SYNTHETIC MACROCYCLIC LIGANDS. V.[1] "CROWNED" DINITROPHENYLAZOPHENOLS: DISSOLVING AND COLORATING AGENT OF ALKALI AND ALKALINE EARTH METAL SALTS IN ORGANIC SOLVENTS†

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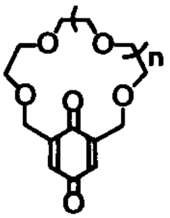
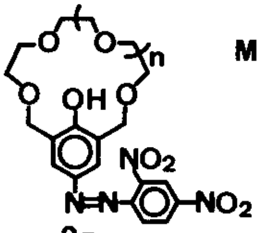
Abstract—The complexations of the title compounds with a series of alkali and alkaline earth metal salts were studied under various conditions, e.g., amine, solvent, etc. A solution of azophenol **2**$_1$-pyridine in chloroform displayed a noticeable metal-cation selective coloration for lithium salts of alkali metal salts.

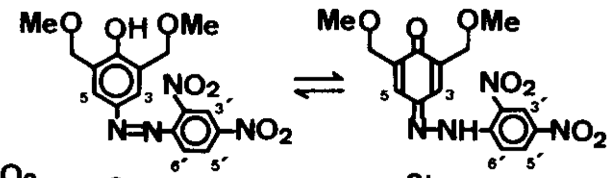
In recent years much attention has been paid on metal-ion selective coloration in macrocyclic ligand chemistry. The synthesis of crown ether dyes for the ion-selective coloration is a stimulative theme.[2] "Crowned" dinitrophenylazophenols **2n**, which are easily derived from "crowned" benzoquinones **1n** previously reported,[3] have unique structural features as follows: 1) the crown ether has in its cavity a phenolic hydroxyl group, the anion of which is capable of affecting the metal cation complexation, and 2) the electron density of phenolate anion contributes to the coloration of the present azopigment. In this communication, we wish to report the cation-dependent coloration of "crowned" azophenols **2n** with various alkali and alkaline earth metal salts.



1n



2n



3a **3b**

Quinone **1n** was treated with 1.1 eq. of 2,4-dinitrophenylhydrazine in ethanol to give the desired "crowned" azophenol **2n**[4] in good yield. An "uncrowned" azophenol **3a**[4] was similarly prepared from the corresponding quinone in 94% yield. NMR study reveals that compound **3** exists in azophenol-hydrazone equilibrium (**3a** : **3b** = 59 : 41 in $CDCl_3$), whereas that **2n** is existing as pure azo-form, indicating the stabilization

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† Dedicated to Professor Herbert C. Brown on the occasion of his 70th birthday

of the phenol form by chelating the phenolic hydrogen with the crown ether moiety. This result is in marked contrast to more than 95% hydrazone content in 2,6-dialkylbenzoquinone dinitrophenylhydrazone.5)

Cation-dependent coloration of the azophenols was studied by means of visible spectrophotometry in the presence of a wide variety of amines.

In Ethanol: **2n** and **3** in ethanol solution partially dissociate to form colored phenolate anions (λ_{max} 586 nm for **2**$_1$, 555 for **2**$_2$, and 586 for **3**). Addition of triethylamine to the solution allows nearly complete dissociation. The resulting blue solution of the phenolate anion was found to change to violet~yellow by addition of crystalline alkali or alkaline earth metal salts. These hypsochromic shifts of the phenolate anions with the salts are summarized in Table. The Table shows the largest hypsochromic shift for **2**$_1$-lithium salt system among alkali metal series and the decreasing order of the shift with the increasing size of metal ions regardless of counter anion species. The phenolate anions of **2**$_2$ and **3** are less susceptible to the hypsochromic shift than that of **2**$_1$.

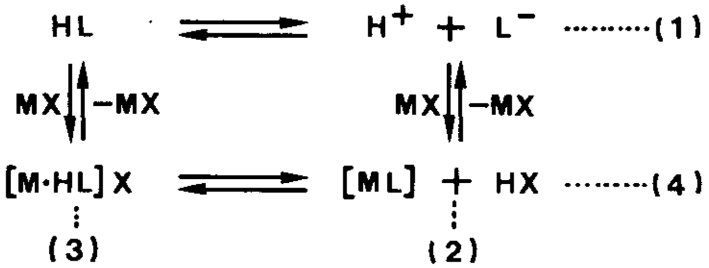
Table. Hypsochromic shift of azophenol-Et$_3$N-metal salt systems in ethanol, $\Delta\lambda=\lambda_{max}$(with salt)-$\lambda_{max}$(salt free)a).6)

Run	Added salt	$\Delta\lambda$/nm b)			Run	Added salt	$\Delta\lambda$/nm b)		
		2$_1$	**2**$_2$	**3**			**2**$_1$	**2**$_2$	**3**
1	LiCl	-50	-30	-11	9	$MgCl_2$	-72	-53	-73
2	$LiClO_4$ c)	-50	-33	-10	10	$Mg(ClO_4)_2$ c)	-111	-61	-78
3	NaCl	-30	-5	0,-5 d)	11	$CaCl_2$	-67	-63	-58
4	$NaClO_4$ c)	-30	-5	-7,-19 e)	12	$Ca(ClO_4)_2$ c,f)	-67	-63	-61
5	KCl	-17	-5	0	13	$SrCl_2\cdot 6H_2O$	-64	-72	-50
6	$KClO_4$	-16	-5	0	14	$BaCl_2\cdot 2H_2O$	-58	-62	-1,-37 d)
7	RbCl	-13	0	0	15	$Ba(ClO_4)_2$ c,g)	-60	-60	-44,-59 e)
8	CsCl	-10	+7	-1					

a) 589 nm for **2**$_1$, 558 for **2**$_2$, and 586 for **3**. b) Error: ±2 nm.
c) Dissolved in the solvent. d) After one day. e) Large excess.
f) Tetrahydrate. g) Trihydrate.

On the other hand, all of alkaline earth metal salts brought about larger hypsochromic effect, compared to those of alkali metal salts. A magnesium perchlorate-**2**$_1$ system shows the largest shift in all the systems examined.

The hypsochromic shift above-stated is affected by phenol dissociation equilibrium [Eq. (1) in Scheme], ion-exchange equilibrium [Eq. (2)], and interaction between phenolate anion and metal cation, which may appreciably influence the transition of azophenol chromophore. In fact, the observed hypsochromic shifts depend upon cation species, amount of salts, reaction time, and, in some cases, counter anion (see runs



Scheme. Equilibrium in azophenol (HL)-metal salt (MX) system.

3, 4, 14, and 15 in Table).

In Chloroform: No phenolate anion in chloroform solution was detected even in the presence of pyridine as a base, in contrast to the case in ethanol. Adding crystalline metal salts to this yellow solution, a color change to orange～purple was observed. Figs. 1-4 show the salt-dependent visible spectra of $\mathbf{2n}$ in chloroform. Especially, Fig. 1 is suggestive of specific coloration of $\mathbf{2}_1$ only with lithium salts among a series of alkali metal salts. A dramatic color change from yellow to purplish red took place rapidly on the addition of lithium chloride or perchlorate to a solution of $\mathbf{2}_1$-pyridine in chloroform. The same lithium ion-specific coloration of $\mathbf{2}_1$ was observed also by using a crystalline mixture of lithium and other alkali metal salts.

The spectral change of $\mathbf{2}_2$ having a larger cavity occurred with cesium chloride as well as lithium salts, as shown in Fig. 2. Figs. 3 and 4 show the color change of

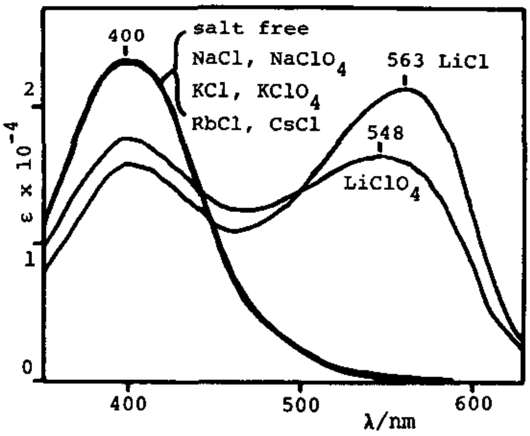


Fig. 1. Visible spectra of $\mathbf{2}_1$-alkali metal salt-pyridine systems in $CHCl_3$.$^{6)}$

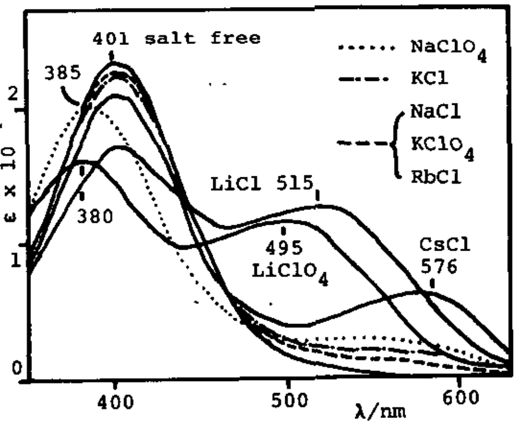


Fig. 2. Visible spectra of $\mathbf{2}_2$-alkali metal salt-pyridine systems in $CHCl_3$.$^{6)}$

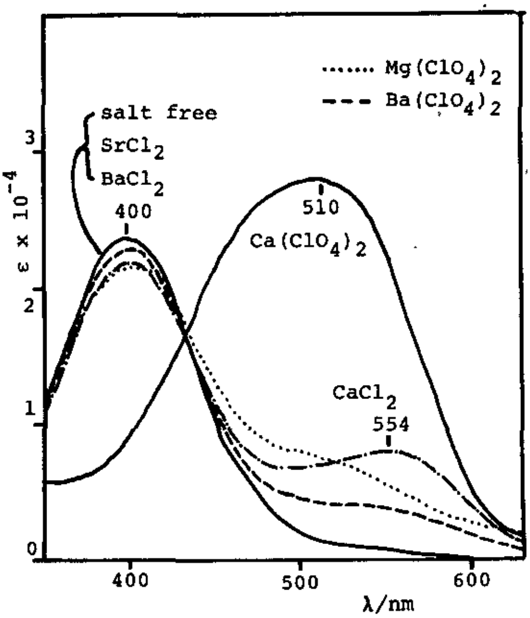


Fig. 3. Visible spectra of $\mathbf{2_1}$-alkaline earth metal salt-pyridine systems in $CHCl_3$.[6)]

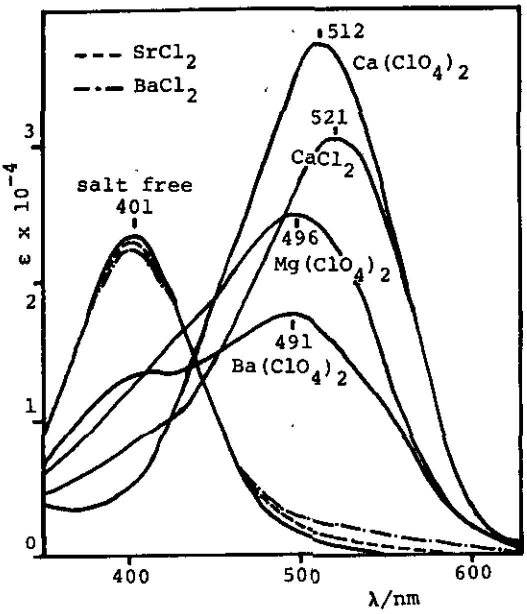


Fig. 4. Visible spectra of $\mathbf{2_2}$-alkaline earth metal salt-pyridine systems in $CHCl_3$.[6)]

2n with relatively small size of alkaline earth metal ions: Mg^{++} and Ca^{++}. It is noteworthy that "uncrowned" azophenol **3a** is inactive to alkali and alkaline earth metal salts except the formation of orange precipitate with magnesium chloride. Since no dissociation of phenol **2n** occurs in pyridine-chloroform, the observed salt-dependent coloration seems to be based on an equilibrium [Eq. (4) in Scheme] between colored salt [ML] and intermediate yellow complex [M·HL]X which may dissociate more easily to give the salt [ML], compared to Eq. (1). The blue shifts of shorter wavelength bands of $\mathbf{2_2}$-$LiClO_4$ and -$NaClO_4$ systems are considered to be due to the formation of [M·HL]ClO_4.

On the basis of the results from this work, further study on cyclic polyether dyes including two phenol groups is in progress.

References and Notes

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4. All new compounds show satisfactory elemental analyses and spectral properties. **2**$_1$: 89% yield, reddish orange crystals from EtOH, mp 167.5-168.5 °C; λ_{max} (log ε in $CHCl_3$) 400 nm (4.37); ^{1}H-NMR (100 MHz, $CDCl_3$) δ 8.76 (d, J=2.5 Hz, 1H, $H_{3'}$), 8.67 (s, 1H, OH), 8.49 (dd, J=2.3, J=9.0 Hz, 1H, $H_{5'}$), 7.81 (d, J=8.9 Hz, 1H, $H_{6'}$), 7.79 (s, 2H, $H_{3,5}$), 4.73 (s, 4H, $ArCH_2$), 3.85-3.56 (m, 8H, OCH_2CH_2O), 3.65 (s, 4H, OCH_2CH_2O). **2**$_2$: 88% yield, orange long plates from MeOH, mp 109.5-110 °C; λ_{max} (log ε in $CHCl_3$) 401 nm (4.28); ^{1}H-NMR (100 MHz, $CDCl_3$) δ 8.96 (bs, 1H, OH), 8.75 (d, J=2.2 Hz, 1H, $H_{3'}$), 8.48 (dd, J=2.3, J=8.9 Hz, 1H, $H_{5'}$), 7.81 (s, 2H, $H_{3,5}$), 7.81 (d, J=8.6 Hz, 1H, $H_{6'}$), 4.76 (s, 4H, $ArCH_2$), 3.87-3.63 (m, 8H, OCH_2CH_2O), 3.71 (s, 8H, OCH_2CH_2O). **3**: purplish red needles from EtOH, mp 123-124.5 °C, λ_{max} (log ε in $CHCl_3$) 400 nm (4.37); ^{1}H-NMR (100 MHz, $CDCl_3$) δ 8.75 (d, J=2.2 Hz, 1H, $H_{3'}$), 8.74 (s, 1H, OH), 8.48 (dd, J=2.4, J=9.0 Hz, 1H, $H_{5'}$), 7.81 (s, 2H, $H_{3,5}$), 7.80 (d, J=8.8 Hz, 1H, $H_{6'}$), 4.68 (s, 4H, $ArCH_2$), 3.51 (s, 6H, Me) for **3a**; 12.18 (bs, 1H, NH), 9.17 (d, J=2.2 Hz, 1H, $H_{3'}$), 8.46 (dd, J=2.4, J=9.3 Hz, 1H, $H_{5'}$), 8.19 (d, J=9.6 Hz, 1H, $H_{6'}$), 7.60-7.50 (m, 1H, H_3 or H_5), 7.43-7.33 (m, 1H, H_3 or H_5), 4.40 (d, J=1.8 Hz, 2H, OCH_2), 4.35 (d, J=1.9 Hz, 2H, OCH_2), 3.54 (s, 3H, Me), 3.50 (s, 3H, Me) for **3b**. After addition of 1 eq. of Et_3N into the tube, the signals due to the hydrazone **3b** were completely disappeared and the following new signals were recorded: δ 8.81 (d, J=2.2 Hz, 1H, $H_{3'}$), 8.45 (dd, J=2.2, J=9.1 Hz, 1H, $H_{5'}$), 7.89 (d, J=8.8 Hz, 1H, $H_{6'}$), 7.74 (s, 2H, $H_{3,5}$), 4.58 (s, 4H, $ArCH_2$), 3.49 (s, 6H, Me).
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6. The visible spectra were measured as follows. After a spoonful of crystalline salt (ca. 10^{-4} mol) was added to a solution (2 ml) of azophenol (ca. 7×10^{-8} mol)-base (ca. 6×10^{-5} mol), the resulting mixture was well shaken for 2 min in a cell and then the spectra were recorded within 5 min.

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