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Synthesis and photochromic properties of crown-containing styryl derivatives of naphthopyrans

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New crown-containing and crownless chromenes were synthesized. Their physical properties and photochemistry were characterized. Crown-containing chromenes form inclusion complexes with Mg^{2+} cation. Two types of photochemical reactions were observed for all the studied chromenes. The photoreaction of the first type is *cis–trans* isomerization of styryl fragment in closed form. Second type of photoreaction is the reversible formation of open form responsible for the photochromism of chromenes. Arrhenius parameters of back reactions are determined. Both crownless and crown-containing chromenes do not demonstrate cation-dependent photochromism, which is explained by the peculiarities of the structure of open form. Copyright © 2009 John Wiley & Sons, Ltd.

Keywords: chromenes; crown ethers; photochromism; *cis–trans* isomerization; electrocyclic reaction

INTRODUCTION

Photochromism is defined as a reversible photoinduced phenomenon in which a photosensitive compound is converted to another isomer having a different absorption spectrum. Spirocompounds (spiropirans, spirooxazines) and chromenes are among the main photochromic families.

Incorporation of crown ether moieties to the photochromic molecules opens a possibility for controlling their properties. This approach is based on the use of complexation with metal cations.[1,2] Binding of metal cations by an ionophore fragment could lead to the change of such properties of photochromic molecules as photostability, sensitivity, and width of working spectral region. Introduction of a crown ether moiety yields in the ion-responsive photochromism of azobenzenes[1,3] diarylethenes,[4] styrylbenzothiazoles,[5–7] spiropyrans,[8–10] spirooxazines,[11–17] and chromenes.[18–20] Potential applications of crown-containing photochromes include[2]:

- optical information storage
- optoelectronic systems
- photoswitching extraction of metal cations
- photoswitching transport through membranes.

Photochromism of spirocompounds is determined by the transitions between colorless (closed) spiro-form and colored (open) form. Complex formation with metal cations can affect both spectral and kinetic properties of an open form.[21] For example, introduction of monoaza-12-crown-4 group into the 5′ position of a spironaphthoxazine (further – SNO) molecule and its complexation with Li^+ ion stabilize the open form of SNO, increasing its lifetime in two orders of magnitude.[12] Reports on crown-containing chromenes are scarce. Oxymethylcrowned chromenes were found to demonstrate ion-responsive photochromism and photoswitchable stoichiometry of complexes with alkali metal cations.[20]

Among the prospective applications of spirocompounds, optical information storage is of greatest interest. To realize it, the non-destructive readout is necessary. Over recent years, two approaches have been pursued in an effort to realize the non-destructive readout. The first approach is to look for systems in which the readout irradiation does not cause the photochemical reactions at all.[22,23] Probably, it could be realized in systems with gated photochemical reactivity.[24] The other approach is to develop two-photon photochromic systems in which irradiation strength and wavelengths are precisely controlled.[25] Some chromene derivatives show such two-photon photochromism.[26–28] Their photochromic reactions proceed between two isomers via an unstable intermediate in a two-step, two-photon process. The recording can be carried out by using a strong beam that converts closed isomers to bicycloisomers via keto intermediates with the two-photon mechanism.[29] Joining two spiroindolino-oxazine and ben-

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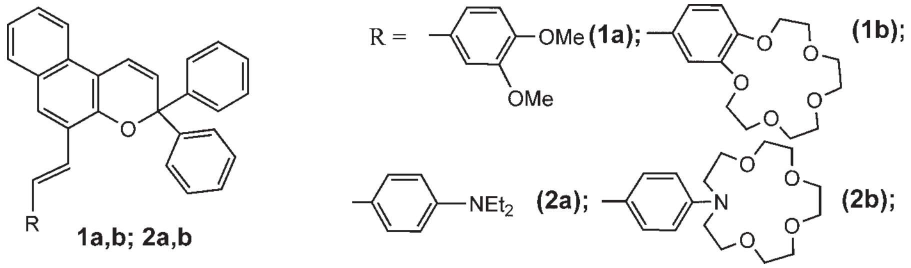


Scheme 1.

zo-[2H]-chromenes or naphthopyran molecules through an ethenic bridge yields a bichromophoric supermolecule, that exhibits photochemical and dynamic properties different from those of the single components.[30] The reaction mechanism for this molecule containing a chromene moiety is characterized by an intermediate, which thermally evolves to different products.

The current work is an extension of authors' efforts on the synthesis and study of crown-containing spirocompounds.[2,5,6,13–18] In this work, the investigation of the photochromic properties of the styrylsubstituted chromene derivatives **1a, b** and **2a, b** (Scheme 1) was carried out aimed to analyze how the phototransformation occurs in the systems possessing two photochromic fragments – styryl fragment (photoreversible *trans–cis*-isomerization) and naphthopyran unit (photoinduced electrocyclic transformation). The studied compounds **1b** and **2b** are additionally supplied by ionophoric crown ether fragment. The presence of binding center in the composition of photochromic molecule opens the way to use the complex formation process to tune of spectral and photochromic characteristics.[17,18,31,32] The change in crown ether structure should lead to change of spectral characteristics of initial photochromic ligand as well as in some difference in complex formation process.

EXPERIMENTAL

Materials

$Mg(ClO_4)_2$ (Aldrich) was used as the source of Mg^{2+} ions. Spectrophotometric grade acetonitrile (Aldrich) was used as a solvent.

Synthesis

All the substances were synthesized using the previously reported procedure.[33] The target compounds **1a,b** and **2a,b** (Scheme 1) were obtained in 35–74% yield from the Wittig olefination of phosphonium salt of 3,3-diphenyl-8-methylene-[3H]-naphtho[2,1-b]pyran **3** using an appropriate formyl derivative **4a,b** or **5a,b** (Scheme 2). The initial compound **3** was prepared as described in.[32]

5-[2-(3,4-dimethoxyphenyl)ethenyl]-3,3-diphenyl-3*H*-benzo[*f*]chromene (1a), 66%, m.p. 56–58 °C. After column chromatography using EtOAc/Cyclohexane = 1/9 as eluent, *cis*- and *trans*-isomer mixture were separated. *cis*-**1a**: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ_H 3.14 (s, 2H, CH_3O-3′), 3.83 (s, 3H, CH_3O-4′), 6.33 (d, 1H, J = 9.9 Hz, H-2), 6.61–6.74 (m, 3H, H-a, 2′, 5′), 6.77–6.87 (m, 2H, H-b, 6′), 7.10-7.55 (m, 14H, H-1, 7, 8, 9, 2 × Ar), 7.60 (s, 1H, H-6), 7.91 (d, 1H, J = 8.6 Hz, H-10).

trans-**1a**: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ_H 3.92 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3), 6.32 (d, 1H, J = 9.9 Hz, H-2), 6.89 (d, 1H, J = 8.0 Hz, H-5′), 7.08–7.60 (m, 17H, H-1, 8, 9, 2′, 6′, a, b, 2 × Ar), 7.72 (d, 1H, J = 8.0 Hz, H-7), 7.87–7.96 (m, 2H, H-6, 10).

$C_{35}H_{28}O_3$. Calcd. C 84.65, H 5.68; found C 84.54, H 5.99.

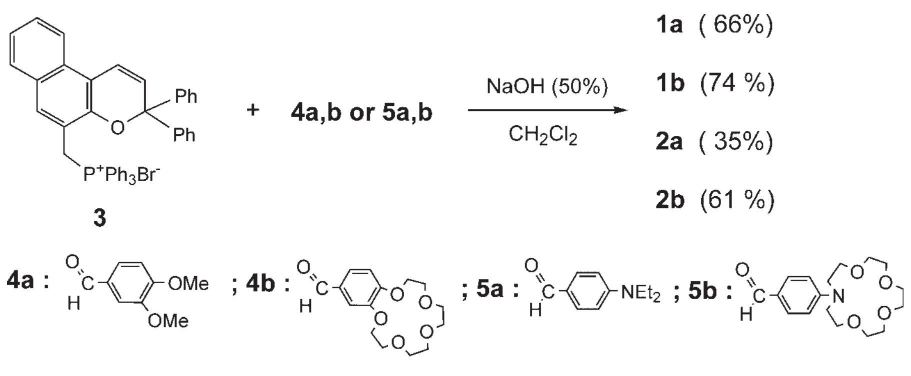
5-[(*E*)-2-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecan-15-yl)ethenyl]-3,3-diphenyl-3*H*-benzo[*f*]chromene (1b), 74%, m.p. 65–70 °C.

cis-**1b**: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ_H 2.44 (m, 4H, 2 × CH_2), 2.55–2.63 (m, 2H, CH_2), 2.65–2.77 (m, 6H, 3 × CH_2), 2.84–2.90 (m, 2H, CH_2), 4.06–4.13 (m, 2H, CH_2), 6.33 (d, 1H, J = 9.1 Hz, H-2), 6.61 (s, 1H, H-2′), 6.67 (d, 1H, J = 8.2 Hz, H-5′), 6.70 (d, 1H, J = 12.3 Hz, H-a), 6.79 (d, 1H, J = .8.2 Hz, H-6′), 6.83 (d, 1H, J = 12.3 Hz, H-b), 7.15–7.63 (m, 13H, H-1, 8, 9, 2 × Ar), 7.65–7.75 (m, 2H, H-6, H-7), 7.92 (d, 1H, J = 8.3 Hz, H-10).

trans-**1b**:^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ_H 3.75–3.83 (m, 8H, 4 × CH_2), 3.91–3.99 (m, 4H, 2 × CH_2), 4.15–4.28 (m, 4H, 2 × CH_2), 6.32 (d, 1H, J = 9.5 Hz, H-2), 6.89 (d, 1H, J = .8.2 Hz, H-5′), 7.10–7.17 (m, 2H, H-2′, H-6′), 7.18–7.62 (m, 15H, H-1, 8, 9, a, b, 2 × Ar), 7.69 (d, 1H, J = 8.1 Hz, H-7), 7.87–7.97 (m, 2H, H-6, H-10).

$C_{41}H_{38}O_6$. Calcd. C 78.57, H 6.11; found C 78.44, H 5.99.

4-[2-(3,3-diphenyl-3*H*-benzo[*f*]chromen-5-yl)ethenyl]-*N*,*N*-4-[2-(3,3-diphenyl-3*H*-benzo[*f*]chromen-5-yl)ethenyl]-*N*,*N*-diethylaniline (2a), viscous oil, 10%, m.p. 70–72°C. After column



Scheme 2.

chromatography using EtOAc/Cyclohexane = 1/19 as eluent, *cis*- and *trans*-isomer mixture were separated.

cis-**2a**: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ_H 1.09 (t, 6H, $J = 7.2$ Hz, $2 \times CH_3$), 3.27 (q, 4H, $J = 7.2$ Hz, $2 \times CH_2$), 6.32 (d, 1H, $J = 9.8$, H-2), 6.42 (d, 2H, $J = 8.9$ Hz, H-3′, 5′), 6.64 (d, 1H, $J = 12.1$ Hz, H-a), 7.05–7.59 (m, 16H, H-1, 8, 9, 2′, 6′, b, $2 \times$ Ar), 7.69 (d, 1H, $J = 8.4$ Hz, H-7), 7.85–7.93 (m, 2H, H-6, 10).

trans-**2a**: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ_H 1.19 (t, 6H, $J = 7.2$ Hz, $2 \times CH_3$), 3.39 (q, 4H, $J = 7.1$ Hz, $2 \times CH_2$), 6.30 (d, 1H, $J = 9.9$, H-2), 6.69 (d, 2H, $J = 8.8$ Hz, H-3′, 5′), 7.15–7.59 (m, 17H, H-1, 8, 9, 2′, 6′, a, b, $2 \times$ Ar), 7.7 (d, 1H, $J = 7.8$ Hz, H-7), 7.85–7.93 (m, 2H, H-6, 10).

$C_{37}H_{23}N_1O_1$. Calcd. C 87.54, H 6.55; found C 87.36, H 6.70.

5-{2-[4-(1,4,7,10-Tetraoxa-13-azacyclopentadecan-13-yl)phenyl]ethenyl}-3,3-diphenyl-3*H*-benzo[*f*]chromene (2b), 35%, m.p. 80–85 °C.

cis-**2b**: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ_H 3.50–3.75 (m, 20H, $10 \times CH_2$), 6.32 (d, 1H, $J = 9.5$Hz, H-2), 6.41 (d, 2H, $J = 8.6$ Hz, H-3′, H-5′), 6.65 (d, 1H, $J = .12.0$ Hz, H-a), 7.11 (d, 2H, $J = 8.6$ Hz, H-2′, 6′), 7.16–7.58 (m, 14H, H-1, H-8, H-9, H-b, $2 \times$ Ar), 7.70 (d, 1H, $J = 8.2$ Hz, H-7), 7.86–7.95 (m, 2H, H-6, H-10).

trans-**2b**: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ_H 3.57–3.72 (m, 1 6H, $8 \times CH_2$), 3.74–3.82 (m, 4H, $2 \times CH_2$), 6.29 (d, 1H, $J = 9.5$ Hz, H-2), 6.68 (d, 2H, $J = 8.6$ Hz, H-3′, H-5′), 7.15–7.59 (m, 17H, H-1, H-8, H-9, H-2′, H-6′, H-a, H-b, $2 \times$ Ar), 7.69 (d, 1H, $J = .8.2$ Hz, H-7), 7.86–7.92 (m, 2H, H-6, H-10).

$C_{43}H_{43}N_1O_5$. Calcd. C 78.99, H 6.63; found C 79.06, H 6.70.

NMR study

^{1}H NMR spectra were recorded on a Bruker DRX-500 instrument (500.13 MHz) for solution in CD_3CN, the solvent being used as the internal reference 1.96 ppm for ^{1}H; for solution in $CDCl_3$, the solvent being used as the internal reference 7.27 ppm for ^{1}H. The COSY and NOESY 2D spectra were recorded using the standard Bruker pulse sequences (cosy45, cosygs, noesytp, roesyprtp) and processed using the Bruker XWINNMR program.

Spectroscopic measurement

UV absorption spectra were recorded using an Agilent HP-8453 spectrophotometer (Agilent Technologies) with the characteristic time of recording *ca.* 2 s. High pressure mercury lamp with the set of glass filters was used as a light source for stationary photolysis. To measure rate constants of the dark reactions with the characteristic time of several seconds, samples were irradiated in the cuvette box of the spectrophotometer. The irradiation was performed till the equilibrium between closed and open forms was achieved. The achievement of photostationary conditions was controlled by the absorption of the open form in the visible spectral region. After that the irradiation was interrupted and the kinetic curves corresponding to the recovery of the system to the initial closed state were recorded.

RESULTS AND DISCUSSION

NMR spectra of chromenes

According to the ^{1}H NMR observation chromenes **1a, b** and **2a, b** form as mixture of *trans*- and *cis*-isomers (see Fig. 1a–c for **1b** as an example). The *cis*-isomers of chromene derivatives **1a, 2a** are stable. It allows the isolation of pure *trans*- and *cis*-isomers by column chromatography. The NMR spectra of pure isomers for these compounds are placed in Experimental part. In the case of crown-containing compounds **1b** and **2b** we failed to separate the individual isomers. But in the NMR spectra the positions of proton signals of *trans*-isomer are different from those of *cis*-isomer. It makes possible to carry out the detailed analysis of the isomer structures. Thus, in NOESY spectrum the interaction of H(2′) ↔ H(Ph) and H(6′) ↔ H(Ph) in *trans*-**1b** points out on the existence of *trans*-**1b** as mixture of A and B conformers (Scheme 3).

Upon the analysis of the signals of *cis*-**1b** the large difference in the position of signals H-α and H-α', H-β, and H-β' was found. This is unusual in comparison with *trans*-isomer (see Fig. 1a–c). The signal of H-2′ proton of *cis*-**1b** is substantially upfield shifted. These facts can be explained assuming that in *cis*-**1b** isomer H-α and H-β protons of crown ether moiety as well as H-2′ proton are under the ring-current effect produced by aromatic naphthalene residue (Scheme 3, structure C). The anisotropic effect of aromatic system on H-2′, H-α, and H-β protons results in the shift of its signals in NMR spectrum to upfield region. Other crown ether protons are located far from the naphthalene ring to avoid the anisotropic effect. The found cross-peak between H-a ↔ H(Ph) in NOESY spectrum of *cis*-**1b** additionally confirms the suggested structure C (Scheme 3).

The NMR observation of chromene **2b** (Fig. 2) showed that the compound is formed as mixture of *trans*- and *cis*-isomers (Scheme 4) with low content of *cis*-isomer (near 15%).

Complexes of crown-containing chromenes with Mg^{2+} cation

Complex formation between chromenes and Mg^{2+} cation was examined. The radius of the cavity of 15-crown-5-ether is 0.85 Å.[34] The radius of the cavity of aza-15-crown-5-ether is in the range of 0.85–1.1 Å.[35] Ionic radius of Mg^{2+} is 0.72 Å,[36] therefore, the position of cation inside the crown ether cavity was expected.

The complex formation was monitored by the UV spectra. No changes in the UV spectra were observed when metal cations were added to crownless chromenes **1a** and **2a**. For crown-containing compounds, the addition of Mg^{2+} cations changes the UV spectra due to the complex formation between chromene and metal ion. Figure 3a demonstrates the formation of **2b** complex with Mg^{2+}. Conservation of the isosbestic points (327 and 350 nm, Fig. 3a) supports an assumption that only two forms containing the chromene coexist in the solution. It allows one to use UV spectra to determine the composition of the complex and to estimate the equilibrium constant.

Job's plots[37] were used to determine the content of the complexes. An example of Job's plots for **2b** complex with Mg^{2+} is shown in Fig. 3b. For the construction of Job's plot, the difference in absorption of the sample at the given concentration of chromene and maximal possible absorption of chromene at a proper wavelength (360 nm) was chosen as a characteristic linear via the complex concentration. According to the Job's plot shown in Fig. 3b, the **2b**:Mg^{2+} ratio is 1:1. The same situation was observed for chromene **1b**. The both studied chromenes form 1:1 complexes with Mg^{2+}. Mg^{2+} cation fits well to the size of the crown ether cavity; therefore, the structure with metal cation situated inside the cavity is essential. The structure of the complex for **1b** is shown in Scheme 5.

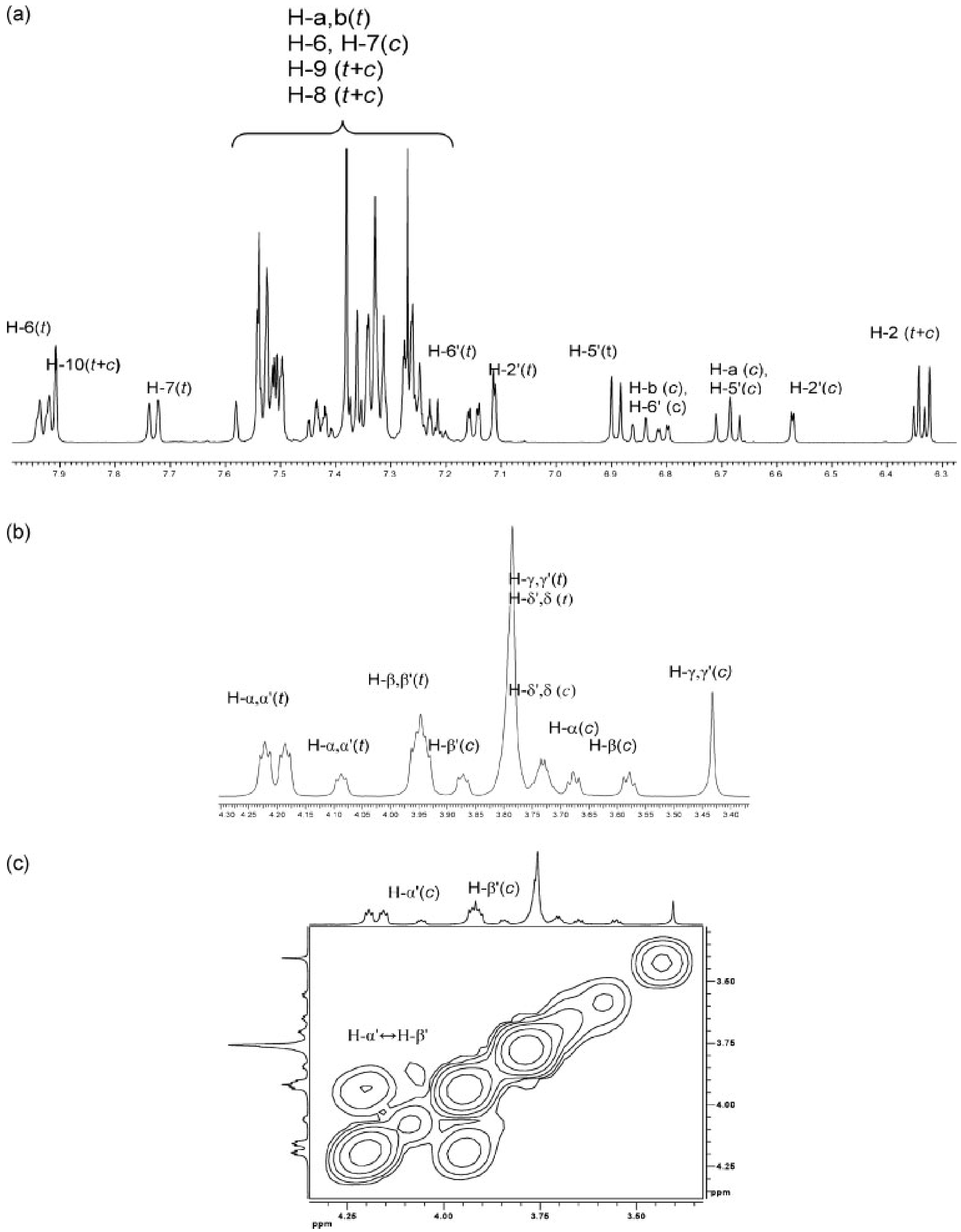
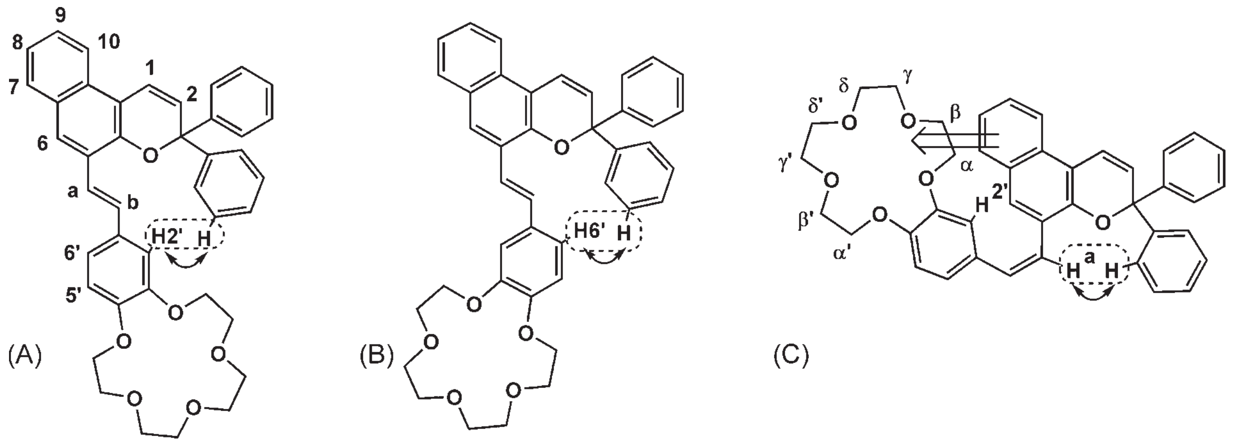


Figure 1. ^{1}H NMR and COSY spectra of chromene **1b**. (a) aromatic part; (b) aliphatic part; (c) COSY spectrum. "Bruker DRX-500", 500 Mhz, in $CDCl_3$, temperature 25 °C. Protons are marked in Scheme 3

The equilibrium constants of the complexes between crown-containing chromenes and metal cation were determined by the comparison of experimental and calculated dependencies of the relative concentration of the complex via initial ratio metal-to-chromene. Figure 4 demonstrates this procedure for an example of (**1b**)-Mg^{2+} complex. Dots with error bars (right axis) represent the experimental relative changes in absorption at a characteristic wavelength (360 nm). Full lines 1, 2 and 3 (left axis)



Scheme 3.

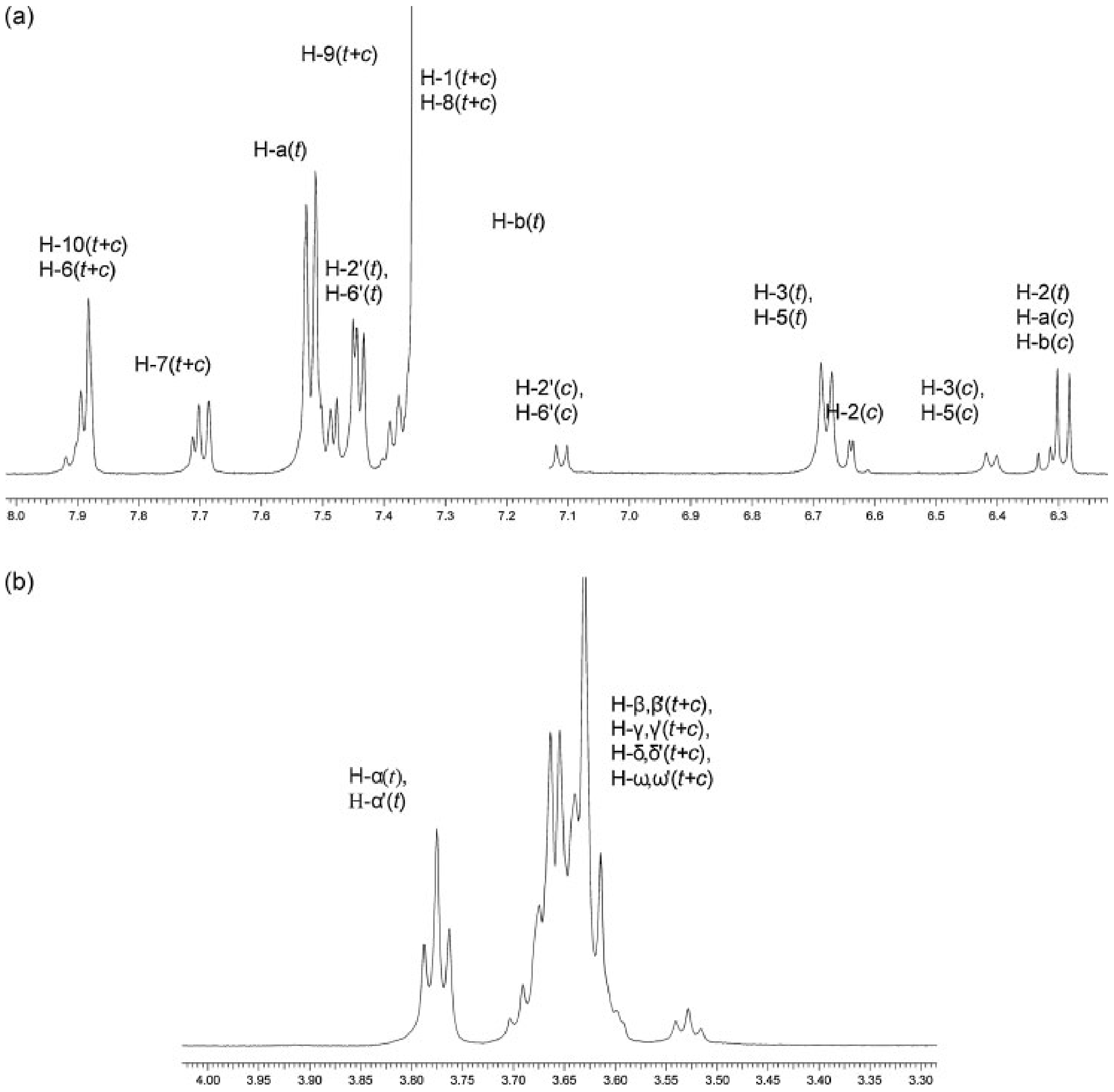
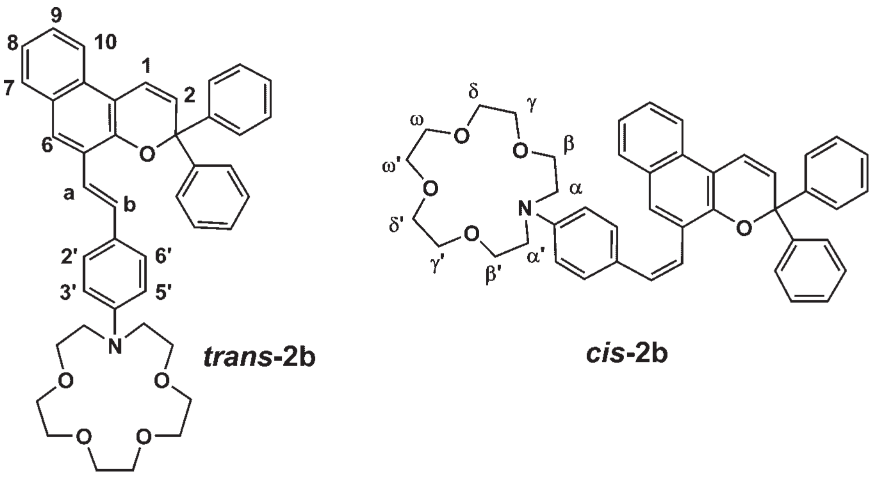


Figure 2. ^{1}H NMR spectrum of chromene **2b**. (a) aromatic part; (b) aliphatic part. "Bruker DRX-500", 500 Mhz, in $CDCl_3$, temperature 25 °C. Protons are marked in Scheme 4



Scheme 4.

represent the calculated relative content of the complex for different values of the equilibrium constant (K_{eq}). The experimental curve (Fig. 4) is satisfactorily fitted with the calculated curve corresponding to the value of $K_{eq} = 5 \times 10^4\,M^{-1}$. The equilibrium constants of (**2b**)-Mg^{2+} complex was found to be $5 \times 10^5\,M^{-1}$.

Photochemistry of chromenes

For crown-containing chromenes and their crownless analogs two types of photochemical reactions were found. First, the continuous irradiation in the region of 313 nm leads to small changes in the UV spectra. An example of these changes for **1b** is shown in Fig. 5. According to NMR data, this reaction is irreversible *cis–trans* isomerization of the closed form. As a result, *cis*-form of chromene in the mixture is completely transformed to *trans*-form.

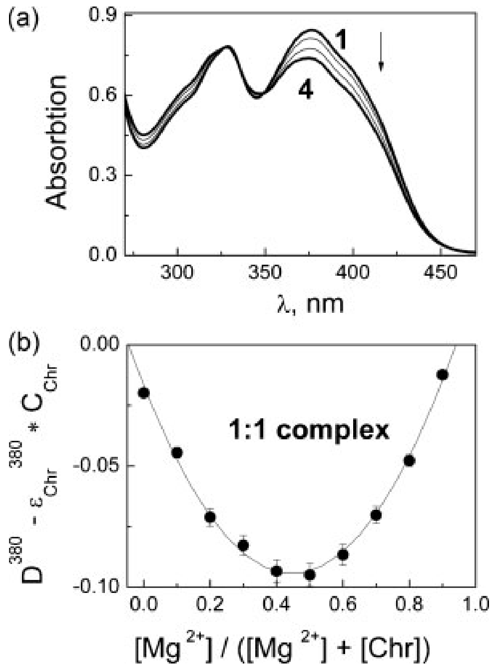
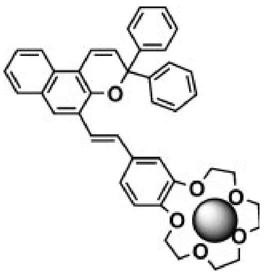


Figure 3. Complex formation between chromene **2b** and Mg^{2+}. (a) changes in the UV spectra. Cuvette 1 cm, 1×10^{-4} M of chromene in CH_3CN, curves 1–4 correspond to 0; 2×10^{-4}; 4×10^{-4}, and 5×10^{-4} M of $Mg(ClO_4)_2$. (b) Job's plot. The sum of concentrations of chromene and Mg^{2+} is 1×10^{-4} M

The photochemical reaction of the second type is the formation of an open form. Irradiation of the closed form of chromenes leads to the formation of absorption band in the region of 450 nm. Figure 6a demonstrates photochemical formation and thermal decay of this absorption for **1b**. This electrocyclic reaction is characteristic for all the chromenes being responsible for their photochromism. The photochemical reactions of both first and second type are shown in Scheme 6.

The electrocyclic reaction is thermally reversible. The characteristic time of the thermal reaction B → A for all the studied chromenes is about tens of seconds at the room temperature. The kinetic curves (Fig. 6b) of the reverse reactions are well fitted by a first order kinetic curve. Arrhenius parameters of the reverse reaction are collected in Table 1. The values of activation energies are always *ca.* 15 kCal $mole^{-1}$, which is typical for all the spirocompounds.[38]

The effect of metal cations on the properties of the open form of chromenes was expected. For example, in the case of spironaphtooxazines the complex formation between an open form of spiro-compound and metal cation affected both spectrum and lifetime of an open form.[17] Moreover, the effects were observed for both crown-containing and crownless spirooxazines. In all cases, the reason of the effects was the complex formation between open form of a spirooxazine and metal cation. Complexes were formed due to the Coulomb interaction between the charge of metal cation and the partial charges (both negative and positive) located on the heteroatoms



Scheme 5.

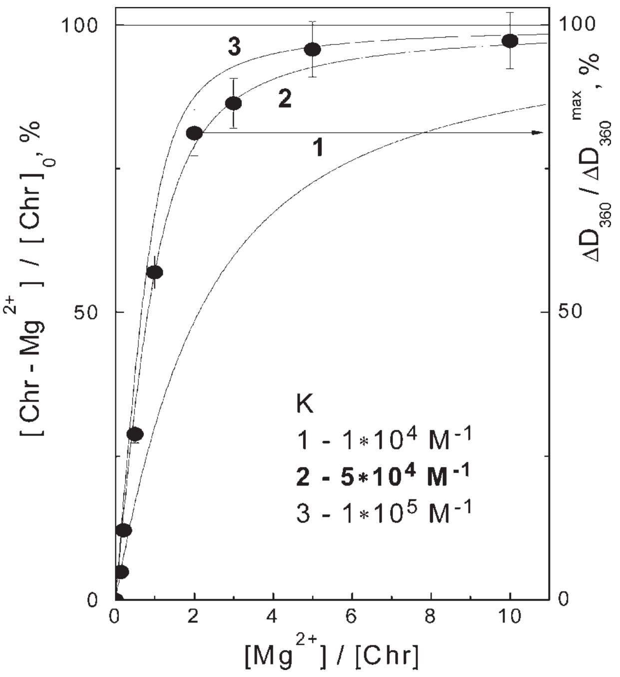


Figure 4. Determination of equilibrium constant of the (**1b**)-Mg^{2+} complex. Relative changes in absorption at 360 nm (dots, right axis) and calculated values of the (**1b**)-Mg^{2+} complex percentage (left axis) *versus* [Mg^{2+}] to [**1b**] ratio. Concentration of chromene is 6.2×10^{-5} M. Curves 1–3 denote to equilibrium constants 1×10^4, 5×10^4, and 1×10^5 M^{-1}

(nitrogen and oxygen) of the open form of the spirooxazine.[17] Earlier the formation of weak complexes between Ca^{2+} cations and merocyanine form of a chromene was found for 3,3-diphenyl-3H-benzo[f]chromenes containing a dimethylamino group.[18]

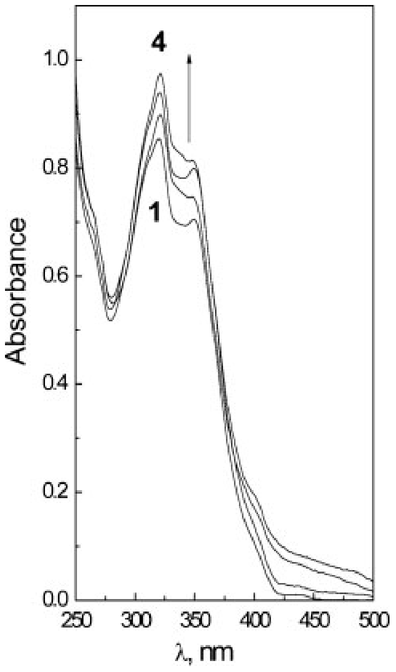


Figure 5. *Cis–trans* isomerization of chromene **1b** in CH_3CN. Changes in the UV spectrum. Cuvette 1 cm, concentration 4.5×10^{-5} M, irradiation at 313 nm. Curves 1–4 correspond to 0; 1; 6; 9 min of irradiation

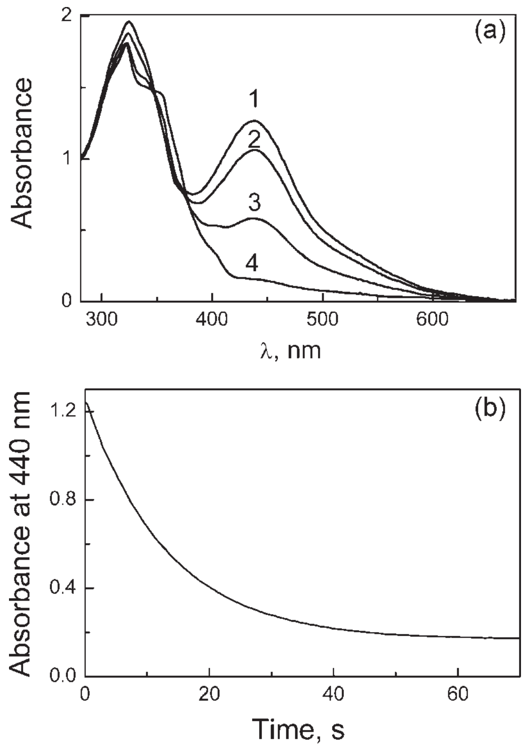
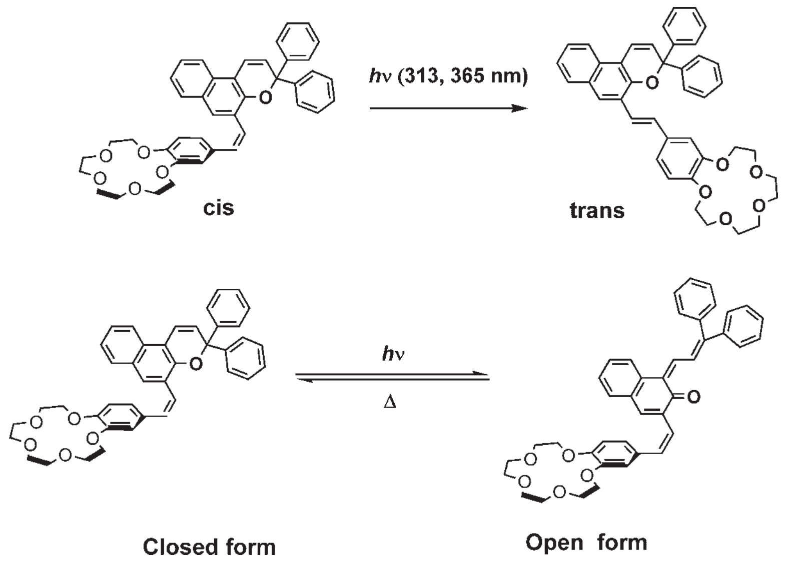


Figure 6. Thermal transition of open form to closed form (temperature 295 K). **1b** in CH_3CN (7.4×10^{-5} M, cuvette 1 cm). (a) changes in the UV spectra. Curve 1: spectrum after 5 s irradiation at 355 nm. Curves 2–4 correspond to 2, 12, and 80 s in dark. (b) kinetic curve of the dark reaction monitored at 440 nm

Nevertheless, in our case the effect of metal cations on the spectral and kinetic properties of an open form was not observed. For crownless chromene **1a** addition of Mg^{2+} up to 8000-fold extent does not shift the position of maximum of the open form absorption band. No influence of metal cations on the lifetime of an open form was observed. It should be noted that the coordination of Mg^{2+} cation to merocyanine oxygen atom with the formation of **1a**-Mg^{2+} complex seems to be essential. The structure of this possible complex (for *cis*-isomer of the open form) is shown in Scheme 7a. The absence of cation effects on both spectrum and lifetime of the open form makes the formation of this complex in our experiments unlikely. Two possible explanations of this fact are given below. The first explanation is based on the kinetic reasons. One can assume that the lifetime of the open form (*ca.* 30 s) is less than the characteristic time of the **1a**-Mg^{2+} complex formation. Second explanation is based on the electronic structure of the open form. It could be assumed that the electron density on oxygen carbonyl atom is low for coordination with Mg^{2+} cations.

For crown-containing chromenes **1b** and **2b** the effect of Mg^{2+} cations on the properties of the open form was not observed up to the great (*ca.* 8000-fold) extent of metal cations. The absence of cation effect on the photochromic properties is probably explained by the peculiarities of the structure of the open form. The effect of the metal cation situated in the crown ether cavity on the properties of the open form (Scheme 7b) could be explained by the Coulomb interaction between the cation and partly charged oxygen atom of the merocyanine form.[17] In our case, the distance between Mg^{2+} and $O^{\delta-}$ is *ca.* 8 Å. This distance



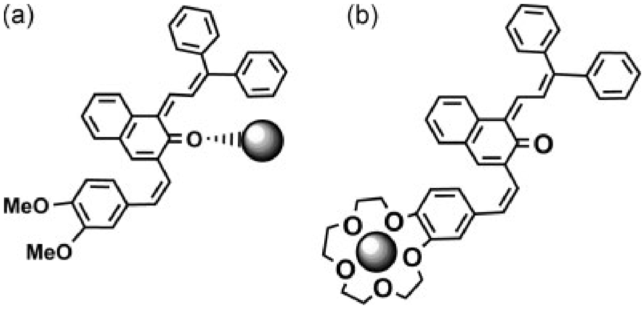
Scheme 6.

is too large for the Coulomb attraction to be effective. As a result, no effect of metal cation on the stability of the open form is observed. When Mg^{2+} cations are taken in a great extent, the possible coordination of second metal cation to merocyanine oxygen atom is not observed due to reasons listed above (either (i) the rate constant of **1b**-Mg^{2+} and **2b**-Mg^{2+} complexes formation is less than the rate constant of their transformation to the open form or (ii) the electron density on oxygen carbonyl atom is low).

Additional explanation of the absence of metal cation effects is possible for *cis*-form of chromenes. The open form of *cis*-isomer probably has non-planar geometry with hindered π-conjugation between styryl fragment and chromene unit. The effect can be attributed to the large size of the benzocrown ether fragment. If the conjugation between the chromene unit and styryl fragment in the open form of chromene is markedly violated, the formation of complexes through the binding of metal cations with crown ether moiety should not affect on the spectral and kinetic properties of the open form.

Table 1. Arrhenius parameters of dark reaction (open form) → (closed form) for chromenes. $k = A \times \exp(-E_{act}/RT)$

Chromene	A, s^{-1}	E_{act}, kCal $mole^{-1}$	k (298 K), s^{-1}
1a	4.2×10^{10}	16 ± 1	0.071
1b	7.1×10^{9}	15 ± 1	0.065
2a	4.1×10^{10}	16 ± 1	0.069
2b	7.7×10^{9}	15 ± 1	0.070



Scheme 7.

CONCLUSIONS

The synthesized crownless and crown-containing chromenes are interesting due to rather complicated photochemistry. Two types of photochemical reactions were found. Occurrence of *cis–trans* isomerization upon the irradiation at 313 and 365 nm light is a characteristic peculiarity of these chromenes. Second type of photochemical reaction is the formation of open form which determines the photochromic behavior of spirocompounds. Complexation of crown-containing chromenes with metal cations was found not to effect on photochromic properties, which is quite unusual. To elucidate this, the study of primary photochemical processes in femtosecond time domain should be necessary.

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