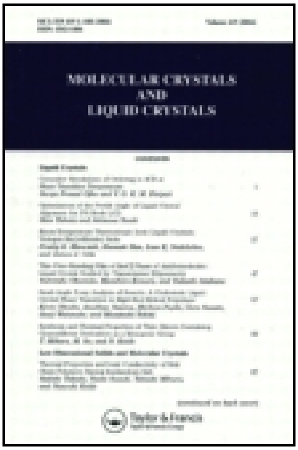

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Investigation of the Azacrown-Ether Substituted Naphtopyranes

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Investigation of the Azacrown-Ether Substituted Naphtopyranes

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The study of the complexation of 3,3-diphenyl-3H-benzo[f]chromenes containing an aza-15-crown-5-ether or morpholine units with Mg^{2+}, Ba^{2+} *and* Pb^{2+} *in acetonitrile are reported. The spectroscopic and kinetic behaviour of the photomerocyanine isomers of these chromenes is strongly affected by complexation with metal cations. In order to interpret the experimental data, a formation of anion-"capped" complexes was supposed.*

Keywords: anion-"capped" complex; aza-18-crown-6 ether; complex formation; 3,3-diphenyl-3*H*-benzo[*f*]chromene; photochromic behaviour

INTRODUCTION

Photochromic compounds have received great interest in the last years due to their application such as ophthalmic lens, transparencies, plastic films, promising materials for the information imaging and

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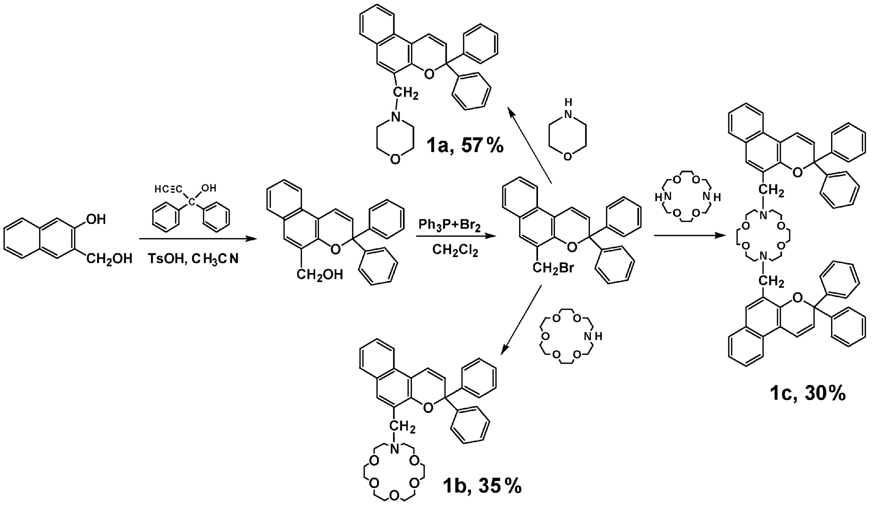
storage, etc [1]. The development of these photochromic systems is aimed at the improved photostability, to obtain higher sensitivity, a wide choice of operating wavelengths and amplification capability. Incorporation of a crown ether moiety which is able to bind metal ions into the naphthopyrans skeleton can be explored to tune the photochromic properties by using complexing process [2].

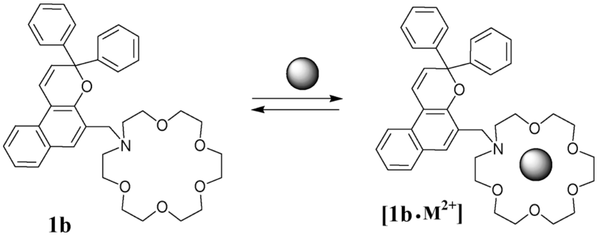
RESULTS AND DISCUSSION

Here we present the results of the spectral and kinetic investigations of the benzochromenes **1a–c** and their complexes with Mg^{2+}, $Ba^{2+}$and Pb^{2+}. The compounds were synthesized according to the three-step procedure [3,4] represented in Scheme 1. The structures attributed to **1a–c** were confirmed by ^{1}H NMR spectroscopy data, mass-spectrometry and elemental analysis (see Experimental part).

Compounds **1a–c** in MeCN exhibited very similar UV/Vis absorption spectra. The addition of Mg^{2+}, Ba^{2+} and Pb^{2+} cations to a solution of **1b,c** led to the small hypsothochromic shift up to 5–10 nm of the long wavelength band, indicating that metal cation is bound by the macrocyclic unit of **1b,c** (Scheme 2). In contrast, the absorption spectrum of **1a** was affected only at a high metal cation concentration (0.1 mol dm^{-3}).



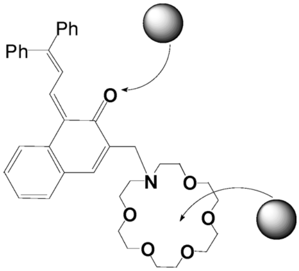
SCHEME 1



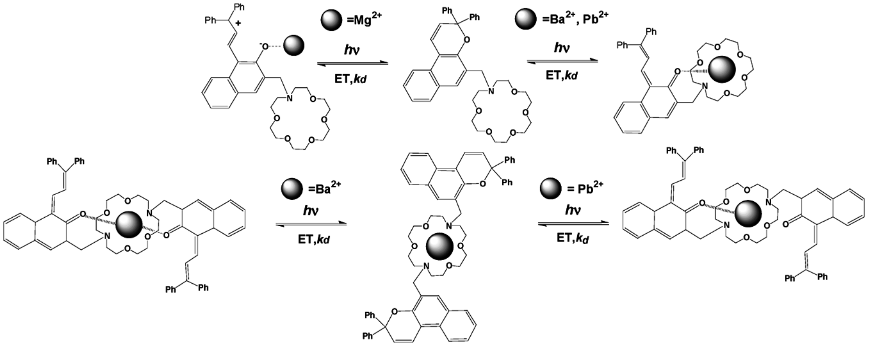
SCHEME 2

UV irradiation of **1a–c** in MeCN resulted in the appearance of a broad absorption band in the visible region, which was assigned to the merocyanine isomer. The dark ring-closure reaction for merocyanine isomer of **1a–c** occurred with a rate constant k_d of about 0.11–0.14 s^{-1} and resulted in the initial chromene. The presence of the metal cations in the solution of photomerocyane form led to a significant change in the dark lifetime of photomerocyanines **1a–c** and caused strong shifts in their absorption spectra, indicating that these compounds were able to bind metal cations (Fig. 1, Table 1).

In the merocyanine form of benzochromenes **1a–c** there are two places for the coordination of metal cations: crown ether fragment (or heteroatoms of nmorpholine residue) and carbonyl oxygen atom [5].



The small changes of $k_\mathrm{d}/\mathrm{s}^{-1}$ observed for the **1a** in the presence of Ba^{2+}, Pb^{2+}cations at relationship ligand:metal cation = 1:1 indicates that in this condition the concentration of complex between **1a** and metal cations is insignificant. The formation of a 1:1 complex between open form of **1a–c** and Mg^{2+} leads to an increase in the rate constant for the dark ring-closure reaction of **1a–c** (Scheme 2). The effect does not depend on the presence of crown ether fragment in molecule. The Mg^{2+} ion is not able to the effective coordination with crown ether fragment, because it has got the cation radii substantially smaller then size of 18-crown-6 ether cavity. Otherwise, the Mg^{2+} cation can



SCHEME 2 (Continued).

bind with carbonyl oxygen atom due to high charge density. The results of the formation of Mg–O coordination should lead to the increase of the polarity of molecule (Scheme 2). In the polar form the dark ring –closure reaction will occur more easily.

The formation of a 1:1 complex between open form of **1b,c** and Ba^{2+}, Pb^{2+} leads to a large bathosochromic effect and the decrease in the rate constant for dark ring-closure reaction. The effect is explained the formation of the anion-"capped" complex of metal cation located

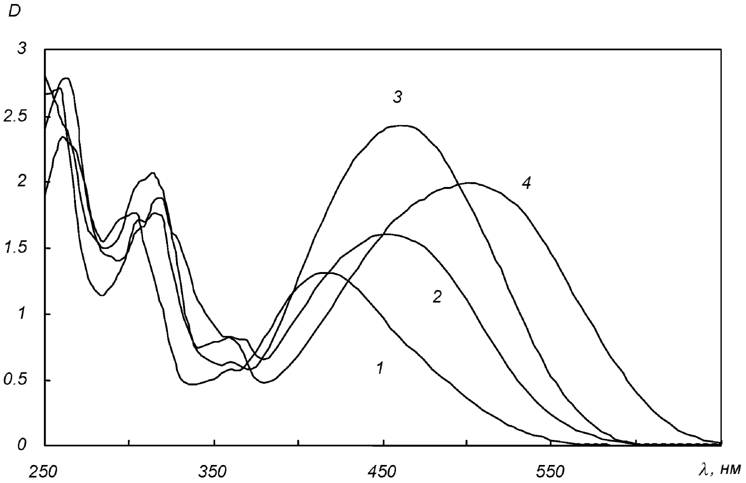


FIGURE 1 UV/V is spectrum of **1b** in acetonitrile (1) free **1b**; (2) in the presence of $Mg(ClO_4)_2$; (3) in the presence of $Ba(ClO_4)_2$; (4) in the presence of $Pb(ClO_4)_2$, prepared by irradiation of solution with light at 365 nm; $[C_L] = [C_M{}^{2+}] = 2 \cdot 10^{-4}$ m/l.

TABLE 1 Effect of the Mg^{2+}, Ba^{2+} and Pb^{2+} Presence on the Rate Constant k_d/s^{-1} of Dark Ring-Closure Reaction, Relationship Ligand:Metal Cations = 1:1

	—	Mg^{2+}	Ba^{2+}	Pb^{2+}
1a	0.11	0.44	0.18	0.12
1b	0.11	0.49	**0.0016**	**0.00035**
1c	0.15	0.19	**0.00034**	**0.00054**

in crown ether cavity with carbonyl oxygen atom (Scheme 2). The effect depends on the nature of metal cations; in case of **1b**, it is larger for Pb^{2+} then for Ba^{2+}. Substantial difference in the changes of magnitude of k_d/s^{-1} (Table 1) was obtained for the complexes of mono- and bischromene **1b,c** with Ba^{2+}. The difference is due to in the complex of **1c** with Ba^{2+} the carbonyl atoms of both chomene units participate in the formation of anion-“capped” complex, whereas, the anion- “capped” complex between **1b** and Ba^{2+} is formed by formation of one coordination bond (Scheme 2). In contrast, for the complexes of mono- (**1b**) and bischromenes (**1c**) with Pb^{2+} the magnitudes of k_d/s^{-1} are closed to each other, what means the participation of only one chromene unit of **1c** in the formation of anion- “capped” complex with Pb^{2+} (Scheme 2).

Thus, the study demonstrates that the spectroscopic and kinetic behaviour of the photomerocyanine isomers of the chromenes **1a–c** is strongly affected by complexation with metal cations. In the photomerocyanine form of compounds **1b,c** the formation of anion-“capped” complexes with Ba^{2+} and Pb^{2+} was found.

EXPERIMENTAL

General Remarks

^1H NMR spectra were recorded on Bruker DRX-500 spectrometer (working frequency 500.13 MHz, 25°C) using TMS as an internal standard and $CDCl_3$ as a solvent. The chemical shifts and the spin-spin coupling constants were determined with an accuracy of 0.01 ppm and 0.1 Hz, respectively. Mass spectra were obtained using a Varian MAT 311 A instrument with an ionisation energy of 70 eV. 5-Bromomethylchromene was prepared according [3], 16-(3,3-diphenyl-3H-benzo[f]chromen-5-ylmethyl)-1,4,7,10,13-pentaoxa-16-aza-cyclooctadecane (**1b**) was obtained according [4], aza-18-crown-6 and diaza-18-crown-6 ethers and morpholine were used as received.

Synthesis of Chromenes. General Procedure

Under nitrogen, aza-substituted crown ether or morpholine (0.2 mmol), 5-bromomethylchromene (80 mg, 0.2 mmol, for diaza-crown ether: 160 mg, 0.4 mmol), triethylamine (60 mg, 0.6 mmol, for diaza-crown ether: 120 mg, 1.2 mmol), and dry THF (25 mL) were placed into a three-necked flask, and the reaction mixture was refluxed for 6 h. The product obtained by solvent evaporation was purified by column chromatography on SiO_2, eluent benzen-MeOH (10:1) or CH_2Cl_2-MeOH (9:1).

4-(3,3-Diphenyl-3H-Benzo[f]Chromen-5-ylmethyl)-Morpholine (1a)

Yield 57%; mp 150–152°C; ^1H NMR (DMSO-d_3): $\delta = 3.3$ (m, 4 H, NCH_2), 3.62 (m, 4 H, OCH_2), 3.74 (s, 2 H, $PhCH_2$), 6.61 (d, $J = 9.7$ Hz, 1 H, CH=), 7.24 (m, 2 H, ArH), 7.34 (m, 5 H, ArH), 7.47 (m, 2 H, ArH, CH=), 7.6 (m, 4 H, ArH), 7.75 (s, 1 H, ArH), 7.8 (d, $J = 8.0$ Hz, 1 H, ArH), 8.06 (d, $J = 8.5$ Hz, 1 H, ArH) ppm. MS: $m/z = 433$ $[M^+]$ (22%), 348 (37%), 266 (100%), 191 (33%), 165 (23%), 115 (22%), 103 (26%), 87 (65%), 69 (51%), 55 (67%). $C_{30}H_{27}NO_2$: calcd. C 83.11, H 6.28, N 3.23; found C 83.18, H 6.32, N 3.19.

7,16-Bis-(3,3-Diphenyl-3H-Benzo[f]Chromen-5-ylmethyl)-1,4,10,13-Tetraoxa-7,16-Diaza-Cyclooctadecane (1c)

Yield 30%; mp 178–182°C; ^1H NMR: $\delta = 2.95$ (t, $J = 5.8$ Hz, 8 H, NCH_2), 3.58 (s, 8 H, OCH_2), 3.67 (t, $J = 5.8$ Hz, 8 H, OCH_2), 3.98 (s, 2 H, $PhCH_2$), 6.25 (d, $J = 10.1$ Hz, 1 H, CH=), 7.25 (m, 2 H, ArH), 7.31–7.37 (m, 6 H, ArH, CH=), 7.44 (m, 1 H, ArH), 7.55 (m, 4 H, ArH), 7.74 (d, $J = 7.8$ Hz, 1 H, ArH), 7.85 (s, 1 H, ArH), 7.95 (d, $J = 8.4$ Hz, 1 H, ArH) ppm. $C_{64}H_{62}N_2O_6$-$2H_2O$: calcd. C 77.55, H 6.71, N 2.83; found C 77.48, H 6.55, N 2.69.

UV/Vis Spectroscopy and Kinetic Measurements

UV/Vis absorption spectra were recorded with a Specord “USB2000” of “Ocean Optics” and a Specord “Cary 50”. The dark lifetimes of photomerocyanines of **1a–c** were measured using an experimental setup with a mercury flash lamp. The time resolution was less than 1 ms. The photostationary absorption spectra of merocyanine isomers were measured with the same setup upon steady-state irradiation of solutions with glass-filtered 365 nm light of a DRSh-250 high-pressure mercury lamp. The range of scanning was 400–750 nm with 1 nm increment.

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