

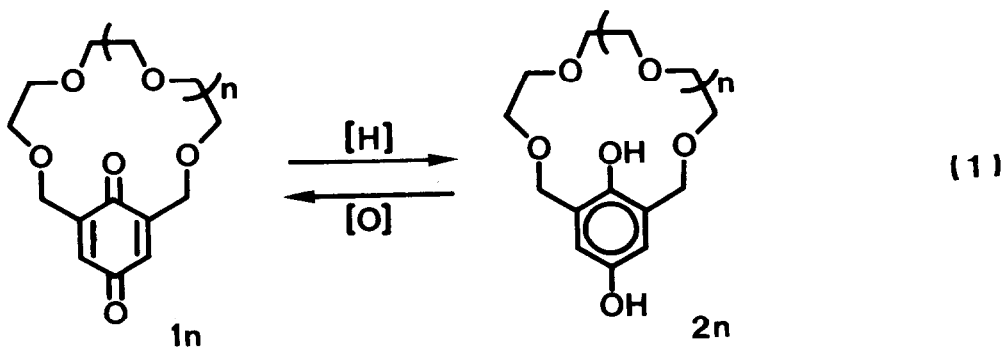
SYNTHETIC MACROCYCLIC LIGANDS. III.¹⁾ SYNTHESIS OF A QUINONE-HYDROQUINONE
REDOX SYSTEM INCORPORATED WITH COMPLEXING ABILITY TOWARD CATIONS

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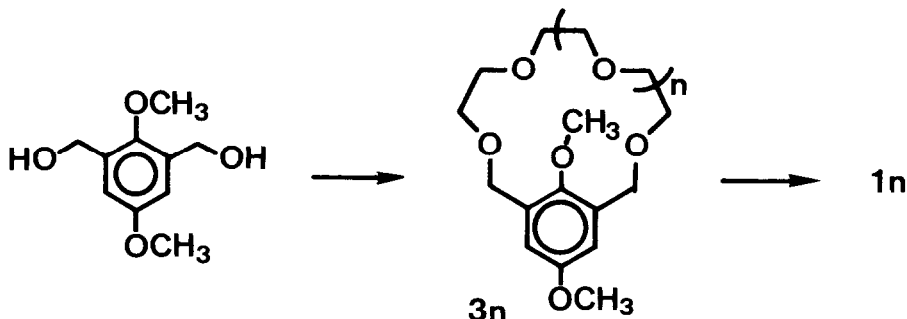
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Summary Two quinones bridged with a polyether chain and the corresponding hydroquinones were synthesized, and their redox reaction and complexations with sodium and potassium ions were observed.

It is well known that quinones are an artificially and naturally momentous class of compounds, the most significant property of which is based on the ready reversibility of the quinone-hydroquinone redox system. When such a redox system is incorporated with complexing ability toward cations, the redox potential of the system can be controlled by closely placed cations. As a model to examine this interesting subject, we chose a "crowned" redox system, equation (1), where $1n$ and/or $2n$ are expected to form a complex with a cation by such a way that the inner one of two oxygen groups attached to the six-membered ring takes part in both the redox reaction and the complexation. We now report the synthesis of the first "crowned" quinone-hydroquinone redox system.²⁾

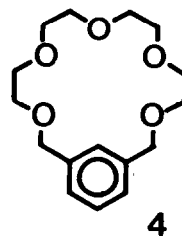


Co-cyclization of 1,3-bis(hydroxymethyl)-2,5-dimethoxybenzene³⁾ with tri- and tetra-ethylene glycol ditosylates afforded cyclic polyethers 3_1 ⁴⁾ and 3_2 ⁴⁾ in 52 and 54% yields, respectively. The cyclic ethers 3_n were oxidatively demethylated with ceric ammonium nitrate⁵⁾ in aqueous acetonitrile at 50°C to give desired "crowned" quinones 1_n , 60% yield for 1_1 ⁴⁾ and 76% for 1_2 .⁴⁾



Reduction of yellow crystalline 1_n in chloroform with aqueous sodium dithionite at room temperature produced a colorless organic layer from which "crowned" hydroquinones 2_n ⁴⁾ were isolated in almost quantitative yields. Reverse oxidation of 2_n with ferric chloride in ethanol at room temperature reproduced the quinones 1_n in good yields, 90% for 1_1 and 84% for 1_2 , indicating the excellent reversibility of this new redox system (1).

The inspection of cycles 1-4 with CPK molecular model suggests that the inner ones of the two substituents (OMe, OH, and C=O) attached to the six-membered rings are capable of flipping up and down through the polyether ring. In fact, the flipping was reflected on singlet patterns of benzylic or allylic protons of 1-4 in NMR spectra, except an AB pattern for 3_1 .



The association constants, K_a , for the 1:1 complex formation of a series of cyclic polyethers 1_n , 2_n , 3_n , and 4 ⁶⁾ and a reference cyclic polyether, 18-crown-6, with Na^+ and K^+ have been determined by potentiometry with cation-selective electrodes. The constants of cycles 1_2 , 2_2 , 3_2 , and 4 having similar size of

cavity to that of 18-crown-6 are summarized in Table. All the cycles show weaker complexations than 18-crown-6 to both ions, and form more stable complexes with K^+ than Na^+ just as 18-crown-6. On the other hand, the constants of smaller cycles 1_1 , 2_1 , and 3_1 are too low to measure by this method.

Table. Association constants for 1:1 complexes in methanol at 25°C.

Polyether	Log K_a ^{a)}	
	Na^+Cl^-	K^+Cl^-
18-crown-6	4.33, 4.32 ^{b)}	6.10, 6.10 ^{b)}
1_2	1.80	2.67
2_2	2.39	3.18
3_2	2.51	3.56
4	1.81	2.82

a) K_a in 1/mol. b) Values of Frensdorff, ref. 7).

The table also shows the magnitude of K_a 's to be the order of $3_2 > 2_2 > 4 > 1_2$. The unexpectedly small values of 1_2 compared to those of 4 clearly indicate that the inner carbonyl oxygen of quinone 1_2 makes no contribution to stabilize the complexes under the given conditions. This is in contrast to the complexation of "crowned" benzimidazolone system where a positive assistance of the ureido carbonyl oxygen was observed.⁸⁾ On the other hand, the inner hydroxylic oxygen of 2_2 shows an effective coordination to the complexed cations, which is manifested by the larger values of 2_2 than those of 1_2 and 4. The effect of cations on the redox potential of the present system will be presented elsewhere.

References and Notes

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- 4) All new compounds show satisfactory elemental analyses and spectral properties. 1_1 : yellow fine needles from hexane, m.p. 137-138°C; $^1\text{H-NMR}$ (100 MHz, CDCl_3) δ 6.69 (s, 2H, =CH), 4.45 (s, 4H, allyl H), 3.80-3.68 (m, 4H, OCH_2), 3.53-3.41 (m, 4H, OCH_2), 3.37 (s, 4H, $\text{OCH}_2\text{CH}_2\text{O}$); IR (nujol mull) 1674, 1658, 1653, 1625, 1619 cm^{-1} . 1_2 : yellow columns from hexane, m.p. 77-78°C; $^1\text{H-NMR}$ (100 MHz, CDCl_3) δ 6.71 (s, 2H, =CH), 4.52 (s, 4H, allyl H), 3.80-3.56 (m, 8H, $\text{OCH}_2\text{CH}_2\text{O}$), 3.53 (s, 8H, $\text{OCH}_2\text{CH}_2\text{O}$); IR (nujol mull) 1677, 1651, 1633 cm^{-1} . 2_1 : colorless fine columns from benzene, m.p. 151-152°C; $^1\text{H-NMR}$ (CDCl_3 -DMSO- d_6 , 100 MHz) δ 6.59 (s, 2H, ArH), 4.52 (s, 4H, ArCH_2), 3.72-3.52 (m, 8H, $\text{OCH}_2\text{CH}_2\text{O}$), 3.61 (s, 4H, $\text{OCH}_2\text{CH}_2\text{O}$); IR (nujol mull) 3387, 3153 cm^{-1} . 2_2 (monohydrated): white crystals from benzene, m.p. 76-80°C; $^1\text{H-NMR}$ (100 MHz, CDCl_3) δ 6.63 (s, 2H, ArH), 4.60 (s, 4H, ArCH_2), 3.68 (s, 8H, $\text{OCH}_2\text{CH}_2\text{O}$), 3.66 (s, 8H, $\text{OCH}_2\text{CH}_2\text{O}$); IR (nujol mull) 3434, 3397, 3153 cm^{-1} . 3_1 : colorless plates from hexane, m.p. 51-52°C, M^+ m/e 312; $^1\text{H-NMR}$ (100 MHz, CDCl_3) δ 6.82 (s, 2H, ArH), 4.90 (d, $J=12.5$ Hz, 2H, ArCH_2), 4.17 (d, $J=12.5$ Hz, 2H, ArCH_2), 3.85 (s, 3H, CH_3), 3.80 (s, 3H, CH_3), 3.72-3.10 (m, 12H, $\text{OCH}_2\text{CH}_2\text{O}$). 3_2 : colorless prisms from hexane- CH_2Cl_2 , m.p. 91°C, M^+ m/e 356; $^1\text{H-NMR}$ (100 MHz, CDCl_3) δ 6.81 (s, 2H, ArH), 4.55 (s, 4H, ArCH_2), 4.04 (s, 3H, inner CH_3), 3.78 (s, 3H, outer CH_3), 3.60 (s, 8H, $\text{OCH}_2\text{CH}_2\text{O}$), 3.48 (s, 8H, $\text{OCH}_2\text{CH}_2\text{O}$).
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