

Syntheses, Cation Complexation, Isomerization and Photochemical Cation-binding Control of Spirobenzopyrans Carrying a Monoazacrown Moiety at the 8-Position

Keiichi Kimura,* Takashi Yamashita and Masaaki Yokoyama

Chemical Process Engineering, Faculty of Engineering, Osaka University, Yamada-oka, Suita, Osaka 565, Japan

Spirobenzopyran derivatives carrying a monoazacrown moiety, such as 12-crown-4, 15-crown-5, and 18-crown-6 moieties, and their acyclic analogue, at the 8-position have been synthesized. Alkali metal ion complexation by the crowned spirobenzopyrans, followed by isomerization to the corresponding merocyanine form, and their photoisomerization, have been studied by cation extraction, absorption spectroscopy, and NMR spectroscopy. Binding of alkali metal ions (Li^+ , Na^+ and K^+) by the crown moieties leads to isomerization of the crowned spirobenzopyrans even under dark conditions. ^7Li and ^{23}Na NMR spectroscopy suggest that in the merocyanine isomer complexing an alkali metal ion, especially Li^+ , the crown-complexed metal ion interacts intramolecularly with the phenolate anion, thus being bound more powerfully than that in the corresponding spiropyran isomer, owing to an additional-binding-site effect. UV-light irradiation in tetrahydrofuran further promotes the isomerization to the merocyanine form, the thermal stability of which depends significantly not only on the ion selectivities of their crown moieties but also on the ease of the intramolecular interaction between the crown-complexed metal ion and the phenolate anion. Under visible-light irradiation, the cation-bound merocyanine form readily reverts to the spiropyran form, releasing the metal ions to some extent. Alternating irradiation with UV and visible light or turning-on and -off of visible light, therefore, causes the isomerization of crowned spirobenzopyrans even in the presence of alkali metal ions, in turn affording control of their cation-complexing abilities.

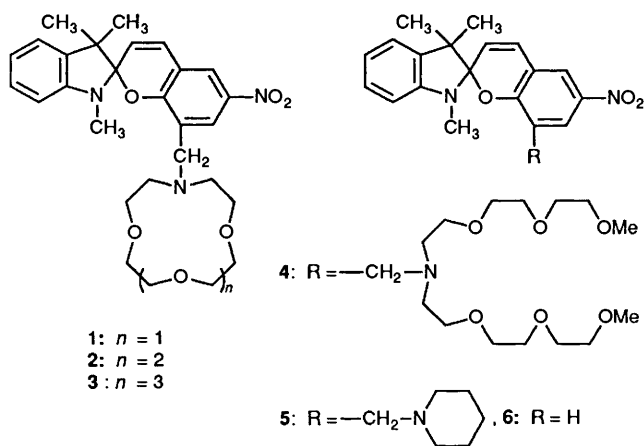
Since spirobenzopyran derivatives undergo reversible isomerization to the corresponding zwitterionic merocyanine form, extensive studies have been devoted to their applications to photochemical control of physical properties in solution. The examples are in photocontrol of membrane transport,^{1,2} membrane potentials,³⁻⁶ and polymer rheology.^{7,8}

Incorporation of a crown ether moiety, which is able to complex metal ions, into the spirobenzopyran skeleton can be expected to provide the parent spirobenzopyran with high functionalities. A few spirobenzopyran derivatives carrying a crown ether moiety at the 1'-position have been synthesized.^{9,10,11} In organic solutions of some of these crowned spirobenzopyrans, cation-induced isomerization was observed, owing to the occurrence of some polar circumstance in the periphery of the spirobenzopyran skeleton by cation binding of the crown moiety.^{9,10} In plasticized polymeric membranes containing one of the crowned spirobenzopyrans, its photo-induced membrane potential change was found to depend on the kind of alkali metal ion present in a measured solution, probably because of the cation-binding effect on the isomerization of its spirobenzopyran skeleton.¹¹

Crowned spirobenzopyrans have also been attractive to us. One of our interests is in photochemical control of cation binding. We have, therefore, designed spirobenzopyran derivatives incorporating a monoazacrown moiety at the 8-position, e.g. **1**, in which cation-binding enhancement can be expected on photoisomerization to their corresponding merocyanine form due to sterically-favourable cooperation of the resulting phenolate anion together with the crown moiety in the cation binding. Actually, a powerful interaction between the phenolate anion and crown-complexed metal ions, especially Li^+ , was found in the merocyanine isomer of **1**.¹²

This paper describes the details of the synthesis, alkali metal ion complexation and isomerization of the spirobenzopyran

derivatives carrying monoaza-12-crown-4, -15-crown-4, and -18-crown-6 moieties, and their acyclic analogue at the 8-position, **1-4**. Photochemical control in the cation binding of the crowned spirobenzopyrans is also discussed.



Results and Discussion

Synthesis of Crowned Spirobenzopyrans.—The syntheses of spirobenzopyran derivatives incorporating a monoazacrown moiety at the 8-position were based on the condensation of 1,3,3-trimethyl-2-methyleneindoline¹³ and a 5-nitrosalicylaldehyde possessing a monoazacrown moiety as shown in Scheme 1. The crowned nitrosalicylaldehydes were obtained by chloromethylation of 5-nitrosalicylaldehyde,¹⁴ followed by reaction with a monoazacrown ether¹⁵ in the presence of triethylamine. The condensation reaction to give crowned spirobenzopyrans was

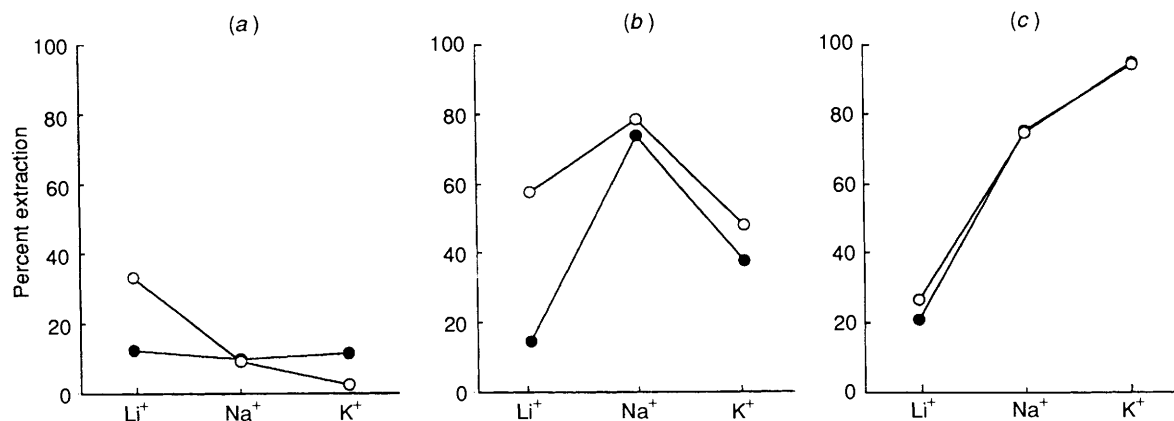
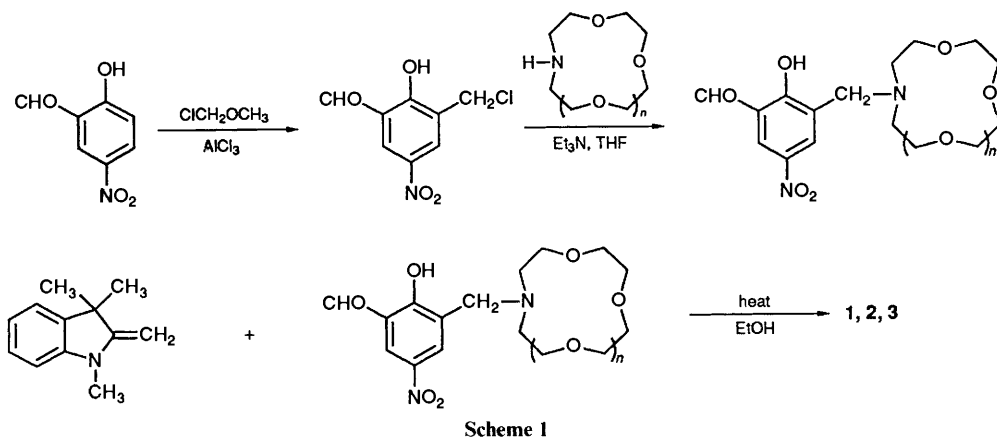


Fig. 1 Cation extraction by crowned spirobenzopyrans 1–3 and comparison with their corresponding model compounds, *N*-benzyl-monoazacrown ethers. Under dark conditions, (a) for monoaza-12-crown-4 systems; 1 (○); 7 (●), (b) for monoaza-15-crown-5 systems; 2 (○), 8 (●), (c) for monoaza-18-crown-6 systems; 3 (○); 9 (●).

performed in refluxing ethanol. Spirobenzopyrans of 12-crown-4 and 15-crown-5, 1 and 2, were off-white crystals, which were readily purified by recrystallization. On the other hand, the spirobenzopyran of 18-crown-6 (3) and acyclic analogue 4 were purified by repeated reversed-phase liquid chromatography to afford analytically pure products as dark-brown viscous liquids.

Cation Extraction Followed by Isomerization.—For estimating cation-complexing abilities of the resulting crowned spirobenzopyrans, 1–4, cation extraction was carried out from an aqueous alkali metal picrate solution with a crowned spirobenzopyran in 1,2-dichloroethane solution under dark conditions.¹⁶ As model compounds of the crowned spirobenzopyrans 1–4, their corresponding *N*-benzyl-monoazacrown ethers and acyclic analogue 7–10 were also employed for comparison in the cation extraction. The results are summarized in Fig. 1, where values of percent extraction are given as a measure of cation-complexing ability. The percent extractions for the systems containing 4 and its model compound 10 could not be determined due to significant loss of these compounds to the aqueous phase. The cation extractabilities for 1–3 reflect the cation-complexing abilities of their parent crown ethers, *i.e.* monoaza-12-crown-4, -15-crown-5, and -18-crown-6, respectively, the order of percent extraction being $\text{Li}^+ > \text{Na}^+ > \text{K}^+$ for 1, $\text{Na}^+ > \text{Li}^+ > \text{K}^+$ for 2, and $\text{K}^+ > \text{Na}^+ > \text{Li}^+$ for 3. Thus, the cation-complexing abilities and extractabilities of crowned spirobenzopyrans originate essentially from those for their corresponding crown moieties. Li^+ affinity is, however, enhanced in all of the crowned spirobenzopyrans compared with their corresponding *N*-benzyl monoazacrown ethers.

Drastic absorption-spectral changes were observed in the organic phase after the cation extraction by the crowned

spirobenzopyrans (Fig. 2). In the absorption spectra for the extraction systems of crowned spirobenzopyrans, a significant peak between 500 and 600 nm, which can be assigned to their corresponding merocyanine isomers (crowned merocyanines), was found, indicating that their isomerization is induced by the cation extraction, *i.e.* the cation complexation. Thus, cation complexation by the crown moiety makes the spirobenzopyran molecule more polar, promoting the formation of the corresponding zwitterionic merocyanine isomer. The order for absorbance of the merocyanine-based peak, which show the degree of isomerization of the crowned spirobenzopyrans, corresponds to that for cation extractability in the 1 system, but it does not necessarily do so in the 2 and 3 systems. The influence of the cation on the isomerization induced by cation extraction implies that alkali metal ions with relatively high charge densities, especially Li^+ , enhance the cation-induced isomerization of crowned spirobenzopyrans. Specifically, in the cation extraction system of 3, the complexation of Li^+ or Na^+ promotes its isomerization to the corresponding merocyanine form more strongly than does complexation of K^+ , despite the much higher extractability of the monoaza-18-crown-6 derivative for K^+ than for Na^+ and Li^+ .

Cation-induced Isomerization in a One-phase System.—Cation complexation-induced isomerization of the crowned spirobenzopyrans also occurred when an alkali metal ion was dissolved directly in an organic solution of a crowned spirobenzopyran under dark conditions. Fig. 3 depicts visible spectra for acetonitrile solutions containing equimolar amounts of a crowned spirobenzopyran and an alkali metal perchlorate. In the one-phase systems, the ' Li^+ effect' on the isomerization of crowned spirobenzopyrans was also remarkable, although the

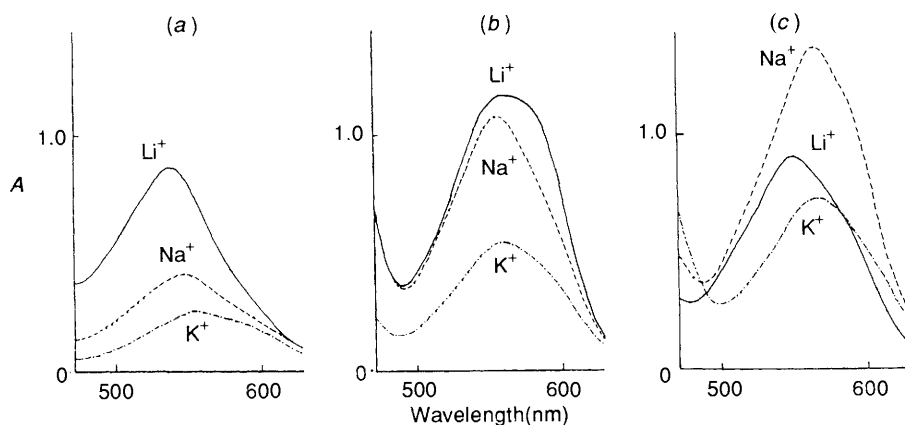


Fig. 2 Isomerization of crowned spirobenzopyrans in organic phase on cation extraction. Under dark conditions, (a) 1 system; (b) 2 system; (c) 3 system.

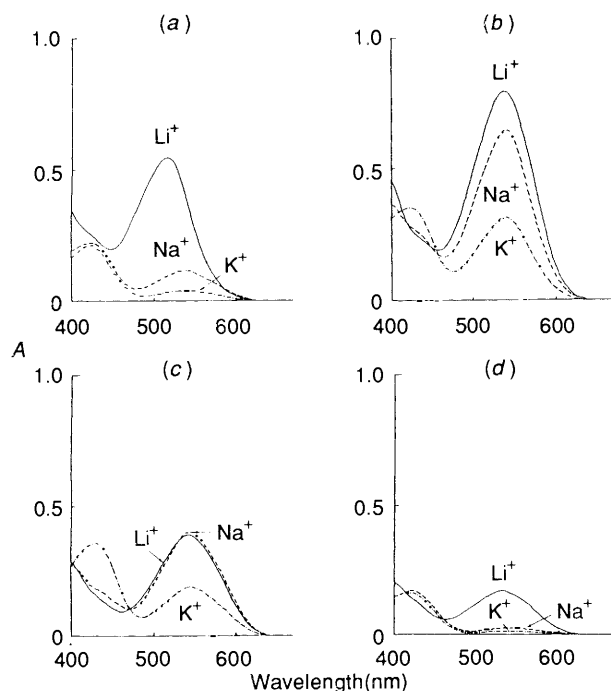


Fig. 3 Cation-induced isomerization of crowned spirobenzopyran in one-phase. Under dark conditions, [crowned spirobenzopyran] and $[\text{MClO}_4]$: $4 \times 10^{-5} \text{ mol dm}^{-3}$ in acetonitrile, (a) 1 system; (b) 2 system; (c) 3 system; (d) 4 system.

cation-binding selectivities of the crown moieties themselves, of course, contribute to the isomerization. Particularly in the **1** and **2** systems, Li^+ addition caused a pronounced absorption peak due to their corresponding merocyanine isomers (**1**: $\lambda_{\text{max}} = 514 \text{ nm}$, $\epsilon = 38\,500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$; **2**: $\lambda_{\text{max}} = 533 \text{ nm}$, $\epsilon = 37\,000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ in $0.019 \text{ mol dm}^{-3} \text{ LiClO}_4$ acetonitrile solution). Even in the acyclic analogue (**4**) system, Li^+ addition promoted the isomerization to its merocyanine form to some extent, while Na^+ and K^+ hardly showed any effect regarding the isomerization. In the systems of spirobenzopyran derivatives containing a piperidinomethyl group and no substituent at the 8-position, **5** and **6**, however, no significant isomerization could be detected spectrophotometrically on the addition of an equimolar amount of alkali metal salt under dark conditions.

^7Li NMR spectroscopy under dark conditions explains the Li^+ -enhancement effect on the isomerization of crowned spirobenzopyrans to their merocyanine form (Fig. 4). An LiClO_4 acetonitrile solution exhibited a peak based on acetonitrile-solvated Li^+ in the ^7Li NMR spectrum (a). Addition of *N*-benzyl-monoaza-12-crown-4 (**7**) to the LiClO_4

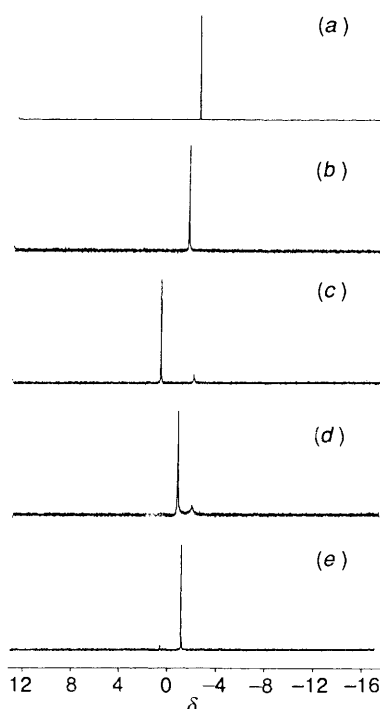


Fig. 4 ^7Li NMR spectra for LiClO_4 acetonitrile solutions in the presence of crowned spirobenzopyrans **1-3**, acyclic analogue **4**, and *N*-benzyl-monoaza-12-crown-4 **7**. Under dark conditions, $[\text{LiClO}_4]$: $2 \times 10^{-2} \text{ mol dm}^{-3}$, (a) without crown compound; (b) $2 \times 10^{-2} \text{ mol dm}^{-3}$ **7**; (c) $1.6 \times 10^{-2} \text{ mol dm}^{-3}$ **1**; (d) $1.6 \times 10^{-2} \text{ mol dm}^{-3}$ **2**; (e) on visible-light irradiation, $1.6 \times 10^{-2} \text{ mol dm}^{-3}$ **1**.

solution caused a continuous shift of the peak to higher frequencies due to Li^+ complexation by the crown ether (b). When the spirobenzopyran of 12-crown-4 (**1**) was added instead, another peak, which never shifts continuously, was observed at a further higher frequency (0.59 ppm with reference to the Li^+ peak for $\text{LiClO}_4\text{-D}_2\text{O}$), besides the peak assigned to crown-complexed Li^+ (c). Increasing the amount of **1** intensified the peak at 0.59 ppm while decreasing the lower-frequency peak, which almost disappeared on addition of an equimolar amount of crowned spirobenzopyran to the LiClO_4 acetonitrile solution. The appearance of the high-frequency peak at 0.59 ppm indicates that a powerful additional interaction with Li^+ complexed by a crown moiety arises on Li^+ binding of the crowned spirobenzopyran, followed by isomerization to its merocyanine form. In a 1:1 mixture of *N*-benzyl-monoaza-12-crown-4 and a spirobenzopyran carrying no crown moiety like a pyridinomethyl derivative **5** or an unsubstituted derivative **6**, such a high-frequency peak as seen in the crowned

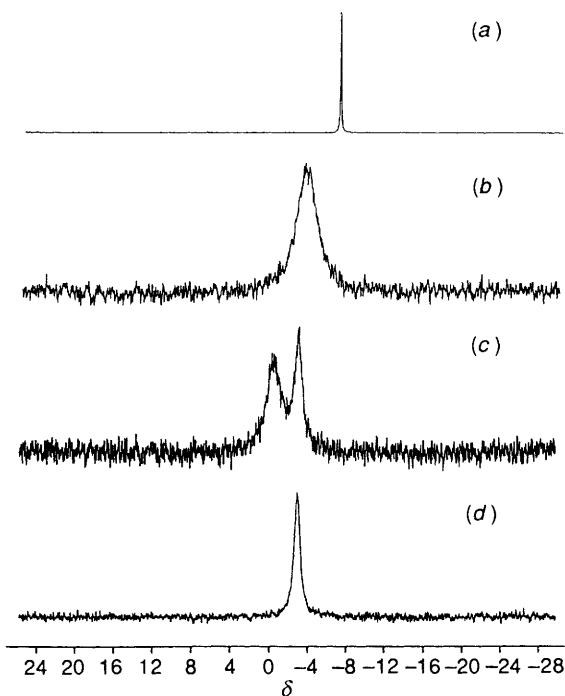
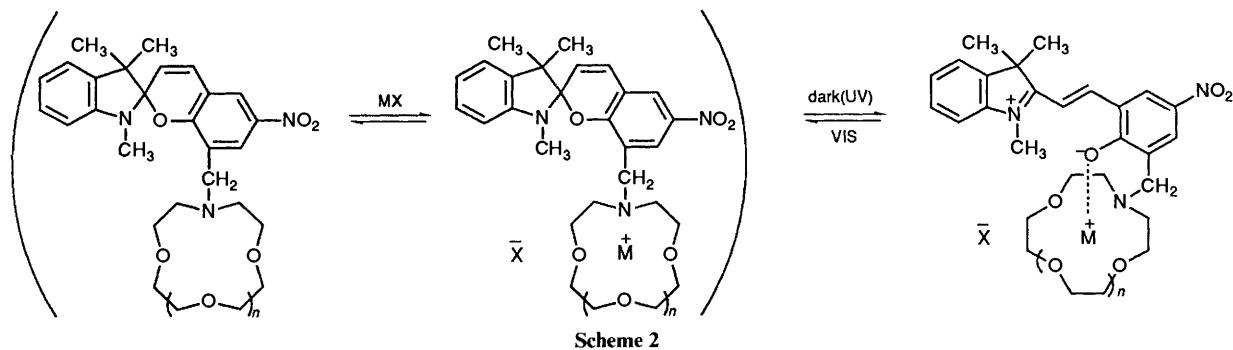


Fig. 5 ^{23}Na NMR spectra for NaClO_4 acetonitrile solutions in the presence of crowned spirobenzopyrans 1–3 and acyclic analogue 4. Under dark conditions, $[\text{NaClO}_4]: 2 \times 10^{-2} \text{ mol dm}^{-3}$, (a) without crown compound; (b) $2 \times 10^{-2} \text{ mol dm}^{-3}$ 1; (c) $2 \times 10^{-2} \text{ mol dm}^{-3}$ 2; (d) on visible-light irradiation, $2 \times 10^{-2} \text{ mol dm}^{-3}$ 2.

spirobenzopyran 1 system was not observed, even under conditions where isomerization of 5 or 6 to their corresponding merocyanine form was extensively promoted by UV-light irradiation. The ^7Li NMR results, therefore, suggest strongly that in the Li^+ -complexation-induced isomerization of crowned spirobenzopyran 1, the crown-complexed Li^+ interacts intramolecularly with its phenolate anion, as demonstrated in Scheme 2. Conceivably, this intramolecular interaction is stabilized by the six-membered chelate formation by the crowning nitrogen and phenolate oxygen atoms with Li^+ . It is thus considered that the intramolecular interaction between the crown-complexed Li^+ and phenolate anion in the merocyanine isomer enhances the cation-induced isomerization of crowned spirobenzopyran. A similar tendency was found in the ^7Li NMR spectra of the spirobenzopyran of 15-crown-5, 2, the intramolecular interaction between a complexed Li^+ and a phenolate ion also taking place in its merocyanine isomer complex. No peak due to the phenolate interacting with Li^+ , however, was observed in the NMR spectra of the spirobenzopyrans of 18-crown-6, 3, and acyclic analogue 4. This means that the merocyanine isomers of 3 and 4 are not able to undergo a powerful intramolecular interaction with Li^+ . Thus, the powerful intramolecular interaction seems to occur only in the

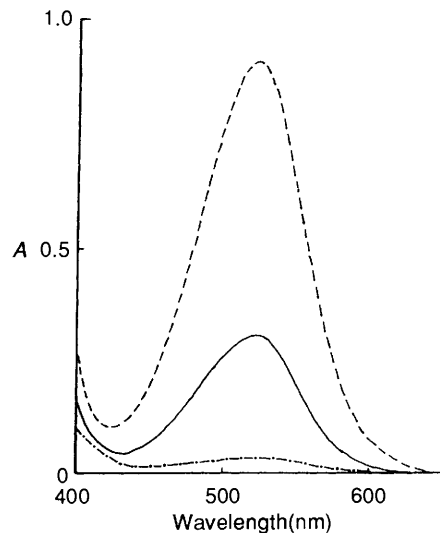


Fig. 6 Photoisomerization of crowned spirobenzopyran 1 in THF in the presence of Li^+ . $[\mathbf{1}]$ and $[\text{LiClO}_4]: 2 \times 10^{-4} \text{ mol dm}^{-3}$, solid line: under dark conditions; broken line: UV-light irradiation; chain line: visible-light irradiation.

merocyanine isomers of crowned spirobenzopyrans of which the crown ring fits Li^+ well.

^{23}Na NMR spectroscopy also shows that a powerful intramolecular interaction between a crown-complexed Na^+ and a phenolate anion happens only in the merocyanine isomer of the spirobenzopyran of 15-crown-5, 2 (Fig. 5). The interaction, however, appears to be weaker than that for the 1-Li^+ systems, as anticipated from the general finding that lower charge-density metal cations are less subject to perturbation by anions. There seems to be only a slight intramolecular interaction between a crown-complexed Na^+ and a phenolate anion in the spirobenzopyrans of 12-crown-4 and 18-crown-6, 1 and 3. Also, no high-frequency peak, which would support the intramolecular interaction of the crown-complexed Na^+ and phenolate anion, was found in the ^{23}Na NMR spectrum of the system for acyclic analogue 4.

Photoisomerization in the Presence of Metal Ions.—Crowned spirobenzopyrans are photochemically isomerized to their corresponding crowned merocyanines in the presence as well as absence of metal ions. As described above, in the presence of Li^+ , even under dark conditions, crowned spirobenzopyran 1 isomerizes partly to the corresponding crowned merocyanine. Particularly in acetonitrile, the isomerization to the merocyanine form proceeded to a great extent with a $[\text{Li}^+]/[\text{crowned spirobenzopyran}]$ ratio of 1. UV-light irradiation, therefore, hardly caused any further isomerization from the spirobenzopyran to merocyanine form under such Li^+ concentrations. Visible-light irradiation, however, gave rise to the

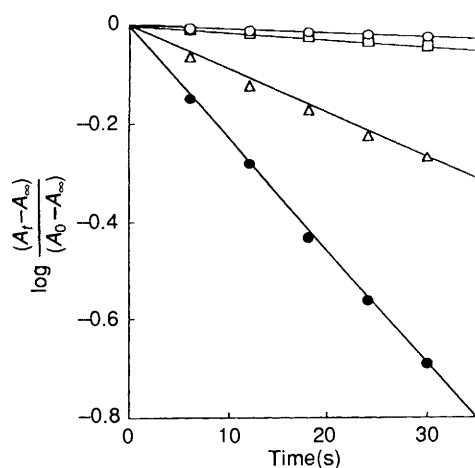


Fig. 7 First-order plots for thermal decolouration of crowned spirobenzopyran **2** in the absence and presence of alkali metal ions. [**2**]: 5×10^{-5} mol dm $^{-3}$, [MClO $_4$]: 2×10^{-4} mol dm $^{-3}$ in THF, after 1 min UV-light irradiation. Without metal ion (●): Li $^+$ (○); Na $^+$ (□); K $^+$ (△).

Table 1 First-order rate constants for thermal decolouration in crowned spirobenzopyrans **1–3** and their acyclic analogue **4** in the presence and absence of alkali metal ions

Metal ion	Rate constant/ 10^{-3} s $^{-1}$ ^a			
	1	2	3	4
None	23	23	19	33
Li $^+$	2.2	0.8	9.9	18
Na $^+$	8.8	1.4	3.3	25
K $^+$	25	9.4	9.6	25

^a Thermal decolouration at 40 °C in THF after 1 min UV-light irradiation, [crowned spirobenzopyran]: 4×10^{-5} mol dm $^{-3}$, [MClO $_4$]: 2×10^{-4} mol dm $^{-3}$.

immediate disappearance of the merocyanine-based absorption peak, indicating that isomerization back to the spiropyran form occurs. In THF, on the other hand, UV-light irradiation enhanced the isomerization to the macrocyanine form, while visible-light irradiation promoted the isomerization to the spiropyran form (Fig. 6). Once the UV and visible lights were turned off, the isomerization equilibrium reverted gradually to the initial one under dark conditions.

In order to elucidate the thermal stability of the crowned merocyanines in the presence and absence of alkali metal ions, their thermal decolouration, *i.e.* isomerization from the merocyanine to spiropyran form, was followed after UV-light irradiation. Since the thermal decolouration was too slow to follow in acetonitrile, the decolouration rates were measured in THF at 40 °C. First-order plots of thermal decolouration for the crowned spirobenzopyran **2** system are depicted in Fig. 7, showing linearity in the initial stages of the thermal decolouration. The first-order thermal-decolouration rate constants are summarized in Table 1. The small rate constants indicate high thermal stabilities of the crowned merocyanines, which in turn reflect the stabilities for crowned merocyanine-metal ion complexes and, in some cases, for the intramolecular phenolate-interacting complexes. The ion selectivities almost correspond to those of the cation-induced isomerization in acetonitrile as seen in Fig. 3. Thus it is again confirmed that the thermal stability of crowned merocyanines is governed not only by the cation-complexing abilities of the crown moieties themselves but also by the strength of the intramolecular interaction between the crown-complexed metal ion and the phenolate anion.

Photochemical Control of Cation Binding.—As illustrated in Fig. 6, crowned spirobenzopyrans **1–3** can be reversibly isomerized to the corresponding crowned merocyanines by photoirradiation, even in the presence of alkali metal ions. Attempts were made to follow the photoisomerization of crowned spirobenzopyrans in the presence of Li $^+$ by 7 Li NMR spectroscopy. A 7 Li NMR spectrum of an acetonitrile solution of **1** (16 mmol dm $^{-3}$) and LiClO $_4$ (20 mmol dm $^{-3}$) exhibited a strong peak at the high frequency (at 0.59 ppm) and a tiny peak at a low frequency under dark conditions [(c) in Fig. 4]. Visible-light irradiation increased the high-frequency peak while decreasing the low-frequency peak with some high-frequency shift of the latter peak [(e) in Fig. 4]. After the visible-light irradiation was ceased, the spectrum reverted to the initial one under dark conditions, gradually at room temperature and immediately on heating at 60 °C. This reversible NMR-spectral change indicates clearly that the cation-binding equilibrium of crowned spirobenzopyran as shown in Scheme 2 can be controlled photochemically. That is to say, under dark conditions (or on UV-light irradiation), the intramolecular interaction with a phenolate anion in the crowned merocyanine promotes Li $^+$ binding due to an additional-binding-site effect, which resembles the 'ariat ether effect'¹⁷ and 'chelate effect'.¹⁸ In contrast, visible-light irradiation induces the isomerization to the spiropyran form and thereby attenuates the additional-binding-site effect, thus diminishing the Li $^+$ binding ability. As a result, photochemical control of cation binding is realized in the crowned spirobenzopyran–Li $^+$ system. Similar, reversible 23 Na NMR-spectral change induced by photo-irradiation was observed in the **2**–Na $^+$ system [(c) and (d) in Fig. 5].

In conclusion, the photochemical control of cation binding by the crowned spirobenzopyrans is quite an intriguing phenomenon and may be useful for photocontrol of cation membrane transport and ion conduction in polymer films.

Experimental

Chemicals.—Unless otherwise specified, all reagents were the best grade and were employed as received. 3',3'-Dimethyl-6-nitro-8-piperidinomethyl-spiro[2*H*-1-benzopyran-2,2'-indoline] or piperidinomethyl spirobenzopyran (**5**) was prepared according to the literature.¹³ 3',3'-Dimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2'-indoline] (**6**) was purchased from Tokyo Kasei. The syntheses of *N*-benzyl-monoazacrown ethers **7–9** and their corresponding acyclic analogue **10** and their debenzoylation were achieved in a similar way to a reported procedure.¹⁵ THF, ethanol and acetonitrile were distilled over LiAlH $_4$, magnesium ethoxide and P $_2$ O $_5$. CH $_2$ Cl $_2$ was purified by distillation. Water was deionized.

Apparatus.—Melting points were determined on a YANACO MP melting point apparatus and were uncorrected. 1 H NMR spectra were recorded as CDCl $_3$ solutions on a JEOL JNM-PS-100 spectrometer. 7 Li and 23 Na NMR spectra were taken as acetonitrile solutions on a JEOL JNM-GSX-400 at the Instrumental Analysis Center of Osaka University. *J* values are in Hz. Mass spectra were obtained on a JEOL JMS-DX303 instrument at the centre. UV and visible spectra were measured with a JASCO 660 spectrophotometer. Preparative reversed-phase liquid chromatography was performed on a JASCO 880-type liquid chromatograph, a Waters R-401 differential refractometer, and a 20 mm × 250 mm column packed with 15 μm octadecylsilanized silica (ODS). UV (300–400 nm) and visible (>490 nm) light for the photoisomerization was obtained by passing light from a 500 W xenon lamp (USHIO 500D-0) through Toshiba UV-D36 and V-Y50 colour filters, respectively.

Synthesis. General Procedure for Preparation of Crowned Spirobenzopyrans.—To a dry THF solution (5 cm³) of a monoazacrown ether (2.9 mmol) and triethylamine (5.9 mmol) was added a dry THF solution (10 cm³) of 3-chloromethyl-5-nitrosalicylaldehyde (2.9 mmol) dropwise while stirring on an ice bath. The stirring was continued overnight at room temperature and then for 3 h under reflux. After filtration of triethylamine hydrochloride, evaporation of the THF afforded crude 3-formyl-2-hydroxy-5-nitrobenzyl monoazacrown ether, which was generally used for the subsequent reaction without further purification. (The solid products can be recrystallized from ethanol.)

A dry ethanol solution (15 cm³) of 1,3,3-trimethyl-2-methyleneindoline (3 mmol) and 3-formyl-2-hydroxy-5-nitrobenzyl monoazacrown ether (3 mmol) was heated under reflux for 8 h. After the reaction, the ethanol was evaporated off to yield a crude product of corresponding crowned spirobenzopyran, which was purified by appropriate liquid chromatography and/or recrystallization.

1',3',3'-Trimethyl-6-nitro-8-[10-(1,4,7-trioxa-10-azacyclododecyl)methyl]spiro[2H-1-benzopyran-2,2'-indoline] [(Monoaza-12-crown-4)ylmethyl spirobenzopyran] **1**. The reaction of 1,3,3-trimethyl-2-methyleneindoline with 3-formyl-2-hydroxy-5-nitrobenzyl monoaza-12-crown-4 afforded compound **1**. Purification by column chromatography (neutral alumina, CHCl₃), followed by recrystallization from ethanol yielded an off-white crystal (23%); m.p. 134 °C; δ_{H} 1.22 (6 H, d, *J* 8, CCH₃), 2.5–3.0 (7 H, m, NCH₃ and NCH₂CH₂O), 3.4–3.9 (14 H, m, OCH₂ and PhCH₂), 5.85 (1 H, d, *J* 10, CH₂=CHPh), 6.54 (1 H, d, *J* 8, CH₂=CHPh), 6.8–7.3 (4 H, m, aromatic H of indoline), 7.8 (1 H, d, *J* 4, 5-H of benzopyran), 8.55 (1 H, d, *J* 4, 7-H of benzopyran); *m/z* (% relative intensity) 510 (M⁺, 27), 335 (100). (Calc. for C₂₈H₃₅N₃O₆: C, 66.00; H, 6.92; N, 8.25. Found: C, 65.7; H, 6.9; N, 8.1%).

1',3',3'-Trimethyl-6-nitro-8-[13-(1,4,7,10-tetraoxa-13-azacyclopentadecyl)methyl]spiro[2H-1-benzopyran-2,2'-indoline] [(Monoaza-15-crown-5)ylmethyl spirobenzopyran] **2**. Compound **2** was prepared by the reaction of 1,3,3-trimethyl-2-methyleneindoline with 3-formyl-2-hydroxy-5-nitrobenzyl monoaza-15-crown-5. Purification by column chromatography (neutral alumina, CHCl₃), followed by recrystallization from ethanol yielded an off-white crystal (22%); m.p. 119–120 °C; δ_{H} 1.22 (6 H, d, *J* 8, CCH₃), 2.5–3.0 (7 H, m, NCH₃ and NCH₂CH₂O), 3.4–3.9 (18 H, m, OCH₂ and PhCH₂), 5.85 (1 H, d, *J* 10, CH₂=CHPh), 6.54 (1 H, d, *J* 8, CH₂=CHPh), 6.8–7.3 (4 H, m, aromatic H of indoline), 7.8 (1 H, d, *J* 4, 5-H of benzopyran), 8.55 (1 H, d, *J* 4, 7-H of benzopyran); *m/z* (% relative intensity) 553 (M⁺, 86), 335 (100). Calc. for C₃₀H₃₉N₃O₆: C, 65.08; H, 7.10; N, 7.59. Found: C, 64.9; H, 7.1; N, 7.5%.

1',3',3'-Trimethyl-6-nitro-8-[16-(1,4,7,10,13-pentaoxa-16-azacyclooctadecyl)methyl]spiro[2H-1-benzopyran-2,2'-indoline] [(Monoaza-18-crown-6)ylmethyl spirobenzopyran] **3**. Compound **3**, prepared from 1,3,3-trimethyl-2-methyleneindoline and 3-formyl-2-hydroxy-5-nitrobenzyl monoaza-18-crown-6 as described in the general procedure, was purified by preparative reversed-phase liquid chromatography [ODS, MeOH–H₂O (90:10)] to yield a dark-brown viscous liquid (29%); δ_{H} 1.22 (6 H, d, *J* 8, CCH₃), 2.5–3.0 (7 H, m, NCH₃ and NCH₂CH₂O), 3.4–3.9 (22 H, m, OCH₂ and PhCH₂), 5.85 (1 H, d, *J* 10, CH₂=CHPh), 6.54 (1 H, d, *J* 8, CH₂=CHPh), 6.8–7.3 (4 H, m, aromatic H of indoline), 7.8 (1 H, d, *J* 4, 5-H of benzopyran), 8.55 (1 H, d, *J* 4, 7-H of benzopyran); *m/z* (% relative intensity) 598 (M⁺, 48), 335 (100). (Calc. for C₃₂H₄₃N₃O₆: C, 64.30; H, 7.25; N, 7.03. Found: C, 63.9; H, 7.1; N, 6.9%).

1',3',3'-Trimethyl-6-nitro-8-[8-(2,5,11,14-tetraaza-8-azapentadecyl)methyl]spiro[2H-1-benzopyran-2,2'-indoline] (Monoazatetraoxapentadecylmethyl spirobenzopyran) **4**. Com-

pound **4**, prepared from 1,3,3-trimethyl-2-methyleneindoline and 8-(3-formyl-2-hydroxy-5-nitrobenzyl)-2,5,11,14-tetraoxa-8-azapentadecane as described in the general procedure, was purified by preparative reversed-phase liquid chromatography [ODS, MeOH–H₂O (90:10)] to yield a dark-brown viscous liquid (32%); δ_{H} 1.22 (6 H, d, *J* 8, CCH₃), 2.5–3.0 (7 H, m, NCH₃ and NCH₂CH₂O), 3.4–3.9 (20 H, m, OCH₂ and PhCH₂), 5.85 (1 H, d, *J* 10, CH₂=CHPh), 6.54 (1 H, d, *J* 8, CH₂=CHPh), 6.8–7.3 (4 H, m, aromatic H of indoline), 7.8 (1 H, d, *J* 4, 5-H of benzopyran), 8.55 (1 H, d, *J* 4, 7-H of benzopyran); *m/z* (% relative intensity) 556 (M⁺, 29), 335 (100). (Calc. for C₃₀H₄₁N₃O₆: C, 64.85; H, 7.44; N, 7.56. Found: C, 64.4; H, 7.3; N, 7.4%).

Cation Extraction.—Equal volumes (3 cm³) of 2.1 × 10⁻³ mol dm⁻³ crowned spirobenzopyran solution (1,2-dichloroethane) and an aqueous solution containing a mixture of 0.1 mol dm⁻³ alkali metal hydroxide and 7.5 × 10⁻⁵ mol dm⁻³ picric acid were introduced into a stoppered vial and shaken by a reciprocating shaker under dark conditions for 15 min.¹⁶ After phase separation, the organic and aqueous phases were subjected to absorption-spectral measurements. The percent extraction was calculated as (A₀ - A)/A₀, where A₀ and A denote absorbances of picrate ion (355 nm) for the aqueous phase before and after the extraction, respectively.

Cation-induced Isomerization in One Phase.—An organic solution containing 4 × 10⁻⁵ mol dm⁻³ crowned spirobenzopyran and 4 × 10⁻⁵ mol dm⁻³ alkali metal perchlorate was allowed to stand for 24 h under dark conditions and its absorption spectrum was then taken. Molar absorptivities for the merocyanine peaks were determined on their complete isomerization induced by addition of a large excess of Li⁺ or Na⁺ salt, which was confirmed by ¹H NMR observation that a doublet peak at δ 1.2, due to 3'-CH₃ protons of the spirobenzopyran isomers, almost completely disappeared with the appearance of a new singlet peak at δ 1.8. Photoisomerization in the one-phase system was carried out by photoirradiation for 1 min.

Thermal Decolouration Rate.—A 4 × 10⁻⁵ mol dm⁻³ crowned spirobenzopyran solution (THF) with and without 2 × 10⁻⁴ mol dm⁻³ alkali metal perchlorate was irradiated by UV light for 1 min. Immediately after the photoirradiation, the absorbance at 530 nm, due to the merocyanine isomer, was continuously monitored at 40 °C. The first-order rate constants of thermal decolouration were determined from the slope of log [(A_t - A_∞)/(A₀ - A_∞)] vs. time (*t*), where A_t, A_∞, and A₀ are the absorbance at *t*, at *t* = 0, and at *t* = infinity, respectively.

⁷Li and ²³Na NMR Spectroscopy.—The sample was a mixture of 2 × 10⁻² mol dm⁻³ LiClO₄ (or NaClO₄) and an appropriate concentration of crowned spirobenzopyran dissolved in CD₃CN–CH₃CN (30/70). The external standard was a 20 mmol dm⁻³ LiClO₄ (or NaClO₄) solution (D₂O). Photoirradiation was conducted for ca. 20 min.

References

- 1 J. Sunamoto, K. Iwamoto, Y. Mohri and T. Kominato, *J. Am. Chem. Soc.*, 1982, **104**, 5502.
- 2 J. D. Winkler, K. Deshayes and B. Shao, *J. Am. Chem. Soc.*, 1989, **111**, 769.
- 3 S. Kato, M. Aizawa and S. Suzuki, *J. Membr. Sci.*, 1976, **1**, 289.
- 4 J. Anzai, A. Ueno and T. Osa, *J. Chem. Soc., Chem. Commun.*, 1984, 688.
- 5 M. Irie, A. Menju and K. Hayashi, *Nippon Kagaku Kaishi*, 1984, 227.

- 6 O. Ryba and J. Petranek, *Makromol. Chem. Rapid Commun.*, 1988, **9**, 125.
- 7 M. Irie, T. Iwayanagi and Y. Taniguchi, *Macromolecules*, 1985, **18**, 2418.
- 8 F. Ciardelli, D. Fabbri, O. Pieroni and A. Fissi, *J. Am. Chem. Soc.*, 1989, **111**, 3470.
- 9 M. Inouye, M. Ueno, T. Kitao and K. Tsuchiya, *J. Am. Chem. Soc.*, 1990, **112**, 8977.
- 10 S. Akabori and Y. Fujimine, 59th National Meeting of the Chemical Society of Japan, 1990, Abstr., No. 1E315.
- 11 H. Sasaki, A. Ueno, J. Anzai and T. Osa, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 1953.
- 12 K. Kimura, T. Yamashita and M. Yokoyama, *Chem. Lett.*, 1991, 965.
- 13 L. D. Taylor, J. Nicolson and R. B. Davis, *Tetrahedron Lett.*, 1967, 1585.
- 14 L. D. Taylor and R. B. Davis, *J. Org. Chem.*, 1963, **28**, 1713.
- 15 M. J. Calverley and J. Dale, *Acta Chem. Scand., Ser. B*, 1982, **36**, 241.
- 16 C. J. Pedersen, *Fed. Proc.*, 1968, **27**, 1305.
- 17 A. Kaifer, D. A. Gustowski, L. Echegoyen, V. J. Gatto, R. A. Schultz, T. P. Cleary, C. R. Morgan, D. M. Goli, A. M. Rios and G. W. Gokel, *J. Am. Chem. Soc.*, 1985, **107**, 1958.
- 18 Y. Katayama, K. Nita, M. Ueda, H. Nakamura and M. Takagi, *Anal. Chim. Acta*, 1985, **173**, 193.

Paper 1/06259J

Received 12th December 1991

Accepted 15th January 1992