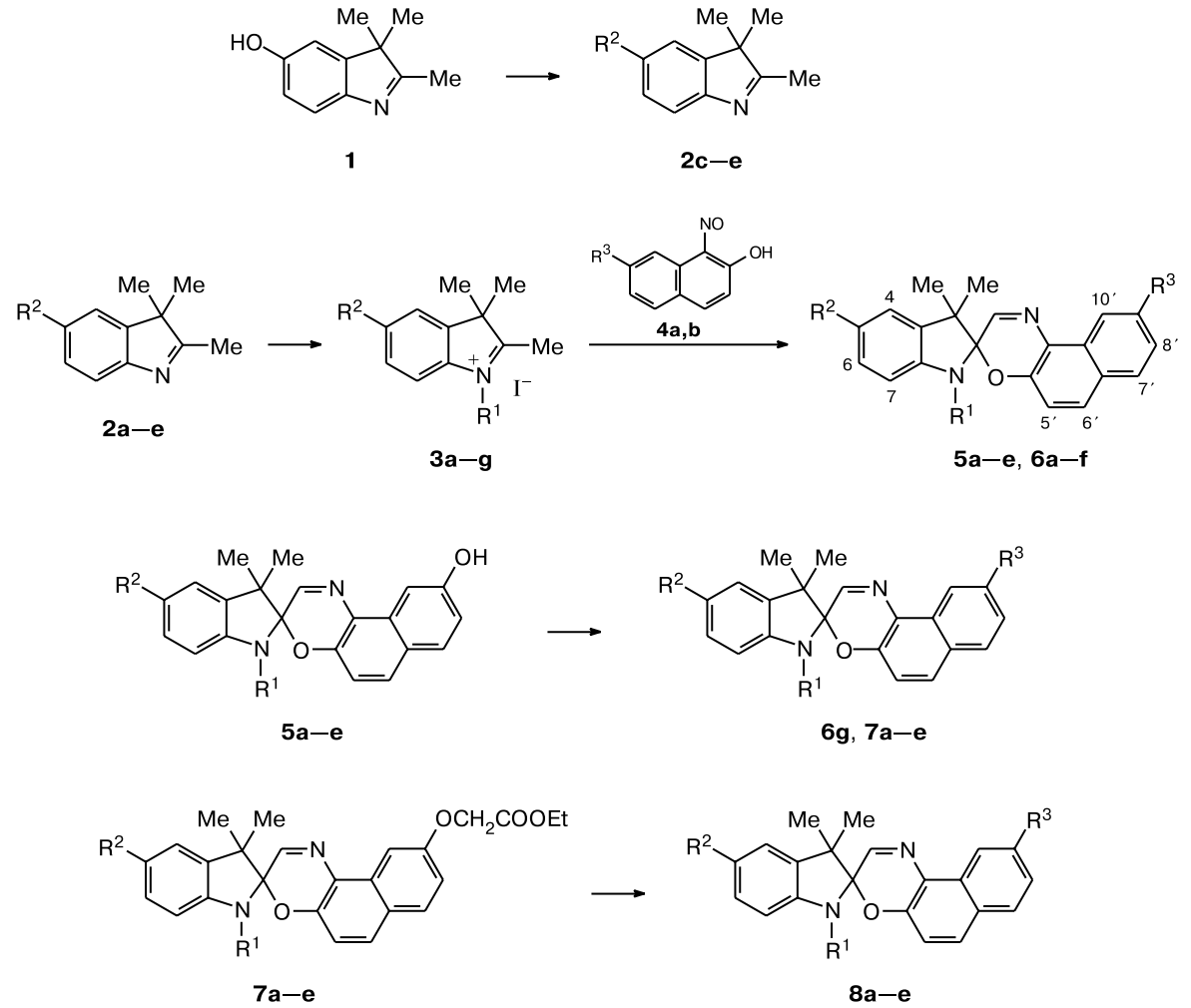
The present study was aimed at synthesizing new spironaphthooxazines containing various substituents at positions 1 and 5 of the indoline fragment and at position 9′ of the oxazine moiety of the molecule and investigating their spectroscopic and kinetic properties.

Synthesis of 9′-substituted spironaphthooxazines. The synthesis of 9′-substituted spirooxazines **5a—e**, **6a—g**, **7a—e**, and **8a—e** containing various substituents in the indoline fragment of the molecule is presented in Scheme 2.

The starting and intermediate indolenines **1** and **2a,b**, 3*H*-indolium iodides **3a,b,f,g**, 2,7-dihydroxy-1-nitrosonaphthalene (**4a**), 7-methoxy-1-nitroso-2-naphthol (**4b**), 1,3,3-trimethylspiro[indoline-2,3′-[3*H*]naphtho[2,1-*b*][1,4]oxazine] (**9**), and 6-nitro-1′,3′,3′-trimethylspiro[[2*H*]-1-benzopyran-2,2′-indoline] (6-nitroBIPS, **10**) were prepared according to procedures described earlier.[1a,b,13,19—21]

Substituents containing a long alkyl chain have a pronounced effect on the photochromic properties of spiropyrans and SPO,[1a,b,3,4,22,23] particularly, in viscous media. Previously unknown 5-alkoxy-substituted indolenines **2c—e** containing lipophilic substituents with different length of the carbon chain in the benzene ring were prepared by phase-transfer catalyzed alkylation of 5-hydroxyindolenine **1** by alkyl iodides in the presence of tetra-

Scheme 2



2: R^2 = H (**a**), OMe (**b**), OPr (**c**), OC_9H_{19} (**d**), $OC_{16}H_{33}$ (**e**)
3: R^1 = Me (**a—e**), Pr (**f**), Bu^i (**g**); R^2 = H (**a**), OMe (**b**, **f**, **g**), OPr (**c**), OC_9H_{19} (**d**), $OC_{16}H_{33}$ (**e**)
4: R^3 = OH (**a**), OMe (**b**)
5: R^1 = Me (**a—e**); R^2 = H (**a**), OMe (**b**), OPr (**c**), OC_9H_{19} (**d**), $OC_{16}H_{33}$ (**e**); R^3 = OH (**a—e**)
6: R^1 = Me (**a—d**, **g**), Pr (**e**), Bu^i (**f**); R^2 = OMe (**a**, **e—g**), OPr (**b**), OC_9H_{19} (**c**), $OC_{16}H_{33}$ (**d**); R^3 = OMe (**a—f**), OPr (**g**)
7: R^1 = Me (**a—e**); R^2 = H (**a**), OMe (**b**), OPr (**c**), OC_9H_{19} (**d**), $OC_{16}H_{33}$ (**e**); R^3 = OCH_2COOEt (**a—e**)
8: R^1 = Me (**a—e**); R^2 = H (**a**), OMe (**b**), OPr (**c**), OC_9H_{19} (**d**), $OC_{16}H_{33}$ (**e**); R^3 = OCH_2COOH (**a—e**)

butylammonium bromide. Alkylation of indolenines **2c—e** by alkyl iodides afforded 3*H*-indolium iodides **3c—e**. 9′-Hydroxy- and 9′-methoxy-substituted spiroindoleninenaphthooxazines **5a—e** and **6a—f** were synthesized by condensation of 3*H*-indolium iodides **3a—g** with the corresponding nitrosonaphthols **4a,b** in the presence of Et_3N.

Spirooxazine **6g** was prepared by alkylation of SPO **5b** by propyl iodide under the conditions of solid-liquid phase transfer catalysis in the presence of 18-crown-6. The reaction proceeded under rather mild conditions, which makes it possible to use alkyl halides containing other functional groups, for example, ester groups. Ethyl spirooxazinyloxyacetates **7a—e** were synthesized by alkylation of SPO **5a—e** by $ClCH_2COOEt$ under analogous conditions. Hydrolysis of the ethoxycarbonyl group of SPO **7a—e** in an alkaline medium gave amphiphilic SPO **8a—e** containing lipophilic substituents with different length of the carbon chain in the indoline fragment and a hydrophilic substituent in the oxazine fragment of the molecule.

The structures of compounds **5b—e**, **6a—g**, **7a—e**, and **8a—e** were established by ^1H NMR spectroscopy and confirmed by elemental analysis.

Spectroscopic and photochemical studies of SPO. The electronic absorption spectra of solutions of SPO **5—8** in EtOH are characterized by a long-wavelength maximum in the region of 320—345 nm with a molar absorption coefficient of 9000—10000 L mol^{-1} cm^{-1} (Table 1). Substituents with different length of the alkyl chain modifying the structure of SPO have virtually no effect on the shapes of absorption bands and positions of their maxima. The most substantial differences were observed on going to 9′-hydroxy-substituted **5b—e** and upon substitution of the H atom at position 5 of the indoline fragment (compounds **7a** and **8a**) by the alkoxy group (compounds **7b—e** and **8b—e**, respectively). In the former case, the spectra of solutions of hydroxy-substituted SPO have a long-wavelength maximum at λ = 345 nm, which is transformed into a shoulder in the spectra of compounds **6a—g**, **7b—e**, and **8b—e**. In the latter case (in the presence of the OAlk group at position 5), the long-wavelength absorption maximum shifts to the short-wavelength region compared to the spectra of derivatives containing the H atom at position 5. Apparently, these spectroscopic differences are associated with changes in the intensity and degree of overlapping of the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ electron transfer bands.

Irradiation of solutions of SPO **5—8** at long-wavelength absorption bands led to their reversible coloration accompanied by the appearance of bands with maxima at λ = 601—621 nm in the electronic absorption spectra in EtOH. The structured character of these bands is of a vibrational nature and is manifested as a shoulder at 575—590 nm (Fig. 1). The presence of the electron-releasing group at position 5 of SPO is the main factor responsible for a bathochromic shift of the long-wavelength absorption maxima of noncyclic isomers **B** in the series of compounds **5—8**. Thus, the absorption band maximum of form **B** in the spectra of SPO **7a** and **8a** is observed in the shorter-wavelength region (λ = 601—604 nm) compared to that in the spectra of 5-alkoxy-substituted SPO (λ = 613—621 nm). By contrast, an enhancement of the electron-releasing properties of substituents at position 9′ of SPO is accompanied by a short-wavelength shift of the absorption band maximum of colored isomer **B**

Table 1. Spectroscopic and kinetic characteristics of SPO **5b—e**, **6a—g**, **7a—e**, and **8a—e**

Compound	Solution in EtOH			In poly(methyl methacrylate) matrix			
	λ_{max}^{A}/nm (ε/L mol^{-1} cm^{-1})	λ_{max}^{B}/nm	$k_{B\rightarrow A} \cdot 10^2$/s^{-1} ($T$ = 295 K)	λ_{max}^{A} / nm	λ_{max}^{B} / nm	$\tau_{1/2}^{B}$/s (T = 293 K)	η
5b	345 (9030)	613	13.7	325	607	98	0.13
5c	345 (9020)	615	12.8	326	608	82	0.09
5d	345 (9560)	616	12.8	326	607	86	0.12
5e	345 (9880)	616	13.2	325	607	87	0.11
6a	317 (9260) 345 sh	619	5.1	321	609	60	0.12
6b	323 (9460) 345 sh	621	5.1	323	613	61	0.11

(*to be continued*)

Table 1 (*continued*)

Compound	Solution in EtOH			In poly(methyl methacrylate) matrix			
	λ_{max}^{A}/nm (ε/L mol^{-1} cm^{-1})	λ_{max}^{B}/nm	$k_{B\to A}\cdot 10^2$/s^{-1} (T = 295 K)	λ_{max}^{A}	λ_{max}^{B}	$\tau_{1/2}^{B}$/s (T = 293 K)	η
				nm			
6c	323 (9620) 347 sh	621	4.4	324	603	74	0.13
6d	325 (9020) 347 sh	621	4.7	324	609	64	0.11
6e	325 (9280) 347 sh	621	4.2	327	613	69	0.16
6f	325 (9130) 347 sh	624	3.8	325	615	62	0.12
6g	325 (8750) 350 sh	621	6.0	325	613	70	0.11
7a	334 (7860)	601	22.3	335	582	75	0.14
7b	322 (9920) 347 sh	619	3.7	322	607	77	0.13
7c	323 (9430) 347 sh	621	3.4	323	610	87	0.12
7d	321 (9860) 347	621	3.5	324	612	78	0.09
7e	322 (10370) 347 sh	621	3.2	323	612	90	0.15
8a	336 (8380)	604	15.2	338	597	21	0.07
8b	321 (9370) 347 sh	621	2.4	322	618	80	0.06
8c	322 (9300) 347 sh	621	2.6	325	621	101	0.06
8d	319 (9190) 347 sh	621	2.0	321	615	85	0.04
8e	320 (9290) 347 sh	621	2.2	324	616	78	0.03

Note. λ_{max}^{A} and λ_{max}^{B} are the long-wavelength absorption maxima of forms **A** and **B**, respectively (see Scheme 1), $k_{B\to A}$ is the rate constant of the thermal reverse reaction, $\tau_{1/2}^{B}$ is the parameter describing the kinetics of thermal decoloration, and η is the relative photocolorability.

(*cf.* 9′-hydroxy-substituted SPO **5b—e** and SPO **6a—g**, **7b—e**, and **8b—e** in Table 1).

The effect of the solvents on the spectroscopic characteristics of photomerocyanines **B** can be characterized by empirical Brooker's parameters of solvents χ_R and χ_B.[24] The parameters χ_R and χ_B describe the transition energies corresponding to the long-wavelengths absorption bands of solutions of merocyanine molecules of two types, *viz.*, with quinoid and bipolar structures, respectively. The correlation between the frequency of the long-wavelength absorption maximum (ν_{max}) of the compound under study and the parameters χ_R and χ_B is indicative of either

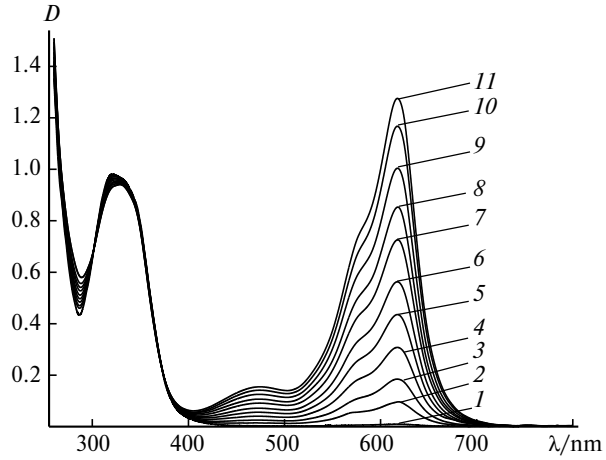


Fig. 1. Electronic absorption spectra of SPO **6a** in EtOH ($C = 1.1 \cdot 10^{-4}$ mol L^{-1}, $T = 293$ K) before (*1*) and after irradiation with light ($\lambda = 365$ nm) for 3 (*2*), 6 (*3*), 11 (*4*), 17 (*5*), 24 (*6*), 34 (*7*), 44 (*8*), 60 (*9*), 90 (*10*), and 137 s (*11*).

a positive or negative solvatochromism, respectively (bathochromic or hypsochromic shifts). For SPO **5** and **6** and unsubstituted **9**, the frequencies of absorption maxima of noncyclic isomers **B** correlate with the parameters χ_R, whereas there is no correlation with the parameters χ_B (Fig. 2). The observed positive solvatochromism indicates that the main state of the compounds under study is weakly polar, *i.e.*, photomerocyanines **B** occur predominantly in the quinoid form.

The kinetics of the thermal relaxation process **B** → **A** in solutions of compounds **5—8** is well described by a monoexponential function and depends on both the nature of substituents in the indoline and oxazine fragments and the polar properties of the solvents. The introduction of electron-releasing groups at position 5 of the indoline moiety of SPO leads to a sharp decrease in the rate constant of the thermal reverse reaction $k_{\mathbf{B}\to\mathbf{A}}$ (see Table 1, *cf.* the series of SPO **7a** and **7b—e**, **8a** and **8b—e**). The enhancement of the electron-releasing properties of the substituents at position 9′ of the naphthooxazine moiety of SPO (see Table 1, *cf.* the series of SPO **8e**, **7e**, **6d**, and **5e**) has an opposite effect. The length of the alkyl chain of the substituents R^1 and R^2 exerts only a slight effect on the rate constant of the thermal reaction and has a steric character. Thus, the constant $k_{\mathbf{B}\to\mathbf{A}}$ tends to decrease as the length and branching of the alkyl chain increases. The dependence of the rate constant of the reverse reaction on the polar properties of the solvent is determined by the relation between the electron-releasing properties of the substituents in the indoline and naphthooxazine fragments. For compounds **5** and **6** containing approximately equally strong electron-releasing substituents in both moieties of the SPO molecule and derivatives **7a** and **8a** bearing electron-releasing groups only in the naphthooxazine fragment as well as for unsubstituted SPO **9**, the rate

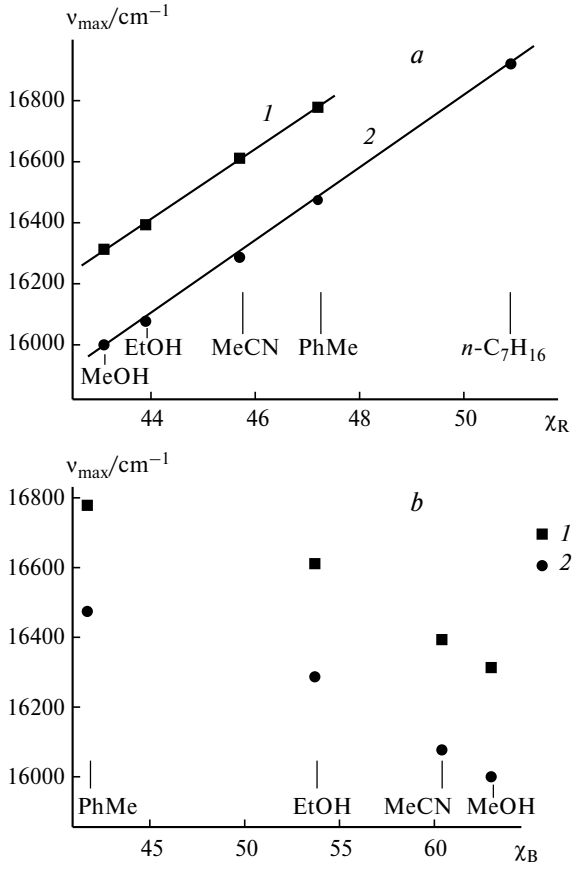


Fig. 2. Dependence of the frequency of the long-wavelength absorption maximum (ν_{max}) of the merocyanine form of spirooxazines **9** (*1*) and **6e** (*2*) on Brooker's parameters of solvents χ_R (*a*) and χ_B (*b*).

constant increases as the polarity of the solvent increases (Fig. 3). For SPO **7b—e** and **8b—e** containing a strong electron-releasing group in the indoline moiety and a

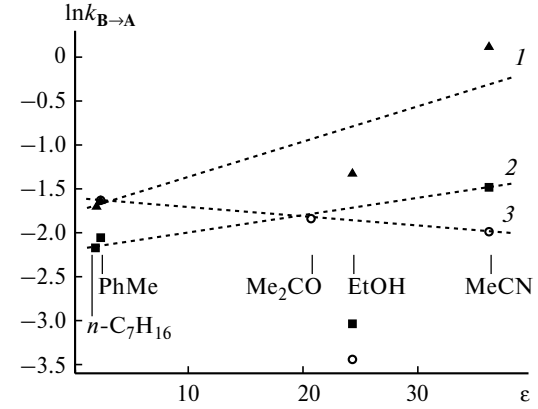


Fig. 3. Logarithm of the rate constant of thermal decoloration ($\ln k_{\mathbf{B}\to\mathbf{A}}$) of solutions of SPO **9** (*1*), **6e** (*2*), and **8d** (*3*) *vs.* the polar properties of the solvent described by the dielectric permeability (ε) at $T = 295$ K (the tendencies for a change, *viz.*, an increase in $\ln k_{\mathbf{B}\to\mathbf{A}}$ with increasing ε for SPO **9** and **6e** and a decrease in $\ln k_{\mathbf{B}\to\mathbf{A}}$ for compound **8d**, are shown by dashed lines).

much weaker electron-releasing group in the naphthooxazine moiety, the rate constant, on the contrary, decreases as the polarity of the solvent increases (see Fig. 3). Apparently, the observed correlations reflect to a certain extent the polar properties of the photomerocyanine structures. It should be noted that the rate constant of the thermal reverse reaction in solvents with specific interactions (for example, in alcohols, which can form intermolecular hydrogen bonds with the photoinduced forms of SPO) can change jumpwise and inadequately to a change in the polar properties of the solvent dependent, for example, on its dielectric permeability (see Fig. 3).

The above-described spectroscopic and kinetic features of the behavior of SPO are determined by the molecular structure of the merocyanine form, *viz.*, the degree of quinoidation or bipolarity, which depends on the electron-releasing properties of substituents in a particular moiety of SPO. Electron-releasing substituents in the indoline moiety of SPO facilitate delocalization of the positive charge on the N atom resulting in stabilization of the bipolar structure. In contrast, the electron-releasing substituents in the naphthooxazine fragment cause an increase in the negative charge on the O atom, as a result of which the bipolar structure becomes thermodynamically unfavorable due to quinoidation of the merocyanine form. The effect of the simultaneous presence of substituents in both moieties of SPO depends on the relation between their electron-releasing properties. For example, in the case of compounds **5**, **6**, and **9**, colored products have quinoid structures, whereas the bipolarity of the merocyanine form is manifested in SPO **7** and **8**.

The anomalous spectral and kinetic behavior was observed upon irradiation of solutions of SPO **8** in heptane. In particular, photoinduced absorption of compound **8d** is characterized by a broad band with a maximum at λ = 540 nm and shoulders at λ = 580 and 630 nm, whereas the absorption band in the spectrum of the photoproduct in toluene has a maximum at λ = 615 nm and a shoulder at λ = 580 nm (Fig. 4). Thermal decoloration of a solution of SPO **8d** in heptane at 297 K, which is formally described by a monoexponential function (the determination coefficient is 0.9992), is characterized by the lifetime of 162 s, the lifetime being increased as the polarity increases in the toluene—acetone—acetonitrile series (5.1, 6.3, and 7.3 s, respectively). Prolonged irradiation of a solution of SPO **8d** in heptane gave rise to a suspension and a red precipitate. The addition of acetonitrile led to dissolution of the precipitate, a change in the color of the solution from red to blue (λ_{max} = 614 nm), and subsequent rapid decoloration, the absorption band of cyclic form **A** of SPO **8d** being restored (λ_{max} = 320 nm). The observed characteristic features are, apparently, associated with the photoinitiated formation of H-type aggregates of the merocyanine forms of SPO **8d** (short-wavelength shift of the absorption maximum with respect to

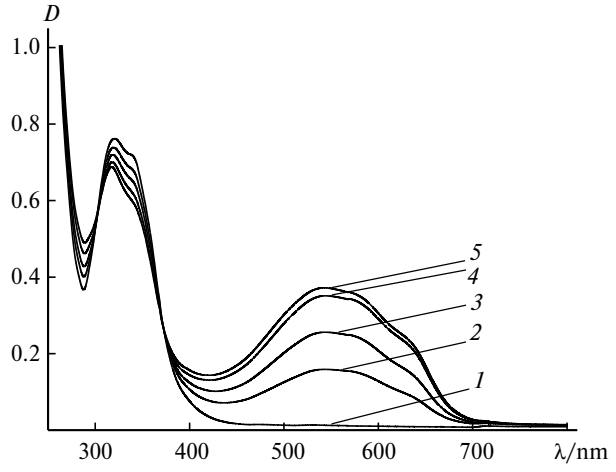


Fig. 4. Electronic absorption spectra of SPO **8d** in heptane ($C = 7.8 \cdot 10^{-5}$ mol L^{-1}, T = 293 K) before (*1*) and after irradiation with light (λ = 365 nm) for 3 (*2*), 8 (*3*), 18 (*4*), and 28 min (*5*).

the absorption maximum of photomerocyanine[25]) in conditions of low solubility of bipolar form **B** in a nonpolar solvent. A similar behavior was observed also for structurally similar compounds **8b,c,e**. Noteworthy also is the role of the long-chain alkyl substituents R^1. Thus, the rate of formation of aggregates increases and sedimentation accelerates as the chain length increases. In the case of SPO **8a** devoid of an electron-releasing group in the indoline fragment, the aggregation appears only slightly and is manifested in the absorption spectrum of photomerocyanine as an additional shoulder at λ = 540 nm (λ_{max} = 614 nm). Under the same conditions, aggregation of SPO **5**—**7** does not occur. The latter observation along with the above-mentioned facts suggest that this processes is structure-dependent, *viz.*, a bipolar structure of the molecules involved in the aggregation is a necessary condition for the aggregation, the presence of long-chain alkyl substituents accelerating the latter process.

To estimate the efficiency of photocoloration of SPO **5**—**8** (with the aim of decelerating the thermal reaction), we prepared their polymeric films based on poly(methyl methacrylate) (PMMA). The dependence of the spectroscopic characteristics of the starting (before irradiation) and colored samples on the structure of SPO is similar to that observed for solutions (see Table 1). The rates of the thermal reverse reactions of compounds **5**—**8** in PMMA are noticeably lower than those in solutions. However, unlike the latter reactions, the kinetics of thermal decoloration is not described by a monoexponential function. Hence, we described this process by the parameter $\tau_{1/2}$ (see Table 1). The relative photocolorability (η) of SPO under study is low (0.03—0.16, see Table 1). The effect of the structure is observed primarily on going from compounds **5**—**7** (η = 0.10—0.16) to compounds **8** (η = 0.03—0.07). This is, apparently, associated with the acidic properties of the OCH_2COOH group, which are

manifested in the step of isomerization of the photoinitiated process **A** → **B** due to interactions with the environment.

To summarize, we developed a procedure for the synthesis of 5-alkoxyindolenines and 9′-alkoxy-substituted spiroindolinenaphthooxazines by phase-transfer catalyzed alkylation of the corresponding hydroxy derivatives by alkyl halides, which extends the scope of structural modifications of SPO. The photochromic properties of the new compounds were studied in solutions and polymeric films. In the series of 9′-substituted SPO, the spectroscopic and kinetic properties were demonstrated to be dictated to a great extent by the structure of the merocyanine form (either quinoid or bipolar), which depends on the relation between the electron-releasing properties of the substituents in the indoline and naphthooxazine fragments of the molecule. The formation of H-aggregates of the bipolar merocyanine forms was observed. The efficiency of this process increases as the length of the alkyl chain of the substituents increases.

Experimental

The ^{1}H NMR spectra were recorded on a Varian Unity-300 spectrometer (300 MHz) in $CDCl_3$ at 20 °C in the mode of internal stabilization at the ^{2}H resonance line; the chemical shifts δ and spin-spin coupling constants were measured with an accuracy of 0.01 ppm and 0.1 Hz, respectively.

The electronic absorption spectra were recorded on Specord M40, Varian Carry 100, and Hewlett—Packard 8452A spectrophotometers at concentrations of $4.0 \cdot 10^{-5}$—$1.2 \cdot 10^{-4}$ mol L^{-1}. The solvents EtOH, MeCN, Me_2CO, PhMe, and heptane were purchased from Aldrich. Photolysis of solutions and polymeric films was carried out with the use of a DRSh-500 mercury lamp using light filters to separate lines of the mercury spectrum. The kinetics of photocoloration and thermal decoloration of SPO in polymeric films was recorded on an apparatus constructed based on a Hitachi Perkin—Elmer 139 spectrophotometer.

Poly(methyl methacrylate) was used as the polymeric matrix. The films were prepared by slow evaporation of $CHCl_3$ from solutions of the polymer and SPO followed by drying of the samples. The concentration of the compounds in the polymeric matrix was $(1—5) \cdot 10^{-3}$ mol L^{-1}.

The efficiency of photocoloration of SPO **5—8** was estimated with the use of the relative photocolorability parameter (η), which was calculated as a ratio between the photocolorabilities of the compound under study (H^X) and the standard (H^E); 6-nitroBIPS (**10**) was used as the standard. The photocolorability is the product of the quantum yield of the formation of colored product **B** ($\Phi_{A\to B}$) by the molar absorption coefficient (ε_{max}) at the maximum of the long-wavelength absorption band of form **B** [17b]

$$\eta = H^X/H^E = (\Phi^X_{A\to B} \cdot \varepsilon_{max}{}^X)/(\Phi^E_{A\to B} \cdot \varepsilon_{max}{}^E).$$

In the general case, irradiation of SPO can lead to three processes: photocoloration ($\Phi_{A\to B}$), photodecoloration ($\Phi_{B\to A}$), and thermal recyclization ($k_{B\to A}$). Since the reverse photoreaction in SPO is generally much less efficient than the direct reaction ($\Phi_{A\to B} \gg \Phi_{B\to A}$),[22] we ignored the former process in our estimations. Taking into account that the thermal reverse reaction at the initial instant of time can be ignored, the photocolorability was calculated according to the equation

$$H = \Phi_{A\to B}\varepsilon^B_{max} = \frac{\left.\frac{dD^B_{max}}{dt}\right|_{t=0} N_A S}{I_0[1-10^{-D^A(\lambda_{irr})}]},$$

where N_A is the Avogadro number, S is the surface of the sample on which the activating radiation impinges, I_0 is the intensity of incident light, and $D^A(\lambda_{irr})$ is the absorbance at the wavelength of irradiation (λ_{irr}) of the starting form of SPO. The value $(dD_{max}{}^B/dt)_{t=0}$ was determined as the slope to the photocolorability curve at the absorption maximum of form **B** at the initial instant of time.

Samples were subjected to photolysis at λ = 365 nm. The intensity of incident light measured on an Aberhrom 540 actinometer was $6 \cdot 10^{15}$ quantum s^{-1}.

The value of H^E thus determined for the standard 6-nitroBIPS (**10**) in PPMA was 23820 L mol^{-1} cm^{-1}.

The thermal decoloration of polymeric films of SPO was characterized with the use of the parameter $\tau_{1/2}{}^B$, *viz.*, the time during which the absorbance at the absorption maximum of colored form **B** is halved.

Synthesis of compounds 2c—e (general procedure). A mixture of indolenine **1** (5 mmol), tetrabutylammonium bromide (0.16 g), PhH (20 mL), THF (15 mL), and a 50% NaOH solution (8 mL) was stirred at 20 °C for 15 min and then the corresponding AlkI (7 mmol) was added. The mixture was stirred at ~20 °C for 10 h. Then PhH (35 mL) and water (20 mL) were added. The organic layer was separated and the aqueous layer was extracted with PhH. The combined extracts were dried with Na_2SO_4 and the solvent was removed *in vacuo*. The resulting indolenine was used without additional purification.

2,3,3-Trimethyl-5-propoxyindolenine (2c). The yield was 86% (oil).

2,3,3-Trimethyl-5-nonyloxyindolenine (2d). The yield was 85% (oil).

5-Hexadecyloxy-2,3,3-trimethylindolenine (2e). The yield was 82% (oil).

Synthesis of compounds 3c—e (general procedure). A mixture of the corresponding indolenine **2c—e** (10 mmol) and MeI (1.7 mL) in diethyl ether (10 mL) was kept at 20 °C for 30 h. The precipitate was filtered off, washed with Et_2O, and used without additional purification.

1,2,3,3-Tetramethyl-5-propoxy-3*H*-indolium iodide (3c). The yield was 88%, m.p. 185—187 °C.

1,2,3,3-Tetramethyl-5-nonyloxy-3*H*-indolium iodide (3d). The yield was 83%, m.p. 154—156 °C.

5-Hexadecyloxy-1,2,3,3-tetramethyl-3*H*-indolium iodide (3e). The yield was 80%, m.p. 153—156 °C.

Synthesis of compounds 5a—e (general procedure). A mixture of the corresponding 3*H*-indolium iodide **3** (1 mmol), nitrosonaphthol **4a** (1.1 mmol), Pr^iOH (7 mL), and Et_3N (1 mmol) was refluxed for 2 h and cooled. The solvent was evaporated and the residue was purified by column chromatography on Al_2O_3 (AcOEt as the eluent).

9′-Hydroxy-1,3,3-trimethylspiro[indoline-2,3′-[3*H*]naphtho[2,1-*b*][1,4]oxazine] (5a). The yield was 42%, m.p. 168—173 °C (*cf.* lit. data[14]: m.p. 168—173 °C).

9′-Hydroxy-5-methoxy-1,3,3-trimethylspiro[indoline-2,3′-[3*H*]naphtho[2,1-*b*][1,4]oxazine] (5b). The yield was 52%, m.p. 197—198 °C (from toluene). Found (%): C, 73.85; H, 6.01; N, 7.35. $C_{23}H_{22}N_2O_3$. Calculated (%): C, 73.78; H, 5.92; N, 7.48. ^{1}H NMR, δ: 1.31 and 1.34 (both s, 3 H each, 2 C(3)Me); 2.68 (s, 3 H, NMe); 3.78 (s, 3 H, OMe); 5.57 (s, 1 H, OH); 6.46 (d, 1 H, H(7), J = 8.2 Hz); 6.70—6.74 (m, 2 H, H(4), H(6)); 6.83 (d, 1 H, H(5′), J = 8.8 Hz); 7.00 (dd, 1 H, H(8′), J = 8.8 Hz, J = 2.5 Hz); 7.56 (d, 1 H, H(7′), J = 8.8 Hz); 7.63 (d, 1 H, H(6′), J = 8.8 Hz); 7.68 (s, 1 H, H(2′)); 7.85 (d, 1 H, H(10′), J = 2.6 Hz).

9′-Hydroxy-1,3,3-trimethyl-5-propoxyspiro[indoline-2,3′-[3*H*]naphtho[2,1-*b*][1,4]oxazine] (5c). The yield was 57%, m.p. 206—207 °C (from toluene). Found (%): C, 74.68; H, 6.45; N, 7.01. $C_{25}H_{26}N_2O_3$. Calculated (%): C, 74.60; H, 6.51; N, 6.96. ^{1}H NMR, δ: 1.03 (t, 3 H, OPr, J = 7.4 Hz); 1.31 and 1.33 (both s, 3 H each, 2 C(3)Me); 1.79 (m, 2 H, OPr); 2.68 (s, 3 H, NMe); 3.88 (t, 2 H, OPr, J = 6.6 Hz); 5.55 (s, 1 H, OH); 6.45 (d, 1 H, H(7), J = 9.1 Hz); 6.70—6.74 (m, 2 H, H(4), H(6)); 6.83 (d, 1 H, H(5′), J = 8.8 Hz); 7.00 (dd, 1 H, H(8′), J = 8.8 Hz, J = 2.6 Hz); 7.56 (d, 1 H, H(7′), J = 8.9 Hz); 7.63 (d, 1 H, H(6′), J = 8.8 Hz); 7.68 (s, 1 H, H(2′)); 7.85 (d, 1 H, H(10′), J = 2.6 Hz).

9′-Hydroxy-1,3,3-trimethyl-5-nonyloxyspiro[indoline-2,3′-[3*H*]naphtho[2,1-*b*][1,4]oxazine] (5d). The yield was 57%, m.p. 125—126 °C (from heptane). Found (%): C, 76.44; H, 7.79; N, 5.72. $C_{31}H_{38}N_2O_3$. Calculated (%): C, 76.51; H, 7.87; N, 5.76. ^{1}H NMR, δ: 0.87 (t, 3 H, OC_9H_{19}, J = 6.6 Hz); 1.24—1.29 (m, 10 H, OC_9H_{19}); 1.31 and 1.33 (both s, 3 H each, 2 C(3)Me); 1.44 and 1.75 (both m, 2 H each, OC_9H_{19}); 2.68 (s, 3 H, NMe); 3.91 (t, 2 H, OC_9H_{19}, J = 6.6 Hz); 5.54 (s, 1 H, OH); 6.44 (d, 1 H, H(7), J = 9.1 Hz); 6.70—6.73 (m, 2 H, H(4), H(6)); 6.82 (d, 1 H, H(5′), J = 8.8 Hz); 6.99 (dd, 1 H, H(8′), J = 8.8 Hz, J = 2.6 Hz); 7.55 (d, 1 H, H(7′), J = 8.9 Hz); 7.62 (d, 1 H, H(6′), J = 8.8 Hz); 7.67 (s, 1 H, H(2′)); 7.85 (d, 1 H, H(10′), J = 2.6 Hz).

5-Hexadecyloxy-9′-hydroxy-1,3,3-trimethylspiro[indoline-2,3′-[3*H*]naphtho[2,1-*b*][1,4]oxazine] (5e). The yield was 56%, m.p. 118—119 °C (from heptane). Found (%): C, 77.96; H, 9.02; N, 4.73. $C_{38}H_{52}N_2O_3$. Calculated (%): C, 78.04; H, 8.96; N, 4.79. ^{1}H NMR, δ: 0.86 (t, 3 H, $OC_{16}H_{33}$, J = 6.6 Hz); 1.23—1.29 (m, 24 H, $OC_{16}H_{33}$); 1.31 and 1.33 (both s, 3 H each, 2 C(3)Me); 1.43 and 1.75 (both m, 2 H each, $OC_{16}H_{33}$); 2.68 (s, 3 H, NMe); 3.90 (t, 2 H, $OC_{16}H_{33}$, J = 6.6 Hz); 5.40 (s, 1 H, OH); 6.44 (d, 1 H, H(7), J = 8.9 Hz); 6.70—6.73 (m, 2 H, H(4), H(6)); 6.83 (d, 1 H, H(5′), J = 8.9 Hz); 6.99 (dd, 1 H, H(8′), J = 8.8 Hz, J = 2.6 Hz); 7.55 (d, 1 H, H(7′), J = 8.9 Hz); 7.63 (d, 1 H, H(6′), J = 8.8 Hz); 7.67 (s, 1 H, H(2′)); 7.84 (d, 1 H, H(10′), J = 2.6 Hz).

Synthesis of compounds 6a—f (general procedure). A mixture of the corresponding 3*H*-indolium iodide **3** (1 mmol), 7-methoxy-1-nitroso-2-naphthol (**4b**) (1.1 mmol), Pr^iOH (10 mL), and Et_3N (1 mmol) was refluxed for 4 h and then cooled. The solvent was evaporated. The residue was purified by column chromatography on Al_2O_3 (PhH as the eluent).

5,9′-Dimethoxy-1,3,3-trimethylspiro[indoline-2,3′-[3*H*]naphtho[2,1-*b*][1,4]oxazine] (6a). The yield was 37%, m.p. 199—200.5 °C (from toluene). Found (%): C, 74.47; H, 5.98; N, 7.01. $C_{24}H_{24}N_2O_3$. Calculated (%): C, 74.21; H, 6.23; N, 7.21. ^{1}H NMR, δ: 1.31 and 1.34 (both s, 3 H each, 2 C(3)Me); 2.69 (s, 3 H, NMe); 3.78 (s, 3 H, C(5)OMe); 3.98 (s, 3 H, C(9′)OMe); 6.46 (d, 1 H, H(7), J = 8.1 Hz); 6.69—6.74 (m, 2 H, H(4), H(6)); 6.83 (d, 1 H, H(5′), J = 8.8 Hz); 7.01 (dd, 1 H, H(8′), J = 8.9 Hz, J = 2.6 Hz); 7.55 (d, 1 H, H(7′), J = 8.8 Hz); 7.61 (d, 1 H, H(6′), J = 8.9 Hz); 7.70 (s, 1 H, H(2′)); 7.84 (d, 1 H, H(10′), J = 2.6 Hz).

9′-Methoxy-1,3,3-trimethyl-5-propoxyspiro[indoline-2,3′-[3*H*]naphtho[2,1-*b*][1,4]oxazine] (6b). The yield was 34%, m.p. 241.5—243 °C (from toluene). Found (%): C, 75.17; H, 7.14; N, 6.69. $C_{26}H_{28}N_2O_3$. Calculated (%): C, 74.98; H, 6.78; N, 6.73. ^{1}H NMR, δ: 1.03 (t, 3 H, OPr, J = 7.4 Hz); 1.31 and 1.34 (both s, 3 H each, 2 C(3)Me); 1.79 (m, 2 H, OPr); 2.68 (s, 3 H, NMe); 3.88 (t, 2 H, OPr, J = 6.6 Hz); 3.98 (s, 3 H, OMe); 6.45 (d, 1 H, H(7), J = 9.1 Hz); 6.70—6.74 (m, 2 H, H(4), H(6)); 6.83 (d, 1 H, H(5′), J = 8.8 Hz); 7.01 (dd, 1 H, H(8′), J = 8.9 Hz, J = 2.6 Hz); 7.55 (d, 1 H, H(7′), J = 8.9 Hz); 7.61 (d, 1 H, H(6′), J = 8.9 Hz); 7.70 (s, 1 H, H(2′)); 7.84 (d, 1 H, H(10′), J = 2.6 Hz).

9′-Methoxy-1,3,3-trimethyl-5-nonyloxyspiro[indoline-2,3′-[3*H*]naphtho[2,1-*b*][1,4]oxazine] (6c). The yield was 33%, m.p. 114—115 °C (from propan-2-ol). Found (%): C, 76.85; H, 7.98; N, 5.64. $C_{32}H_{40}N_2O_3$. Calculated (%): C, 76.77; H, 8.05; N, 5.60. ^{1}H NMR, δ: 0.87 (t, 3 H, OC_9H_{19}, J = 6.6 Hz); 1.24—1.29 (m, 10 H, OC_9H_{19}); 1.31 and 1.34 (both s, 3 H each, 2 C(3)Me); 1.45 and 1.75 (both m, 2 H each, OC_9H_{19}); 2.68 (s, 3 H, NMe); 3.90 (t, 2 H, OC_9H_{19}, J = 6.6 Hz); 3.98 (s, 3 H, OMe); 6.44 (d, 1 H, H(7), J = 9.0 Hz); 6.70—6.73 (m, 2 H, H(4), H(6)); 6.83 (d, 1 H, H(5′), J = 8.8 Hz); 7.01 (dd, 1 H, H(8′), J = 8.9 Hz, J = 2.6 Hz); 7.55 (d, 1 H, H(7′), J = 8.9 Hz); 7.61 (d, 1 H, H(6′), J = 8.9 Hz); 7.69 (s, 1 H, H(2′)); 7.84 (d, 1 H, H(10′), J = 2.6 Hz).

5-Hexadecyloxy-9′-methoxy-1,3,3-trimethylspiro[indoline-2,3′-[3*H*]naphtho[2,1-*b*][1,4]oxazine] (6d). The yield was 34%, m.p. 103—104 °C (from propan-2-ol). Found (%): C, 78.16; H, 9.14; N, 4.63. $C_{39}H_{54}N_2O_3$. Calculated (%): C, 78.22; H, 9.09; N, 4.68. ^{1}H NMR, δ: 0.86 (t, 3 H, $OC_{16}H_{33}$, J = 6.6 Hz); 1.24—1.29 (m, 24 H, $OC_{16}H_{33}$); 1.31 and 1.34 (both s, 3 H each, 2 C(3)Me); 1.44 and 1.75 (both m, 2 H each, $OC_{16}H_{33}$); 2.68 (s, 3 H, NMe); 3.90 (t, 2 H, $OC_{16}H_{33}$, J = 6.6 Hz); 3.98 (s, 1 H, OMe); 6.44 (d, 1 H, H(7), J = 9.1 Hz); 6.70—6.73 (m, 2 H, H(4), H(6)); 6.83 (d, 1 H, H(5′), J = 8.8 Hz); 7.01 (dd, 1 H, H(8′), J = 8.9 Hz, J = 2.6 Hz); 7.55 (d, 1 H, H(7′), J = 8.9 Hz); 7.61 (d, 1 H, H(6′), J = 8.9 Hz); 7.69 (s, 1 H, H(2′)); 7.84 (d, 1 H, H(10′), J = 2.6 Hz).

5,9′-Dimethoxy-3,3-dimethyl-1-propylspiro[indoline-2,3′-[3*H*]naphtho[2,1-*b*][1,4]oxazine] (6e). The yield was 36%, m.p. 146—147 °C (from heptane). Found (%): C, 75.17; H, 6.89; N, 6.83. $C_{26}H_{28}N_2O_3$. Calculated (%): C, 74.98; H, 6.78; N, 6.73. ^{1}H NMR, δ: 0.89 (t, 3 H, Pr, J = 7.4 Hz); 1.29 and 1.33 (both s, 3 H each, 2 C(3)Me); 1.65 (m, 2 H, Pr); 3.07 (t, 2 H, Pr, J= 7.4 Hz); 3.77 (s, 3 H, C(5)OMe); 3.98 (s, 3 H, C(9′)OMe); 6.48 (d, 1 H, H(7), J = 9.0 Hz); 6.68—6.72 (m, 2 H, H(4), H(6)); 6.81 (d, 1 H, H(5′), J = 8.8 Hz); 7.00 (dd, 1 H, H(8′), J = 8.9 Hz, J = 2.6 Hz); 7.54 (d, 1 H, H(7′), J = 8.8 Hz); 7.60 (d, 1 H, H(6′), J = 8.9 Hz); 7.70 (s, 1 H, H(2′)); 7.83 (d, 1 H, H(10′), J = 2.6 Hz).

1-Isobutyl-5,9′-dimethoxy-3,3-dimethylspiro[indoline-2,3′-[3*H*]naphtho[2,1-*b*][1,4]oxazine] (6f). The yield was 35%, m.p. 155—156 °C (from heptane). Found (%): C, 75.28; H, 6.92; N, 6.70. $C_{27}H_{30}N_2O_3$. Calculated (%): C, 75.32; H, 7.02; N, 6.51. ^{1}H NMR, δ: 0.87 (d, 3 H, Bu^i, J = 6.6 Hz); 0.96 (d, 3 H, Bu^i, J = 6.6 Hz); 1.19 and 1.28 (both s, 3 H each, 2 C(3)Me);

2.04 (m, 1 H, Bu^i); 2.83 (dd, 1 H, Bu^i, J = 14.4 Hz, J = 9.6 Hz); 3.00 (dd, 1 H, Bu^i, J = 14.4 Hz, J = 5.7 Hz); 3.78 (s, 3 H, C(5)OMe); 3.98 (s, 3 H, C(9′)OMe); 6.47 (d, 1 H, H(7), J = 9.1 Hz); 6.67—6.71 (m, 2 H, H(4), H(6)); 6.80 (d, 1 H, H(5′), J = 8.8 Hz); 7.00 (dd, 1 H, H(8′), J = 8.9 Hz, J = 2.6 Hz); 7.54 (d, 1 H, H(7′), J = 8.8 Hz); 7.60 (d, 1 H, H(6′), J = 8.9 Hz); 7.71 (s, 1 H, H(2′)); 7.82 (d, 1 H, H(10′), J = 2.6 Hz).

Synthesis of compounds 6g and 7a—e (general procedure). A mixture of the corresponding hydroxyoxazine **5** (1 mmol), K_2CO_3 (0.18 g), 18-crown-6 (0.0054 g), AlkHal (1.5 mmol), and PhMe (10 mL) was refluxed for 5 h. The solvent was evaporated. The residue was purified by column chromatography on Al_2O_3 (PhH as the eluent).

5-Methoxy-1,3,3-trimethyl-9′-propoxyspiro[indoline-2,3′-[3*H*]naphtho[2,1-*b*][1,4]oxazine] (6g). The yield was 57%, m.p. 150—151 °C (from heptane). Found (%): C, 75.25; H, 6.96; N, 6.62. $C_{26}H_{28}N_2O_3$. Calculated (%): C, 74.98; H, 6.78; N, 6.73. ^{1}H NMR, δ: 1.07 (t, 3 H, OPr, J = 7.4 Hz); 1.31 and 1.34 (both s, 3 H each, 2 C(3)Me); 1.88 (m, 2 H, OPr); 2.98 (s, 3 H, NMe); 3.78 (s, 3 H, OMe); 4.12 (t, 2 H, OPr, J = 6.7 Hz); 6.46 (d, 1 H, H(7), J = 8.1 Hz); 6.69—6.74 (m, 2 H, H(4), H(6)); 6.82 (d, 1 H, H(5′), J = 8.8 Hz); 7.02 (dd, 1 H, H(8′), J = 8.9 Hz, J = 2.6 Hz); 7.54 (d, 1 H, H(7′), J = 8.8 Hz); 7.60 (d, 1 H, H(6′), J = 8.9 Hz); 7.69 (s, 1 H, H(2′)); 7.82 (d, 1 H, H(10′), J = 2.6 Hz).

Ethyl 1,3,3-trimethylspiro[indoline-2,3′-[3*H*]naphtho[2,1-*b*][1,4]oxazine]-9′-yloxyacetate (7a). The yield was 62%, m.p. 167—168 °C (from propan-2-ol). Found (%): C, 72.46; H, 6.14; N, 6.55. $C_{26}H_{26}N_2O_4$. Calculated (%): C, 72.54; H, 6.09; N, 6.51. ^{1}H NMR, δ: 1.32 (t, 3 H, OCH_2COOEt, J = 7.1 Hz); 1.33 and 1.34 (both s, 3 H each, 2 C(3)Me); 2.76 (s, 3 H, NMe); 4.31 (q, 2 H, OCH_2COOEt, J = 7.1 Hz); 4.81 (s, 2 H, OCH_2COOEt); 6.56 (d, 1 H, H(7), J = 7.8 Hz); 6.85 (d, 1 H, H(5′), J = 8.8 Hz); 6.88 (dt, 1 H, H(5), J = 7.4 Hz, J = 0.9 Hz); 7.07 (dd, 1 H, H(4), J = 7.3 Hz, J = 1.0 Hz); 7.13 (dd, 1 H, H(8′), J = 8.9 Hz, J = 2.6 Hz); 7.20 (dt, 1 H, H(6), J = 7.7 Hz, J = 1.0 Hz); 7.56 (d, 1 H, H(7′), J = 8.9 Hz); 7.64 (d, 1 H, H(6′), J = 8.9 Hz); 7.68 (s, 1 H, H(2′)); 7.81 (d, 1 H, H(10′), J = 2.6 Hz).

Ethyl 5-methoxy-1,3,3-trimethylspiro[indoline-2,3′-[3*H*]naphtho[2,1-*b*][1,4]oxazine]-9′-yloxyacetate (7b). The yield was 68%, m.p. 165—166 °C (from propan-2-ol). Found (%): C, 70.47; H, 6.04; N, 6.15. $C_{27}H_{28}N_2O_5$. Calculated (%): C, 70.42; H, 6.13; N, 6.08. ^{1}H NMR, δ: 1.31 (s, 3 H, C(3)Me); 1.32 (t, 3 H, OCH_2COOEt, J = 7.1 Hz); 1.34 (s, 3 H, C(3)Me); 2.68 (s, 3 H, NMe); 3.78 (s, 3 H, OMe); 4.31 (q, 2 H, OCH_2COOEt, J = 7.1 Hz); 4.81 (s, 2 H, OCH_2COOEt); 6.46 (d, 1 H, H(7), J = 8.1 Hz); 6.69—6.74 (m, 2 H, H(4), H(6)); 6.86 (d, 1 H, H(5′), J = 8.9 Hz); 7.12 (dd, 1 H, H(8′), J = 8.9 Hz, J = 2.6 Hz); 7.56 (d, 1 H, H(7′), J = 8.9 Hz); 7.64 (d, 1 H, H(6′), J = 8.9 Hz); 7.67 (s, 1 H, H(2′)); 7.81 (d, 1 H, H(10′), J = 2.6 Hz).

Ethyl 1,3,3-trimethyl-5-propoxyspiro[indoline-2,3′-[3*H*]naphtho[2,1-*b*][1,4]oxazine]-9′-yloxyacetate (7c). The yield was 66%, m.p. 129.5—131 °C (from propan-2-ol). Found (%): C, 71.32; H, 6.56; N, 5.82. $C_{29}H_{32}N_2O_5$. Calculated (%): C, 71.29; H, 6.60; N, 5.73. ^{1}H NMR, δ: 1.03 (t, 3 H, OPr, J = 7.4 Hz); 1.31 (s, 3 H, C(3)Me); 1.32 (t, 3 H, OCH_2COOEt, J = 7.1 Hz); 1.34 (s, 3 H, C(3)Me); 1.79 (m, 2 H, OPr); 2.67 (s, 3 H, NMe); 3.88 (t, 2 H, OPr, J = 6.6 Hz); 4.31 (q, 2 H, OCH_2COOEt, J = 7.1 Hz); 4.81 (s, 2 H, OCH_2COOEt); 6.45 (d, 1 H, H(7), J = 9.1 Hz); 6.70—6.74 (m, 2 H, H(4), H(6)); 6.85 (d, 1 H, H(5′), J = 8.8 Hz); 7.12 (dd, 1 H, H(8′), J = 8.9 Hz, J = 2.6 Hz); 7.56 (d, 1 H, H(7′), J = 8.8 Hz); 7.64 (d, 1 H, H(6′), J = 8.9 Hz); 7.67 (s, 1 H, H(2′)); 7.81 (d, 1 H, H(10′), J = 2.6 Hz).

Ethyl 1,3,3-trimethyl-5-nonyloxyspiro[indoline-2,3′-[3*H*]naphtho[2,1-*b*][1,4]oxazine]-9′-yloxyacetate (7d). The yield was 71%, m.p. 120—121 °C (from propan-2-ol). Found (%): C, 73.35; H, 7.81; N, 4.77. $C_{35}H_{44}N_2O_5$. Calculated (%): C, 73.40; H, 7.74; N, 4.89. ^{1}H NMR, δ: 0.87 (t, 3 H, OC_9H_{19}, J = 6.6 Hz); 1.24—1.29 (m, 10 H, OC_9H_{19}); 1.30 (s, 3 H, C(3)Me); 1.32 (t, 3 H, OCH_2COOEt, J = 7.1 Hz); 1.33 (s, 3 H, C(3)Me); 1.44 and 1.75 (both m, 2 H each, OC_9H_{19}); 2.67 (s, 3 H, NMe); 3.90 (t, 2 H, OC_9H_{19}, J = 6.6 Hz); 4.30 (q, 2 H, OCH_2COOEt, J = 7.1 Hz); 4.81 (s, 2 H, OCH_2COOEt); 6.45 (d, 1 H, H(7), J = 9.1 Hz); 6.70—6.74 (m, 2 H, H(4), H(6)); 6.85 (d, 1 H, H(5′), J = 8.8 Hz); 7.12 (dd, 1 H, H(8′), J = 8.9 Hz, J = 2.6 Hz); 7.56 (d, 1 H, H(7′), J = 8.9 Hz); 7.64 (d, 1 H, H(6′), J = 8.9 Hz); 7.67 (s, 1 H, H(2′)); 7.81 (d, 1 H, H(10′), J = 2.6 Hz).

Ethyl 5-hexadecyloxy-1,3,3-trimethylspiro[indoline-2,3′-[3*H*]naphtho[2,1-*b*][1,4]oxazine]-9′-yloxyacetate (7e). The yield was 69%, m.p. 197—198 °C (from propan-2-ol). Found (%): C, 75.14; H, 8.79; N, 4.23. $C_{42}H_{58}N_2O_5$. Calculated (%): C, 75.19; H, 8.71; N, 4.18. ^{1}H NMR, δ: 0.86 (t, 3 H, $OC_{16}H_{33}$, J = 6.6 Hz); 1.24—1.29 (m, 24 H, $OC_{16}H_{33}$); 1.30 (s, 3 H, C(3)Me); 1.32 (t, 3 H, OCH_2COOEt, J = 7.1 Hz); 1.33 (s, 3 H, C(3)Me); 1.44 and 1.75 (both m, 2 H each, $OC_{16}H_{33}$); 2.67 (s, 3 H, NMe); 3.90 (t, 2 H, $OC_{16}H_{33}$, J = 6.6 Hz); 4.30 (q, 2 H, OCH_2COOEt, J = 7.1 Hz); 4.81 (s, 2 H, OCH_2COOEt); 6.45 (d, 1 H, H(7), J = 9.1 Hz); 6.70—6.74 (m, 2 H, H(4), H(6)); 6.85 (d, 1 H, H(5′), J = 8.8 Hz); 7.12 (dd, 1 H, H(8′), J = 8.9 Hz, J = 2.6 Hz); 7.56 (d, 1 H, H(7′), J = 8.9 Hz); 7.64 (d, 1 H, H(6′), J = 8.9 Hz); 7.67 (s, 1 H, H(2′)); 7.80 (d, 1 H, H(10′), J = 2.6 Hz).

Synthesis of compounds 8a—e (general procedure). A mixture of the corresponding spirooxazine **7** (1 mmol), KOH (0.08 g), water (0.35 mL), and MeOH (30 mL) was refluxed for 3 h. The solvent was distilled off *in vacuo*. The residue was diluted with water (30 mL), acidified with dilute HCl to pH 6, and extracted with AcOEt. The extract was dried with Na_2SO_4 and the solvent was removed *in vacuo*.

1,3,3-Trimethylspiro[indoline-2,3′-[3*H*]naphtho[2,1-*b*][1,4]oxazine]-9′-yloxyacetic acid (8a). The yield was 63%, m.p. 177—178 °C (from propan-2-ol). Found (%): C, 71.74; H, 5.56; N, 6.88. $C_{24}H_{22}N_2O_4$. Calculated (%): C, 71.63; H, 5.51; N, 6.96. ^{1}H NMR, δ: 1.33 and 1.36 (both s, 3 H each, 2 C(3)Me); 2.67 (s, 3 H, NMe); 5.06 (s, 2 H, OCH_2COOH); 6.52 (d, 1 H, H(7), J = 7.8 Hz); 6.86 (d, 1 H, H(5′), J = 8.9 Hz); 6.87 (dt, 1 H, H(5), J = 7.4 Hz, J = 0.9 Hz); 7.06 (dd, 1 H, H(4), J = 7.3 Hz, J = 0.9 Hz); 7.17 (dd, 1 H, H(8′), J = 8.9 Hz, J = 2.6 Hz); 7.18 (dt, 1 H, H(6), J = 7.7 Hz, J = 1.3 Hz); 7.60 (d, 1 H, H(7′), J = 8.9 Hz); 7.68 (d, 1 H, H(6′), J = 8.9 Hz); 7.69 (d, 1 H, H(10′), J = 2.6 Hz); 8.08 (s, 1 H, H(2′)).

5-Methoxy-1,3,3-trimethylspiro[indoline-2,3′-[3*H*]naphtho[2,1-*b*][1,4]oxazine]-9′-yloxyacetic acid (8b). The yield was 62%, m.p. 171—172 °C (from propan-2-ol). Found (%): C, 69.39; H, 5.53; N, 6.56. $C_{25}H_{24}N_2O_5$. Calculated (%): C, 69.43; H, 5.59; N, 6.48. ^{1}H NMR, δ: 1.34 (s, 6 H, 2 C(3)Me); 2.61 (s, 3 H, NMe); 3.77 (s, 3 H, OMe); 5.05 (s,

2 H, OCH_2COOH); 6.42 (d, 1 H, H(7), J = 8.6 Hz); 6.68—6.72 (m, 2 H, H(4), H(6)); 6.87 (d, 1 H, H(5′), J = 8.8 Hz); 7.17 (dd, 1 H, H(8′), J = 8.9 Hz, J = 2.5 Hz); 7.60 (d, 1 H, H(7′), J = 8.9 Hz); 7.67 (d, 1 H, H(6′), J = 8.8 Hz); 7.70 (d, 1 H, H(10′), J = 2.5 Hz); 8.06 (s, 1 H, H(2′)).

1,3,3-Trimethyl-5-propoxyspiro[indoline-2,3′-[3*H*]naphtho[2,1-*b*][1,4]oxazine]-9′-yloxyacetic acid (8c). The yield was 59%, m.p. 176—177 °C (from propan-2-ol). Found (%): C, 70.45; H, 4.98; N, 8.36. $C_{27}H_{28}N_2O_5$. Calculated (%): C, 70.42; H, 6.13; N, 6.08. ^{1}H NMR, δ: 1.02 (t, 3 H, OPr, J = 7.4 Hz); 1.33 (s, 6 H, 2 C(3)Me); 1.77 (m, 2 H, OPr); 2.60 (s, 3 H, NMe); 3.86 (t, 2 H, OPr, J = 6.6 Hz); 5.05 (s, 2 H, OCH_2COOH); 6.40 (d, 1 H, H(7), J = 9.1 Hz); 6.68—6.71 (m, 2 H, H(4), H(6)); 6.86 (d, 1 H, H(5′), J = 8.8 Hz); 7.17 (dd, 1 H, H(8′), J = 8.9 Hz, J = 2.5 Hz); 7.60 (d, 1 H, H(7′), J = 8.9 Hz); 7.67 (d, 1 H, H(6′), J = 8.9 Hz); 7.69 (d, 1 H, H(10′), J = 2.5 Hz); 8.06 (s, 1 H, H(2′)).

1,3,3-Trimethyl-5-nonyloxyspiro[indoline-2,3′-[3*H*]naphtho[2,1-b][1,4]oxazine]-9′-yloxyacetic acid (8d). The yield was 64%, m.p. 154—155 °C (from propan-2-ol). Found (%): C, 72.80; H, 7.48; N, 5.09. $C_{33}H_{40}N_2O_5$. Calculated (%): C, 72.77; H, 7.40; N, 5.14. ^{1}H NMR, δ: 0.86 (t, 3 H, OC_9H_{19}, J = 6.6 Hz); 1.24—1.29 (m, 10 H, OC_9H_{19}); 1.33 (s, 6 H, 2 C(3)Me); 1.43 and 1.74 (both m, 2 H each, OC_9H_{19}); 2.59 (s, 3 H, NMe); 3.88 (t, 2 H, OC_9H_{19}, J = 6.6 Hz); 5.07 (s, 2 H, OCH_2COOH); 6.40 (d, 1 H, H(7), J = 9.1 Hz); 6.68—6.71 (m, 2 H, H(4), H(6)); 6.86 (d, 1 H, H(5′), J = 8.8 Hz); 7.18 (dd, 1 H, H(8′), J = 8.9 Hz, J = 2.5 Hz); 7.60 (d, 1 H, H(7′), J = 8.9 Hz); 7.67 (d, 1 H, H(6′), J = 8.9 Hz); 7.68 (d, 1 H, H(10′), J = 2.5 Hz); 8.09 (s, 1 H, H(2′)).

5-Hexadecyloxy-1,3,3-trimethylspiro[indoline-2,3′-[3*H*]naphtho[2,1-*b*][1,4]oxazine]-9′-yloxyacetic acid (8e). The yield was 60%, m.p. 146—147 °C (from propan-2-ol). Found (%): C, 74.65; H, 8.52; N, 4.31. $C_{40}H_{54}N_2O_5$. Calculated (%): C, 74.73; H, 8.47; N, 4.36. ^{1}H NMR, δ: 0.86 (t, 3 H, $OC_{16}H_{33}$, J = 6.6 Hz); 1.24—1.29 (m, 24 H, $OC_{16}H_{33}$); 1.33 (s, 6 H, 2 C(3)Me); 1.44 and 1.75 (both m, 2 H each, $OC_{16}H_{33}$); 2.60 (s, 3 H, NMe); 3.88 (t, 2 H, $OC_{16}H_{33}$, J = 6.6 Hz); 5.06 (s, 2 H, OCH_2COOH); 6.40 (d, 1 H, H(7), J = 9.1 Hz); 6.68—6.71 (m, 2 H, H(4), H(6)); 6.86 (d, 1 H, H(5′), J = 8.8 Hz); 7.18 (dd, 1 H, H(8′), J = 8.9 Hz, J = 2.5 Hz); 7.60 (d, 1 H, H(7′), J = 8.9 Hz); 7.67 (d, 1 H, H(6′), J = 8.9 Hz); 7.68 (d, 1 H, H(10′), J = 2.5 Hz); 8.08 (s, 1 H, H(2′)).

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