Spiropyrans and spirooxazines
5.* Synthesis of photochromic 8-(4,5-diphenyl-1,3-oxazol-2-yl)-substituted spiro[indoline-benzopyrans]**

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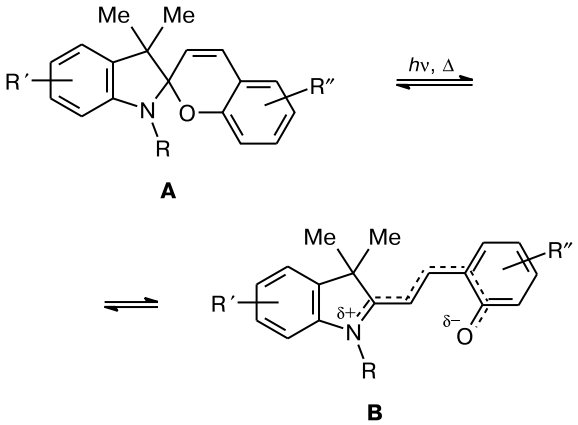
Photochromic spiro[indoline-benzopyrans] containing 4,5-diphenyloxazolyl group at position 8 of the benzopyran fragment have been obtained. New diphenyloxazolyl-substituted spiropyrans manifest considerably higher thermal stability of the merocyanine isomers than their naphthopyran analogs.

Key words: triaryloxazole, spiropyrans, merocyanines, photochromism.

The synthesis and studies of new efficient photochromic systems, prospective for development of polyfunctional materials for molecular electronics on their basis, is an actual problem.[2,3] Among the most well-known classes of photochromic compounds, spiropyrans are of particular interest since, depending on molecular structures, they manifest spectro-kinetic characteristics varying in a wide range, as well as due to the relative easiness of their synthesis.[3—5]

Mechanism of photochromic transformations of spiropyrans (SPP) (Scheme 1) includes the thermally and photochemically reversible process of heterolytic cleavage of the C_{Sp}—O bond of the cyclic isomer **A** with subsequent *cis—trans*-isomerization to the metastable merocyanine form **B**.[3—5]

Scheme 1



On the basis of SPP by introduction of the corresponding functional fragments, it is possible to obtain polyfunctional molecular systems displaying, along with photochromism, fluorescent,[6] magnetic,[7] and complex-forming properties switching by optical irradiation.[8] Earlier,[9] we reported on the synthesis of photochromic 5′-(4,5-diphenyl-1,3-oxazol-2-yl)-substituted spiro[indoline-naphthopyran], the merocyanine form of which reversibly forms complexes with bivalent cations of heavy metals. In continuation of this research, the present work deals with the synthesis and description of photochromic properties of a number of spirobenzopyrans containing diphenyloxazolyl group at position 8 of the benzopyran fragment.

Results and Discussion

There are two general methods for the synthesis of SPP. The first of them (method I) includes a condensation of corresponding heterocyclic cations with *o*-hydroxyaromatic aldehydes in acidic medium, isolation of salts of *o*-hydroxystyryl derivatives, and spirocyclization of the latter under the action of a base. Method II, used the most often for the preparation of indoline SPP, consists in condensation of a methylene base (or the corresponding heterocyclic immonium salt in the presence of a base) with *o*-hydroxyaromatic aldehydes. Both methods have been used for the synthesis of indoline SPP containing diphenyloxazolyl substituent (Scheme 2).

* For Part 4, see Ref. 1.
** Dedicated to Academician A. I. Konovalov on his 75th birthday.

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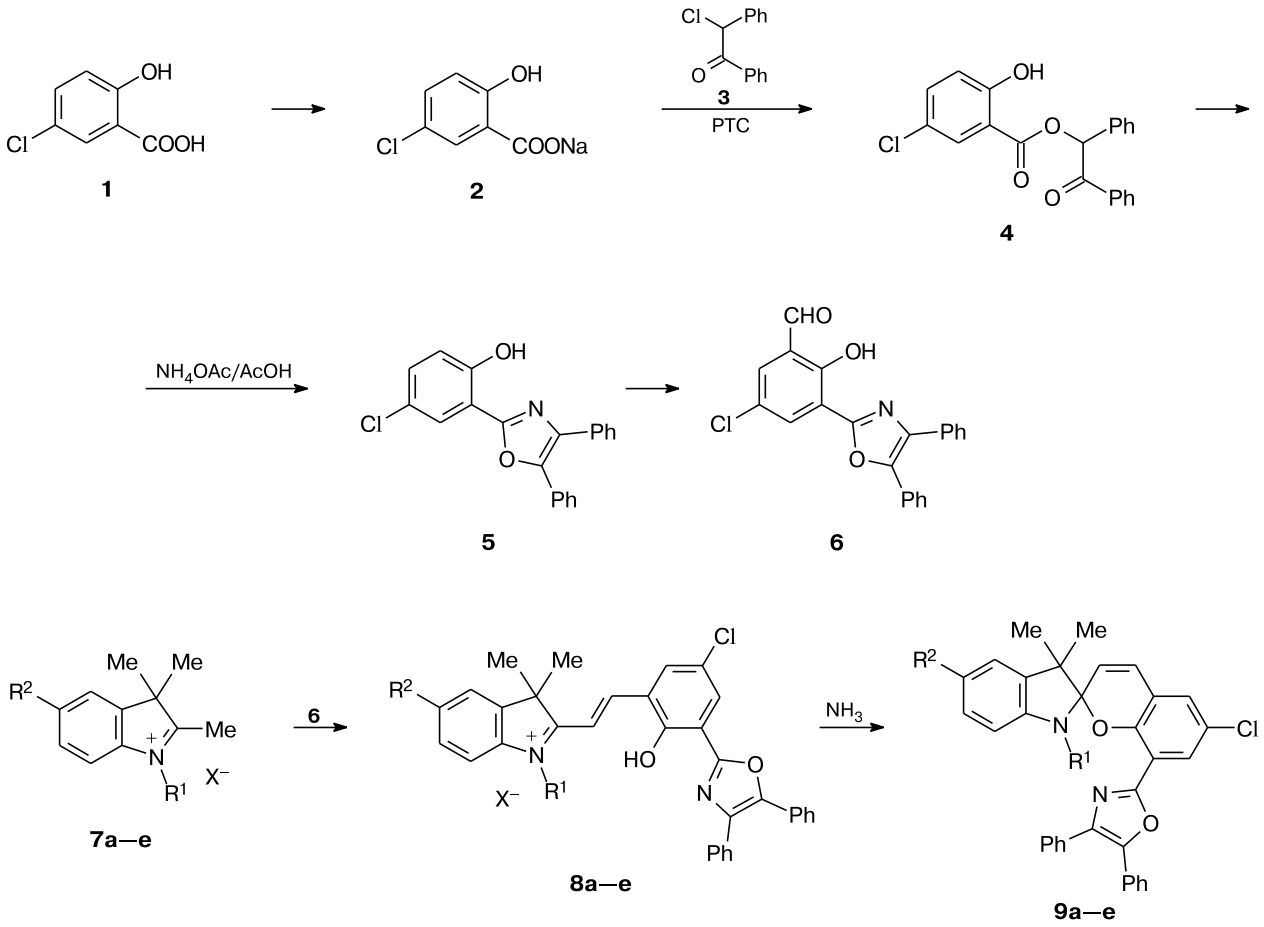
Scheme 2



PTC means phase-transfer catalysis

7: R^1 = Me (**a—d**), Pr (**e**), All (**f**), Bu^i (**g**); R^2 = H (**a,e—g**), Cl (**b**), Me (**c**), OMe (**d**); X = I (**a,c—g**), ClO_4 (**b**);
8: R^1 = Me (**a—d**), Pr (**e**); R^2 = H (**a,e**), Cl (**b**), Me (**c**), OMe (**d**); X = I (**a,c—e**), ClO_4 (**b**);
9: R^1 = Me (**a—d**), Pr (**e**), All (**f**), Bu^i (**g**); R^2 = H (**a,e—g**), Cl (**b**), Me (**c**), OMe (**d**)

Cyclization of aromatic acid benzoin esters (desyl esters) by the Davidson method is a convenient method for preparing 2,4,5-triaryl-1,3-oxazoles.[10] The synthesis of the corresponding desyl esters, which can be obtained by acylation of unsubstituted or symmetrically substituted benzoin (in the case of unsymmetrically substituted benzoin, formation of isomeric acylation products is possible), also is not difficult.[11] However, in the case of 2-(hydroxyaryl)-4,5-diphenyl-1,3-oxazoles, the synthesis of the corresponding desyl esters by this method is complicated by the necessity to obtain acyl chlorides of hydroxy-substituted arylcarboxylic acids and possible side acylation reactions. In this case, preparation of the corresponding desyl esters by the alkylation of carboxylic acid salts with desyl chloride under phase-transfer catalysis conditions is the most preferable.[12]

5-Chloro-2-hydroxybenzoic acid (**1**) was the starting compound (see Scheme 2). The reaction of acid **1** with sodium methoxide in methanol led to sodium salt **2**, the alkylation of which with 2-chloro-1,2-diphenylethanone (**3**) under conditions of phase-transfer catalysis in the system solid phase—liquid in the presence of 15-crown-5

led to desyl ester **4**. The reaction of desyl ester **4** with ammonium acetate in acetic acid by the Davidson method[10] afforded diphenyloxazolyl-substituted phenol **5**, the Duff formylation of which in trifluoroacetic acid gave *o*-hydroxybenzaldehyde **6**.

8-Diphenyloxazolyl-substituted spirobenzopyrans were obtained by the two-step method (method I): *viz.*, by the reaction of 3*H*-indolium salts **7a—e** with diphenyloxazolyl-substituted hydroxybenzaldehyde **6** in acetic acid, the isolation of salts of *o*-hydroxystyryl derivatives **8a—e**, and treatment of the latter with ammonia, which finally leads to SPP **9a—e**. Spiropyrans **9f,g** were synthesized by the one-step method (method II): *viz.*, by the condensation of 3*H*-indolium salts **7f,g** with *o*-hydroxybenzaldehyde **6**, which is formed by the formylation of 2-(2-hydroxyphenyl)-4,5-diphenyloxazole **5**, in the presence of triethylamine as the base (see Scheme 2). Diphenyloxazolyl-substituted aldehyde **6** was obtained by formylation of 2-(2-hydroxyphenyl)-4,5-diphenyloxazole (**5**).

Colorless or lightly colored 8-diphenyloxazolyl-substituted spirobenzopyrans **9a—g** was purified by chromatography and recrystallized. The structures of compounds **4—6** and **9a—g** were established by ^{1}H NMR spectroscopy and confirmed by the elemental analysis data.

^{1}H NMR spectroscopy is a convenient method for the structural identification of SPP since it allows one to quickly and accurately establish the structure of a compound obtained from characteristic shifts, spin-spin coupling constants, and number of protons of various types. The signals of such characteristic (indicative) groups as *gem*-dimethyl group, *N*-alkyl substituent, protons at the double bond C(3)=C(4) usually can be easily identified and they have different chemical shifts for open and cyclic forms.[13—15]

According to the ^{1}H NMR spectroscopic data, the SPP synthesized exist in solution ($CDCl_3$) in the spirocyclic form.

The downfield region of SPP spectrum includes easily identifiable two signals from the magnetically nonequivalent geminal methyl groups, the signal for the *N*-alkyl substituent (Me, Pr, All, Bu^i), and the signals for the corresponding indicative groups of substituents (Me, OMe) of SPP.

Prochirality of the methyl groups and the protons of the methylene group of the *N*-isobutyl substituent (SPP **9g**) and the methylene group of the *N*-allyl substituent (SPP **9f**) leads to the diastereotopic splitting of signals for these groups.

Two doublets at δ 0.90 and 0.91 and two doublets of doublets at δ 2.93 and 3.04 correspond to the diastereotopic protons of the methyl and methylene groups of the *N*-isobutyl substituent of SPP **9g**, respectively. A multiplet of the signal for the proton of the CH group is recorded around δ 2.04.

The diastereotopic protons of the methylene group of the *N*-allyl-substituted SPP **9f** resonate as a triplet of doublets of doublets in the region δ 3.77 and 3.99. The signals for the protons of the terminal CH_2 group, each resonating as quartet of doublets, are in the region δ 5.01 and 5.16. The proton of the CH group is recorded as a multiplet at δ 5.89.

The upfield portion of the SPP **9a—g** spectra includes several groups of mutually interacting signals for protons related to the indoline and pyran fragments of the molecule and the signals for two groups (each consisting of five interacting nuclei) related to the phenyl groups of the diphenyloxazolyl substituent. In contrast to diphenyloxazolyl-substituted phenol **5** and aldehyde **6**, in the ^{1}H NMR spectra of which the signals for the ten protons of two phenyl rings of the diphenyloxazolyl group resonate as four- and six-proton multiplets, in the ^{1}H NMR spectra of the diphenyloxazolyl-substituted spirobenzopyrans, the signals for the protons of two phenyl rings of the benzoxazole group form a complex picture of four multiplets with the integral intensities being 2 : 3 : 3 : 2.

The ^{1}H NMR spectroscopic data (the two signals from the magnetically nonequivalent geminal methyl groups, the signals for the protons of the phenyl rings of the diphenyloxazolyl group, the diastereotopic splitting of the signals for the protons of the *N*-alkyl substituent, the chemical shift values, and the spin-spin coupling constant values for the diastereotopic protons of the *N*-isobutyl and *N*-allyl substituents, the protons of the double bond of the pyran fragment, and the protons of the indoline and pyran fragments) unambiguously confirm the structure of the SPP obtained. The absence of the signals for the *N*-methyl and *gem*-dimethyl groups, *trans*-vinylic protons, and other protons of the indoline and pyran fragments in the regions of the spectrum characteristic of the open plane merocyanine form without asymmetric center suggests that the compounds obtained exist in solution ($CDCl_3$) mainly in the spirocyclic form.

Electronic absorption spectra of cyclic forms **A** of SPP **9a—g** in the region of spectral transparency of toluene are characterized by the presence of two bands. The more intensive one, a short-wave band with molar extinction coefficient in the maximum being 19300—24200 L mol^{-1} cm^{-1}, is susceptible to the changes in the SPP structure (substituents R^1 and R^2) and has the maximum in the region 300—312 nm (Table 1). In contrast to this, position of the maximum of the less intensive (ε = 11800—13700 L mol^{-1} cm^{-1}) long-wave absorption band of SPP **9a—g** does not depend on the nature of substituents R^1 and R^2 in the indoline part of SPP and is localized at 358 nm. This fact agrees with the suggestion on the additivity of absorption spectra of acoplanar fragments of SPP and on localization of the electron transition, responsible for the more long-wave absorption band, on the benzopyran part of the molecule. Method of structural simulation showed that the electronic absorption spectra of SPP can be represented as a linear combination of absorption spectra of the composing fragments, that becomes possible due to the weak interaction of the mutually orthogonal fragments. In this case, the long-wave absorption band corresponds to the photochemically active benzopyran fragment, whereas

Table 1. Absorption spectra data and kinetic properties of compounds **9a—g** in toluene, $T = 283$ K

SPP	λ_{max}^{A}/nm (ε/L mol^{-1} cm^{-1})		λ_{max}^{B}/nm		$\tau^{B\rightarrow A}$ /s
	1	2	1	2	
9a	301 (19300)	358 (11800)	450	648	25.5
9b	309 (22800)	358 (13700)	470	650	9.8
9c	306 (23700)	358 (13100)	440	650	45.6
9d	312 (24200)	358 (12300)	440	655	61.0
9e	302 (21600)	358 (12600)	440	650	40.0
9f	300 (20000)	358 (12500)	445	650	14.1
9g	302 (21800)	358 (12900)	445	650	37.4

the more short-wave one, to the absorption of the heterocyclic part of the molecule.[16]

It was found that the cyclic forms of SPP do not possess fluorescent properties at 293 K.

On irradiation of toluene solutions of SPP **9a—g** in the region of the long-wave absorption of cyclic forms **A**, their coloration is observed accompanied by the appearance in the electronic absorption spectra of bands (Fig. 1, see Table 1) characteristic of acyclic merocyanine isomers **B** of SPP.[3—5] It should be noted that SPP **9f** undergoes irreversible photodegradation on the constant UV irradiation.

Electronic absorption spectra of the merocyanine isomers **B** of SPP **9a—g** in the visible region of the spectrum include two bands: more intensive long-wave one with the maximum at 648—655 nm and less intensive, with maximum at 440—470 nm corresponding to the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions, respectively. Position of the maximum of the long-wave absorption band of the merocyanine form **B** in the series of SPP **9a—g** is considerably shifted to the long-wave region of the spectrum on introduction of the electron-donating MeO group at position 5 of the indoline part of SPP (SPP **9d**).

The absorption spectra of SPP **9a—g** in toluene at room temperature do not contain absorption band of the merocyanine form, that suggests the absence of the ring-chain equilibrium **A** $\rightleftharpoons$ **B** in the ground state, which is observed for the structural analogs of compounds under study, 5′-(4,5-diphenyl-1,3-oxazol-2-yl)-substituted spironaphthopyrans.[9]

On stopping the irradiation of solutions of SPP **9a—g**, their discoloration occurs, which is caused by the thermal recyclization **B** → **A**. The kinetic curves of the relaxation processes in the dark are satisfactoryly described by the monoexponential function, which is confirmed by the linear dependence of the logarithm of relative change of optical density in the long-wave absorption band maxima of the merocyanine isomers of SPP **9a—g** from the thermal discoloration time presented in Figure 2. The time constant values obtained from the kinetic curves of thermal discoloration (lifetime) are presented in Table 1. In comparison with 5′-(4,5-diphenyl-1,3-oxazol-2-yl)-substituted spiro[indoline-naphthopyran] having a high rate of discoloration in the dark and characterizing by the lifetime of the colored form of less than 1 s,[9] compounds **9a—g**, being its benzopyran analogs, manifest considerably higher thermal stability of the merocyanine isomers with the lifetime of 10—60 s at $T = 283$ K (see Table 1).

The lifetimes of the merocyanine forms **B** depend on the nature of substituents at positions 1 and 5 of the indoline fragment. The presence of electron-donating group at position 5 leads to the retardation of the thermal process of discoloration. Thus, on going from 5-chloro derivative (SPP **9b**) to the unsubstituted at position 5 SPP **9a** and further to SPP **9c** and **9d** including electron-donating substituents, a considerable increase in the lifetime of photoinduced isomers **B** is observed. An elongation of the alkyl radical chain at the nitrogen atom (R^1), apparently, creating sterical hindrance in the process of

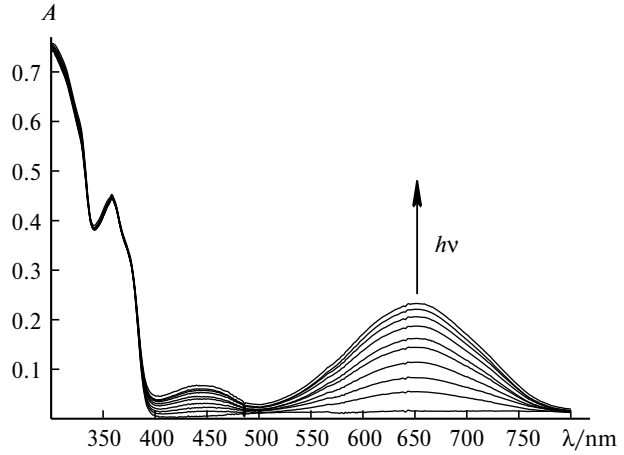


Fig. 1. Electronic absorption spectra of SPP **9g** in toluene on irradiation with light with λ = 365 nm ($C = 3.49 \cdot 10^{-5}$ mol L^{-1}, $T = 283$ K).

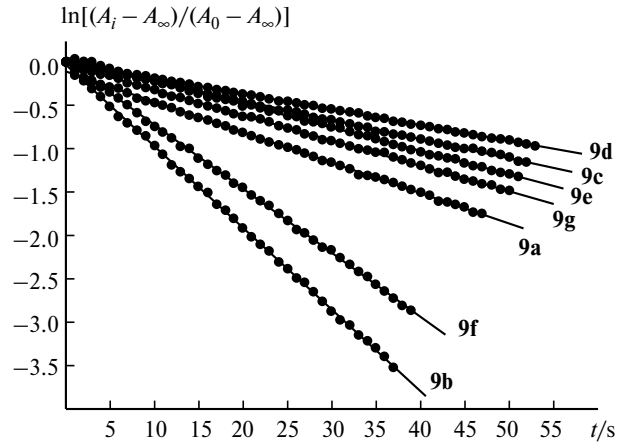


Fig. 2. Linear anamorphoses of kinetic curves obtained in the process of thermal discoloration of the merocyanine isomers of compounds **9a—g** in toluene, $T = 283$ K.

the pyran ring formation, stabilizes the merocyanine form **B**. This is confirmed by the lifetime values for SPP **9a** (R^1 = Me), **9e** (R^1 = Pr), and **9g** (R^1 = Bu^i), which are 25, 40, and 37 s, respectively.

In conclusion, new 8-(4,5-diphenyl-1,3-oxazol-2-yl)-substituted spiro[indoline-benzopyrans] are obtained displaying photochromic properties in solutions. It was found that, in contrast to naphthopyran analogs, the spirobenzopyrans synthesized are characterized by significantly higher thermal stability of the merocyanine isomers.

Experimental

^{1}H NMR spectra were recorded on a Varian Unity-300 spectrometer (300 MHz) at 20 °C in $CDCl_3$, δ values were determined to within 0.01 ppm, spin-spin coupling constants, within 0.1 Hz.

Electronic absorption spectra and kinetic curves of thermal recyclization reactions of compounds under study were recorded on an Agilent 8453 spectrophotometer equipped with a thermostated cell. Photolysis of solutions was carried out by the mercury DRSh-250 lamp supplied with a set of interferential light filters. Toluene of spectrophotometric grade (Aldrich) was used for preparation of solutions.

1,2-Diphenyl-2-chloroethanone (3) was obtained according to the known procedure.[17]

3*H*-Indolium iodides **7a,c—g** were synthesized according to the methods described earlier.[18—21]

Sodium 5-chloro-2-hydroxybenzoate (2). A mixture of 5-chloro-2-hydroxybenzoic acid **1** (8.63 g, 50 mmol) and sodium methoxide (2.70 g, 50 mmol) in methanol (40 mL) was refluxed for 2 h. Methanol was half evaporated *in vacuo* followed by the addition of ether (30 mL). A precipitate was filtered off, dried *in vacuo*, and used further without additional purification. The yield was 8.47 g (87%).

2-Oxo-1,2-diphenylethyl 2-hydroxy-5-chlorobenzoate (4). A mixture of sodium salt **2** (6.42 g, 33 mmol), 15-crown-5 (1 mL), and acetonitrile (50 mL) was stirred for 0.5 h at 70 °C followed by the addition of desyl chloride **3** (6.93 g, 30 mmol). The mixture was stirred under reflux for 10 h and then poured into icy water. A precipitate formed was filtered off, washed with water, and dried. Ester **4** obtained was recrystallized from propan-2-ol—isooctane (3 : 1). The yield was 9.02 g (82%), m.p. 123—124 °C. Found (%): C, 68.63; H, 4.21. $C_{21}H_{15}ClO_4$. Mol. weight 366.80. Calculated (%): C, 68.77; H, 4.12. ^{1}H NMR, δ: 6.94 (d, 1 H, H(3), J = 8.9 Hz); 7.08 (s, 1 H, 1-COOC<u>H</u>(Ph)C(O)Ph); 7.40—7.47 (m, 6 H, H(4), PhH); 7.53—7.58 (m, 3 H, PhH); 7.93 (d, 1 H, H(6), J = 2.7 Hz); 7.96—7.99 (m, 2 H, PhH); 10.38 (s, 1 H, 2-OH).

4-Chloro-2-(4,5-diphenyl-1,3-oxazol-2-yl)phenol (5). A mixture of desyl benzoate **4** (7.34 g, 20 mmol), ammonium acetate (9.24 g, 0.12 mol), and acetic acid (40 mL) was refluxed for 4 h and poured into ice (500 g). A precipitate was filtered off, washed with water, and dried. Phenol **5** obtained was recrystallized from propan-2-ol. The yield was 4.87 g (70%), m.p. 136—137 °C. Found (%): C, 72.38; H, 3.95; N, 4.11. $C_{21}H_{14}ClNO_2$. Mol. weight 347.80. Calculated (%): C, 72.52; H, 4.06; N, 4.03. ^{1}H NMR, δ: 7.04 (d, 1 H, H(6), J = 8.9 Hz); 7.32 (dd, 1 H, H(5), J = 8.9 Hz, J = 2.6 Hz); 7.39—7.46 (m, 6 H, PhH); 7.68—7.71 (m, 4 H, PhH); 7.89 (d, 1 H, H(3), J = 2.6 Hz); 11.23 (s, 1 H, OH).

5-Chloro-2-hydroxy-3-(4,5-diphenyl-1,3-oxazol-2-yl)benzaldehyde (6). A mixture of phenol **5** (3.48 g, 10 mmol), hexamethylenetetramine (5.60 g, 40 mmol), and trifluoroacetic acid (30 mL) was refluxed for 13 h under inert atmosphere and cooled followed by the addition of a mixture of conc. hydrochloric acid (14 mL) and water (28 mL). The reaction mixture was poured into water (130 mL), a precipitate was filtered off, washed with water, and dried. Benzaldehyde **6** obtained was recrystallized from benzene. The yield was 2.67 g (71%), m.p. 184—185.5 °C. Found (%): C, 70.46; H, 3.64; N, 3.67. $C_{22}H_{14}ClNO_3$. Mol. weight 375.81. Calculated (%): C, 70.31; H, 3.75; N, 3.73. ^{1}H NMR, δ: 7.42—7.48 (m, 6 H, PhH); 7.67—7.72 (m, 4 H, PhH); 7.89 (d, 1 H, H(4), J = 2.7 Hz); 8.11 (d, 1 H, H(6), J = 2.7 Hz); 10.55 (s, 1 H, 1-CHO); 12.12 (s, 1 H, 2-OH).

8-(4,5-Diphenyl-1,3-oxazol-2-yl)-3′,3′-dimethylspiro-[2*H*-1-benzopyran-2,2′-indolines] 9a—e (method I, general procedure). A mixture of 3*H*-Indolium salt **7a—e** (1 mmol), aldehyde **6** (1 mmol), and glacial acetic acid (8 mL) was refluxed for 5.5 h and kept for 12 h at ~20 °C. A precipitate formed was filtered off, washed with ether, dried, and used further without additional purification. A flow of dry ammonia was bubbled through a suspension of salt **8a—e** obtained in benzene (20 mL) until dissolution of the precipitate, the solvent was evaporated, the residue was purified by column chromatography on Al_2O_3 (eluent, benzene) and recrystallized.

6-Chloro-8-(4,5-diphenyl-1,3-oxazol-2-yl)-1′,3′,3′-trimethylspiro[2*H*-1-benzopyran-2,2′-indoline] (9a). The yield was 49%, m.p. 188—189 °C (from heptane—toluene, 2 : 1). Found (%): C, 77.09; H, 5.01; N, 5.45. $C_{34}H_{27}ClN_2O_2$. Mol. weight 531.05. Calculated (%): C, 76.90; H, 5.12; N, 5.28. ^{1}H NMR, δ: 1.21, 1.39 (both s, 3 H each, 3′-Me); 2.79 (s, 3 H, 1′-Me); 5.85 (d, 1 H, H(3), J = 10.3 Hz); 6.58 (d, 1 H, H(7′), J = 7.7 Hz); 6.86 (d, 1 H, H(4), J = 10.3 Hz); 6.93 (dt, 1 H, H(5′), J = 7.4 Hz, J = 0.9 Hz); 7.02—7.05 (m, 2 H, PhH); 7.12 (dd, 1 H, H(4′), J = 7.3 Hz, J = 1.2 Hz); 7.13 (d, 1 H, H(5), J = 2.6 Hz); 7.20—7.27 (m, 4 H, H(6′), PhH); 7.30—7.38 (m, 3 H, PhH); 7.56—7.59 (m, 2 H, PhH); 8.04 (d, 1 H, H(7), J = 2.6 Hz).

5′,6-Dichloro-8-(4,5-diphenyl-1,3-oxazol-2-yl)-1′,3′,3′-trimethylspiro[2*H*-1-benzopyran-2,2′-indoline] (9b). The yield was 52%, m.p. 215—216 °C (from heptane—toluene, 2 : 1). Found (%): C, 72.04; H, 4.71; N, 4.87. $C_{34}H_{26}Cl_2N_2O_2$. Mol. weight 565.50. Calculated (%): C, 72.21; H, 4.63; N, 4.95. ^{1}H NMR, δ: 1.21, 1.38 (both s, 3 H each, 3′-Me); 2.75 (s, 3 H, 1′-Me); 5.82 (d, 1 H, H(3), J = 10.3 Hz); 6.46 (d, 1 H, H(7′), J = 8.2 Hz); 6.87 (d, 1 H, H(4), J = 10.3 Hz); 7.07 (d, 1 H, H(4′), J = 2.2 Hz); 7.08—7.11 (m, 2 H, PhH); 7.13 (d, 1 H, H(5), J = 2.6 Hz); 7.16 (dd, 1 H, H(6′), J = 8.2 Hz, J = 2.2 Hz); 7.27—7.39 (m, 6 H, PhH); 7.55—7.59 (m, 2 H, PhH); 8.05 (d, 1 H, H(7) J = 2.6 Hz).

6-Chloro-8-(4,5-diphenyl-1,3-oxazol-2-yl)-1′,3′,3′,5′-tetramethylspiro[2*H*-1-benzopyran-2,2′-indoline] (9c). The yield was 42%, m.p. 194—195.5 °C (from heptane—toluene, 2 : 1). Found (%): C, 77.01; H, 5.23; N, 5.28. $C_{35}H_{29}ClN_2O_2$. Mol. weight 545.08. Calculated (%): C, 77.12; H, 5.36; N, 5.14. ^{1}H NMR, δ: 1.20, 1.36 (both s, 3 H each, 3′-Me); 2.34 (s, 3 H, 5′-Me); 2.76 (s, 3 H, 1′-Me); 5.84 (d, 1 H, H(3), J = 10.3 Hz); 6.48 (d, 1 H, H(7′), J = 7.8 Hz); 6.84 (d, 1 H, H(4), J = 10.3 Hz); 6.91 (s, 1 H, H(4′)); 7.02—7.08 (m, 3 H, H(6′), PhH); 7.12 (d, 1 H, H(5) J = 2.6 Hz); 7.16—7.25, 7.31—7.38 (both m, 3 H each, PhH); 7.56—7.60 (m, 2 H, PhH); 8.04 (d, 1 H, H(7) J = 2.6 Hz).

6-Chloro-8-(4,5-diphenyl-1,3-oxazol-2-yl)-5′-methoxy-1′,3′,3′-trimethylspiro[2*H*-1-benzopyran-2,2′-indoline] (9d). The yield was 46%, m.p. 204.5—205.5 °C (from heptane—toluene, 2 : 1). Found (%): C, 77.15; H, 5.11; N, 5.14. $C_{35}H_{29}ClN_2O_3$. Mol. weight 561.08. Calculated (%): C, 74.92; H, 5.21; N, 4.99. ^{1}H NMR, δ: 1.22, 1.38 (both s, 3 H each, 3′-Me); 2.72 (s, 3 H, 1′-Me); 3.79 (s, 3 H, 5′-OMe); 5.84 (d, 1 H, H(3), J = 10.3 Hz); 6.47 (d, 1 H, H(7′), J = 8.2 Hz); 6.74 (dd, 1 H, H(6′), J = 8.2 Hz, J = 2.6 Hz); 6.76 (d, 1 H, H(4′), J = 2.6 Hz); 6.85 (d, 1 H, H(4), J = 10.3 Hz); 7.04—7.08 (m, 2 H, PhH); 7.12 (d, 1 H, H(5), J = 2.6 Hz); 7.22—7.26, 7.31—7.38 (both m, 3 H each, PhH); 7.56—7.60 (m, 2 H, PhH); 8.05 (d, 1 H, H(7) J = 2.6 Hz).

6-Chloro-8-(4,5-diphenyl-1,3-oxazol-2-yl)-3′,3′-dimethyl-1′-propylspiro[2*H*-1-benzopyran-2,2′-indoline] (9e). The yield was 44%, m.p. 186—187.5 °C (from heptane—toluene, 2 : 1). Found (%): C, 77.20; H, 5.69; N, 4.90. $C_{36}H_{31}ClN_2O_2$. Mol. weight 559.11. Calculated (%): C, 77.34; H, 5.59; N, 5.01. ^{1}H NMR, δ: 0.87 (t, 3 H, 1′-Pr, J = 7.4 Hz); 1.20, 1.37 (both s, 3 H each, 3′-Me); 1.63, 3.20 (both m, 2 H each, 1′-Pr); 5.85 (d, 1 H, H(3), J = 10.3 Hz); 6.59 (d, 1 H, H(7′), J = 7.7 Hz); 6.82 (d, 1 H, H(4), J = 10.3 Hz); 6.90 (dt, 1 H, H(5′), J = 7.4 Hz, J = 0.9 Hz); 7.02—7.06 (m, 2 H, PhH); 7.10—7.12 (m, 2 H, H(4′), H(5)); 7.18—7.24 (m, 4 H, H(6′), PhH); 7.30—7.38 (m, 3 H, PhH); 7.56—7.60 (m, 2 H, PhH); 8.04 (d, 1 H, H(7), J = 2.6 Hz).

8-(4,5-Diphenyl-1,3-oxazol-2-yl)-3′,3′-dimethylspiro[2*H*-1-benzopyran-2,2′-indolines] 9f,g (method II, general procedure). A mixture of 3*H*-Indolium salt **7f,g** (1 mmol), triethylamine (0.14 mL, 1 mmol), and aldehyde **6** (1 mmol) in benzene (8 mL) and propan-2-ol (2 mL) was refluxed for 10 h, concentrated, and the residue was purified by column chromatography on Al_2O_3 (eluent, benzene) and recrystallized.

1′-Allyl-6-chloro-8-(4,5-diphenyl-1,3-oxazol-2-yl)-3′,3′-dimethylspiro[2*H*-1-benzopyran-2,2′-indoline] (9f). The yield was 47%, m.p. 172.5—174 °C (from heptane). Found (%): C, 77.79; H, 5.12; N, 4.95. $C_{36}H_{29}ClN_2O_2$. Mol. weight 557.09. Calculated (%): C, 77.62; H, 5.25; N, 5.03. ^{1}H NMR, δ: 1.23, 1.39 (both s, 3 H each, 3′-Me); 3.77 (tdd, 1 H, 1′-C$\underline{H}_2$CH=CH$_2$, J = 17.3 Hz, J = 5.3 Hz, J = 1.6 Hz, J = 1.6 Hz); 3.99 (tdd, 1 H, 1′-C$\underline{H}_2$CH=CH$_2$, J = 17.3 Hz, J = 4.2 Hz, J = 2.0 Hz, J = 2.0 Hz); 5.01 (qd, 1 H, 1′-CH$_2$CH=C$\underline{H}_2$, J = 10.3 Hz, J = 1.7 Hz, J = 1.7 Hz, J = 1.7 Hz); 5.16 (qd, 1 H, 1′-CH$_2$CH=C$\underline{H}_2$, J = 17.2 Hz, J = 1.8 Hz, J = 1.8 Hz, J = 1.8 Hz); 5.85 (d, 1 H, H(3), J = 10.3 Hz); 5.89 (m, 1 H, 1′-CH$_2$C$\underline{H}$=CH$_2$); 6.59 (d, 1 H, H(7′), J = 7.7 Hz); 6.82 (d, 1 H, H(4), J = 10.3 Hz); 6.92 (dt, 1 H, H(5′), J = 7.4 Hz, J = 0.9 Hz); 7.02—7.06 (m, 2 H, PhH); 7.10—7.14 (m, 2 H, H(4′), H(5)); 7.18—7.24 (m, 4 H, H(6′), PhH); 7.31—7.38 (m, 3 H, PhH); 7.56—7.60 (m, 2 H, PhH); 8.04 (d, 1 H, H(7) J = 2.6 Hz).

6-Chloro-8-(4,5-diphenyl-1,3-oxazol-2-yl)-1′-isobutyl-3′,3′-dimethylspiro[2*H*-1-benzopyran-2,2′-indoline] (9g). The yield was 45%, m.p. 182—183 °C (from heptane). Found (%): C, 77.41; H, 5.65; N, 4.97. $C_{37}H_{33}ClN_2O_2$. Mol. weight 573.13. Calculated (%): C, 77.54; H, 5.80; N, 4.89. ^{1}H NMR, δ: 0.90 (d, 3 H, 1′-CH$_2$CH(C$\underline{H}_3$)$_2$, J = 6.7 Hz); 0.91 (d, 3 H, 1′-CH$_2$CH(C$\underline{H}_3$)$_2$, J = 6.6 Hz); 1.23, 1.38 (both s, 3 H each, 3′-Me); 2.04 (m, 1 H, 1′-CH$_2$C$\underline{H}$(CH$_3$)$_2$); 2.93 (dd, 1 H, 1′-C$\underline{H}_2$CH(CH$_3$)$_2$, J = 14.5 Hz, J = 9.4 Hz); 3.04 (dd, 1 H, 1′-C$\underline{H}_2$CH(CH$_3$)$_2$, J = 14.5 Hz, J = 5.7 Hz); 5.88 (d, 1 H, H(3), J = 10.3 Hz); 6.59 (d, 1 H, H(7′), J = 7.7 Hz); 6.81 (d, 1 H, H(4), J = 10.3 Hz); 6.90 (dt, 1 H, H(5′), J = 7.4 Hz, J = 0.9 Hz); 7.03—7.07 (m, 2 H, PhH); 7.11 (dd, 1 H, H(4′), J = 7.3 Hz, J = 1.1 Hz); 7.12 (d, 1 H, H(5), J = 2.6 Hz); 7.21 (dt, 1 H, H(6′), J = 7.6 Hz, J = 1.3 Hz); 7.22—7.26, 7.31—7.38 (both m, 3 H each, PhH); 7.55—7.59 (m, 2 H, PhH); 8.02 (d, 1 H, H(7), J = 2.6 Hz).

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