Crown-Containing Styryl Derivatives of Naphthopyrans: Complexation with Alkaline-Earth Metal Cations and Photochemistry¹

A. B. Smolentsev^a, V. V. Korolev^{a, b}, E. M. Glebov^{a, b}, V. P. Grivin^{a, b},
V. F. Plyusnin^{a, b}, A. I. Kruppa^{a, b}, A. V. Chebun'kova^c, S. V. Paramonov^c,
O. A. Fedorova^c, V. Lokshin^d, and A. Samat^d

^a Institute of Chemical Kinetics and Combustion, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia

^b Novosibirsk State University, Novosibirsk, 630090 Russia

^c Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, 119991 Russia ^d Centre Interdisciplinaire de Nanoscience de Marseille (CINaM, CNRS), Marseille, 13288 France

e-mail: s_art@ngs.ru

Received January 25, 2011

Abstract—The photochemistry and complexation with alkaline-earth metal cations of two crown-containing naphthopyrans and their crownless analogues are reported. Two types of photoreactions occur in the system, namely, the reversible formation of the open form, which is responsible for the photochromism of these compounds, and the geometric isomerization of the closed form. The photochromic properties (UV spectrum and lifetime) of the naphthopyrans do not change upon complexation with metal cations. This is explained by the specific features of the structure of the open form and by the kinetic parameters of the processes.

DOI: 10.1134/S0023158412010144

Photochromism is a reversible photoinduced phenomenon in which a photosensitive compound transforms to another isomer having a different absorption spectrum. Photochromic compounds are promising for creation of photosensitive systems: optical variable-transmission materials, optical information storage systems, and photoswitchers [1-4]. The naphthopyrans (chromenes) are one of the most interesting families of organic photochromes since many of them have a high fatigue resistance [3]. The photochromism of chromenes is caused by the transformation of the colorless closed (S) form to the colored open merocyanine (M) form (Scheme 1). The change in color is due to the molecule changing its geometry from spatial to planar [1-6].



Open merocyanine (M) form

Scheme 1.

Incorporation of crown-ether moieties into photochromic molecules opens up the possibility of controlling their properties via complex formation with metal cations. The properties of crown-containing organic photochromic compounds have been actively investigated in the last two decades. The binding of the metal cations by the crown-ether moiety leads to changes in the photochromic properties of azobenzenes [7, 8],

¹ The article was translated by the authors.

diarylethenes [9], styrylbenzothiazoles [10–12], spiropyranes [13–15], spirooxazines [16–22] and chromenes [23–25]. This approach opensup the possibility of creating photocontrolled receptors. Complex formation with metal cations can affect the parameters of the S \leftrightarrow M reaction [5, 21]. For instance, the complexation of crown-containing spironaphthooxazine with Li⁺ cations extends the lifetime of the open form by two orders of magnitude [16]. In this work, complexation with alkaline-earth metal cations and the effect of complexation on the photochromic properties were studied for two types of crown-containing naphthopyrans (compounds **1b** and **2b** on the Scheme 2). For comparison, similar experiments were carried out on cromenes that do not contain a macrocyclic moiety (model compounds **1a** and **2a** in Scheme 2). This work continues a series of studies initiated by Glebov et al. [26].



Scheme 2.

EXPERIMENTAL

The synthesis, physical properties, and NMRspectra of **1a** (5-[2-(3,4-dimethoxyphenyl)ethenyl]-3,3-diphenyl-3H-benzo[f]chromene), 1b (5-[(E)-2-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecan-15-yl)ethenyl]-3,3-diphenyl-3Hbenzo[f]chromene), 2a (4-[2-(3,3-diphenyl-3Hbenzo[f]chromen-5-yl)ethenyl]-N,N-4-[2-(3,3-diphenyl-3H-benzo[f]chromen-5-yl)ethenyl]-N,N-diethylaniline), and **2b** (5-{2-[4-(1,4,7,10-tetraoxa-13-azacyclopentadecan-13-yl)phenyl]ethenyl}-3,3-diphenyl-3H-benzo[f]chromene) have been reported in [26]. According to NMR data, all of the synthesized compounds are a mixture of *trans* and *cis* isomers (Scheme 3). The cis isomers of chromene derivatives 1a and 2a are stable. This allowed the pure trans and cis isomers to be isolated chromatographically. In the case of crowncontaining compounds 1b and 2b, we failed to isolate the individual isomers. According to NMR data, naphthopyrans 1b and 2b are a mixture of cis and trans isomers in a ratio of 5:2 and 5:1, respectively.

 $Mg(ClO_4)_2$ and $Ba(ClO_4)_2$ (Aldrich) were used as the sources of Mg^{2+} and Ba^{2+} ions. Spectrophotometric-grade acetonitrile (Aldrich) was used as the solvent. Isomers of the closed form of 1b



UV absorption spectra and kinetic curves on the second and minute time scales were recorded on an Agilent HP-8453 spectrophotometer (Agilent Technologies) with a characteristic spectrum recording time of about 2 s. A high-pressure mercury lamp with a set of glass filters was used as the light source for stationary photolysis. To measure the rate constants of the thermal reaction of naphthopyrans ($M \rightarrow S$), samples were irradiated in the cuvette box of the spectro-



Fig. 1. (a) Changes in the UV spectrum of **1b** as a result of complexation with Mg^{2+} cations; the **1b** concentration in acetonitrile is 4.55×10^{-5} mol/l; the $Mg(ClO_4)_2$ concentration is (1) 0, (2) 3.0×10^{-5} , (3) 6.0×10^{-5} , (4) 1.2×10^{-4} , and (5) 6.0×10^{-4} mol/l. (b) Job's plot; the sum of the chromene and Mg^{2+} concentrations is 9.0×10^{-5} mol/l; the proper wavelength is 360 nm.

photometer (optical path length of 1 cm). Irradiation was performed until the equilibrium between the closed and open forms was established (equilibration was monitored as the absorption of the open form in the blue spectral region). After the establishment of the equilibrium, irradiation was ceased and kinetic curves characterizing the return of the system to the initial closed state were recorded.

The pure *cis* isomer of naphthopyran **1a** was used to measure the quantum yield of geometric isomerization. Measurements were performed in the initial segments of the kinetic curves of photolysis, where the absorption of the *trans* isomer is negligible. A modified ferrioxalate actinometer was used to measure the intensity of the mercury lamp [27].

Laser flash photolysis experiments were carried out using a setup with YAG : Nd^{3+} laser (355 nm, pulse duration of 5 ns, pulse energy of 0.5–2 mJ) similar to that described previously [28]. All experiments were performed in standard quartz cuvettes (optical path length of 1 cm) at room temperature. If necessary, oxygen was removed from the samples by blowing argon for 15 min.

The composition of the complexes of crown-containing naphthopyrans with metal cations was determined using Job's method [29]. For construction of Job's plot, measurements were carried out on a series of solutions in which the sum of metal and ligand concentrations ($C_L + C_M = C_0$) was constant, while the $x = C_M$: C_0 ratio was varied. Let us assume that the metal ion M and the ligand L form only the complex M_pL_q :

$$p\mathbf{M} + q\mathbf{L} \leftrightarrow \mathbf{M}_{p}\mathbf{L}_{q}.$$
 (1)

The largest amount of the complex M_pL_q forms when the components are combined in the proportion equal to the ratio of the stoichiometric coefficients *p* and *q*, i.e. when $C_M : C_L = p : q$,

$$C_{\rm L}: C_{\rm M} = (1 - x_{\rm max})/x_{\rm max} = q: p.$$
 (2)

Job's plot has an extremum at $x = x_{max}$. In our case, the experimental parameter that is linear with respect to the complex concentration is the absorbance of the complex at a given wavelength, $A(\lambda)$, which is equal to the difference between the absorbance of the sample at the given concentrations of chromene $C_{\rm L}$ and metal $C_{\rm M}$ ($A_{\rm exp}$) and the maximum possible absorbance of chromene at this concentration.

The proper wavelength was chosen soas to maximize the change in absorbance due to complexation (i.e. the $A(\lambda)$ value). The dependence of $A(\lambda)$ on $C_{\rm M}/(C_{\rm L} + C_{\rm M})$ was plotted. The position of the extremum depends on the stoichiometry of the complex: if the extremum is observed at $C_{\rm M}/(C_{\rm L} + C_{\rm M}) = 0.5, 0.33$ or 0.67, this means that the stoichiometry is 1 : 1, 1 : 2, or 2 : 1.

The dependences of absorbance at the chosen wavelength $\Delta A = A(z) - A_0$ (where A_0 is absorbance in the absence of metal cations) on the relative concentration of the reactants, $z = C_M/C_L$, were used to estimate the stability constants of the 1 : 1 complexes. As the metal concentration is increased, ΔA tends to the limiting value ΔA_{max} , which corresponds to the situation in which the entire ligand is in the metal complex. For each value of C_M at a fixed C_L , we determined the value of $y(\%) = \Delta A/\Delta A_{\text{max}} \times 100\%$. If the metal and chromene form only the complex 1 : 1, then

$$y(z) = 50 \left[(1 + z + 1/K_1C_L) - \sqrt{(1 + z + 1/K_1C_L)^2 - 4z} \right], \quad (3)$$

where $K_1 = [ML]/[M][L]$. The optimal value of the stability constant K_1 was determined by fitting the experimental y(z) dependence to Eq. (3).

In the case of stepwise complex formation, the dependences of absorbance at different wavelengths,



Fig. 2. Changes in the UV spectrum of **1b** as a result of complexation with Ba^{2+} cations; the **1b** concentration in acetonitrile is 4.36×10^{-5} mol/l; the $Ba(ClO_4)_2$ concentration is (1) 0, (2) 5.4×10^{-6} , (3) 7.3×10^{-6} , (4) 1.1×10^{-5} , and (5) 4.4×10^{-5} mol/l.

 $A(\lambda)$, on the total metal cation content of the solution (C_{Ba}) at a constant total naphthopyran content (C_L) were analyzed to estimate the stability constants of complexes with Ba²⁺ cations. The iterative procedure for estimating the stability constants is detailed in [30]. The experimental $A(\lambda)$ dependences were fitted to Eqs. (4) and (5):

$$A(\lambda) = \frac{C_{\rm L}(\varepsilon_{\rm L} + \varepsilon_1 K_1 [{\rm Ba}^{2+}] + \varepsilon_2 K_1 K_2 [{\rm Ba}^{2+}]^2)}{1 + K_1 [{\rm Ba}^{2+}] + 2K_1 K_2 [{\rm Ba}^{2+}]^2} l, \quad (4)$$

$$K_{1}K_{2}[Ba^{2+}]^{3} + (K_{1} + 2C_{L}K_{1}K_{2} - K_{1}K_{2}C_{Ba})[Ba^{2+}]^{2} + (1 + K_{1}C_{L} - K_{1}C_{Ba})[Ba^{2+}] - C_{Ba} = 0,$$
(5)

where $K_2 = [ML_2]/[ML][L]$; ε_L , ε_1 , and ε_2 are the extinction coefficients of the initial naphthopyran and the 1 : 1 and 2 : 1 complexes, respectively; and *l* is the optical path length.

The sought parameters $(K_1, K_2, \varepsilon_1(\lambda), \varepsilon_2(\lambda))$ were estimated by fitting the experimental dependences. These procedures were carried out at several wavelengths. The stability constants determined at different

KINETICS AND CATALYSIS Vol. 53 No. 1 2012

wavelengths coincided within the experimental error, and this was evidence of the adequacy of the algorithm.

RESULTS AND DISCUSSION

Complexation of the Closed Form of Naphthopyrans with Metal Cations

Addition of alkali-earth metal cations to the solutions of crownless naphthopyrans does not affect their UV absorption spectra. For crown-containing compounds, the addition of cations was found to change in their UV spectra. Figure 1a demonstrates the spectral changes in the course of complex formation between chromene **1b** and Mg^{2+} cations. The persistence of isosbestic points in the UV spectra (at 325, 336 and 347 nm) indicates that, in the concentration range examined, only two forms of chromene coexist in solution. This makes it possible to determine the composition of the complex by Job's method [29].

In the case of Mg²⁺ cations, the minimum of Job's plot for compounds **1b** and **2b** was observed at $x = C_M/C_0 = 0.5$ (Fig. 1b). This indicates the formation of a 1 : 1 complex (complex A in Scheme 4). This com-

position of the complex corresponds to the location of the metal cation inside the crown ether cavity. The ionic radius of the Mg²⁺ cation is 0.72 Å [31], while the radius of the 15-crown-5–ether cavity is 0.85 Å [32] and the radius of the cavity in aza-15-crown-5-ether falls in the 0.85–1.1 Å range [33].

For the **1b**–Ba²⁺ system, no well-defined isosbestic points were observed while adding metal cations to the

solution (Fig. 2), which indicated the formation of complexes with different stoichiometries. The Ba²⁺ cation, whose ionic radius is 1.36 Å [31], forms two complexes with chromene **1b**, in which $[Ba^{2+}]$: **[1b]** = 1 : 1 and 1 : 2. The latter ratio corresponds to the sandwich structure of the complex (Scheme 4). Geometrically, the sandwich complex can have both *syn* and *anti* structures (complexes **B** and **C** in Scheme 4).





Scheme 4.

In contrast to compound **1b**, naphthopyran **2b**, which contains an aza-crown moiety, forms only a 1 : 1 complex with the Ba²⁺ cation. Generally, sandwich complex formation is not typical of aza-crown-containing compounds [23]. This is probably explained by the steric hindrance caused by the nonplanar structure of the molecules. In particular, the *syn* structure, which seems to be energetically more favorable because of the stacking interaction between chromophores [5], cannot be realized.

The experimental dependence of $\Delta A/\Delta A_{\text{max}} \times 100\%$ on C_{Ba}/C_{2b} for the 1 : 1 complex **2b**-Ba²⁺ fits satisfactorily to Eq. (3) with the equilibrium constant

 $K_1 = 4 \times 10^3$ l/mol (Fig. 3, curve *I*). Curves 2 and 3 in Fig. 2 correspond to equilibrium constants of 3×10^3 and 5×10^3 l/mol. In the determination of the stepwise stability constants for the **1b**-Ba²⁺ system, it was found that experimental curves at different wavelengths can be satisfactorily fitted to Eqs. (4) and (5) with similar stability constants (table).

The results of the determination of the stoichiometry and stability constants of the complexes are presented in the table. The stability constants for the complexes of naphthopyrans with the Mg^{2+} cation coincide with the same constants reported in [26], where a slightly different computational procedure

was used. Note that the stability constant for the 2b– Mg^{2+} complex, in which the cation is located inside the crown ether cavity, is two orders of magnitude higher than that for the 2b– Ba^{2+} complex, in which the cation is located outside the cavity.

Photochromism of the Naphthopyrans

Irradiation of all of the chromenes in the region of the long-wavelength absorption band (355 nm) gives rise to characteristic absorption at 450 nm (Fig. 4a), which makes the colorless solution yellow. According to the literature, the absorption band at 450 nm is due to the open form of the chromene [3]. After the cessation of irradiation, the open form transforms thermally to the closed form, which results in the restoration of the initial UV spectrum.

An example of a kinetic curve for the photochemical formation of the open form and its thermal conversion to the closed form (for compound 1b at room temperature) is shown in Fig. 4b (the beginning of the descent of the curve corresponds to the instant the exciting irradiation was switched off). The kinetic curves for the $M \rightarrow S$ thermal reactions are exponential. The characteristic lifetime of the open form for all of the naphthopyrans is several tens of seconds at room temperature. The rate constants for the thermal $M \rightarrow S$ reaction were determined at different temperatures in the 270-300 K range. This allowed us to calculate the activation energies for the reverse reactions of naphthopyrans. The Arrhenius parameters of this process were reported in [26]. The activation energy for all of the chromenes was about 15 kcal/mol, which is typical of spirocompounds [34].

The degree of photodegradation per excitation thermal reaction cycle is small for all of the naphthopyranes. After 10 cycles, the absorbance of the initial compound at 450 nm increased by 0.05 (Fig. 5). The absorbance of the open form in the photostationary state therewith did not changed significantly.

Photoinduced Geometric Isomerization of the Closed Form of Naphthopyrans

As it was mentioned in Experimental, the closed form of crown-containing naphthopyrans in solution is a mixture of *trans* and *cis* isomers. Prolonged irradiation of the solutions in the region of long-wavelength absorption band (313 nm) results in changes in their ¹H NMR spectra. An analysis of the initial and final NMR spectra of **1b** demonstrated that the signals from the protons of the *cis* isomer of the closed form disappeared entirely as a result of photolysis. At the same time, a moderate increase in the intensity of signals from the protons of the *trans* isomer was observed. Therefore, the observed reaction is the *cis–trans* isomerization of the closed form. As was shown in [26], the *cis–trans* isomerization of the closed form of

* Reported in [26].



Fig. 3. Dependence of the relative change of absorbance at 380 nm (dots, left scale) and the calculated percentage of the complex (lines, right scale) on the $[Ba^{2+}]/[2b]$ ratio (chromene concentration of 5×10^{-5} mol/l): (1) results of fitting the experimental data to Eq. (3) with a stability constant of $K_1 = 4000 \text{ l/mol}/$, (2) $K_1 = 3 \times 10^3 \text{ l/mol}$, and (3) $K_1 = 5 \times 10^3 \text{ l/mol}$.

naphthopyran **1b** leads to an increase in UV absorbance at 300–400 nm.

By contrast, for naphthopyran **2b** UV absorbance at 300–400 nm decreases markedly upon irradiation

Stoichiometry and stability constants of the complexes of the crown-containing naphthopyrans (closed form) with alkaline-earth metal cations

Complex	Composi-	$\log K_1$	$\log K_2$	$\log K = \log K_1 + \log K_2$
	tion	[l/mol]		
$1b-Mg^{2+}$	1:1	$4.7\pm0.2^*$	_	_
$2b-Mg^{2+}$	1:1	$5.7\pm0.2*$	_	_
1b -Ba ²⁺	1 : 1 and 2 : 1	4.7 ± 0.4	5.6 ± 0.4	10.3 ± 0.8
2b -Ba ²⁺	1:1	3.6 ± 0.2	—	—



Fig. 4. (a) Changes in the UV spectrum as a result of the thermal reaction M → S of 1b in acetonitrile in the presence of Ba²⁺ cations; $C_{1b} = 6 \times 10^{-5}$ mol/l; $C_{Ba(CIO_4)_2} = 0.01$ mol/l; time elapsed after the cessation of irradiation, s: (*I*) 0 (UV spectrum after 10-s-long irradiation at 365 nm), (*2*) 2, (*3*) 5, (*4*) 10, (5) 20, and (*6*) spectrum of naphthopyrane **1b** before irradiation. (b) Kinetics of the thermal reaction S ↔ M (430 nm, 298 K).

(Fig. 6). This is accompanied by an increase of the signals from *cis* isomer protons and by a decrease of the signals from *trans*—isomer protons. However, the signals from *trans*—isomer protons dot not disappear completely. Therefore, the photolysis of naphthopyran **2b** at 313 nm results in *trans—cis* isomerization, which leads to a new equilibrium distribution of the isomers of the closed form. The composition of the equilibrium mixture is determined by the photolysis quantum yields and molar absorption coefficients of the *trans* and *cis* forms at the irradiation wavelength.

For compound **1a**, the pure *trans* and *cis* isomers of the closed form were separated, which allowed us to determine the quantum yield for geometric isomerization. The spectral changes in the course of the photolysis (313 nm) of the *cis* isomer testify that *cis*-*trans* isomerization occurs. From the initial portion of the



Fig. 5. Photostability of naphthopyran 1a. The cycle is sample irradiation at 365 nm until the establishment of the photostationary state and the subsequent dark stage until the end of the reaction $M \rightarrow S$. The naphthopyran concentration in acetonitrile is 4×10^{-5} mol/l.

plot of absorbance at 350 nm versus irradiation time, we determined the quantum yield for the *cis*-*trans* isomerization of the closed form of **1a** to be 0.05 ± 0.01 .

The open form of the naphthopyrans can result from both the *trans* isomer and *cis* isomer of the closed form. This clearly demonstrates that the geometric isomerization of the closed form and the appearance of the open form are parallel photochemical reactions. No effect of the isomer composition of the closed form on the spectrum and lifetime of the open form was experimentally observed.

Primary Processes in Naphthopyran Photochemistry

Primary photochemical processes for naphthopyranes were studied by means of laser flash photolysis ($\lambda_{ex} = 355 \text{ nm}$) with 50 ns time resolution. For **1a** and **1b**, only an instantaneous change in absorbance was observed in the time interval examined (50 ns-10 ms).

The spectrum of this instantaneous change (with a maximum at 450 nm) coincides with the spectra of the open form of the naphthopyrans. Therefore, all processes leading to the appearance of the open form come to completion within <50 ns at room temperature.

For the compounds examined, the dependences of the appearing absorbance of the open form on the laser pulse energy were obtained. All of these dependencies were linear. Therefore, the photochemical reaction is a one-quantum process.

The primary processes in the photochemistry of chromenes were studied in [6, 35-38] by means of femtosecond pump-probe spectroscopy. In all cases, it was shown that the overall time of the formation of the metastable isomer of the open form did not exceed 10 ps. The mechanism of the formation of the open

form of naphthopyran (Scheme 5), proposed in [6], is usually confirmed by femtosecond experiments.

According to [6], C–O bond cleavage occurs under the action of light, leading to the primary intermediate **A**, which displays the properties of a zwitterion. The characteristic time of zwitterion formation is several hundreds of femtoseconds. Next, the **A** intermediate transforms into the **B** intermediate having a *cisoid ortho*-quinodal structure. The characteristic time of this process is about 1 ps. The lifetime of the **B** intermediate is determined by the rate of mutual rotation around the C(3)–C(4) bond. This rotation leads to the formation of the metastable isomer of the open form (**C**). This isomer has a *transoid* geometry. Its absorption spectrum coincides with the spectra observed in stationary photolysis. Therefore, the **C** form is the experimentally observable open form of naphthopyran.



For several chromenes, the formation of a triplet state of the initial molecule was observed, with the triplet state quantum yield being less than 10% of the total quantum yield of photolysis [6, 38]. In our experiments on laser flash photolysis of oxygen-free solutions of nitrogen-containing naphthopyrans (**2a** and **2b**), we observed the appearance of short-lived transient absorption (Fig. 7). This absorption was not observed upon the photolysis of oxygen-containing solutions. This testifies that this transient absorption is most likely due to the triplet state of the closed form.

In the case of **1a** and **1b**, the removal of oxygen does not result in such an effect.

Figure 7a demonstrates the transient absorption spectra of an oxygen-free solution of chromene **2b** obtained 0.1 and 50 μ s after the laser pulse. The kinetic curves at all the wavelengths (Fig. 7b) are satisfactorily fitted to a monoexponential function with a characteristic time of $3.5 \pm 0.5 \mu$ s. When experiments were performed at different laser pulse energies, a fourfold increase in the initial amplitude of the transient absorption signal did not change its characteristic



Fig. 6. Changes in the UV spectra of naphthopyrans during the photoinduced *cis-trans* isomerisation. (a) Photolysis of chromene **1b** $(4.5 \times 10^{-5} \text{ mol/l})$ in acetonitrile. The irradiation time (313 nm) is (*I*) 0, (*2*) 1, (*3*) 6, and (*4*) 9 min. (b) Photolysis of chromene **2b** $(4.5 \times 10^{-5} \text{ mol/l})$ in acetonitrile. The irradiation time (313 nm) is (*I*) 0, (*2*) 1, (*3*) 3, (*4*) 6, (*5*) 10, and (*6*) 15 min.

decay time. This means that second-order reactions do not make any measurable contribution to the transient absorption decay kinetics. The transient absorption spectrum of the oxygen-free sample 20 μ s after the laser pulse coincides with the spectrum of the open form.

According to [6], one might hypothesize that the observed reaction is the transition of the triplet state of the closed form to the open form. If this were the case, the quantum yield of the appearance of the open form in oxygen free solutions would be higher than in solutions with the natural oxygen content. In our experiments, the relative quantum yield of the appearance of the open form (derived from the final absorbance at the band maximum) was not oxygen-dependent. Therefore, the triplet states of the closed forms of 2a and 2b do not turn into the open forms (as distinct from the chromenes studied in [6]).



Fig. 7. Laser flash photolysis (355 nm) of naphthopyran **2b** (6×10^{-5} mol/l) in acetonitrile in the absence of oxygen. (a) Transient absorption spectra recorded (*1*) 0.1 and (*2*) 50 µs after a laser pulse. (b) Kinetic curves recorded at 520 and 400 nm (experimental curves and their fits to monoexponential functions).

Effect of Metal Cations on the Photochromic Properties of the Naphthopyrans

Based on the literature data on the photochemistry of chromenes, one could expect a sufficient effect of metal cations on the parameters of the electrocyclic reaction $M \rightarrow S$ [5, 16, 21, 23]. For example, for chromenes studied in [23], the rate constant of the reverse reaction $M \rightarrow S$ at $[Ca^{2+}]$: [Chr] = 1000 was smaller by a factor of 5 for crown-containing compounds and by a factor of 2 for their crownless analogues. This effect is explained by complex formation due to the Coulomb interaction between the partial negative charge on the carbonyl oxygen atom and the positive charge of the metal cation, which can be located either in the solution bulk or in the crown ether cavity (Scheme 6) [21, 23, 34].

However, in our case both the position of the absorption band of the open form and its lifetime did

not change even at $[Me^{2+}]$: [Chr] = 6000. This was true both for the crown-containing naphthopyrans and for the crownless ones.

The absence of a metal cation effect on the lifetimes of the open forms of model compounds **1a** and **2a** testifies that the complex, in which the metal cation is coordinated to the carbonyl oxygen atom (Scheme 6a), is unlikely to appear. This can be due to the competition between the two possible reactions of the merocyanine form of naphthopyran, namely, the complexation of the metal cation and conversion into the closed form. The characteristic time of complex formation seems to be much shorter than the lifetime of the open form (about 30 s at room temperature).



For compounds 1b and 2b, the absence of the influence of the metal cation (located inside the crown ether cavity) on the properties of the open form is probably explicable in terms of molecular structure. The cause of the possible effect is the Coulomb interaction between the charge of the cation and the partial negative charge of an oxygen atom (Scheme 6b). In our case, the distance between the Mg²⁺ and $O^{\delta-}$ cations is ca. 8 Å, and the Coulomb interaction over this distance is weak. When metal cations are taken in great excess, the coordination of a second metal cation seems to be possible (Scheme 6a). However, the absence of observable results of this coordination indicates that, as in the case of the crownless naphthopyranes, the lifetime of the open form is insufficient for the complex to appear.

An alternative explanation of the absence of a metal cation effect on the properties of the open form of crown-containing naphthopyrans is possible for the case of *cis* isomers (Scheme 3). The open form of the cis isomer is likely nonflat, and this decreases the conjugation of the π -electronic systems of the styryl and benzo–crown moieties of the molecule. In this case, the lpresence of a metal cation inside the crown ether

cavity should not affect the properties of the open form.

Thus, the naphthopyrans examined are involved in two parallel photochemical reactions, namely, the geometric isomerization of the closed form and the formation of the merocyanine (open) form. Geometric isomerization does not affect the lifetime of the open form. The naphthopyrans form complexes of different compositions with Mg^{2+} and Ba^{2+} cations. Complex formation exerts an effect on the spectral characteristics of crown-containing chromenes in closed form but does not change the properties of the open form. This fact indicates the independence of the two photochromic parts of the molecule. In spite of the conjugation of these molecular moieties, the metal cations located in the styryl moiety cannot effect the electrocyclic reaction of the naphthopyran moiety.

ACKNOWLEDGMENTS

The work was supported by the Russian Foundation for Basic Research (grant nos. 11-03-00268 and 09-03-00283).

- Gromov, S.P., *Ross. Nanotekhnol.*, 2006, vol. 1, nos. 1–2, p. 29.
- Queiroz, M.-J.R.P., Plasencia, P.M.S., Dubest, R., Aubard, J., and Guglielmetti, R., *Tetrahedron*, 2003, vol. 59, no. 14, p. 2567.
- 3. Organic Photochromic and Thermochromic Compounds, Crano, J.C. and Guglielmetti, R.J., Eds., New York: Plenum, 1998, p. 111.
- Favaro, G., Chidichimo, G., Formoso, P., Manfredi, S., Mazzucato, U., and Romani, A., J. Photochem. Photobiol., A, 2001, vol. 140, no. 3, p. 229.
- 5. Ushakov, E.N., Alfimov, M.V., and Gromov, S.P., *Usp. Khim.*, 2008, vol. 77, no. 1, p. 39.
- 6. Gentili, P.L., Danilov, E., Ortica, F., Rodgers, M.A.J., and Favaro, G., *Photochem. Photobiol. Sci.*, 2004, vol. 3, no. 9, p. 886.
- Shinkai, S., Nakaji, T., Ogawa, T., Shigematsu, K., and Manabe, O., *J. Am. Chem. Soc.*, 1981, vol. 103, no. 1, p. 111.
- Wei, W., Tomohoro, T., Kodaka, M., and Okuno, H., J. Org. Chem., 2000, vol. 65, no. 26, p. 8979.
- Takeshita, M. and Irie, M., J. Org. Chem., 1998, vol. 63, no. 19, p. 6643.
- 10. Sasaki, H., Ueno, A., Anzai, J.-I., and Osa, T., *Bull. Chem. Soc. Jpn.*, 1986, vol. 59, no. 6, p. 1953.
- 11. Fedorov, Yu.V., Fedorova, O.A., Gromov, S.P., Bobrovskii, M.V., Andryukhina, E.N., and Alfimov, M.V., *Izv. Akad. Nauk, Ser. Khim.*, 2002, vol. 51, no. 5, p. 789.
- Fedorov, Yu.V., Fedorova, O.A., Andryukhina, E.N., Gromov, S.P., Alfimov, M.V., Kuzmina, L.G., Churakov, A.V., Howard, J.A.K., and Aaron, J.-J., *New J. Chem.*, 2003, vol. 27, no. 2, p. 280.
- 13. Kimura, K., Yamashita, T., and Yokoyama, M., J. Chem. Soc., Perkin Trans. 2, 1992, no. 5, p. 613.
- Tanaka, M., Ikeda, T., Xu, Q., Ando, H., Shibutani, Ya., Nakamura, M., Sakamoto, H., Yajima, S., and Kimura, K., J. Org. Chem., 2002, vol. 67, no. 7, p. 2223.
- 15. Liu, Z., Jiang, L., Liang, Z., and Gao, Y., J. Mol. Struct., 2005, vol. 737, no. 3, p. 267.
- Kimura, K., Kaneshige, M., Yamashita, T., and Yokoyama, M., *J. Org. Chem.*, 1994, vol. 57, no. 20, p. 5377.
- Inouye, M., Ueno, M., Tsuchiya, K., Nakayama, N., Konishi, N., and Kitao, T., *J. Org. Chem.*, 1992, vol. 59, no. 6, p. 1251.
- Fedorova, O.A., Gromov, S.P., Pershina, Yu.A., Sergeev, S.S., Strokach, Yu.P., Barachevsky, V.A., Alfimov, M.V., Pepe, G., Samat, A., and Guglielmetti, R., *J. Chem. Soc., Perkin Trans.* 2, 2000, no. 3, p. 563.
- Feofanov, A.V., Alaverdian, Yu.S., Gromov, S.P., Fedorova, O.A., and Alfimov, M.V., *J. Mol. Struct.*, 2001, vols. 563–564, p. 193.
- Fedorova, O.A., Strokach, Yu.P., Gromov, S.P., Koshkin, A.V., Valova, T.M., Alfimov, M.V., Feofanov, A.V., Alaverdian, I.S., Lokshin, V.A., Samat, A., Gugliel-

metti, R., Girling, R.B., Moore, J.N., and Hester, R.E., *New J. Chem.*, 2002, vol. 26, no. 9, p. 1137.

- Korolev, V.V., Vorobyev, D.Yu., Glebov, E.M., Grivin, V.P., Plyusnin, V.F., Koshkin, A.V., Fedorova, O.A., Gromov, S.P., Alfimov, M.V., Shklyaev, Yu.V., Vshivkova, T.S., Rozhkova, Yu.S., Tolstikov, A.G., Lokshin, V.A., and Samat, A., *Mendeleev Commun.*, 2006, vol. 16, no. 6, p. 302.
- Korolev, V.V., Vorobyev, D.Yu., Glebov, E.M., Grivin, V.P., Plyusnin, V.F., Koshkin, A.V., Fedorova, O.A., Gromov, S.P., Alfimov, M.V., Shklyaev, Yu.V., Vshivkova, T.S., Rozhkova, Yu.S., Tolstikov, A.G., Lokshin, V.A., and Samat, A., *J. Photochem. Photobiol.*, *A*, 2007, vol. 192, no. 2, p. 75.
- Fedorova, O.A., Maurel, F., Ushakov, E.N., Nazarov, V.B., Gromov, S.P., Chebunkova, A.V., Feofanov, A.V., Alaverdyan, I.S., Alfimov, M.V., and Barigelletti, F., *New J. Chem.*, 2003, vol. 27, no. 12, p. 1720.
- 24. Ahmed, S.A., Tanaka, M., Ando, H., and Kimura, K., *Eur. J. Org. Chem.*, 2003, no. 13, p. 2437.
- 25. Ahmed, S.A., Tanaka, M., Ando, H., Iwamoto, H., and Kimura, K., *Tetrahedron*, 2004, vol. 60, no. 14, p. 3211.
- Glebov, E.M., Smolentsev, A.B., Korolev, V.V., Plyusnin, V.F., Chebunkova, A.V., Paramonov, S.V., Fedorova, O.A., Lokshin, V., and Samat, A., *J. Phys. Org. Chem.*, 2009, vol. 22, no. 5, p. 537.
- 27. Kurien, K.C., J. Chem. Soc. B, 1971, vol. 75, no. 14, p. 2081.
- Pozdnyakov, I.P., Plyusnin, V.F., Grivin, V.P., Vorobyev, D.Yu., Bazhin, N.M., and Vauthey, E., J. Photochem. Photobiol., A, 2006, vol. 182, no. 1, p. 75.
- 29. Beck, M. and Nagypal, I., *Chemistry of Complex Equilibria*, Budapest: Academiai Kiado, 1989, p. 130.
- 30. Hargrove, A., Zhong, Z., Sessler, J., and Anslyn, E., *New J. Chem.*, 2010, vol. 34, no. 2, p. 348.
- 31. Lur'e, Yu.Yu., *Spravochnik po analiticheskoi khimii* (Handbook of Analytical Chemistry), Moscow: Khimiya, 1979.
- 32. Arnaud-Neu, F., Delgado, R., and Chaves, S., *Pure Appl. Chem.*, 2003, vol. 75, no. 1, p. 71.
- 33. Thomas, K.J., Thomas, K.G., Manojkumar, T.K., Das, S., and George, M.V., *Proc. Indian Acad. Sci.* (*Chem. Sci.*), 1994, vol. 106, no. 6, p. 1375.
- 34. Lokshin, V., Samat, A., and Metelitsa, A.V., Usp. Khim., 2002, vol. 71, no. 11, p. 1015.
- 35. Aubard, J., Maurel, F., Buntinx, G., Poizat, O., Levi, G., Guglielmetti, R., and Samat, A., *Mol. Cryst. Liq. Cryst.*, 2000, vol. 345, p. 215.
- Hobley, J., Malatesta, V., Hatanaka, K., Kajimoto, S., Williams, S.L., and Fukumura, H., *Phys. Chem. Chem. Phys.*, 2002, vol. 4, no. 2, p. 180.
- 37. Favaro, G., Mazzucato, U., Ottavi, G., and Becker, R.S., *Mol. Cryst. Liq. Cryst.*, 1997, vol. 298, p. 137.
- Ortica, F., Smimmo, P., Favaro, G., Mazzucato, U., Delbaere, S., Venec, D., Vermeersch, G., Frigoli, M., Moustrou, C., and Samat, A., *Photochem. Photobiol. Sci.*, 2004, vol. 3, no. 9, p. 878.