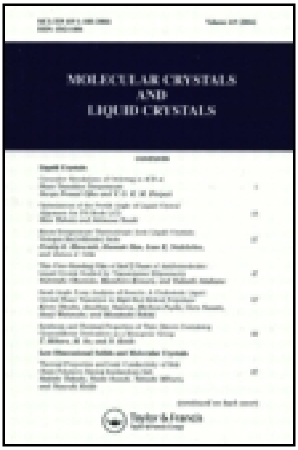

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Lithium-Ion Facilitated Photoisomerization of Spirobenzothiapyran Derivative Incorporating a Monoaza-12-Crown-4 Moiety

Mutsuo Tanaka [a], Kenji Kamada [a] & Keiichi Kimura [b]

[a] Osaka National Research Institute, AIST, 1-8-13, Midorigaoka, Ikeda, Osaka, 563-8577, Japan

[b] Department of Applied Chemistry, Faculty of Systems Engineering, Wakayama University, Sakaedani 930, Wakayama, 640-8510, Japan

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MUTSUO TANAKA[a], KENJI KAMADA[a] and KEIICHI KIMURA[b]

[a]*Osaka National Research Institute, AIST, 1–8–13, Midorigaoka, Ikeda, Osaka 563–8577, Japan and* [b]*Department of Applied Chemistry, Faculty of Systems Engineering, Wakayama University, Sakae-dani 930, Wakayama 640–8510, Japan*

A spirobenzothiapyran derivative bearing a monoaza-12-crown-4 moiety shows remarkable stabilization of its photoinduced colored isomer (merocyanine form) by complexation of a metal ion, especially Li^+ and Ag^+. Comparison of the crowned spirobenzothiapyran with its corresponding spirobenzopyran derivative indicates that the stabilization of the merocyanine form in the presence of Li^+ and Ag^+ are derived mainly from the metal-ion complexing ability of its crown ether moiety and the metal-ion affinity of its merocyanine thiophenolate anion, respectively.

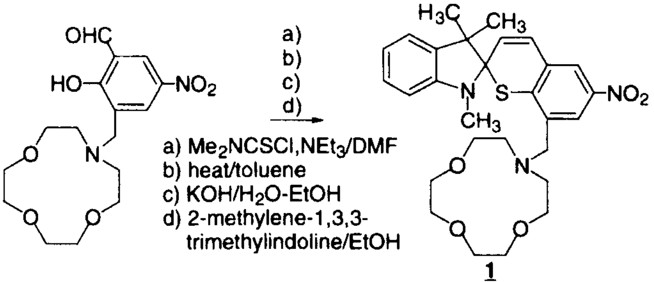
Keywords: spirobenzothiapyran; crown ether; metal-ion complexation; photoisomerization; enhanced stability of open colored form

INTRODUCTION

Spirobenzopyrans and spirobenzothiapyrans are well-known photochromic compounds, which isomerize to their corresponding merocyanine forms by UV light, and *vice versa* by visible light or heat.[1] Such kinds of compounds have been studied extensively for applications to photochromic devices. Incorporation of a crown ether moiety to a spirobenzopyran skeleton has been found to facilitate the spiropyran-ring opening by the metal-ion complexation of the crown ether moiety.[2] In our preliminary study, [3] we have reported that a spirobenzothiapyran bearing a monoaza-12-crown-4 moiety (crowned spirobenzothiapyran) shows a similar behavior in the thiapyran-ring opening of crowned spirobenzopyrans. In this paper, we discuss in details about the metal-ion-induced stabilization of the open colored form in the crowned spirobenzothiapyran, which is compared with its corresponding spirobenzopyran derivative.

RESULTS AND DISCUSSION

The synthesis of crowned spirobenzothiapyran **1** was accomplished as follows.[3]



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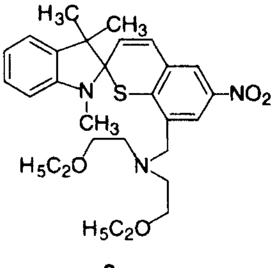

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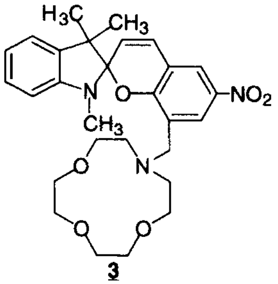

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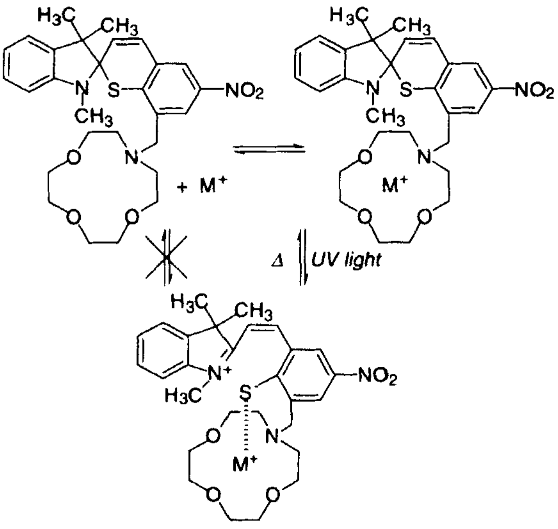
For comparison, a spirobenzothiapyran derivative bearing an oligooxyethylene moiety, **2**, was synthesized in a similar way to **1**, and a crowned spirobenzopyran, **3**, was prepared according to a previously reported method.[2a,b] Absorption spectra of **1**, **2**, and **3** were measured in acetonitrile (2×10^{-4} M for **1** and **2**, 1×10^{-4} M for **3**; under dark conditions, at room temperature) in the presence and absence of a metal ion, which was added as a perchlorate of Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} or a nitrate for Ag^+, Pb^{2+}, Tl^+, Hg^+, Cu^{2+}, and Zn^{2+}. Similarly, absorption spectra were measured on irradiation of 365-nm UV light.[3]

Under dark conditions, the absorption spectra of **1** and **2** solutions were hardly changed on addition of an equimolar amount of metal ions, except Hg^+, Cu^{2+}, and Zn^{2+}, which prevented reversible photochromism of the spirobenzothiapyran derivative. Only a slight color change for the both solutions was observed on addition of alkaline-earth metal ions and Ag^+ (even after one day). On the other hand, the spectra of **3** showed a drastic change with Li^+, alkaline-earth metal ions, Pb^{2+}, and Tl^+. This means that the isomerization of **1** to its merocyanine form by the thiapyran-ring opening cannot be induced simply by the metal-ion complexation of its crown-ether ring under dark conditions. The



isomerization behavior of 1 is very different from that of 3, the pyran ring of which can be opened readily by metal-ion complexation even under dark conditions, probably due to the polarity increase induced by the metal-ion binding.

The irradiation of 365-nm UV light on the 1 solution containing Li^+ (FIGURE 1) and Ag^+ (FIGURE 2) caused a drastic change in the absorption spectra. Such a drastic spectral change was also observed in the 2 solution with Ag^+ (FIGURE 3), but not with Li^+. On the contrary, the solution of 3 showed a significant spectral change with Li^+ but not with Ag^+ under dark conditions. These results indicate that the metal-ion complexing ability of the crown ether moiety of 1 to Li^+ stabilizes the merocyanine form. The stabilization of its merocyanine form in the presence of Ag^+ can, however, be attributed mainly to the affinity of the thiophenolate anion in the merocyanine form to Ag^+.

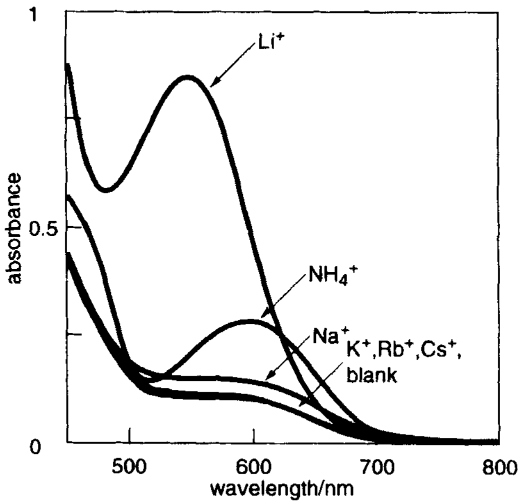


FIGURE 1. Absorption spectra of 1 with alkali-metal ions.

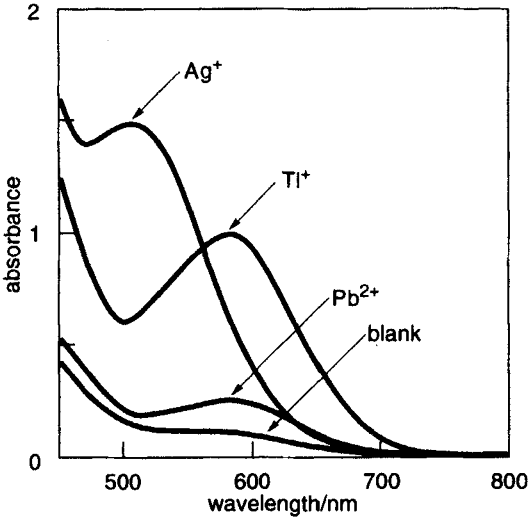


FIGURE 2. Absorption spectra of 1 with heavy metal ions.

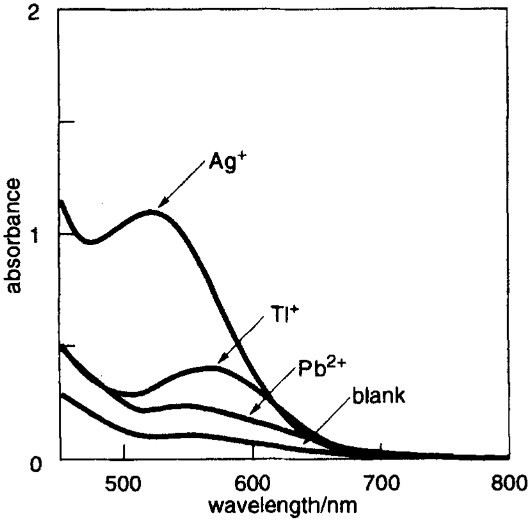


FIGURE 3. Absorption spectra of 2 with heavy metal ions.

In order to evaluate the thermal stability of the open colored merocyanine form of crowned spirobenzothiapyran **1** in acetonitrile, the first-order thermal decoloration rates were measured in the presence or absence of a metal ion, at room temperature after turning off UV light (TABLE 1). In the presence of Li^+ and Ag^+, the thermal isomerization back to the spirobenzothiapyran form proceeded very slowly as compared with other alkali and heavy metal ions, respectively. The results are consistent with the above-mentioned absorption-spectral data.

TABLE 1. Thermal decoloration rate constants. (10^{-2} s^{-1})

blank	1.6	Mg^{2+}	1.0	Ag^+	0.21
Li^+	0.46	Ca^{2+}	0.29	Pb^{2+}	1.5
Na^+	1.6	Sr^{2+}	0.43	Tl^+	0.38
K^+	1.7	Ba^{2+}	0.46	Hg^{2+}	-a)
Rb^+	1.8			Cu^{2+}	-a)
Cs^+	1.9			Zn^{2+}	-a)
NH_4^+	1.4				

a) not determined

Thus, in the crowned spirobenzothiapyran **1**, the stabilization of its photoinduced open colored isomer (merocyanine form) was enhanced by metal-ion complexing ability of the crown-ether moiety, especially to Li^+, and by the metal-ion affinity of the thiophenolate anion in the merocyanine form, especially to Ag^+.

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