Spiropyrans and spirooxazines

3.* Synthesis of photochromic 5′-(4,5-diphenyl-1,3-oxazol-2-yl)-spiro[indoline-2,3′-naphtho[2,3-*b*]pyran]

N. A. Voloshin, A. V. Chernyshev, A. V. Metelitsa, I. M. Raskita, E. N. Voloshina, and V. I. Minkin*

Institute of Physical and Organic Chemistry,
Rostov State University,
194/2 prosp. Stachki, 344090 Rostov-on-Don, Russian Federation.
Fax: +7 (863 2) 43 4667. E-mail: photo@ipoc.rsu.ru

The reaction of 2-hydroxy-3-(4,5-diphenyl-1,3-oxazol-2-yl)-1-naphthaldehyde with 1,2,3,3-tetramethyl-3*H*-indolium perchlorate afforded photochromic spiro[indoline-2,3′-naphthopyran] containing a 4,5-diphenyloxazole group in position 5′ of the naphthopyran fragment. The merocyanine form of the spiropyran gave complexes with bivalent heavy cations.

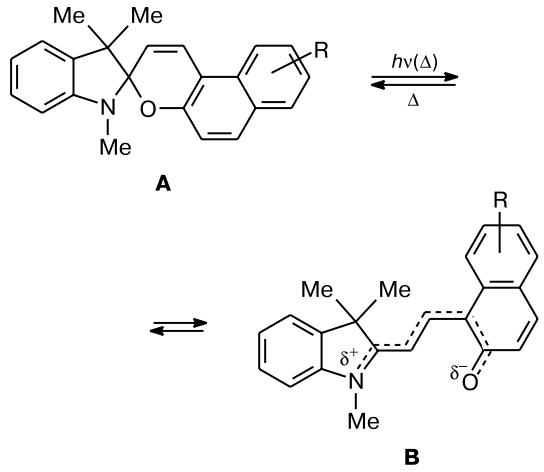
Key words: spiropyrans, photochromism, metal complexes.

Photochromic organic molecules (including spiropyrans and spirooxazines) have been under intense study in the last few years because they can be used in optical systems for recording and displaying information, as well as in sensors, optobio- and optoelectronics, transport systems, and catalysis.[2—5]

Photochromic transformations of spironaphthopyrans (Scheme 1) and spirooxazines involve thermally and photochemically reversible cleavage of the C_{spiro}—O bond of the cyclic isomer **A** followed by *cis-trans*-isomerization into metastable merocyanine form **B**. The latter spontaneously or when exposed to visible light changes to the starting spiro form.[2,3]

In recent years, isomerization of spiropyrans and spirooxazines in the presence of certain chemical species (specific substrates such as, *e.g.*, metal cations[6]) has attracted great interest. In this case, spiropyran and spirooxazine molecules usually contain an ionophore fragment in the *ortho*-position relative to the pyran/oxazine O atom, while the phenoxide O atom of the colored isomer provides additionally coordination to the metal cation. Much research is devoted to spirocyclic photochromes containing ionophore crown-ether fragments,[7—9] the isomerization of which is substantially affected by alkali and alkaline-earth metal cations. The number of spiro compounds the transformations of which are affected by transition and rare-earth ions is much smaller. Among them are spirobenzopyranindolines with methoxy,[10—12] piperidinomethyl,[13] and other electron-donating substituents[14] in position 8 and quinolinespiropyranindolines.[15—19] Recently, 5′-benzothiazolylspirooxazines have been synthesized and found promising for use as photochromic chelating reagents.[20]

Scheme 1



Oxazole derivatives, especially those containing aromatic or heterocyclic substituents in positions 2 and 5, are good fluorophore systems.[21] They are widely used as fluorescent bleaching agents and can form complexes with transition element ions.[22]

The present work was devoted to the synthesis and study of the coordinative power of 5′-(diphenyloxazolyl)spironaphthopyran (**11**).

* For Part 2, see Ref. 1.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 3, pp. 693—697, March, 2005.

1066-5285/05/5403-0705

Results and Discussion

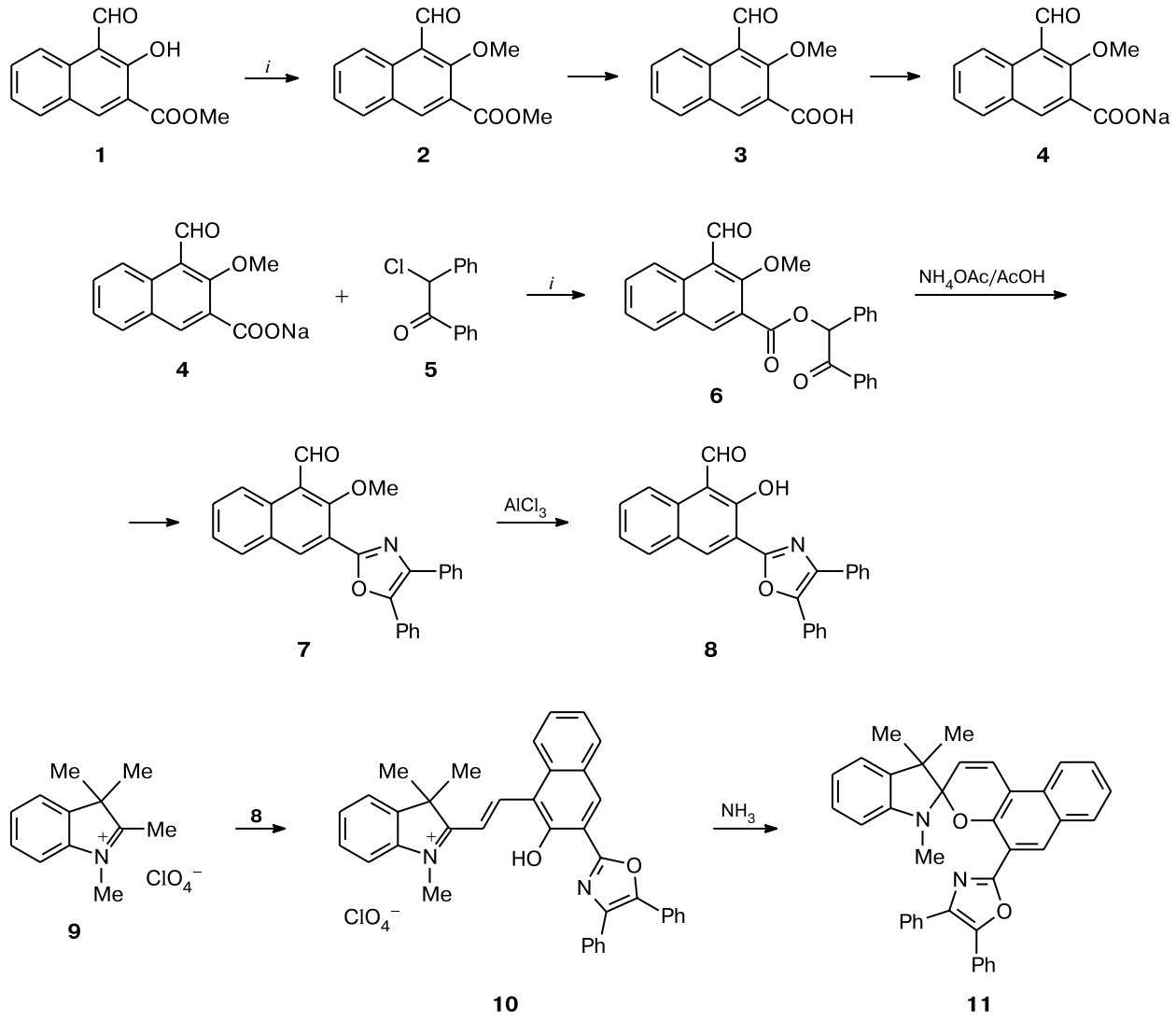
Spiro compound **11** was obtained in two steps as shown in Scheme 2 by the reaction of tetramethyl-3*H*-indolium perchlorate (**9**) with 3-(4,5-diphenyloxazolyl)-2-hydroxynaphthaldehyde (**8**) in AcOH followed by treatment of 2-hydroxynaphthylvinylindolium perchlorate (**10**) with ammonia.

The starting material for the synthesis of 2-hydroxynaphthaldehyde **8** was sodium 4-formyl-3-methoxy-2-naphthoate (**4**). Its alkylation with 2-chloro-1,2-diphenylethanone (**5**) under the conditions of phase-transfer catalysis yielded desyl ester (**6**). The latter was refluxed with ammonium acetate in acetic acid according to the Davidson method[23] to give 3-(4,5-diphenyloxazol-2-yl)-2-methoxynaphthaldehyde (**7**). Demethylation of aldehyde **7** with $AlCl_3$ led to 2-hydroxy derivative **8**. The synthesis of compound **4** involved alkylation of methyl 4-formyl-3-hydroxy-2-naphthoate (**1**) with iodomethane under the conditions of solid—liquid PTC in the presence of 18-crown-6, hydrolysis of the corresponding methoxynaphthoate **2** into naphthoic acid **3**, and the reaction of the latter with NaOMe.

Compounds **2**, **3**, **6**—**8**, and **11** were identified by ^{1}H NMR spectroscopy; their structures were confirmed by elemental analysis data.

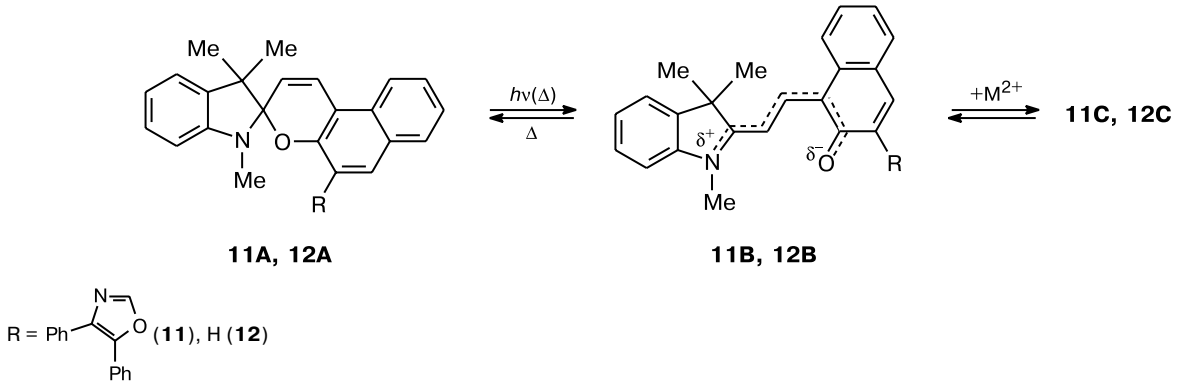
Spectroscopic and photochemical properties. The spectroscopic and photochemical properties of spironaphthopyrans were examined in toluene, acetone, acetonitrile, and ethanol. Unsubstituted spironaphthopyran

Scheme 2



i. Phase-transfer catalysis in the presence of 18-crown-6.

Scheme 3



(**12**) was used as a standard compound in comparative experiments.

In toluene and acetone, both spironaphthopyrans exist virtually entirely as cyclic isomers **A** (Scheme 3): their spectra show no noticeable absorption in the visible range, as distinct from acyclic merocyanine structures **B**.[1,2]

The spectrum of the cyclic form of spironaphthopyran **12** in toluene contains a structured absorption band with the maxima at 346 (ε 13 590) and 362 nm (ε 11 930). The spectrum of compound **11A** shows an absorption band at 342 nm (ε 22 150) and, because of the presence of the heterocyclic substituent, an additional longer-wavelength band at 370 to 420 nm (Fig. 1). In more polar solvents, the absorption bands undergo a slight hypsochromic shift. Isomer **11A** fluoresces weakly at 430 nm. At 77 K, phosphorescence was observed; the maxima of its structured band appear at 580 and 630 nm. In contrast to **11A**, compound **12A** show no luminescence. At low temperatures, both spironaphthopyrans exhibit photochromic properties, which are not observed under normal conditions

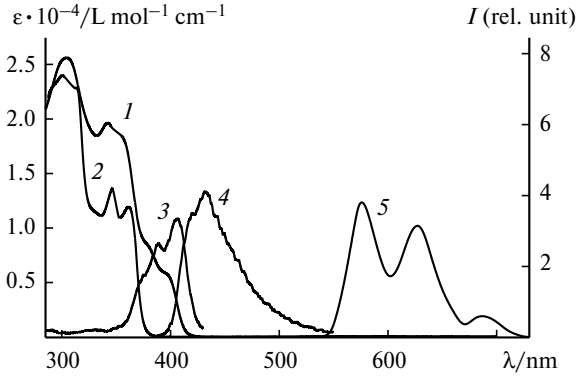


Fig. 1. Absorption spectra of compounds **11** (*1*) and **12** (*2*), the fluorescence excitation (*3*) and emission spectra (*4*) of compound **12** (toluene, 293 K). The phosphorescence spectrum of compound **11** (*5*) (toluene—EtOH—Et_2O, 77 K).

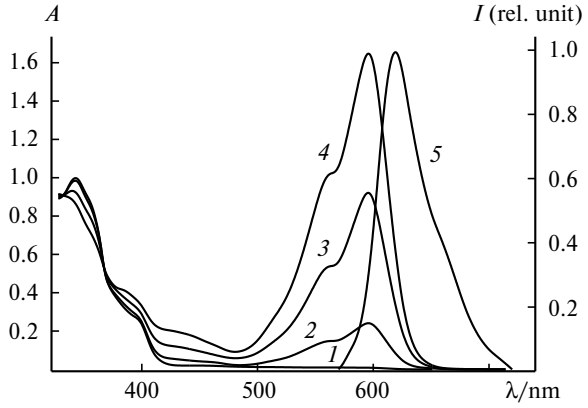


Fig. 2. Photoinduced changes in the absorption spectra of compound **12** upon the irradiation with the light wavelength λ = 365 nm for 0 (*1*), 30 (*2*), 60 (*3*), and 120 s (*4*) and the fluorescence spectrum of open form **12B** ($C = 1.13 \cdot 10^{-4}$ mol L^{-1}, toluene, 200 K) (*5*).

because of a high-rate reverse thermal reaction of ring closure. For instance, when irradiated with UV light at 200 K, colorless solutions of spironaphthopyran turned colored due to the formation of acyclic structures **B** (Fig. 2). Under these conditions, both isomers **11B** and **12B** are stable and intensely fluoresce at 550 to 720 nm; the spectrum of compound **11B** is bathochromically shifted by 20 nm relative to compound **12B**.

Cation-induced isomerization. Addition of equivalent amounts of Zn^{2+}, Cu^{2+}, Mn^{2+}, Co^{2+}, and Ni^{2+} salts to a virtually colorless solution of spironaphthopyran **11** in acetone significantly changed the spectral pattern. In the near UV range of the spectrum, the absorption increases insignificantly, while the visible range contains new intense bands at different λ values, depending on the type of the ions added (Table 1). The band maxima of metal-containing solutions of spironaphthopyran are shifted hypsochromically relative to the band of the merocyanine isomer. The largest shift (29 nm) was observed for solu-

Table 1. Spectroscopic properties of merocyanines **11** and **12** and their complexes in acetone

M	**11**			**12**		
	$\lambda^{abs}{}_{max}$/nm	$-\Delta\lambda^{abs}{}_{max}$	$\lambda^{fl}{}_{max}$/nm	$\lambda^{abs}{}_{max}$/nm	$\Delta\lambda^{abs}{}_{max}$	$\lambda^{fl}{}_{max}$/nm
—*	588	—	620	562	—	600
Mn	582	6	—	—	—	—
Co	571	17	—	—	—	—
Ni	580	8	—	—	—	—
Cu	559	29	—	—	—	—
Zn	566	22	625	558	–4	605
Cd	586	2	628	—	—	—

* Metal-free.

tions containing Cu^{2+} ions (Table 1). The reactions of metal ions with spiropyran **11** are fairly contrast ones. Addition of alkali and alkaline-earth ions even in a 100-fold excess with respect to the spiropyran virtually did not change the spectral pattern, which indicates that no complexation occurs. In the presence of Cd^{2+} ions, coloration was noticeable only with a 20-fold excess of the metal. In contrast to compound **11**, a solution of spiropyran **12** changed color only upon addition of a 100-fold excess of Zn^{2+} ions. The absorption band of the product also experienced a blue shift relative to the band of the corresponding merocyanine.

Spiroheterocyclic photochromes can react with metal ions in two known ways: either through complexation between their merocyanine isomers and a metal ion or through participation in a redox reaction.[24] In both cases, reaction products absorb in the visible range of the spectrum. Obviously, in contrast to complex formation, a redox process is irreversible. To check the reversibility of reactions of spironaphthopyran with metal ions, a competitive complexone, namely, a disodium salt of ethylenediaminetetraacetic acid (EDTA), was added to colored solutions.[25] In all cases, the solutions became colorless and the spectra resumed their original shapes characteristic of the cyclic isomer. Hence, the reactions of spiropyrans with metal ions yield complex compounds **11C** and **12C**.

Colored solutions of Zn^{2+} and Cd^{2+} complexes with spironaphthopyran **11** weakly fluoresced at 628 and 625 nm, respectively (see Table 1). In the case of Cu^{2+}, Mn^{2+}, Co^{2+}, and Ni^{2+} complexes, no fluorescence was observed.

Thus, we developed the method for the synthesis of 3-(4,5-diphenyl-1,3-oxazol-2-yl)-2-hydroxy-1-naphthaldehyde and 5´-(4,5-diphenyl-1,3-oxazol-2-yl)spiro[indoline-2,3´-naphthopyran], which exhibits photochromic properties in solutions at $T < 250$ K. The merocyanine form of compound **11** yields intensely colored complexes with Cu^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, and Cd^{2+} cations. The spironaphthopyran obtained is of interest as a photochrome sensitive to the presence of heavy metal cations in solution.

Experimental

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

Electronic absorption spectra were recorded on a Varian, Carry 100 spectrophotometer. Luminescence emission and excitation spectra were recorded on a Shimadzu RF-5001 PC spectrofluorimeter. The solvents were MeOH, EtOH, MeCN, acetone, toluene (Aldrich), heptane, and Et_2O (reagent grade). Photolysis of solutions was carried out with a DRSh-250 mercury lamp with a set of interference light filters for isolation of the spectral lines of mercury. Metal ions were added to solutions as perchlorates. The constant ionic strength ($\mu = 0.01$) of photometrically studied solutions was maintained by adding 0.2 *M* Bu_4NClO_4 (Acros).

Compounds **1**,[26] **5**,[27] and **12** [28] were prepared according to known procedures.

Methyl 4-formyl-3-methoxy-2-naphthoate (2). A mixture of ester **1** (2.30 g, 10 mmol), K_2CO_3 (1.66 g, 12 mmol), 18-crown-6 (0.053 g, 0.2 mmol), and iodomethane (0.75 mL, 12 mmol) in toluene (35 mL) was refluxed for 10 h. The precipitate was filtered off, the filtrate was concentrated, and the residue was purified by column chromatography on Al_2O_3 with $CHCl_3$ as an eluent. The solvent was removed and the residue was recrystallized from hexane. The yield of compound **2** was 1.93 g (79%), m.p. 83—84 °C. Found (%): C, 68.77; H, 5.06. $C_{14}H_{12}O_4$. Calculated (%): C, 68.85; H, 4.95. ^{1}H NMR, δ: 4.02 (s, 3 H, 2-$COOCH_3$); 4.06 (s, 3 H, 3-OCH_3); 7.56 (m, 1 H, H(7)); 7.74 (m, 1 H, H(6)); 7.90 (m, 1 H, H(8)); 8.66 (s, 1 H, H(1)); 9.22 (m, 1 H, H(5)); 10.84 (s, 1 H, 4-CHO).

4-Formyl-3-methoxy-2-naphthoic acid (3). A mixture of ester **2** (1.96 g, 8 mmol) and NaOH (0.38 g, 9.5 mmol) was refluxed in water (8 mL) for 2 h. The reaction mixture was cooled and acidified with dilute HCl to pH ~2. The precipitate was filtered off, washed with cold water, and dried. The yield of compound **3** was 1.80 g (92%), m.p. 199—200 °C (from propan-2-ol—water, 1 : 1). Found (%): C, 67.90; H, 4.46. $C_{13}H_{10}O_4$. Calculated (%): C, 67.82; H, 4.38. ^{1}H NMR, δ: 4.16 (s, 3 H,

3-OCH_3); 7.62 (m, 1 H, H(7)); 7.80 (m, 1 H, H(6)); 7.98 (d, 1 H, H(8), J = 8.1 Hz); 8.93 (s, 1 H, H(1)); 9.21 (d, 1 H, H(5), J = 8.7 Hz); 10.86 (s, 1 H, 4-CHO).

2-Oxo-1,2-diphenylethyl 4-formyl-3-methoxy-2-naphthoate (6). A mixture of acid **3** (2.30 g, 10 mmol) and NaOMe (0.54 g, 10 mmol) was refluxed in MeOH (17 mL) for 1 h. The solvent was evaporated *in vacuo* to half the initial volume and ether (10 mL) was added. The precipitate was filtered off and dried *in vacuo*. The yield of sodium salt **4** was 2.24 g (89%). A mixture of salt **4** (2.52 g, 11 mmol) and PEG-400 (2 mL) in MeCN (20 mL) was stirred at 70 °C for 0.5 h. Desyl chloride **5** (2.31 g, 10 mmol) was added and the reaction mixture was refluxed with stirring for 7 h and poured into water with ice (50 mL). The precipitate that formed was filtered off, washed with water, and dried. The resulting ester **6** was purified by column chromatography on Al_2O_3 with $CHCl_3$ as an eluent and recrystallized from heptane—toluene (1 : 1). The yield of compound **6** was 2.46 g (58%), m.p. 161—162 °C. Found (%): C, 76.56; H, 4.87. $C_{27}H_{20}O_5$. Calculated (%): C, 76.40; H, 4.75. ^{1}H NMR, δ: 4.03 (s, 3 H, 3-OCH_3); 7.16 (s, 1 H, 2-COOR); 7.37—7.47 (m, 5 H, PhH); 7.50—7.60 (m, 4 H, H(7), PhH); 7.71 (m, 1 H, H(6)); 7.90 (m, 1 H, H(8)); 7.98—8.02 (m, 2 H, PhH); 8.78 (s, 1 H, H(1)); 9.20 (m, 1 H, H(5); 10.81 (s, 1 H, 4-CHO).

3-(4,5-Diphenyl-1,3-oxazol-2-yl)-2-methoxy-1-naphthaldehyde (7). A mixture of desyl naphthoate **6** (2.12 g, 5 mmol) and ammonium acetate (2.31 g, 30 mmol) was refluxed in acetic acid (10 mL) for 4 h. The reaction mixture was poured into ice (100 g). The precipitate was filtered off, washed with water, dried, and purified by column chromatography on Al_2O_3 with $CHCl_3$ as an eluent. The yield of compound **7** was 1.12 g (55%), m.p. 158—159 °C (from propan-2-ol—toluene, 3 : 1). Found (%): C, 79.84; H, 4.81; N, 3.34. $C_{27}H_{19}NO_3$. Calculated (%): C, 79.98; H, 4.72; N, 3.45. ^{1}H NMR, δ: 4.12 (s, 3 H, 2-OCH_3); 7.37—7.46 (m, 6 H, PhH); 7.55 (m, 1 H, H(6)); 7.70 (m, 1 H, H(7)); 7.72—7.79 (m, 4 H, PhH); 7.93 (m, 1 H, H(5)); 8.89 (s, 1 H, H(4)); 9.22 (m, 1 H, H(8)); 10.92 (s, 1 H, 1-CHO).

3-(4,5-Diphenyl-1,3-oxazol-2-yl)-2-hydroxy-1-naphthaldehyde (8). Anhydrous $AlCl_3$ (2.0 g, 15 mmol) in methylene dichloride (15 mL) was stirred at ~20 °C for 2 h. A solution of aldehyde **7** (2.03 g, 5 mmol) in methylene dichloride (15 mL) was added dropwise and the reaction mixture was stirred at ~20 °C for 3 h and poured into dilute HCl. The product was extracted with chloroform. The solvent was removed and the residue was purified by column chromatography on Al_2O_3 with $CHCl_3$ as an eluent and recrystallized from acetonitrile—benzene (1 : 1). The yield of compound **8** was 67%, m.p. 213—214 °C. Found (%): C, 79.93; H, 4.50; N, 3.49. $C_{26}H_{17}NO_3$. Calculated (%): C, 79.78; H, 4.38; N, 3.58. ^{1}H NMR, δ: 7.40—7.47 (m, 7 H, H(6), PhH); 7.66 (m, 1 H, H(7)); 7.70—7.75 (m, 4 H, PhH); 7.86 (m, 1 H, H(5)); 8.67 (s, 1 H, H(4)); 9.23 (m, 1 H, H(8)); 11.04 (s, 1 H, 1-CHO); 12.47 (s, 1 H, 2-OH).

5′-(4,5-Diphenyl-1,3-oxazol-2-yl)-1,3,3-trimethylspiro(indoline-2,3′-[3*H*]naphtho[2,1-*b*]pyran) (11). A mixture of perchlorate **9** (0.27 g, 1 mmol) and aldehyde **8** (0.39 g, 1 mmol) was refluxed in glacial acetic acid (8 mL) for 5 h and left at ~20 °C for 12 h. The precipitate that formed was filtered off, washed with ether, dried, and used subsequently without additional purification. A flow of dry ammonia was passed through a suspension of the resulting perchlorate **10** in benzene (20 mL) until the precipitate dissolved. The solvent was removed and the residue was purified by column chromatography on Al_2O_3 with benzene as an eluent. The yield of compound **11** was 0.29 g (53%), m.p. 200—201 °C (from heptane—toluene, 3 : 1). Found (%): C, 83.60; H, 5.36; N, 5.02. $C_{38}H_{30}N_2O_2$. Calculated (%): C, 83.49; H, 5.53; N, 5.12. ^{1}H NMR, δ: 1.25, 1.42 (both s, 3 H each, 3-Me); 2.79 (s, 3 H, 1-Me); 5.90 (d, 1 H, H(2′), J = 10.5 Hz); 6.57 (d, 1 H, H(7), J = 7.7 Hz); 6.89 (td, 1 H, H(5), J = 7.4 Hz, J = 0.9 Hz); 7.10—7.14 (m, 3 H, H(4), PhH); 7.20 (td, 1 H, H(6), J = 7.6 Hz, J = 1.2 Hz); 7.22—7.40 (m, 7 H, H(8′), PhH); 7.56 (m, 1 H, H(9′)); 7.60—7.63 (m, 2 H, PhH); 7.66 (d, 1 H, H(1′), J = 10.5 Hz); 7.86 (d, 1 H, H(7′), J = 8.1 Hz); 8.05 (d, 1 H, H(10′), J = 8.5 Hz); 8.61 (s, 1 H, H(6′)).

This work was financially supported by the Civilian Research and Development Foundation of the United States (CRDF) and the Ministry of Education of the Russian Federation (Project RO-004-X1), the Russian Foundation for Basic Research (Project No. 03-03-32154), and the International Scientific and Technical Center (Grant 2117).

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Received November 2, 2004;
in revised form March 9, 2005