Cation-specific Isomerization of Crowned Spirobenzopyrans

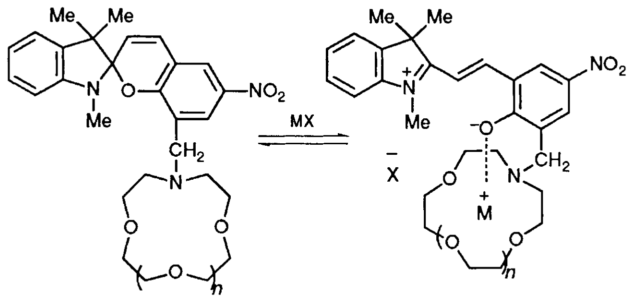
Keiichi Kimura,* Takashi Yamashita and Masaaki Yokoyama

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

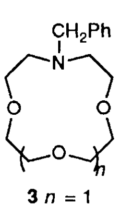
Novel spirobenzopyran derivatives carrying monoazacrown moieties at the 8-position undergo selective complexation of alkali metal ions and thereby isomerization to their corresponding merocyanine form in the dark; the isomerization is enhanced especially by Li^+ that is likely to interact with the phenolate anion intramolecularly when bound to the crown rings.

Spirobenzopyran derivatives are typical photochromic compounds which are generally converted to the corresponding zwitterionic merocyanine isomers by UV irradiation.[1] In a spirobenzopyran derivative possessing a piperidinomethyl group at the 8-position, the isomerization to the corresponding merocyanine form proceeds in the presence of metal ions such as Zn^{2+} even under dark conditions, since the merocyanine form is stabilized to some extent by chelate formation with the metal cations.[2] It occurred to us that incorporation of monoazacrown moieties at the 8-position of the spirobenzopyran skeleton instead of the piperidine ring may provide spirobenzopyran derivatives with complexing abilities towards alkali metal ions, thus drastically affecting their isomerization equilibrium between the spiropyran and merocyanine forms. Here we report the selective alkali metal ion complexation and isomerization of crowned spirobenzopyrans **1** and **2**.

The crowned spirobenzopyrans were synthesized by the condensation reaction of 1,3,3-trimethyl-2-methyleneindoline with 1-(3-formyl-2-hydroxy-5-nitrobenzyl)-monoaza-12-crown-4 and -monoaza-15-crown-5, respectively (reflux, in ethanol, 8 h), which were in turn obtained by treating 3-chloromethyl-5-nitrosalicylaldehyde with the corresponding monoazacrown ethers [reflux, in tetrahydrofuran (THF), 8 h].† In order to elucidate the cation-binding abilities of the crowned spirobenzopyrans, extraction of alkali metal picrates (Li^+, Na^+ and K^+) was carried out under dark conditions according to Pedersen's method[3] using a 1,2-dichloroethane–water system (Fig. 1). For comparison, the corresponding model compounds, 1-benzylmonoaza-12-crown-4 **3** and -15-crown-5 **4** were also employed for cation extraction. Crowned spirobenzopyrans **1** and **2** selectively extract Li^+ and Na^+, respectively. The ion selectivities in the cation extraction almost correspond to those of the respective parent monoazacrown rings, since compounds **3** and **4** possess high affinities towards Li^+ and Na^+, respectively. The selectivity ratios of Li^+ over Na^+ and Li^+ over K^+ for **1** and **2**, are, however, higher than those for **3** and **4**, respectively, implying some enhancement in the Li^+ affinity of the crowned spirobenzopyrans as compared with **3** and **4**. Absorption spectra for the organic phase after the extraction showed a peak at 530–560 nm, based on the merocyanine form of the crowned spirobenzopyrans (Fig. 2). This clearly indicates that the cation complexation of the crown moieties provides ionic character to the spirobenzopyran derivatives, thus leading to isomerization of **1** and **2** to the corresponding merocyanine isomers. The degree of isomerization of **1** in the organic phase almost reflects the Li^+ selectivity in its cation extractability. On the other hand, the isomerization of **2** decreased in the order $Li^+ \geqslant Na^+ > K^+$. These results suggest that the complexation of Li^+ by the crown moieties stabilizes the merocyanine isomers strongly.



1 $n = 1$
2 $n = 2$



3 $n = 1$
4 $n = 2$

^7Li NMR spectroscopy gave some information on the

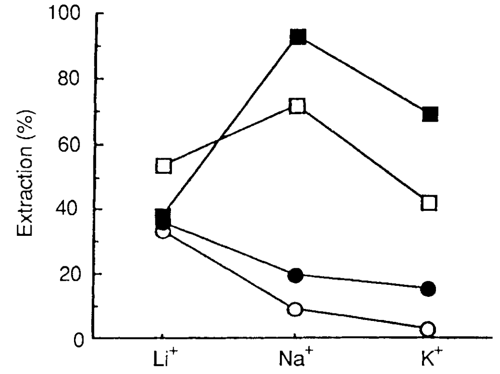


Fig. 1 Extraction of alkali metal picrates with crowned spirobenzopyrans **1** (○) and **2** (□) and benzylmonoazacrown ethers **3** (●) and **4** (■) (2.1×10^{-3} mol dm^{-3}) in $ClCH_2CH_2Cl$, 0.1 mol dm^{-3} metal hydroxide and 7×10^{-5} mol dm^{-3} picric acid in H_2O; 15 min extraction in the dark

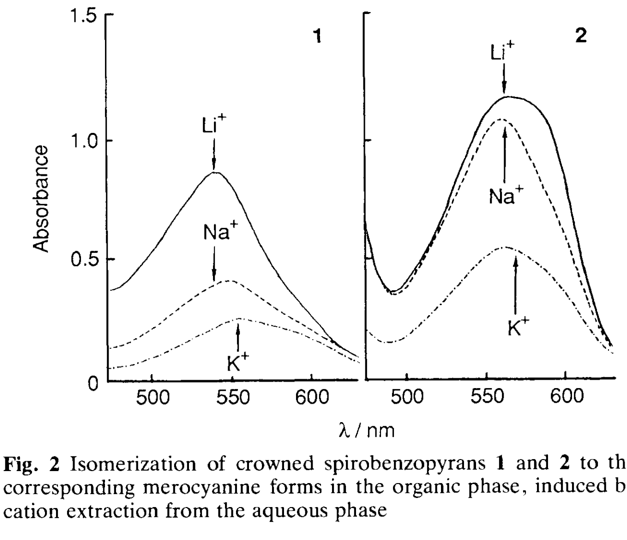


Fig. 2 Isomerization of crowned spirobenzopyrans **1** and **2** to the corresponding merocyanine forms in the organic phase, induced by cation extraction from the aqueous phase

---

† Satisfactory analytical data.

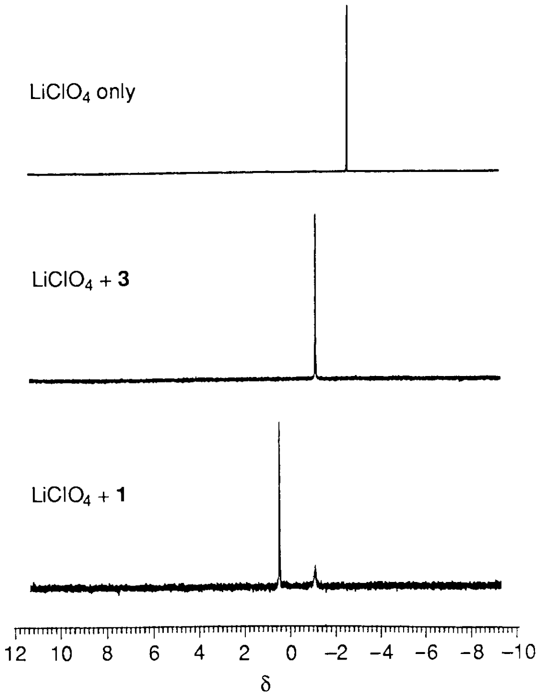


Fig. 3 Comparison of ^{7}Li NMR spectra of solutions of $LiClO_4$ in acetonitrile with and without crowned spirobenzopyran **1** and model compound **3**; 0.02 mol dm^{-3} $LiClO_4$ and crown compounds in CD_3CN–CH_3CN (30:70); external standard: 0.02 mol dm^{-3} $LiClO_4$ in D_2O

crown-complexed Li^+ in the merocyanine form **1** (Fig. 3).‡ A solution of $LiClO_4$ in acetonitrile showed a peak due to acetonitrile-solvated Li^+. Addition of 1 mol. equiv. of the benzylmonoazacrown ether **3** to the solution caused a shift of the peak to higher frequency, indicating Li^+ complex formation with **3**. In a $LiClO_4$–acetonitrile solution containing crowned spirobenzopyran **1**, a strong peak was observed at a further higher frequency besides a weak peak attributable to an equilibrium between Li^+ complexed simply by the crown moiety and Li^+ solvated by acetonitrile. These NMR data are indicative of intramolecular interaction between the crown-complexed metal ion and the phenolate anion in the merocyanine form. Specifically, Li^+ which possesses the highest charge density of the alkali metal ions, when complexed by the crown moiety, may participate in formation of a stable six-membered ring chelate by the nitrogen atom on the crown ring and the phenolate anion. This, in turn, seems to promote the Li^+ complex formation and the isomerization to the merocyanine form.

Thus, the crowned spirobenzopyrans undergo ion-specific isomerization to the corresponding merocyanine forms by the cation complexation of their crown moieties. In other words, the isomerization and thereby the colouration of the crowned spirobenzopyrans can be controlled easily by the addition of alkali metal ions, especially Li^+. Also, the crowned spirobenzopyrans may be useful for Li^+ detection and analysis. The isomerization of the crowned spirobenzopyrans on photoirradiation is being studied.

Received, 5th October 1990; Com. 0/04500D

---

‡ The NMR data were obtained on a JEOL JNM-GSX-400 spectrometer at the Instrumental Analysis Centre.

References

1 R. C. Bertelson, 'Photometric Process Involving Heterocyclic Cleavage, in *Photochromism*, G. H. Brown, Wiley–Interscience, New York, 1971, ch. III.
2 L. D. Taylor, J. Nicholson and R. B. Davis, *Tetrahedron Lett.*, 1967, 1585.
3 C. J. Pedersen, *Fed. Proc.*, 1968, **27**, 1305.