

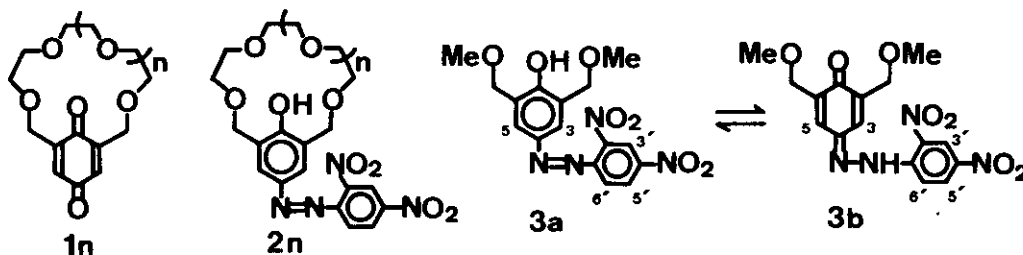
SYNTHETIC MACROCYCLIC LIGANDS. V.¹⁾ "CROWNED" DINITROPHENYLAZO-PHENOLS: DISSOLVING AND COLORATING AGENT OF ALKALI AND ALKALINE EARTH METAL SALTS IN ORGANIC SOLVENTS[†]

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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_n-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 2_n, which are easily derived from "crowned" benzoquinones 1_n 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 2_n with various alkali and alkaline earth metal salts.



Quinone 1_n was treated with 1.1 eq. of 2,4-dinitrophenylhydrazine in ethanol to give the desired "crowned" azophenol 2_n⁴⁾ in good yield. An "uncrowned" azophenol 3_a⁴⁾ was similarly prepared from the corresponding quinone in 94% yield. NMR study reveals that compound 3 exists in azophenol-hydrazone equilibrium (3_a : 3_b = 59 : 41 in CDCl₃), whereas that 2_n is existing as pure azo-form, indicating the stabilization

† 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: $\underline{2}$ and $\underline{3}$ in ethanol solution partially dissociate to form colored phenolate anions (λ_{\max} 586 nm for $\underline{2}_1$, 555 for $\underline{2}_2$, and 586 for $\underline{3}$). 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 $\underline{2}_1$ -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 $\underline{2}_2$ and $\underline{3}$ are less susceptible to the hypsochromic shift than that of $\underline{2}_1$.

Table. Hypsochromic shift of azophenol-Et₃N-metal salt systems in ethanol, $\Delta\lambda = \lambda_{\max}(\text{with salt}) - \lambda_{\max}(\text{salt free})$ a), 6)

Run	Added salt	$-\Delta\lambda/\text{nm}^{\text{b)}$			Run	Added salt	$-\Delta\lambda/\text{nm}^{\text{b)}$		
		$\underline{2}_1$	$\underline{2}_2$	$\underline{3}$			$\underline{2}_1$	$\underline{2}_2$	$\underline{3}$
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 ·6H ₂ O	-64	-72	-50
6	KClO ₄	-16	-5	0	14	BaCl ₂ ·2H ₂ O	-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					

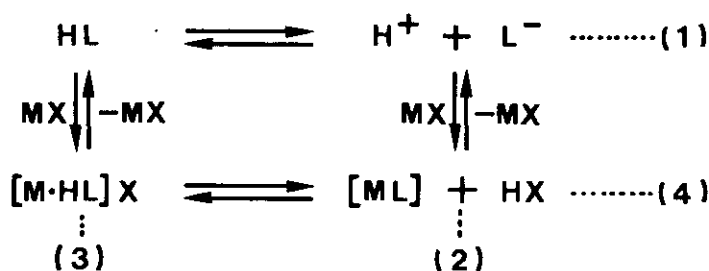
a) 589 nm for $\underline{2}_1$, 558 for $\underline{2}_2$, and 586 for $\underline{3}$. b) Error: ± 2 nm.

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- $\underline{2}_1$ 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 $\underline{2}_1$ in chloroform. Especially, Fig. 1 is suggestive of specific coloration of $\underline{2}_1$ 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 $\underline{2}_1$ -pyridine in chloroform. The same lithium ion-specific coloration of $\underline{2}_1$ was observed also by using a crystalline mixture of lithium and other alkali metal salts.

The spectral change of $\underline{2}_2$ 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

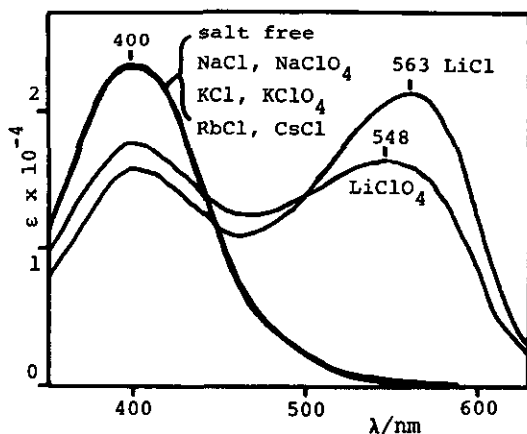


Fig. 1. Visible spectra of $\underline{2}_1$ -alkali metal salt-pyridine systems in CHCl_3 .⁶⁾

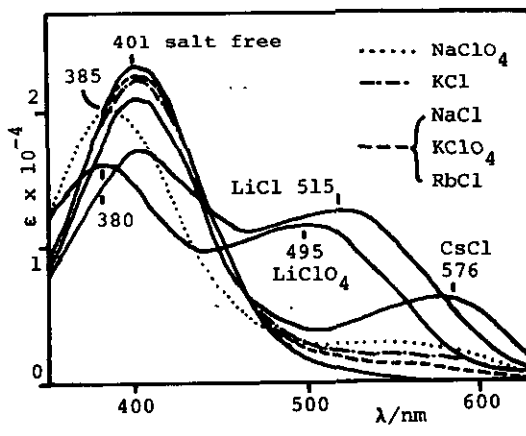


Fig. 2. Visible spectra of $\underline{2}_2$ -alkali metal salt-pyridine systems in CHCl_3 .⁶⁾

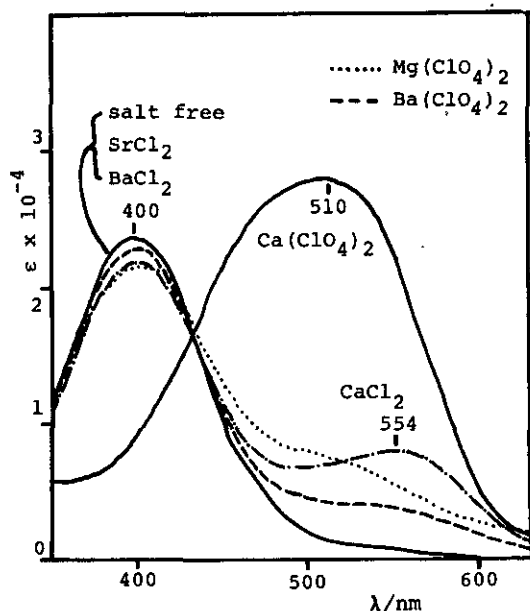


Fig. 3. Visible spectra of 2_1 -alkaline earth metal salt-pyridine systems in CHCl_3 .⁶⁾

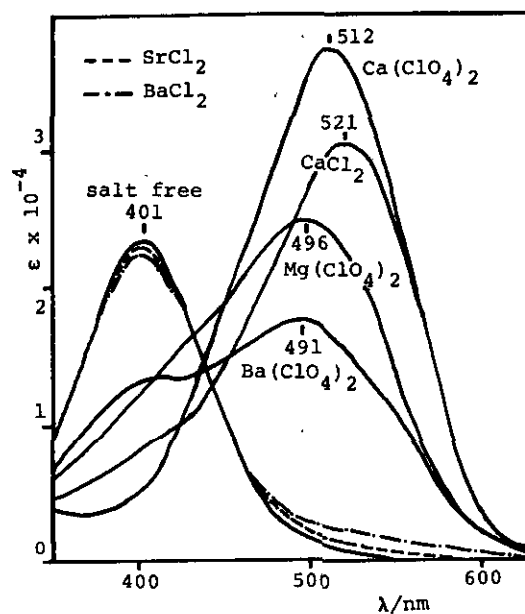


Fig. 4. Visible spectra of 2_2 -alkaline earth metal salt-pyridine systems in CHCl_3 .⁶⁾

2_n with relatively small size of alkaline earth metal ions: Mg^{++} and Ca^{++} . It is noteworthy that "uncrowned" azophenol 3_a is inactive to alkali and alkaline earth metal salts except the formation of orange precipitate with magnesium chloride.

Since no dissociation of phenol 2_n 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 $[\text{M}\cdot\text{HL}]\text{X}$ which may dissociate more easily to give the salt [ML], compared to Eq. (1). The blue shifts of shorter wavelength bands of 2_2 - LiClO_4 and $-\text{NaClO}_4$ systems are considered to be due to the formation of $[\text{M}\cdot\text{HL}]\text{ClO}_4$.

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. 2₁: 89% yield, reddish orange crystals from EtOH, mp 167.5-168.5 °C; λ_{\max} (log ϵ in CHCl₃) 400 nm (4.37); ¹H-NMR (100 MHz, CDCl₃) δ 8.76 (d, J=2.5 Hz, 1H, H₃), 8.67 (s, 1H, OH), 8.49 (dd, J=2.3, J=9.0 Hz, 1H, H₅), 7.81 (d, J=8.9 Hz, 1H, H₆), 7.79 (s, 2H, H_{3,5}), 4.73 (s, 4H, ArCH₂), 3.85-3.56 (m, 8H, OCH₂CH₂O), 3.65 (s, 4H, OCH₂CH₂O). 2₂: 88% yield, orange long plates from MeOH, mp 109.5-110 °C; λ_{\max} (log ϵ in CHCl₃) 401 nm (4.28); ¹H-NMR (100 MHz, CDCl₃) δ 8.96 (bs, 1H, OH), 8.75 (d, J=2.2 Hz, 1H, H₃), 8.48 (dd, J=2.3, J=8.9 Hz, 1H, H₅), 7.81 (s, 2H, H_{3,5}), 7.81 (d, J=8.6 Hz, 1H, H₆), 4.76 (s, 4H, ArCH₂), 3.87-3.63 (m, 8H, OCH₂CH₂O), 3.71 (s, 8H, OCH₂CH₂O). 3: purplish red needles from EtOH, mp 123-124.5 °C, λ_{\max} (log ϵ in CHCl₃) 400 nm (4.37); ¹H-NMR (100 MHz, CDCl₃) δ 8.75 (d, J=2.2 Hz, 1H, H₃), 8.74 (s, 1H, OH), 8.48 (dd, J=2.4, J=9.0 Hz, 1H, H₅), 7.81 (s, 2H, H_{3,5}), 7.80 (d, J=8.8 Hz, 1H, H₆), 4.68 (s, 4H, ArCH₂), 3.51 (s, 6H, Me) for 3a; 12.18 (bs, 1H, NH), 9.17 (d, J=2.2 Hz, 1H, H₃), 8.46 (dd, J=2.4, J=9.3 Hz, 1H, H₅), 8.19 (d, J=9.6 Hz, 1H, H₆), 7.60-7.50 (m, 1H, H₃ or H₅), 7.43-7.33 (m, 1H, H₃ or H₅), 4.40 (d, J=1.8 Hz, 2H, OCH₂), 4.35 (d, J=1.9 Hz, 2H, OCH₂), 3.54 (s, 3H, Me), 3.50 (s, 3H, Me) for 3b. After addition of 1 eq. of Et₃N 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, H₃), 8.45 (dd, J=2.2, J=9.1 Hz, 1H, H₅), 7.89 (d, J=8.8 Hz, 1H, H₆), 7.74 (s, 2H, H_{3,5}), 4.58 (s, 4H, ArCH₂), 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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