Efficient Synthesis of Alkoxyanthraquinones from Fluoroanthraquinones and Their Preliminary Electrochemistry

L. Echegoyen,*,† Yehia Hafez,‡ Raphael C. Lawson,† J. de Mendoza,*,‡ and T. Torres*,‡

Department of Chemistry, University of Miami, Coral Gables, Florida 33124, and Departamento de Química, Universidad Autônoma de Madrid, Cantoblanco, 28049-Madrid, Spain

Received September 15, 1992

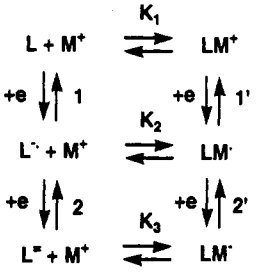
The reaction of 1,8-dichloroanthraquinone with CsF in DMSO under anhydrous conditions affords improved yields of the corresponding difluoro derivative **2**. Nucleophilic displacement reactions using simple alkoxide nucleophiles or crown ether derivatives on **2** allows the preparation of 1,8-dialkoxyanthraquinones **5–10** in good to excellent yields. Compounds **8** and **10** exhibit enhanced sodium binding properties upon reduction to the corresponding mono- and dianions. Cation binding enhancements are larger than those previously observed for structurally related systems.

Introduction

Anthraquinone-substituted ligands (podands, crown ethers, and cryptands) have been used as electrochemically-switched systems capable of enhanced cation binding and enhanced transport across model membranes.[1,2] The operating principle leading to these enhancements is the coupling of the redox processes of the quinones to the cation binding equilibria.[1,2] These multiple equilibria can be represented by Scheme I. The electrochemical processes 1, 1′, 2, and 2′ correspond to the reduction steps of the free ligand (1 and 2) and to those of the ligand-cation complex (1′ and 2′). These are coupled to the cation binding equilibria of the ligand: K_1 for the neutral complexant, K_2 for the anion radical, and K_3 for the dianion. The binding enhancements K_2/K_1 and K_3/K_2 are typically $\leq 10^3$ [1,2] and have been used to enhance cation binding transport rates across model liquid membranes.[2] Since the reduced states of the anthraquinone group are stable in aqueous environments at neutral pH, these anthraquinone-containing ligands are potentially useful as cation-, electron-, and proton-transporting systems across membranous materials.[2]

The major obstacle encountered in these studies has been the lack of convenient and effective synthetic methods for the preparation of the necessary substituted anthraquinones. For example, the preparation of 1-alkoxy derivatives from the readily accessible 1-hydroxyanthraquinone with the appropriate halide or tosylate is very difficult.[1c] Direct displacement of chlorine from the 1-position by alkoxides is also complicated, and the resulting yields are very low. Recently, Gokel et al.[3] have reported enhanced yields for nucleophilic aromatic substitutions of anthraquinones when the nucleophile is a poly(ethyleneoxy) derivative. They also reported that once these ethyleneoxy substituents are attached to the quinone they can be displaced by nucleophiles which do not displace chlorine. Other substituents such as alkynols exhibit similar properties. The overall process may be made catalytic. Moderate to good yields were obtained by these procedures, which depended largely on the nature of the alkoxide used as nucleophile and on the catalyst. Consequently, the development of a general procedure for the preparation of 1-alkoxyanthraquinones, especially in good yields, was still needed.

Scheme I



Additions of side chains to anthraquinone systems have involved displacements of fluoride by amines,[4,5] but nucleophilic aromatic substitutions of this halide by alkoxides have not received much attention. Due to our continued interest in the electrochemical properties of anthraquinone-containing cation complexing systems, and their potential application as redox-switched cation and electron "shuttles" across membranes, we wanted to develop a convenient and effective synthetic method to prepare 1,8-dialkoxyanthraquinones. We report here an improved procedure for the synthesis of 1,8-difluoroanthraquinone from commercially available 1,8-dichloroanthraquinone. We also report efficient nucleophilic displacement of the halide atoms by alkoxides derived from simple alcohols and lariat ether macrocycles to yield 1,8-dialkoxyanthraquinones **5–7** and **9** in good to excellent yields. The same strategy has been used to prepare 1-alkoxyanthraquinone derivatives **8** and **10** from 1-fluoroanthraquinone. Preliminary electrochemical results for the later two ligands, previously unknown, are also reported here.

† University of Miami.

‡ Universidad Autónoma de Madrid.

(1) (a) Echegoyen, L.; Gustowski, D. A.; Gatto, V. J.; Gokel, G. W. *J. Chem. Soc., Chem. Commun.* **1986**, 220–222. (b) Gustowski, D. A.; Delgado, M.; Gatto, V. J.; Echegoyen, L.; Gokel, G. W. *Tetrahedron Lett.* **1986**, *27*, 3487–3490. (c) Gustowski, D. A.; Delgado, M.; Gatto, V. J.; Echegoyen, L.; Gokel, G. W. *J. Am. Chem. Soc.* **1986**, *108*, 7553–7560. (d) Delgado, M.; Gustowski, D. A.; Yoo, H. K.; Gokel, G. W.; Echegoyen, L. *J. Am. Chem. Soc.* **1988**, *110*, 119–124.

(2) (a) Echeverria, L.; Delgado, M.; Gatto, V. J.; Gokel, G. W.; Echegoyen, L. *J. Am. Chem. Soc.* **1986**, *108*, 6825–6826. (b) Echegoyen, L. E.; Yoo, H. K.; Gatto, V. J.; Gokel, G. W.; Echegoyen, L. *J. Am. Chem. Soc.* **1989**, *111*, 2440–2443. (c) Chen, Z.; Gokel, G. W.; Echegoyen, L. *J. Org. Chem.* **1991**, *56*, 3369–3372.

(3) (a) Yoo, H. K.; Davis, D. M.; Chen, Z.; Echegoyen, L.; Gokel, G. W. *Tetrahedron Lett.* **1990**, *31*, 55–58. (b) Lu, T.; Yoo, H. K.; Zhang, H.; Bott, S.; Atwood, J. L.; Echegoyen, L.; Gokel, G. W. *J. Org. Chem.* **1990**, *55*, 2269–2270. (c) Fang, J.; Lu, T.; Kim, H.; Delgado, I.; Geoffroy, P.; Atwood, J. L.; Gokel, G. W. *J. Org. Chem.* **1991**, *56*, 7059–7065.

(4) Bayer, O. Anthrachinone. In *Houben-Weyl, Methoden der Organischen Chemie*, 4th ed.; Müller, O., Ed.; Georg Thieme Verlag: Stuttgart, 1979; Vol. 7/3c.

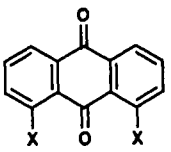
(5) Ossowski, T.; Schneider, H. *Chem. Ber.* **1990**, *123*, 1673–1677.

0022-3263/93/1958-2009$04.00/0

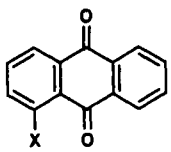
Results and Discussion

1,8-Difluoroanthraquinone (2) has been previously prepared from 1,8-dichloroanthraquinone (1) by treatment with potassium fluoride at 230 °C under pressure[6] or with cesium fluoride in DMSO solution.[7] Attempts to prepare 2 using the first method failed in our hands. Only unsubstituted 9,10-anthraquinone was isolated as a reaction product. Using the second method compound 2 was obtained, as described, in low yield (35%).[7] We have found that a slight modification of this method, mainly by using extremely anhydrous conditions of all reactants and solvents, reduces the presence of reaction intermediates in the final product to afford 1,8-difluoroanthraquinone (2) in good yield (60%). Similarly, 1-fluoroanthraquinone (4)[8,9] was obtained from 1-chloroanthraquinone (3) in 78% yield. Attempts to displace chloride with fluoride using anhydrous tetrabutylammonium fluoride[10] afforded lower yields of the corresponding fluoroanthraquinone.

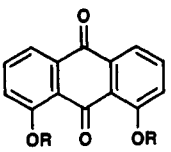
The reaction of 1,8-difluoroanthraquinone (2) with different alcohols (propanol, decanol, and hexadecanol) using standard conditions (NaH/THF, reflux) afforded 70–90% yields of the corresponding disubstituted derivatives 5–7. These results are in pronounced contrast with



1 X = Cl
2 X = F



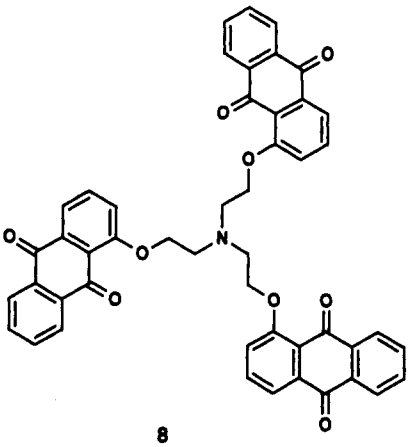
3 X = Cl
4 X = F



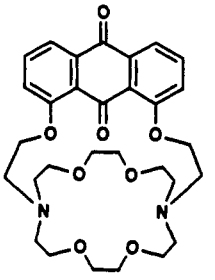
5 R = C_3H_7
6 R = $C_{10}H_{21}$
7 R = $C_{16}H_{33}$

the low yields (all under 20%) reported for the nucleophilic substitution reactions of single 1-chloroanthraquinone using similar alkoxide nucleophiles in the absence of any catalyst.[3c] Our results clearly indicate the convenience of using fluorine instead of chlorine in the nucleophilic aromatic substitution reactions at the 1-position of anthraquinone derivatives.

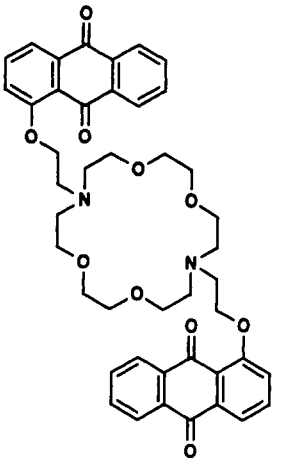
The same methodology has been used to prepare the more complicated anthraquinone derivatives 8–10. In all of these cases the reaction seems to be essentially quantitative. Unfortunately, isolated yields (68% for 8, 71% for 9.NaI, and 53% for 10) are lower due to isolation problems associated with the formation of sodium complexes and their water solubility. It should be pointed out that the recent report of the preparation of 9 using a two-step synthesis afforded a much lower yield than that reported here.[11]



8



9



10

As in previous electrochemical work with substituted anthraquinones,[1,2] compounds 8 and 10 exhibit additional and time-resolved redox pairs upon addition of aliquots of sodium tetraphenylborate. Before addition of the Na^+ salt, only two quasireversible redox pairs are observed in each case, which correspond to the one- and two-electron reduction of each of the essentially independent and uncoupled quinone groups to its corresponding anion radical and dianion, respectively (see steps 1 and 2 in Scheme I). Thus, in the case of 8 the first reduction corresponds to a three-electron wave, one for each of the equivalent quinone groups in the structure. The second wave is also a three-electron process, leading to the formation of a hexaanion. In the case of 10, these two waves correspond to two-electron processes each, for a total of four electrons. Therefore, Scheme I can be applied in all cases as long as it is remembered that the single-electron process represents one such reduction per quinone group in the particular compound under study.

After the addition of the Na^+ salt, two additional redox couples are observed simultaneously, which correspond to steps 1′ and 2′ in Scheme I (remember that the number of electrons for each of these two additional processes is really equal to the number of quinone groups in the particular structure). Such an observation is somewhat unexpected, especially for compound 8, since it is not expected to have a particularly high binding affinity for Na^+. Surprisingly, all four redox couples were resolved. This was also the case for 10, the voltammograms of which are presented in Figure 1. It should be pointed out that most other electrochemical work with simple quinones

(6) Hoeschst, A. G., Brit. Patent 755668, Aug. 22, 1956; *Chem. Abstr.* 1957, *51*, 9686h.
(7) Yamamoto, G.; Oki, M. *Bull. Chem. Soc. Jpn.* 1981, *54*, 473–480.
(8) Valkanas, G.; Hopff, H. *J. Org. Chem.* 1962, *27*, 3680–3682.
(9) Yamamoto, G.; Suzuki, M.; Oki, M. *Bull. Chem. Soc. Jpn.* 1983, *56*, 306–313.
(10) Cox, D. P.; Terpinski, J.; Lewrynowicz, W. *J. Org. Chem.* 1984, *49*, 3216–3219.
(11) Chen, Z.; Schell, O. F.; Alcala, M.; Li, Y.; Gokel, G. W.; Echegoyen, L. *J. Am. Chem. Soc.* 1992, *114*, 444–451.

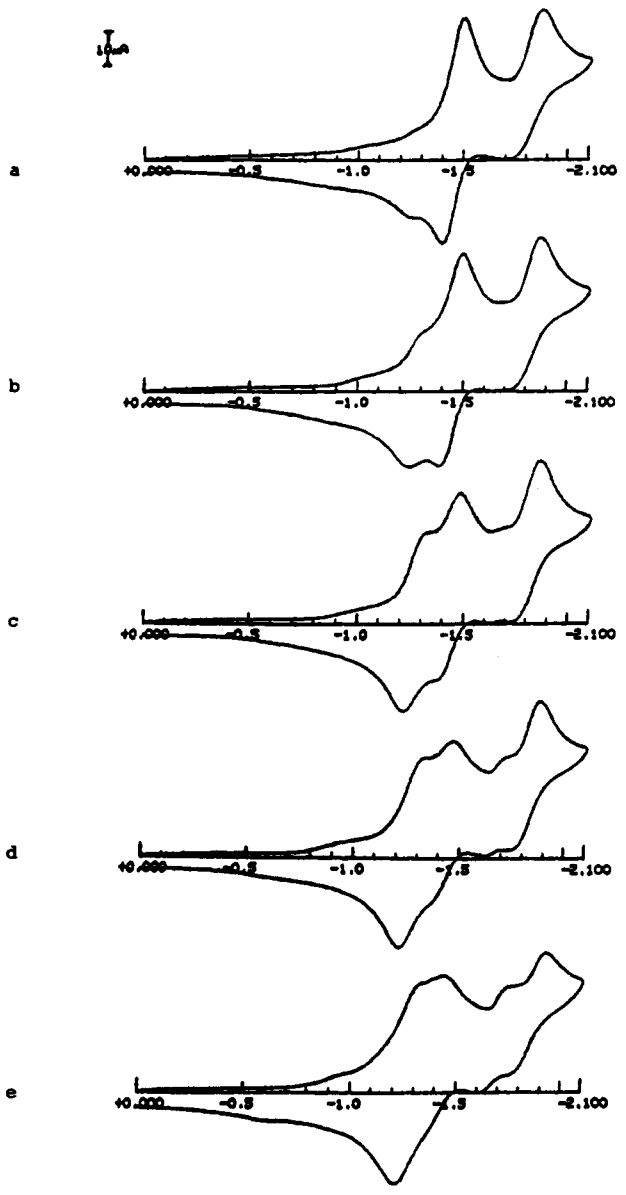
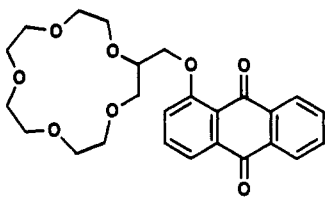


Figure 1. Cyclic voltammograms for **10** in CH_2Cl_2 containing 0.1 M $TBAPF_6$ (a) in the absence of Na^+, (b) in the presence of 0.5 equiv of Na^+, (c) in the presence of 1.0 equiv of Na^+, (d) in the presence of 1.5 equiv of Na^+, and (e) in the presence of 2.0 equiv of Na^+.

shows the usual potential shifts of the redox couple (instead of its split into two couples) as a function of added metal ion concentrations.[12] That is to say, electrochemical steps 1 and 1′ are averaged together, as are steps 2 and 2′ for each of the quinone groups present in the structure. Figure 1 clearly shows the appearance of two additional redox waves as the Na^+ concentration is increased.

On the basis of the individual measurement of all potentials for these four waves, it was possible to determine the apparent ratios K_2/K_1 and K_3/K_2, as previously described.[1] These values correspond to the cation binding enhancements resulting from electrochemical switching of the ligand to its multiply reduced states. These states are considerably more negatively charged than the corresponding neutral ligands. The values measured for **8** are as follows: 8.7×10^2 for K_2/K_1 and 6.9×10^2 for K_3/K_2. For **10**, the corresponding enhancements are as follows: 1.4×10^3 (K_2/K_1) and 7.5×10^2 (K_3/K_2). These enhancements were calculated from the corresponding $E_{1/2}$ values for each of the waves, which in turn were determined from the average of the cathodic and anodic peak potentials [$(E_p^a + E_p^c)/2$]. The enhancements are relatively large when compared with those of structurally related systems.[1c] For example, the sodium binding enhancement observed for **11** was 2.3×10^2 (K_2/K_1), while no K_3/K_2 enhancement was detected. These results are not so surprising when one considers that the overall reduction steps for **10** involve twice as many electrons per molecule as the corresponding ones for **11**.



11

This evidence indicates that both sidearms in **10** are participating in the binding of the macrocycle-bound cation, probably with each sidearm approaching from opposite sites of the macroring plane. Further evidence for this is that the voltammogram does not change appreciably (although some change is noted) when the equivalent amount of added Na^+ is increased from 1 to 2; see Figure 1. Further studies are needed to confirm these conclusions.

Experimental Section

Melting points are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Bruker WP 200 SY instrument, MS spectra on VG Autospec and Varian MAT 312 spectrometers, and IR spectra on a Perkin-Elmer 257. Aldrich neutral alumina, Brockmann I, 150 mesh was used for purification. Except in the cases indicated, solvents were purified and dried by standard procedures, and reagents (Aldrich) were used as received without further purification.

Electrochemical experiments were performed using a Bioanalytical Systems 100 analyzer, equipped with IR compensation, and recorded on a Houston DMP-40 plotter. A glassy carbon electrode was used as the working electrode and a platinum wire was used as a counter electrode. The reference electrode was a piece of silver immersed in a 0.1 M tetra-*n*-butylammonium hexafluorophosphate solution containing 5 mM $AgNO_3$ in dichloromethane–acetonitrile (9:1). The experiments were run at room temperature under a dry nitrogen atmosphere. The electroactive species was present in ~1 mM concentrations. All voltammograms were recorded using full IR compensation. The cation-containing salt was added in half-equivalent increments as the tetraphenylborate salt. Voltammograms were recorded after each successive addition. The potential was scanned at a rate of 100 mV/s.

1,8-Difluoroanthraquinone (2). A mixture of well-dried (60 °C, 3 h, 0.1 Torr) 1,8-dichloroanthraquinone (**1**) (8.00 g, 28.8 mmol) and anhydrous cesium fluoride (155 °C, 8 h, 0.05 Torr) (16.00 g, 105.2 mmol) in thoroughly dried DMSO (35 mL) (CaH_2, 18 h, distillation in vacuo, 4-Å molecular sieves) was stirred for 10 h at 135 °C under an argon atmosphere. After being cooled the mixture was poured into ice–water. The precipitate was filtered, washed successively with water (4 × 250 mL) and methanol (50 mL), and dried in vacuo. The crude material was chromatographed on alumina with dichloromethane–hexane (1:1) as eluent affording 4.22 g (60%) of 1,8-difluoroanthraquinone (**2**) as yellow crystals: mp 228–229 °C (dichloromethane–hexane) (lit.[7] mp 227–228 °C); IR (KBr) 1670, 1590, 1440 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.15 (dd, 2 H, H-4, H-5), 7.75 (ddd, 2 H, H-3, H-6), 7.50

(12) (a) Nagaoka, T.; Okazaki, S.; Fujinaga, T. *J. Electroanal. Chem.* **1982**, *133*, 89–99. (b) Nagaoka, T.; Okazaki, S.; Fujinaga, T. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1967–1968.

(ddd, 2 H, H-2, H-7) ppm; ^{13}C NMR ($CDCl_3$) δ 181.4 (C-10), 180.2 (C-9), 161.2 (C-1, C-8), 135.7 (C-11, C-14), 134.3 (C-3, C-6), 127.0 (C-12, C-13), 124.9 (C-4, C-5), 119.3 (C-2, C-7) ppm; MS *m/z* (relative intensity) 244 (M^+, 100), 216 (78), 188 (74). Anal. Calcd for $C_{14}H_6F_2O_2$: C, 68.86; H, 2.48. Found: C, 68.89; H, 2.39.

1-Fluoroanthraquinone (4). Obtained as above from 1-chloroanthraquinone (6.98 g, 28.8 mmol) and cesium fluoride (7.99 g, 52.6 mmol): yield 5.00 g (78%); pale yellow crystals, mp 228–229 °C (dichloromethane–hexane) (lit.[10] mp 228–230 °C); IR (KBr) 1680, 1595, 1450, 1340 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.32 (m, 2 H, H-5, H-8), 8.19 (dd, 1 H, H-4), 7.8 (m, 3 H, H-2, H-6, H-7), 7.5 (m, 1 H, H-3) ppm; MS *m/z* (relative intensity) 226 (M^+, 100), 198 (79), 170 (74). Anal. Calcd for $C_{14}H_7FO_2$: C, 74.34; H, 3.12. Found: C, 74.47; H, 3.19.

General Procedure for the Preparation of 1,8-Dialkoxyanthraquinones 5–7. A solution of the corresponding alcohol (2 mmol) in dry THF (3 mL) was added over a well stirred suspension of sodium hydride (0.20 g, 5 mmol of 60% oil dispersion, thoroughly washed with dry hexane) in dry THF (2 mL) under argon, and the mixture was heated to reflux for 45 min. After the mixture was cooled at room temperature, 1,8-difluoroanthraquinone (**2**) (0.12 g, 0.5 mmol) was added under argon, and the flask was rinsed with dry THF (3 mL). The mixture was stirred and refluxed for 6, 8, and 24 h for **3**, **4**, and **5**, respectively. Evaporation of the solvent afforded a residue which was treated with water (10 mL). The suspension was extracted with dichloromethane (3 × 25 mL), and the organic phase was washed successively with water (3 × 100 mL), brine (3 × 25 mL), and water (3 × 100 mL) and then dried over anhydrous sodium sulfate. The solvent was evaporated to afford crude 1,8-dialkoxyanthraquinone that was purified by column chromatography on alumina, using dichloromethane–hexane (1:1) as eluent. Analytical samples were obtained by recrystallization from ethanol.

1,8-Dipropoxyanthraquinone[13] **(5)**: yield 81%; mp 143–145 °C; IR (KBr) 1670, 1590, 1440 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.83 (dd, 2 H, H-4, H-5), 7.59 (dd, 2 H, H-3, H-6), 7.29 (dd, 2 H, H-2, H-7), 4.10 (t, 4 H, OCH_2), 1.94 (m, 4 H, OCH_2CH_2), 1.12 (t, 6 H, CH_3) ppm; ^{13}C NMR ($CDCl_3$) δ 184.2 (C-10), 182.1 (C-9), 158.8 (C-1, C-8), 134.7 (C-11, C-14), 133.4 (C-3, C-6), 124.6 (C-12, C-13), 119.5 (C-4, C-5), 118.7 (C-2, C-7), 71.2 (OCH_2CH_2), 22.5 (OCH_2CH_2), 10.4 (CH_2CH_3) ppm; MS *m/z* (relative intensity) 324 (M^+, 1), 295 (1), 281 (100), 263 (29). Anal. Calcd for $C_{20}H_{20}O_4$: C, 74.06; H, 6.22. Found: C, 74.21; H, 6.26.

1,8-Bis(decyloxy)anthraquinone (6): yield 70%; mp 101–102 °C; IR (KBr) 1680, 1590, 1310, 1280, 1215 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.82 (dd, 2 H, H-4, H-5), 7.58 (dd, 2 H, H-3, H-6), 7.29 (dd, 2 H, H-2, H-7), 4.12 (t, 4 H, OCH_2), 1.90 (m, 4 H, OCH_2CH_2), 1.65 (m, 4 H, $OCH_2CH_2CH_2$), 1.31 (m, 24 H, CH_2), 0.87 (t, 6 H, CH_3) ppm; ^{13}C NMR ($CDCl_3$) δ 184.3 (C-10), 182.2 (C-9), 158.9 (C-1, C-8), 134.8 (C-11, C-14), 133.4 (C-3, C-6), 124.7 (C-12, C-13), 119.6 (C-4, C-5), 118.8 (C-2, C-7), 69.8 (OCH_2), 31.9, 29.6, 29.4, 29.1, 25.9, 22.7 (CH_2), 14.1 (CH_3) ppm; MS *m/z* (relative intensity) 520 (M^+, 2), 379 (100). Anal. Calcd for $C_{34}H_{48}O_4$: C, 78.42; H, 9.29. Found: C, 78.45; H, 9.11.

1,8-Bis(hexadecyloxy)anthraquinone (7): yield 88%; mp 105–106 °C; IR (KBr) 1670, 1590, 1460, 1310, 1290, 1215 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.82 (dd, 2 H, H-4, H-5), 7.58 (dd, 2 H, H-3, H-6), 7.27 (dd, 2 H, H-2, H-7), 4.12 (t, 4 H, OCH_2), 1.9 (m, 4 H, OCH_2CH_2), 1.55 (m, 4 H, $OCH_2CH_2CH_2$), 1.25 (m, 48 H, CH_2), 0.87 (t, 6 H, CH_3) ppm; ^{13}C NMR ($CDCl_3$) δ 184.2 (C-10), 182.1 (C-9), 158.8 (C-1, C-8), 134.8 (C-11, C-14), 133.4 (C-3, C-6), 124.6 (C-12, C-13), 119.5 (C-4, C-5), 118.7 (C-2, C-7), 69.8 (OCH_2), 31.9, 29.7, 29.3, 29.1, 25.9, 22.6 (CH_2), 14.1 (CH_3) ppm; MS *m/z* (relative intensity) 688 (M^+, 3), 463 (100). Anal. Calcd for $C_{46}H_{72}O_4$: C, 80.18; H, 10.53. Found: C, 80.28; H, 10.50.

Tris[2-(1-anthraquinonyloxy)ethyl]amine (8). According to the general procedure for the preparation of 1,8-dialkoxyanthraquinones described above, starting from triethanolamine (0.10 g, 0.66 mmol) in dry THF (3 mL), sodium hydride (5 mmol) in dry THF (2 mL), and 1-fluoroanthraquinone (**4**) (0.50 g, 2.2 mmol), compound **8** was obtained as a greenish-yellow solid: yield 1.15 g (68%); mp 220–221 °C (ethyl acetate–hexane); IR (KBr) 1665, 1585, 1445, 1320, 1280, cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.19 (m, 6 H, H-5, H-8), 7.86 (dd, 3 H, H-4), 7.70 (m, 6 H, H-6, H-7), 7.58 (dd, 3 H, H-3), 7.47 (dd, 3 H, H-2), 4.44 (t, 6 H, OCH_2), 3.50 (t, 6 H, NCH_2) ppm; ^{13}C NMR ($CDCl_3$) δ 183.2 (C-10), 182.0 (C-9), 159.7 (C-1), 135.5 (C-12), 134.8 (C-7), 134.1 (C-3, C-14), 133.1 (C-6), 132.4 (C-11), 126.9 (C-8), 126.6 (C-5), 121.3 (C-13), 119.6 (C-4), 119.2 (C-2), 69.2 (OCH_2), 55.0 (NCH_2) ppm; MS *m/z* (relative intensity) 768 (M^+ + 1, 28), 544 (77); high-resolution FAB-MS calcd for $C_{48}H_{33}NO_9$ 768.223, found 768.225.

Preparation of [Anthraquinone.2.2]cryptand Sodium Iodide Complex (9·NaI). *N,N'*-Bis(2-hydroxyethyl)-4,13-diaza-18-crown-6 sodium iodide salt[14] (0.25 g, 0.5 mmol) was added to a well-stirred suspension of sodium hydride (0.24 g, 60% oil dispersion, 6 mmol, thoroughly washed with dry hexane) in 4 mL of dry THF under argon, and the mixture was heated at reflux for 45 min. After the mixture was cooled to room temperature, 1,8-difluoroanthraquinone (**2**) (0.122 g, 0.5 mmol) was added under argon and the flask was rinsed with 2 mL of dry THF. The reaction mixture was heated to 60 °C for 24 h, and after being cooled at room temperature, it was treated with 30 mL of water. The suspension was extracted with dichloromethane (3 × 100 mL), and the organic phase was washed with water (3 × 100 mL) and dried over anhydrous sodium sulfate. The solvent was removed, and the residue was triturated with ether to give a brownish-yellow solid that was recrystallized from a concentrated solution of NaI in acetone–ether affording 0.25 g of a brownish-yellow crystalline solid: yield 71%; mp 134–136 °C; IR (KBr) 1670, 1630, 1590, 1445, 1360 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.90 (dd, 2 H, H-4, H-5), 7.73 (dd, 2 H, H-3, H-6), 7.48 (dd, 2 H, H-2, H-7), 4.40 (m, 4 H, OCH_2CH_2N-crown), 3.7–3.5 (m, 8 H, OCH_2CH_2N), 3.63 (broad s, 8 H, OCH_2CH_2O), 3.0 (m, 4 H, OCH_2CH_2N-crown), 2.75 (m, 8 H, NCH_2CH_2O) ppm; ^{13}C NMR ($CDCl_3$) δ 183.1 (C-10), 181.5 (C-9), 158.2 (C-1, C-8), 134.9 (C-2, C-7), 134.6 (C-11, C-14), 122.4 (C-12, C-13), 119.9 (C-4, C-5), 119.4 (C-3, C-6), 68.3, 68.0, 66.8 (OCH_2), 54.2, 53.4 (NCH_2) ppm; MS *m/z* (relative intensity) 577 (M^+, 18). Anal. Calcd for $C_{30}H_{38}N_2O_8$·NaI: C, 51.14; H, 5.44; N, 3.97. Found: C, 50.90; H, 5.49; N, 3.82.

[Anthraquinone.2.2]cryptand (9) Free Ligand. Obtained as above with the following modification: After 1,8-difluoroanthraquinone was added, the reaction mixture was stirred at room temperature for 86 h and the solvent was evaporated to afford a residue that was treated with ice–water (20 mL). The resulting suspension was extracted as described above: yield 50%; mp 126–127 °C (chloroform–hexane); ^{1}H NMR ($CDCl_3$) δ 7.89 (dd, 2 H, H-4, H-5), 7.58 (dd, 2 H, H-3, H-6), 7.24 (dd, 2 H, H-2, H-7), 4.18 (m, 4 H, OCH_2CH_2N-crown), 3.72 (m, 8 H, OCH_2CH_2N), 3.61 (s, 8 H, OCH_2CH_2O), 3.31 (m, 4 H, OCH_2CH_2N-crown), 3.0 (m, 8 H, NCH_2CH_2O) ppm; purification by column chromatography on alumina (5% methanol/chloroform) is possible but the yield is drastically reduced; high-resolution FAB-MS calcd for $C_{30}H_{38}N_2O_8$ 555.271, found 555.263.

7,16-Bis[2-(1-anthraquinonyloxy)ethyl]-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (10). Obtained as above from *N,N'*-bis(2-hydroxyethyl)-4,13-diaza-18-crown-6 sodium iodide salt (0.25 g, 0.5 mmol), sodium hydride (0.12 g, 3 mmol), and 1-fluoroanthraquinone (0.23 g, 1 mmol). The reaction mixture was refluxed for 14 h, and the solvent was evaporated. The residue was treated with water (10 mL), and the resulting suspension was extracted with dichloromethane (3 × 75 mL). The organic phase was successively washed with water (3 × 100 mL), brine (50 mL), and water (3 × 100 mL) and then dried over anhydrous magnesium sulfate. The solvent was removed to afford a greenish-yellow solid that was recrystallized from the ethyl acetate–hexane mixture to give 0.4 g of **10**: yield 53%; mp 149–151 °C; IR (KBr) 1665, 1585, 1280 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.23 (m, 4 H, H-5, H-8), 7.96 (dd, 2 H, H-4), 7.74 (m, 6 H, H-6, H-7, H-3), 7.62 (dd, 2 H, H-2), 4.25 (t, 4 H, OCH_2CH_2N-crown), 3.68 (m, 8 H, OCH_2CH_2N), 3.63 (s, 8 H, OCH_2CH_2O), 3.18 (t, 4 H, OCH_2CH_2N-crown), 2.97 (t, 8 H, NCH_2CH_2O) ppm; FAB-MS *m/z* (relative intensity) 763 (M^+ + 1, 30). Anal. Calcd for $C_{44}H_{46}N_2O_{10}$: C, 69.27; H, 6.07; N, 3.67. Found: C, 69.15; H, 6.09; N, 3.62.

Acknowledgment. L.E. and R.C.L. wish to thank the Chemistry Division of the National Science Foundation (CHE-9011901) for support of this work.

(13) Miura, C.; Nagasaka, H.; Oshima, A. *Jpn. Patent* 78134421; *Chem. Abstr.* **1979**, *90*, 160154g.

(14) Gatto, V. J.; Gokel, G. W. *J. Am. Chem. Soc.* **1984**, *106*, 8240–8244.