Synthesis and Properties of Crown Compounds Containing Anthraquinone Nuclei[1)]

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Synopsis. 2,5,8,20,23,26-Hexaoxa[7.7]- and 2,5,8,11,23,26,29,32-Octaoxa[10.10](1,8)anthraquinonophanes (**2** and **3**) were synthesized, examined for complexation behavior with alkali and alkaline earth metal cations, and observed to show significant selectivity among the cations studied. The electroreduction of **2** by cyclic voltammetry was studied with the related compounds.

Crown compounds including a quinone-hydroquinone redox system in the molecule demonstrate complexation behavior. Recently, Vögtle *et al.* synthesized 4,7,10-trioxa-1,13-dithia[13](9,10)anthraquinonophane[2a)] and 1,4,7,10,13-pentaoxa[13]- and 1,4,7,10,13,16-hexaoxa-[16](1,2)anthraquinonophanes.[2b)] Misumi *et al.* have reported the synthesis of "crowned" quinone-hydroquinone redox systems, for which the 2,4-dinitrophenylhydrazone derivatives exist only as tautometric "crowned" dinitrophenylazophenols. They showed cation selectivity for Li(I).[3a,b)] These compounds were applied to the spectrophotometric determination of Li(I).[3c)]

Here, we report the synthesis of a new series of "crowned" anthraquinone (**1**, **2**, **3**, and **6**) according to Chart 1.

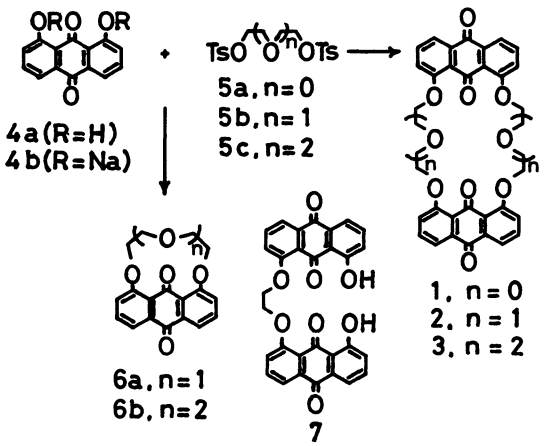

Chart 1.

TABLE 1. RESULTS OF SOLVENT EXTRACTION AT 20 °C

Ion	2(%)	3(%)	7(%)	Ionic radius/Å
Li^+	5.8	12.8	0.7	0.60
Na^+	9.9	22.6	2.1	0.95
K^+	12.8	56.6	2.8	1.33
Rb^+	28.6	49.9	3.1	1.48
Cs^+	25.5	35.7	2.7	1.69
Mg^{2+}	2.4	3.2	1.4	0.65
Ca^{2+}	3.8	7.1	2.6	0.99
Sr^{2+}	3.4	4.0	2.4	1.13
Ba^{2+}	5.4	30.4	2.3	1.35

Treatment of the sodium salt (**4b**) of 1,8-dihydroxyanthraquinone with ethylene glycol ditosylate (**5a**) in the presence of NaOH in xylene under reflux for 10—15 h did not gave the cyclic ether **1** but the acyclic ether **7** in 2.5% yield. On the other hand the reactions of **4b** with **5b** and **5c** afforded **2** (8.9%) and **3** (0.6%). Neither the expected **6a** and **6b** were obtained. An attempt to synthesize **6** ($n=1$ or 2) by the reaction of **4b** with the corresponding **5b** or **5c** was unsuccessful. The structures of **2**, **3**, and **7** obtained here, were identified by elemental analyses, IR, mass spectra, and ^1H NMR. The complex formation between a macrocyclic polyether (**2** or **3**) and a variety of alkali and alkaline earth metal salts could be readily established by Pedersen's solvent extraction method.[4)] Results obtained by the solvent extraction of the complexed crowns from a mixture of picric acid, alkali, or alkaline earth metal salt (Li^+, Na^+, K^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, or Ba^{2+}) and the crown (**2** or **3**) in CH_2Cl_2–H_2O are shown in Table 1.

Appreciable selectivity was shown by **2** for Rb^+ and Cs^+, and by **3** for K^+, Rb^+, and Cs^+ among alkali cations and also by **3** for Ba^{2+} among alkaline earth metal cations. It was also clear that the acyclic diol **7** did not participate significantly in the extraction. These facts seem to be related to the relative size of the cations and the cavity of **2** or **3**.[5)]

Electrochemical properties of **2** were studied by cyclic voltammetry together with related quinones.[6)] The reduction potentials of these quinones are summarized in Table 2. The acyclic compound **7** has two redox couples (−0.66 and −1.35 V), whose difference ($E_{p1}-E_{p2}$) corresponds well to that of 9,10-anthraquinone. In contrast the cyclic voltammogram of **2** gave a well-defined three wave pattern contrary to that expected for two or four redox couples. The differences between the redox potentials ($E_{p1}-E_{p2}$ and $E_{p2}-E_{p3}$) of **2** were characteristically very small, *i.e.*, 0.22 and 0.33 V, respectively. This behavior of **2** is not completely explained but seems to be related to the easy delocalization of the electron(s) in the corresponding dianion species (dianion or dianion diradical) arising from the reduction of **2**. Thus, the dianion species appear to be more stabilized by delocalization than the corresponding mono-, tri-, or tetraanion species

TABLE 2. ELECTROCHEMICAL REDUCTION POTENTIALS (V *vs.* SCE)

Compound	E_{p1}	E_{p2}	E_{p3}	$E_{p1}-E_{p2}$	$E_{p2}-E_{p3}$
9,10-Anthraquinone	−0.96	−1.67	—	0.71	—
7	−0.66	−1.35	—	0.69	—
2	−0.85	−1.07	−1.40	0.22	0.33

derived from **2**.

Experimental

Ultraviolet absorption (UV) spectra and IR spectra were measured on Shimadzu UV-300 and JASCO IRA-2 spectrometers, respectively. ^{1}H NMR spectra were obtained on a JEOL FX 90Q spectrometer. The chemical shifts are in ppm using TMS as an internal standard. Mass spectra were obtained with a JEOL JMS-01SG mass spectrometer.

General Procedure. *Polyethylene glycol ditosylate* (**5a**, **5b**, or **5c**, 80 mmol) was added to a solution of disodium 9,10-dioxo-1,8-anthracenediolate prepared by azeotropic distillation of a mixture of aqueous NaOH solution (160 mmol), 1,8-dihydroxyanthraquinone (19.20 g, 80 mmol), and xylene (500 ml). The above mixture was refluxed for 10—15 h. The reaction mixture was filtered and the residue washed thoroughly with xylene (100 ml). The combined xylene solution was evaporated *in vacuo* and the solid residues were washed with acetone to give **2**, **3**, and **7**, respectively. The unreacted tosylate was recovered from the filtrate. The compounds (**2**, **3**, and **7**) were recrystallized from toluene.

2,5,8,20,23,26-Hexaoxa[7.7](1,8)anthraquinonophane (**2**): Yellow crystals; mp 190 °C; IR (KBr): 1670, 1630, and 1585 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ=4.04—4.36 (m, 16H, $-CH_2-$) and 7.15—7.98 (m, 12H, aromatic H); UV (CH_2Cl_2): 396 nm (ε 9750); Found: C, 69.70; H, 5.00%; M$^+$, 620. Calcd for $C_{36}H_{28}O_{10}$: C, 69.67; H, 4.55%; M, 620.

2,5,8,11,23,26,29,32-Octaoxa[10.10](1,8)anthraquinonophane (**3**): Pale yellow crystals; mp 278—280 °C; IR (KBr): 1670, 1625, and 1590 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ=3.60—4.22 (m, 24H, $-CH_2-$) and 7.12—7.83 (m, 12H, aromatic H); UV (CH_2Cl_2): 380 nm (ε 8490); Found: C, 66.10; H, 4.99%: M$^+$, 708. Calcd for $C_{40}H_{36}O_{12}\cdot H_2O$: C, 66.11; H, 5.27%; M, 708.

1,1′-Bis(8-hydroxy-9,10-dioxo-1-anthryloxy)ethylene (**7**): Yellow crystals; mp 280 °C decomp; IR (KBr): 3400, 1675, 1635, and 1585 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ=4.74 (s, 4H, $-CH_2-$), 12.72 (s, 2H, OH), and 7.25—7.96 (m, 12H, aromatic H); UV (CH_2Cl_2): 411 nm (ε 11000); Found: C, 73.48; H, 4.54%; M$^+$, 506. Calcd for $C_{30}H_{18}O_8\cdot 1/2C_7H_8$: C, 73.69; H, 4.18%; M 506.

Solvent Extraction Experiments of Metal Ions by **2**, **3**, *and* **7**:[4] After a mixture of picric acid (7×10^{-5} M, 5 ml of aqueous solution; 1 M=1 mol dm^{-3}), metal chloride (0.1 equiv., 5 ml of aqueous solution) was shaked vigorously with **2**, **3**, or **7** (7×10^{-4} M, 5 ml of CH_2Cl_2 solution), the absorbance of the aqueous layer was measured. The extraction ratios obtained by the reduced absorbance to that of the original aqueous layer are shown in Table 1.

Electrochemical Measurements of the Quinones: According to Ref. 6 all measurements were carried out in *N,N*-dimethylformamide containing 0.1 M tetrabutylammonium perchlorate at 20±0.2 °C using a three electrode cell.

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5) The cavity sizes of **2** and **3** were estimated by using the CPK model: **2**, 2.6×3.6 Å; **3**, 4.2×5.4 Å.

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