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Photochromic and Cation-Binding Properties of New Crowned Spiropyrans

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Spectral properties of new crowned spiropyrans and their cationic complexes are described.

Keywords: benzocrown ethers; crowned spiropyrans; ionophore; spectral data

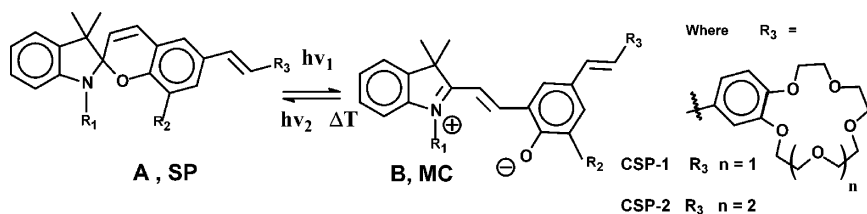
INTRODUCTION

The photochromic properties of spiropyrans (SPs) have been extensively studied due to their potential applications in high-density

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optical data storage and non-linear optical devices [1] as well as photo-switchable molecular receptors [1,2]. Most of the previous studies have been focused on the derivatives having a strong electron-withdrawing substituent, such as nitro group at the 6'-position of SP, so as to increase the life-time of the photoinduced coloured merocyanine (MC) form, whereas much less attention has been paid to SP derivatives, which lack a strong electron withdrawing substituent in the benzopyran ring [2,3]. Our research is devoted to the investigation of photochromic properties of the SP molecules, which possess the ionophoric moiety for effective cation binding.



In this paper, we describe the synthesis and properties of a series of new crowned SPs with different macroheterocycle size (**CSP-1** and **CSP-2**, where $R_1 = \text{CH}_3$, $R_2 = \text{H}$ and R_3 is an ionophore residue). The molecules contained either of two crown-ether ionophores (mono-benzo-5(6)-crown-15(18)), which was bound via a C=C-spacer to the 6'-position of the pyran moiety instead of the nitro group.

EXPERIMENTAL

The spectral - kinetic study of CSPs was conducted in acetonitrile solutions ($C \approx 2 \cdot 10^{-4} \text{ M}$). The electronic spectra of samples were measured on a Cary-50 spectrophotometer (Varian), and the kinetic curves of photoinduced and spontaneous change of solution optical density were recorded on the special kinetic set-up. The photochemical transformations were carried out under filtered radiation of the SVD-120 or DRSH-250 mercury lamps using the standard glass light filters.

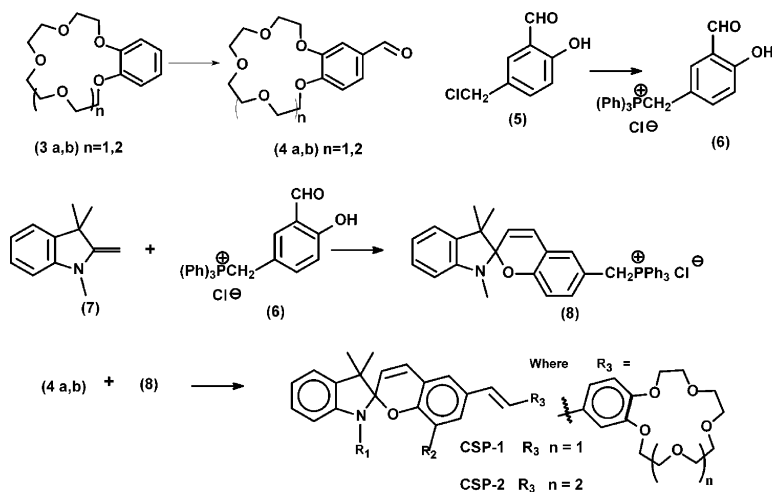
RESULTS AND DISCUSSION

Synthesis

Thus far, most studies have been focused on the design of approaches for introducing an ionophore fragment, either at the

6-position, or at the N atom of the indoline cycle, or at the 8'-position of the benzopyrane ring of CSPs containing monoazacrown ether or 15-crown-5 ether moieties [2]. In our case, the ionophoric group was attached to the 6'-position of the pyran moiety via C=C-spacer. We proposed a new effective approach to ionophore introduction into the SP molecule involving the Wittig olefination of 4'-formyl-crowns (**4 a,b**) with the ylide, generated from phosphonium salt (**8**) under phase transfer catalysis conditions (see Scheme 1). The starting compounds (**4 a,b**) were obtained by Duff formylation of benzo-15-crown-5 or benzo-18-crown-6, as described previously [4]. Phosphonium salt (**8**) was prepared with 80% yield by condensation of Fischer's base (**7**) with correspondent salicylaldehyde derivative (**6**) [5].

The key reaction used to prepare **CSP-1**, **CSP-2** consists in the Wittig olefination of 4'-formyl-crowns (**4 a,b**) with the ylide, generated from triphenylphosphonium salt (**8**) under phase-transfer catalysis conditions (CH_2Cl_2 , K_2CO_3 , 18-crown-6, 3–5 days), which were developed in our earlier study [6]. It was found that the Wittig olefination follows preferably *E*-selectivity for the newly formed bond and gives moderate yields of products. The pure *E*-isomers were obtained by column chromatography and recrystallization. The structure of all compounds was confirmed unambiguously by IR; UV; ^1H NMR-spectroscopy and mass-spectrometry.



SCHEME 1

Photochromic Properties

Earlier, it was shown using pulse irradiation that SPs without electron-withdrawing substituents undergo photochromic transformations between initial colorless spiroform (A, SP) and photoinduced coloured merocyanine forms (B, MC) due to fast relaxation of the photoinduced MC form at room temperature ($k = 11,5 \text{ s}^{-1}$ in cyclohexane [3]). A spectral - kinetic study of CSPs has shown that they display photochromic properties in contrast to the unsubstituted derivatives (Fig. 1).

It can be seen from Figure 1 that the initial **CSP-1** acetonitrile solution is already coloured as a result of partial shift of the equilibrium toward the MC form taking place in the dark. Successive exposure of solution to the UV- and visible filtered light of a SVD-120 mercury lamp induces interconversion of the two forms ($\text{SP} \leftrightarrow \text{MC}$) of the photochromic compound. The λ_{max} value for the absorption band of the photoinduced MC form equals 470 nm. The thermal bleaching proceeds extremely slowly (Fig. 2), in contrast to that in unsubstituted SPs. This can be explained by the effect of the electronic and steric factors of the crown macroheterocycle.

The similar properties are detected for the **CSP-2** compound. The related spectral changes are observed upon the introduction of La^{+3} ions into a solution (Fig. 3). They are enhanced during storage of the sample solution in the dark. These observable spectral changes are caused by the gradual shift of equilibrium toward the MC form. As

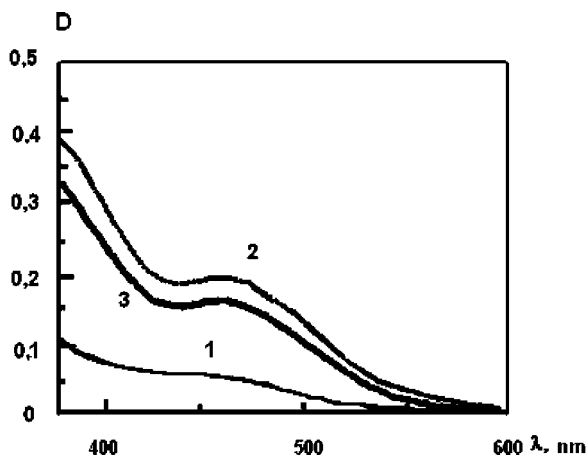


FIGURE 1 Absorption spectra of **CSP-1** in acetonitrile ($C \ 2 \cdot 10^{-4} \text{ M}$): before (1), and under UV- (2) and visible light (3).

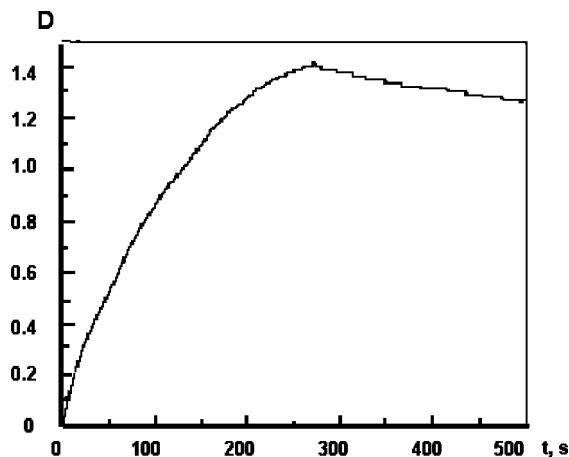


FIGURE 2 Kinetic curve of the photoinduced changes in the optical density of **CSP-1** in acetonitrile under UV-light of a DRSH-250 lamp and after switching-off illumination.

soon as the formation of the cation-ionophore complex has completed, the obtained solution no longer exhibit the photochromic properties. It can be explained by the strong electrostatic interaction between

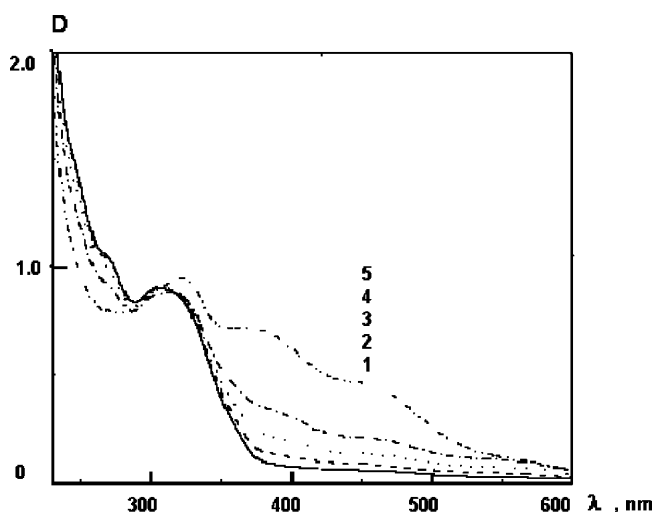


FIGURE 3 Absorption spectra of **CSP-1** in acetonitrile ($C \ 2 \cdot 10^{-4} \text{ M}$) measured: before (1), and within 5 (2), 20 (3), and 60 min (4), and 25 h 15 min (5) after the introduction of the La^{+3} salt, respectively. The concentration ratio $C_{\text{CSP-1}}/C_{\text{La}^{+3}} = 1:100$.

phenoxide ion of the MC form and La^{+3} /ionophore complex. The solution of the complex with low La^{+3} concentration partly retains its photochromic properties, due to the residual concentration of photochromic molecules not involved in complexation.

A comparative study of the complexation efficiency for **CSP-1** molecule with two metal ions has shown that this is somewhat higher for La^{+3} than for Mg^{+2} . **CSP-2** is slightly more effective than **CSP-1** as regards complexation with La^{+3} ions. This is due to the good match between the sizes of the interacting species. It was found that their stability against irreversible phototransformations increases after introduction of Mg^{+2} ions into solution about the concentration ratio $C_{\text{CSP-1}}/C_{\text{Mg}^{+2}} = 1:10$ (Fig. 4.). Probably, it is a sequent of high light resistance of coloured non-photochromic complexes.

CONCLUSIONS

An effective synthetic approach to CSPs containing an ionophoric group linked to the 6'-position of pyran moiety via a C=C-spacer was proposed.

Photochromic properties of the SP molecules with the ionophoric fragment at the $\text{C}_{6'}$ – position of the pyran ring were detected at room temperature, being due to retardation of thermal relaxation rate of the MC form.

It was shown for the CSPs, that after completion of the cation-ionophore complex formation, the resulting samples do not exhibit

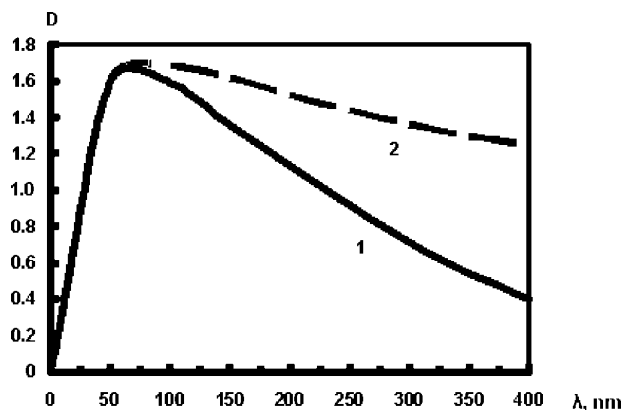


FIGURE 4 Kinetic curves of optical density changes of photocoloration and photodegradation processes of **CSP-1** in acetonitrile: without (1) and in the presence of a Mg^{+2} salt (2). Concentration ratio: $C_{\text{CSP-1}}/C_{\text{Mg}^{+2}} = 1:10$.

photochromic properties. The absorption spectra of these non-photochromic species were almost identical to those of photoinduced MC form solutions without addition of metal salts. Also, solutions of these species were found to exhibit higher stability against irreversible photochemical transformations. It was found that at low metal ion concentrations, the photochromic properties are partly retained due to the residual concentration of photochromic molecules not involved in the complexation process.

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