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DIRECT NUCLEOPHILIC AROMATIC SUBSTITUTION REACTIONS IN THE SYNTHESES OF ANTHRAQUINONE DERIVATIVES: CHEMISTRY AND BINDING OF PODANDS, CROWN ETHERS, AND A CRYPTAND

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The direct nucleophilic aromatic substitution reactions of anthraquinones have permitted the syntheses of more than 30 novel podands, crown ethers and lariat ethers. Anthraquinones having (ethyleneoxy)$_n$ sidearms were obtained by direct displacement of chloride by the anion of $CH_3(OCH_2CH_2)_nOH$. The ethyleneoxy-substituted anthraquinones could, in turn, undergo direct replacement by nucleophiles that failed to displace chloride. This approach has been used for the preparation of two-armed podand derivatives and several novel crown derivatives of anthraquinone. Binding comparisons are presented for several of these new anthraquinones. Direct substitution did not prove successful in the preparation of anthraquinone-[2·2]-cryptand which was obtained by alkylation. The crystal structure of the latter reveals an orientation of ring and anthraquinone appropriate for cation binding, a fact confirmed by cation binding constant measurements.

INTRODUCTION

In previous work, we have demonstrated the utility of the anthraquinone nucleus to serve as the redox-switchable component of podands,[1] lariat ethers[2] and, recently, an anthraquinone cryptand.[3] The utility of the anthraquinone subunit is increasingly apparent from the number of novel structures that incorporate it. We have recently devoted considerable attention to the preparation of simple anthraquinones in the hope that general synthetic methodology and a unifying mechanism would emerge.[4] While the previous reports of our efforts in this area have been detailed, they have focused on methodology rather than targets. We report here the extension of the direct nucleophilic substitution methodology to the preparation of podands, lariat ethers, crown ethers and the first anthraquinone-containing cryptand. Cation binding information for several of these compounds and a solid-state structure are reported.

RESULTS AND DISCUSSION

Anthraquinones are richly represented among both natural and synthetic[5] products, but access has long suffered from the difficulties of preparation.[6] In recent work, we have demonstrated that direct nucleophilic aromatic substitution of chloroanthraquinone is successful with oligoethyleneoxy and alkynyl nucleophiles although alkanols and alkenols fail in this approach.[4] Moreover, alkynols and oligoethylene glycols serve as leaving groups as well as nucleophiles. Our need for certain disubstituted anthraquinone derivatives led us to exploit the approach shown in equation (1) for the preparation of various derivatives as detailed in the sections below.

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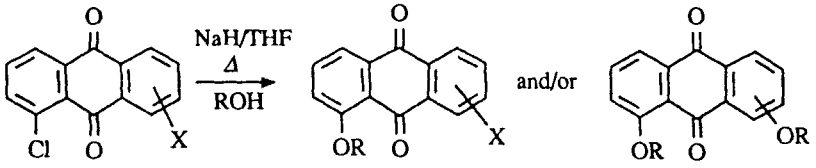


(1)

Anthraquinone podands

Our studies of redox-switchable systems have, in recent years, favored anthraquinone over nitrobenzene as the redox-sensitive moiety because the former is stable in water whereas the later is not. In addition, two successive one-electron reductions are possible with anthraquinones whereas only a single electron is readily added to nitrobenzene. The podands represent the simplest of the redox-switchable cation binding systems and succeed admirably in their designed function while the corresponding nitrobenzene derivatives fail.[7] Alkylation of nitrobenzene is, however, straightforward and alkylation of anthraquinones is generally difficult. We have previously reported the use of both 1,5- and 1,8-anthraquinone podands having $(CH_2CH_2O)_{3,4}CH_3$ sidearms in this context but have not elaborated their syntheses.[2]

The (ethyleneoxy)$_n$-sidearmed podands proved fairly easy to prepare in comparison with simple alkyl derivatives. When $R(OCH_2CH_2)_nO^-$ was the nucleophile, chloride was a suitable nucleofuge but not when simple alkoxides were used as nucleophiles. In contrast, when $(CH_2CH_2O)_{3,4}OCH_3$ was the sidearm (nucleofuge), most primary alcohols proved to be good nucleophiles. Secondary alcohols were apparently too hindered to be successful in this transformation. The ethyleneoxy sidearm is thus an excellent nucleophile and nucleofuge, a fact that we originally attributed to its potential to complex a proximate cation. We have recently described several simple examples of these single sidearm replacement reactions. We now show that both sidearms may be displaced from the same anthraquinone and, indeed, that unsymmetrical products can arise from a single reaction.

The results for more than a dozen double sidearm displacements are shown in Table 1. The starting 1,5- and 1,8-disubstituted anthraquinone podands were prepared from the corresponding, commercially available 1,5- or 1,8-dichlorides. When $CH_3(OCH_2CH_2)_nOH$ ($n = 3$ or 4) was the nucleophile, reasonable yields (39–72%) of the double displacement product were obtained. Yields for the 1,8-disubstitution products are generally better than those for the corresponding 1,5-substitution pattern. This suggests interchain cooper-

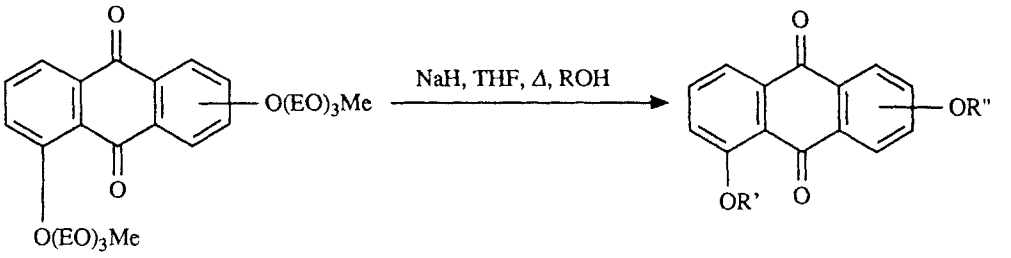
Table 1. Podands by nucleophilic substitution of anthraquinones

Cpd. No.	Substitution pattern	Sidearm[a]	Leaving group	Sidearm	Group	Yield (%)	M.p. (°C)
5	1,5	$OEOEOEOCH_3$	Cl	$OEOEOEOEOCH_3$	Cl	39	50–51
6	1,8	$OEOEOEOCH_3$	Cl	$OEOEOEOEOCH_3$		64	Oil
7	1,5	$OEOEOEOEOCH_3$	Cl	$OEOEOEOEOCH_3$		72	Oil
8	1,8	$OEOEOEOEOCH_3$	Cl	$OEOEOEOEOCH_3$	Cl	53	Oil
9	1	OEOEOEOEOH	Cl	–	–	62	Oil
10	1	OEOEOEOEO-1-anthraquinyl	Cl	–	–	10	157·5–158·5
12	1	$OEOEOEOEOC_{18}H_{37}$	Cl	–	–	79	68–69
13	1	$OEOEOEOEOC_{15}H_{31}$	**9**	–	–	72	64·5–66·0
14	1,5	$OEOEOEOCH_3$	Cl	Cl	Cl	37	67·5–68·5
15	1,5	$OC_{16}H_{33}$	**14**	$OC_{16}H_{33}$	**14**	10	98·0–98·5
15	1,5	$OC_{16}H_{33}$	**5**	$OC_{16}H_{33}$	**5**	36	98·0–98·5
16	1,5	$OEOEOEOEOCH_3$		OH	Cl[b]	10	85·0–86·0
17	1,5	$OC_{17}H_{35}$	**16**	OH	**16**	72	72·5–73·5
18	1,5	$OC_{17}H_{35}$	**17**	$OCOCH_3$	**17**	70	120–121·5
19	1,8	$OCH_2CH_2CH_3$	**6**	$OCH_2CH_2CH_3$	**6**	49	137–139
20	1,8	$O(CH_2)_7CH_3$	**6**	$O(CH_2)_7CH_3$	**6**	72	105–106
21	1,8	$OC_{16}H_{33}$	**6**	$OC_{16}H_{33}$	**6**	86	107–108
22	1,5	$OC_{16}H_{33}$	**5**	$OC_{16}H_{33}$	**5**	25	79–80
23	1,5	$OC_{10}H_{21}$	**5**	$OC_{10}H_{21}$	**5**	31	93–94
24	1,5	$OC_{10}H_{21}$	**5**	$OEOEOEOCH_3$	**5**	19	60–61

[a] E = ethyl.

[b] The reaction may involve direct exchange of HO for Cl or may involve the intermediate formation of $OEOEOEOEOCH_3$ followed by HO displacement.

Table 2. Double substitutions of anthraquinones

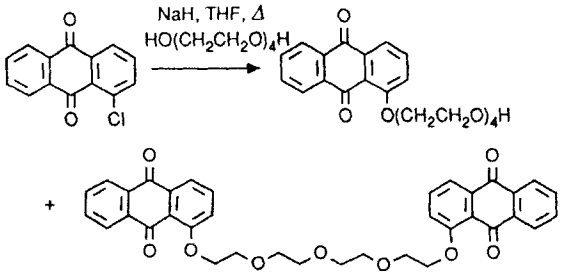


Substitution	R	R′	5-R″	8-R″	Yield (%)
1,8	C_3H_7	C_3H_7	–	C_3H_7	49
1,8	C_8H_{17}	C_8H_{17}	–	C_8H_{17}	72
1,8	$C_{16}H_{33}$	$C_{16}H_{33}$	–	$C_{16}H_{33}$	86
1,5	$C_{10}H_{21}$	$(EO)_3Me$	$C_{10}H_{21}$	–	25%
		$C_{10}H_{21}$	$C_{10}H_{21}$		36%
1,5	$C_{16}H_{33}$	$(EO)_3Me$	$C_{16}H_{33}$	–	19%
		$C_{16}H_{33}$	$C_{16}H_{33}$		31%

ation, the generality of which has thus far proved impossible to confirm.

Some interesting differences in behavior were noted between the 1,5- and 1,8-disubstituted systems. These are exemplified by the reactions shown in Table 2. When the $O(CH_2CH_2O)_3CH_3$ sidearms were disposed 1,8- (i.e. on the same side of the anthraquinone), double substitution was clean and yields appeared to increase with increasing lipophilicity although a three-reaction sample cannot be generalized with confidence. When the ethyleneoxy substituents were on opposite sides of the anthraquinone, product mixtures were obtained in both of the cases studied. If the Na^+ cation is playing a coordinating role that assists either entry of the nucleophile or exit of the nucleofuge, it should do so more effectively when both podand chains are proximate.

Several anthraquinones bearing mixed hydrophobic–hydrophilic sidearms were also prepared in the expectation that they would ultimately be used for redox-switched cation transport. These compounds could be obtained either by the preparation of a hydrocarbon-terminated $(ethyleneoxy)_n$ unit such as $AQ—O(CH_2CH_2O)_4C_{18}H_{37}$, or by acylating with palmitic acid the hydroxy terminus of $AQ—(OCH_2CH_2)_4OH$ [$\rightarrow AQ—(OCH_2CH_2O)_4COC_{15}H_{31}$]. Both approaches proved successful. The latter course is less satisfactory in fulfilling the cation transport goal owing to ester hydrolysis that occurs in the aqueous membrane phases. We therefore do not discuss the latter compound further. It is interesting that when 1-chloroanthraquinone was treated with $H_{37}C_{18}O(CH_2CH_2O)_4H$ in the presence of NaH and THF, the hydrophobic/hydrophilic podand, 1-$AQ—O(CH_2CH_2O)_4C_{18}H_{37}$, was isolated in 80 ± 2% yield (two runs). When 1-chloroanthaquinone was treated with tetraethylene glycol under comparable conditions, both $AQ—O(CH_2CH_2O)_4H$ and the bis(anthraquinone) $AQ—O(CH_2CH_2O)_4—AQ$ were isolated as shown below. Although the latter is a *mechanistically* obvious product, it is, to our knowledge, the first example of a bis(anthraquinyl) podand. Note that if cation organization involving sidearm and carbonyl oxygen is playing a critical role, formation of the bis(anthraquinone) product should be disfavored because the nucleophilic end of AQ—OEOEOEOEOH should be wrapped back on itself.



The double substitution reactions of anthraquinones are generally fairly successful from the preparative perspective. They require, so far as is currently known, a poly(ethyleneoxy) chain either as the nucleophile or electrophile. This may have to do with cation coordination either during nucleophile entry or nucleofuge

departure. It seems reasonable to assume that cation binding will generally be greater if the two sidearms are *syn* than if they are *anti*. This is not borne out, however, by homogeneous cation binding studies (see below). Moreover, we have found that when a single sidearm is present, yields for alkynyl-substituted anthraquinones are similar to those for $(ethyleneoxy)_n$ derivatives and both are far better than when the sidearm is either alkyl or alkenyl. We have been unable to rationalize this behavior in any obvious terms. If cation coordination plays the key role, then an ethyleneoxy sidearm must be more efficacious than alkyl, alkenyl or alkynyl groups. If the double bond plays a special role, alkenes and alkynes should be superior to alkyl or ethyleneoxy derivatives. Hence the tempting cation coordination rationale of higher yields for 1,8- compared with 1,5-disubstituted anthraquinones, if correct at all, cannot be the sole explanation.

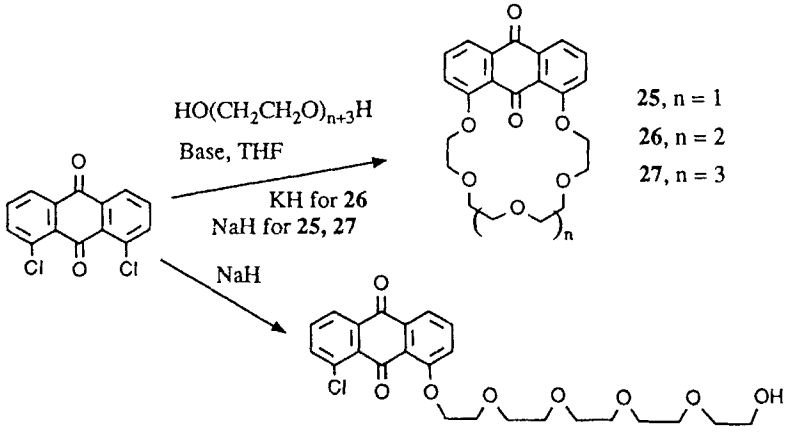
Anthraquinone crown ethers

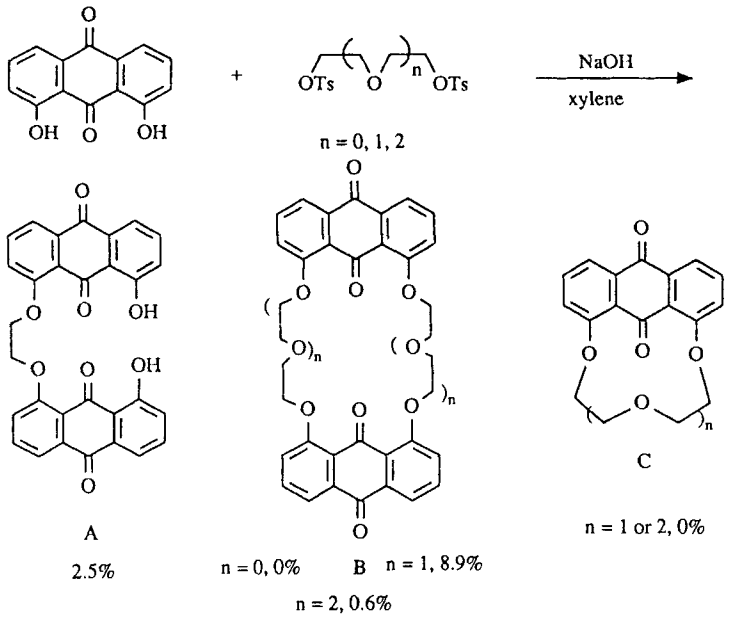
Wolf and Cooper[8] and Togo *et al.*[9] have shown that the redox behavior of 1,4-benzoquinone crown ethers reflects cation binding strength by the neutral crown. Other crown ethers possessing the anthraquinone subunit were reported by Vögtle and co-workers,[10] who noted UV shifts on cation complexation. These alizarin-derived systems were prepared by reaction of the phenolic alizarin hydroxyls with the appropriate polyethylene glycol ditosylates in 4–8% yield. Although Vögtle and co-workers' anthraquinone crown ethers are of obvious interest, they are not directly related to those described here.

Anthraquinone crown ethers (**25**–**27**) possessing different cavity sizes were synthesized by the reaction of 1,8-dichloroanthraquinone with one equivalent of the corresponding tetra-, penta- and hexaethylene glycol. These compounds have six, seven or eight oxygen atoms in the crown cavity, including an anthraquinone carbonyl. Yields ranged from 30 to 45% when NaH or KH was used as base in THF. All products were isolated as yellow solids and further purified by crystallization from absolute ethanol. A similar preparation using NaH as base was attempted in the expectation of forming crown ether **27**. Instead, the oily major product isolated was 1-{2-[2-(2-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}ethoxy)]}-8-chloroanthraquinone. This podand was identified from the NMR spectrum, in which the integral ratio for the aromatic region to the ethoxy region was 1 : 4, and from the OH stretch observed in the IR spectrum.

Related work has been reported by Nakatsuji *et al.*[11] They synthesized bis(anthraquinone) derivatives by the reaction of 1,8-dihydroxyanthraquinone with the corresponding mono-, di- or triethylene glycol ditosylate in the presence of NaOH in xylene. They reported that when $n = 1$, the cyclic bis(anthraquinone) B was not obtained but acyclic bis(anthraquinone) A was isolated in 2·5% yield. On the other hand, when $n = 2$ or 3, cyclic bis(anthraquinone)s (B) were isolated in 8·9% and 0·6% yields, respectively. None of the expected monoanthraquinones (C, $n = 1$ or 2) were obtained. Molecular models (CPK) suggest that the latter compounds possess cavities (four or five oxygen atoms) that are too congested to form or to be stable. The models suggested to us that at least four ethyleneoxy units are required to form a structure of type C.

Our attempt to prepare bis(anthraquinone)-containing crowns by the reactions of 1,8-dichloroanthraquinone with mono-, di- or triethylene glycol in the presence of NaH failed.

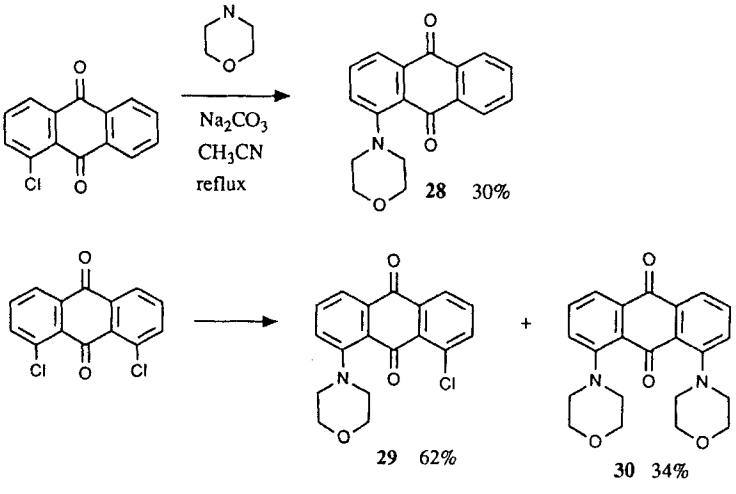


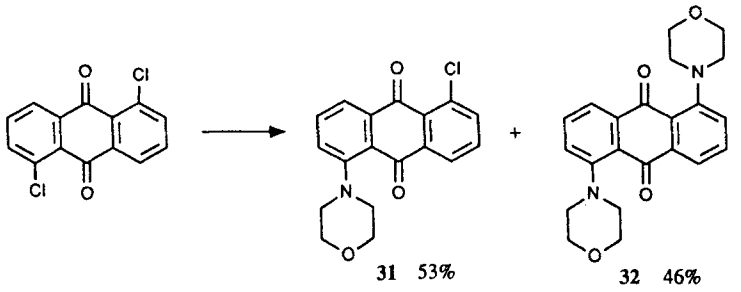


Anthraquinone derivatives bearing nitrogen substituents

Morpholine-substituted anthraquinones were prepared by the reaction of morpholine with the corresponding chloroanthraquinone as shown below. An excess (2 equivalents) of morpholine reacted with 1-chloroanthraquinone in the presence of Na_2CO_3 to give 1-morpholinoanthraquinone (**28**) in 30% yield. When 1,8-dichloroanthraquinone was reacted with 2 equivalents of morpholine, the only product isolated was 1-chloro-5-morpholinoanthraquinone (**29**) (11%). When 8 equivalents of morpholine were employed, mono- and disubstituted products (**29** and **30**) were obtained in 62% and 34% yields, respectively. This was also true with 1,5-substitution; mono- and disubstituted anthraquinones **31** and **32** were prepared in 53% and 46% yields in the presence of 8 equivalents of morpholine. Compounds **28**–**32** were all obtained as purple solids.

Bis(1-morpholinoanthraquinone) podand **33** was prepared by the reaction of 1-chloro-5-morpholinoanthraquinone (**31**) with triethylene glycol in the presence of NaH in THF. After work-up, followed by recrystallization from EtOAc, compound **33** was obtained as a purple solid (m.p. 166·0–167·0 °C) in 69% yield. The two morpholino derivatives obtained





had weak but different cation binding strengths, suggesting that when two morpholines were present in the 1,8-positions (i.e. **30**), they could cooperate.

Bis(aza-15-crown-5)anthraquinone

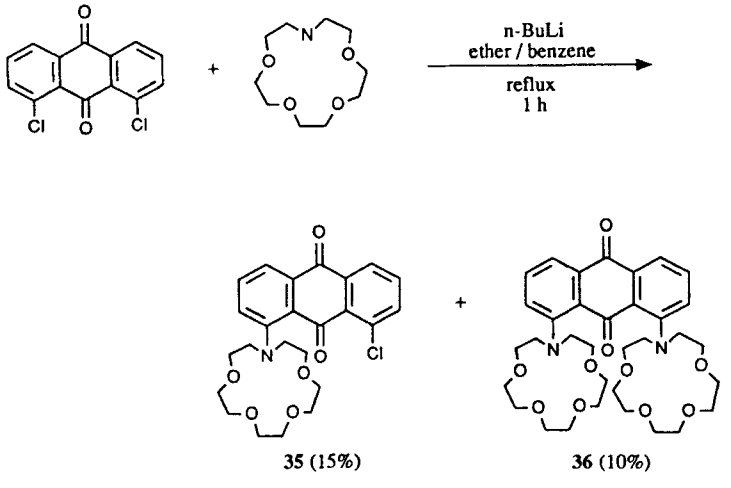
The reaction of 1,8-dichloroanthraquinone with 2 equivalents of aza-15-crown-5 in the presence of *n*-BuLi gave the mono- and disubstituted anthraquinone shown. Aza-15-crown-5 was dissolved in anhydrous diethyl ether, to which was added 1·1 equivalent of *n*-butyllithium (1·6 M solution in hexane). The reaction mixture was stirred for 15 min, then 1,8-dichloroanthraquinone dissolved in dry benzene was added. The reaction mixture was heated under reflux for 1 h; work-up, followed by column chromatography (SiO_2, EtOAc then 25% MeOH–CH_2Cl_2), yielded two products, **35** and **36**, in 15% and 10% yields, respectively.

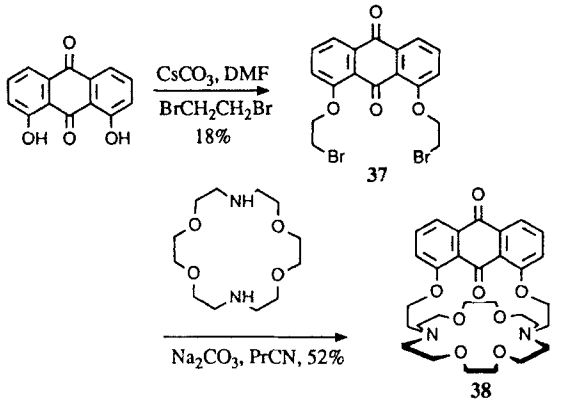
Dix and Vögtle[10d] had previously prepared 1-chloro-5-(aza-15-crown-5)-anthraquinone **35** in 12% yield by this reaction but they apparently did not isolate **36**. This may be due to the fact that **35** is crystalline (purple, m.p. 106–107 °C) whereas **36** is a viscous oil.

Anthraquinone cryptand and structure

When reduced, considerable electron density is localized on anthraquinone's carbonyl oxygen atoms. These highly directional carbonyl groups could be strong donors for cations if appropriately located. Placing the anthraquinone residue over a crown ring with a carbonyl directed to the center of the macrocycle was an appealing prospect. We therefore undertook the synthesis of anthraquinone-[2.2]-cryptand.

Based on our previous successes, the obvious approach appeared to be to use *N,N'*-bis(2-hydroxyethyl)-4,13-diaza-18-crown-6 as a nucleophile to substitute 1,8-dichloroanthraquinone. Several attempts using this approach failed, perhaps because it is difficult for the rigid system to undergo final ring closure. The opposite approach, using 1,8-dihydroxyanthraquinone as nucleophile, was then tried and proved successful. 1,8-Bis(2-bromoethoxy)anthraquinone was prepared from 1,8-dihydroxyanthraquinone and 1,2-dibromoethane (Cs_2CO_3, DMF) to give **37** as yellow needles in 18% yield (m.p. 152–153 °C) after crystallization from ethyl acetate. This approach has the advantage that the cesium salt of anthraquinone is soluble in DMF. Reaction of **37** with





4,13-diaza-18-crown-6 ($CH_3CH_2CH_2CN$, Na_2CO_3, catalytic NaI) gave the cryptand (**38**, 52%) after chromatography and crystallization as green crystals.

The crystals originally isolated gradually changed in color from green to mustard-yellow, and finally to light brown. Combustion analytical data and 400 MHz ^{1}H NMR studies produced no discernible difference among these three samples. The discoloration occurred even in the dark and cannot be explained.

Two views of the solid-state structure of **38** are shown in Figure 1. Three cavities can be distinguished in the system, identified as distances A, B, and C on Figure 1. They span internuclear distances of 8·2–8·5 Å (A, C=O···CH_2), 6·2–6·5 Å (B, CH_2···CH_2) and 4·8–5·5 Å (C). The distance between nitrogen atoms is approximately 6·5 Å, longer than observed for diaza-18-crown-6 (5·8 Å) or for the related ferrocenyl[2,2]-cryptand (5·5 Å). The carbonyl group proximal to the macroring is canted by 20°. These deviations from the structure expected when a cation is bound are generally those that can be attributed to packing forces. The deviation of the anthraquinone's carbonyl group from the anthraquinone plane is relatively minor. We have

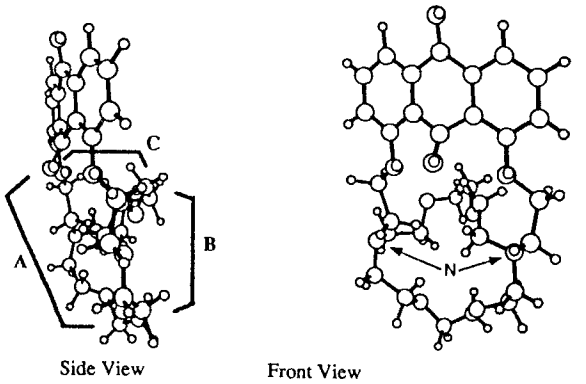


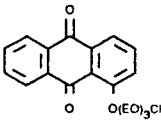
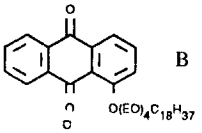
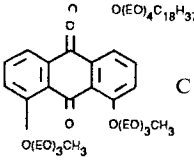
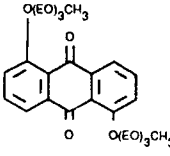
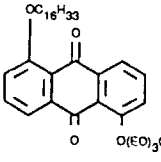
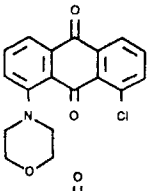
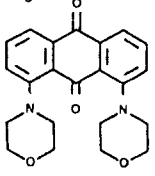
Figure 1. Two views of the solid-state structure of **38**

recently demonstrated that **38** does, in fact, exhibit novel electrochemically switched complexation behavior, the details of which are reported elsewhere.[3]

Cation binding studies

Representative cation binding data for the anthraquinone derivatives studied are given in Table 3. A number of interesting points can be made. First,

Table 3. Cation binding in anthraquinone derivatives

Compound		Log K_S (methanol) Na^+	K^+	NH_4^+
	A	1·8	2	<1·5
	B	2·33	2·2	<1·5
	C	2·30	2·45	ND
	D	2·35	2·26	<1·5
	E	2·32	1·5	<1·5
	F	<2	<2	ND
	G	2·3	2·2	ND

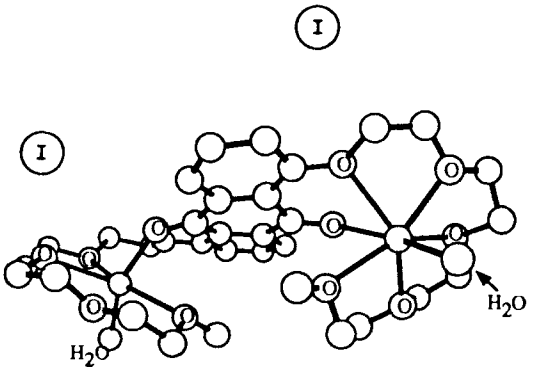
ammonium ion binding is poor for all of the systems analyzed. Sodium and K^+ cation binding are more revealing. Compounds A–D in Table 3 show the effect of sidearm placement and different numbers of oxygen donors. Structures A and B differ in hydrophobicity and the number of donors. In studies of diaza-18-crown-6-derivatives,[12] we have found that hydrophobic sidechains did not significantly alter cation binding. If that observation is extensible to this system, then the added oxygen donor in B causes the binding enhancement of about $10^{0.5}$. Comparison of binding for A and E, however, suggests that this system may behave differently from diaza-crowns. A comparison of B, C and D is particularly interesting. In C and D, the number of donors is identical but they are disposed on opposite sides of the anthraquinone residue. Nevertheless, their Na^+ binding strengths are essentially identical and the K^+ binding constants differ little. This suggests a dominant role for the carbonyl oxygens in either case.

The fact that binding for B, C and D differs so little suggests that only one cation may be bound irrespective of sidearm position. We have previously shown[4b] that when four-oxygen sidearms are disposed 1,5-, a pseudo-bis(crown) complex of the type podand·2NaI·$(H_2O)_2$ forms; each Na^+ ion is bound by an anthraquinone oxygen, four ethers and a water molecule. Thus each Na^+ is hexacoordinate. Perhaps when both sidearms are present in the 1,8-positions, the second arm fills the coordination shell created primarily by a single sidearm. When the anthraquinone is substituted 1,5-, water or methanol may fulfil this role.

Solid-state structure of 7

A solid-state structure was obtained for compound **7** as described in the Experimental section. In it, the anthraquinone is at the center of two coils, each coil containing an Na^+ cation. In both cases, sodium is six-coordinate. Four of the donors are ether oxygen atoms contributed by the sidearm. A bound water molecule and the anthraquinone carbonyl oxygen complete the binding array. It is interesting that the anthraquinone carbonyl oxygens are bent out of the aromatic plane in each case to better accommodate the cation. A view of the structure which includes the relatively remote iodide anions is shown.

In the preliminary report of this work,[4b] we suggested that the structure reflected the mechanism by which the ethyleneoxy sidearms served so effectively as both nucleophiles and leaving groups. Subsequent studies have shown that alkynols are also effective nucleophiles and leaving groups but alkanols and alkenols are not.[4c] Hence the evidence has shown that although a cation coordination mechanism may indeed operate in this system, it cannot be a universal mechanism for transformations involving anthraquinones.



Cation complexation properties of anthraquinone crowns

Log K_S values are shown in Table 4 for the anthraquinyl crowns **25**–**27** and cryptand **37** along with values for the 3*n*-crown-*n*-structures having $n = 5$–8. The number of oxygens specified for the anthraquinone compounds refers to those that point inward, i.e. the *anti*-carbonyl group is not considered. Because one of the carbonyl groups intrudes on the cation binding hole, cavity sizes are much diminished compared with simple crowns having comparable number of oxygen atoms. The binding profile shows something approaching a 'hole-size selectivity', undoubtedly reflecting the rigidity of anthraquinone. Of all the binding constant values, those for **27** seem most surprising since log K_S in this case is barely better than that observed for the acyclic 1,5-bis(podands).

Of all the compounds studied, the anthraquinone cryptand appears to have the greatest binding strength and selectivity. In accord with its rigidity and cavity size, it binds K^+ with a constant (log K_S) of 6·31. The K^+/Na^+ selectivity is *ca* 80-fold in favor of the former.

Table 4. Cation binding for simple and anthraquinyl crowns

Compound	No. of oxygens[a]	Estimated cavity diameter (Å)	Log K_S[d]	
			Na^+	K^+
25	6	1·6–2·0[b]	3·52	3·41
26	7	2·8–3·6[b]	3·04	4·26
27	8	4·0–4·6[b]	2·31	3·38
15-Crown-5	5	1·7–2·2[c]	3·25	3·34
18-Crown-6	6	2·6–3·2[c]	4·35	6·10
21-Crown-7	7	3·4–4·3[c]	2·54	4·35
24-Crown-8	8	4·4–4·8[b]	2·35	3·53
Cryptand **38**	7	~3	4·41	6·31

[a] No. of oxygens in the cavity including the anthraquinone carbonyl.
[b] Cavity diameters are measured from CPK molecular models (1·25 cm ≡ 1 Å).
[c] Ref. 10.
[d] Measured in absolute MeOH at 25°C.

CONCLUSIONS

Interest in anthraquinone chemistry is growing owing to its electrochemical switching ability[13] and the possibility of one- and/or two-electron reduction to give water-stable derivatives capable of electrochemically mediated membane transport. We have developed potential anthraquinone carriers containing podand sidearms or a macroring. Syntheses of more than 30 novel anthraquinone cation binders reported here were generally accomplished by direct nucleophilic displacement of chloride leaving groups by $(ethyleneoxy)_n$ alkoxide derivatives. The remarkable multiple, direct nucleophilic subsitutions are illustrated for podand, morpholine, crown ether and lariat ether derivatives. Cation complexation by these systems is reported along with two solid-state structures that offer insight the complexation and substitution mechanisms but which are currently inconclusive. Nevertheless, synthetic access is effective and important potential uses of these systems is obvious.

EXPERIMENTAL

^{1}HNMR spectra were recorded at 60 or 400 MHz in $CDCl_3$ unless specified otherwise. Chemical shifts are reported in ppm (δ) downfield from internal $(CH_3)_4Si$, and are reported in the order chemical shift, spin multiplicity (b = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration and assignment. Infrared (IR) spectra in cm^{-1}, recorded as KBr pellets, were calibrated against the 1601 cm^{-1} band of polystyrene. Combustion analyses (C, H, N) were performed by Atlantic Microlabs (Atlanta, GA). Melting points were determine on a capillary apparatus and are uncorrected. Thin-layer chromatographic analyses were performed on aluminium oxide 60 F-254 neutral (type E) or silica gel 60 F-254 with a 0·2 mm layer thickness. Preparative chromatographic columns were packed with aluminium oxide, activated, neutral Brockmann 1 (150 mesh, standard grade), or Kieselgel 60 (70–230 mesh, chromatographic grade). Chromatotron chromatography was performed on a Chromatotron using 4 mm thickness circular plates prepared from Kieselgel 60 PG-254. All the reactions were performed under a nitrogen atmosphere. All reagents were of the best grade commercially available and were used without further purification unless specified otherwise. Tetrahydrofuran (THF) was distilled in the presence of CaH_2 or sodium metal.

All reactions were conducted under dry nitrogen unless noted otherwise. All reagents were of the best grade commercially available and were distilled, recrystallized or used without further purification, as appropriate. Molecular distillation temperatures refer to the oven temperature of a Kugelrohr apparatus. Combustion analyses were performed by Atlantic Microlab and are reported as percentages.

Cation binding constants were measured in absolute methanol at 25 ± 1·0 °C using a Corning 476210 electrode and an Orion Model 701A Ionalyzer meter according to the method of Frensdorff[14] as described more recently in detail.[15] Values for the equilibrium constants are reported as log K_S. Samples suitable for single-crystal x-ray analysis were grown by slow cooling of a warm saturated solution, by evaporation of a saturated solution or by vapor diffusion.

1-Chloroanthraquinone (**1**), 1,5-dichloroanthraquinone (**2**) and 1,8-dichloroanthraquinone (**3**) were purchased from Aldrich Chemical.

Tetraethylene glycol monomethyl ether (**4**). To a vigorously stirred suspension of NaH (60% 3·0 g, 75·0 mmol) in THF (20 ml) was added triethylene glycol monomethyl ether (10·0 g, 60·9 mmol). Benzyloxyethyl tosylate (20·1 g, 65·6 mmol) in THF (30 ml) was added slowly at reflux, and heating was continued for 3 days. The mixture was cooled, concentrated *in vacuo*, the residue dissolved in CH_2Cl_2 (200 ml), washed with H_2O (2 × 75 ml), the organic layer concentrated *in vacuo*, chromatographed (alumina, 5% propan-2-ol–hexane) and the residue distilled (Kugelrohr, 155 °C, 0·2 Torr), to give 2-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}ethyl benzyl ether as a colorless oil (17·4 g, 95%). ^{1}H NMR: 3·33 (s, 3H, OCH_3), 3·62 (m, 16H, OCH_2), 4·51 (s, 2H, OCH_2Ar), 7·38 (s, 5H, ArH). A Parr bottle was charged with the ether (above, 13·0 g, 43·3 mmol), 10% Pd–C (1·0 g), and absolute EtOH (90 ml), shaken (H_2, 60 psi, 24 h), filtered, concentrated *in vacuo* and Kugelrohr distilled (100 °C, 0·2–0·3 Torr) to give **4** as a colorless oil (7·9 g, 87%). ^{1}H NMR: 3·35 (s, 3H, OCH_3), 3·63 (m, 17H, OCH_2, OH).

1,5-Bis{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}anthracene-9,10-dione(**5**) *and 1,8-bis{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}anthracene-9,10-dione*(**6**). These were prepared as described previously.[2]

*1,5 - Bis(2 - {2 - [2 - (2 - methoxyethoxy)ethoxy]ethoxy}ethoxy)*anthracene-9,10-dione(**7**). A solution of **2** (1·85 g, 6·68 mmol) and **4** (3·0 g, 14·41 mmol) in THF (45 ml) was added dropwise to a vigorously stirred and refluxed suspension of NaH (60% oil dispersion, 0·9 g, 22·5 mmol) in THF (5 ml). The reaction mixture was stirred for 5 h. After work-up as described for **8**, column chromatography (silica, 2% MeOH–CH_2Cl_2) gave **7** (3·4 g, 72%) as a yellow oil. ^{1}H NMR: 3·32 (s, 6H, OCH_3), 3·56–4·40 (m, 32H, OCH_2), 7·20–8·95 (m, 6H, ArH). IR (neat): 2900, 1685, 1605, 1450, 1335, 1295, 1215, 1110 cm^{-1}. Analysis: calculated for $C_{32}H_{44}O_{12}$, C 61·91, H 7·16; found, C 61·73, H 7·24%.

Crystal structure data for $7 \cdot 2H_2O \cdot 2NaI$. A solution containing **7** and 10 equivalents of NaI deposited crystals (45%) of the complex. Crystallization from ethanol gave the bis-sodium dihydrate complex of **7**, m.p. 173–174 °C. Analysis: calculated for $C_{32}H_{44}O_{12} \cdot 2NaI \cdot 2H_2O$, C 40·18, H 5·07; found, C 40·49, H 5·29%. The same had the following crystal data: FW 959·59, space group *Cc*, $a = 11 \cdot 429(5)$ Å, $b = 16 \cdot 153(6)$ Å, $c = 22 \cdot 472(6)$ Å, $Z = 4$, $d_c = 1 \cdot 57$ cm^{-1}, Mo Kα($\mu = 16 \cdot 14$ cm^{-1}) $R = 0 \cdot 060$ for 1836 unique reflections with $I > 2\sigma(I)$ (of 2803 unique data) measured with an Enraf–Nonius CAD4 x-ray spectrometer by $\omega - 2\theta$ scans, $2° < \theta < 42°$.

1,8 - Bis(2 - {2 - [2 - (2 - methoxyethoxy)ethoxy] ethoxy} ethoxy)anthracene-9,10-dione (**8**). A solution of **3** (1·75 g, 6·32 mmol) and **4** (3·0 g, 14·41 mmol) in THF (30 ml) was added dropwise to NaH (60%, 0·9 g, 22·5 mmol) in THF (10 ml). The mixture was refluxed (4 h) cooled, reduced to minimum volume *in vacuo*, diluted with H_2O (100 ml), extracted with CH_2Cl_2 (200 ml then 100 ml), dried over $MgSO_4$, evaporated and chromatographed (silica, 2% MeOH–CH_2Cl_2) to give **8** as its monohydrate (2·09 g, 53·3% viscous yellow oil). ^{1}H NMR: 3·35 (s, 6H, OCH_3), 3·55–4·50 (m, 32H, OCH_2), 7·25–7·90 (m, 6H, ArH). IR (neat): 2910, 1680, 1605, 1455, 1330, 1290, 1120 cm^{-1}. Analysist calculated for $C_{32}H_{44}O_{12}H_2O$, C 60·16, H 7·27; found, C 60·31, H 7·52%.

1-(2-{2-[2-(2-Hydroxyethoxy)ethoxy] ethoxy} ethoxy) anthracene-9,10-dione (**9**). A solution of tetraethylene glycol (5·20 g, 21·8 mmol) in THF (10 ml) was added to of NaH (0·54 g, 13·5 mmol) in THF (10 ml). The reaction mixture was stirred for 10 min, **1** (2·37 g, 9·77 mmol) in THF (50 ml) was added dropwise, refluxe continued for 4 h and the mixture cooled concentrated *in vacuo*. The residue was dissolved in CH_2Cl_2 (200 ml), washed with H_2O (2 × 100 ml), brine (100 ml), the solvent evaporated and the residue was dissolved in EtOAc and filtered though alumina and washed EtOAc to give 1,8-bis(1 - oxyanthracene - 9,10 - dione) - 3,6,9 - trioxaundecane (**10**) (0·6 g, 10%) as a yellow solid (m.p. 157·5 °C). The filtrate was concentrated *in vacuo* to afford **9** as a yellow oil (1·41 g, 62%), which was used without further purification in the following reaction. ^{1}H NMR: 2·82 (s, 1H, OH), 3·15–4·43 (m, 16H, OCH_2), 7·20–8·30 (m, 7H, ArH). IR (neat): 2890, 2640, 1590, 1430, 1450, 1265, 1100, 800, 700 cm^{-1}.

Tetraethylene glycol monooctadecyl ether (**11**). To a suspension of NaH (60%, 1·10 g, 27·5 mmol) in THF (10 ml) was added tetraethylene glycol (10·33 g, 53·2 mmol). The mixture was refluxed for 30 min, 1-bromooctadecane (6·00 g, 18·0 mmol) in THF (15 ml) was added and refluxing was continued overnight. The mixture was concentrated, the residue dissolved in CH_2Cl_2 (100 ml), washed with H_2O (3 × 50 ml), concentrated and chromatographed (alumina, CH_2Cl_2 then 2% MeOH–CH_2Cl_2) to give **11** (4·8 g, 59%) as a white solid: m.p. 41·0–42·0 °C. ^{1}H NMR: 0·70–1·50 [m, 35H, $(CH_2)_{16}CH_3$], 2·75 (b, 1H, OH), 3·30–3·80 (m, 18H, OCH_2). IR: 3500, 2950, 2880, 1480, 1110, 915, 735 cm^{-1}.

1-(2-{2-[2-(2-Octadecyloxyethoxy)ethoxy] ethoxy} ethoxy)anthracene-9,10-dione (**12**). To a suspension of NaH (60%, 0·29 g, 7·25 mmol) in THF (10 ml) was added **11** (2·15 g, 4·81 mmol) in THF (10 ml). After 30 min, a solution of **1** (1·28 g, 5·28 mmol) in THF (20 ml) was added slowly, reflux continued for 10 h, cooled, evaporated and the crude residue was dissolved in CH_2Cl_2 (25 ml), washed with H_2O (2 × 15 ml), brine (15 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo*. Column chromatography (silica, 2% MeOH–CH_2Cl_2) followed by recrystallization (absolute EtOH) gave **12** (2·73 g, 79%) as a yellow solid: m.p. 68·0–69·0 °C. ^{1}H NMR: 0·80–1·75 [m, 35H, $(CH_2)_{16}CH_3$], 3·25–4·45 (m, 20H, OCH_2), 7·20–8·35 (m, 7H, ArH). ^{13}C NMR (22·6 MHz, $CDCl_3$): 183·9, 182·0, 159·7, 135·0, 134·8, 134·1, 133·1, 132·5, 127·1, 126·5, 120·0, 71·5, 71·1, 70·6, 71·1, 70·0, 69·5, 31·9, 29·6, 26·1, 22·6, 14·0 ppm. IR (KBr): 2840, 1685, 1600, 1270, 1110 cm^{-1}. Analysis: calculated for $C_{40}H_{60}O_7$, C 73·57, H 9·28; found, C 73·41, H 9·31%.

*1 - (2{2 - [2 - (2 - Palmitoyloxyethoxy)ethoxy] ethoxy} ethoxy)anthracene-9,10-dione (***13***).* Palmitoyl chloride (0·30 g, 1·091 mmol) was added dropwise to **9** (0·35 g, 0·874 mmol) dissolved in CH_2Cl_2 (10 ml). The mixture was stirred at room temperature overnight, H_2O (10 ml) was added and the organic phase was washed with H_2O (2 × 10 ml). Removal of solvent, followed by recrystallization (hexane), gave **13** (0·4 g, 72%) as a light yellow solid: m.p. 64·5–66·0 °C. ^{1}H NMR: 0·80–1·50 (m, 29H, CH_2CH_3), 2·30 (t, 2H, COCH), 3·60–4·45 (m, 16H, OCH_2), 7·10–8·30 (m, 7H, ArH). IR (KBr): 2900, 2840, 1740, 1670, 1585, 1305, 1255, 1120, 700 cm^{-1}. Analysis: calculated for $C_{38}H_{54}O_8$, C 71·43, H 8·54% found, C 71·58, H 8·55%.

1-Chloro-5-{2-[2-(2-methoxyethoxy)ethoxy] ethoxy} anthracene-9,10-dione (**14**). A solution of **2** (3·17 g, 11·44 mmol), triethylene glycol monomethyl ether (1·90 g, 11·57 mmol) in the THF (100 ml) and NaH (60%, 0·52 g, 13·0 mmol) was refluxed for 5 h. After work-up as described above, column chromatography (silica, 3% MeOH–CH_2Cl_2) afforded **14** and **6** (0·61 g, 10%). Crystallization of **14** from hexane gave the product (1·73 g, 37%) as a yellow solid: m.p. 67·5–68·5 °C. ^{1}H NMR: 3·35 (s, 3H, OCH_3),

3·45–4·45 (m, 12H, OCH_2), 7·15–8·35 (m, 6H, ArH). IR (KBr): 2900, 1680, 1595, 1580, 1310, 1290, 1255, 1100, 700 cm^{-1}. Analysis: calculated for $C_{21}H_{21}ClO_6$, C 62·29, H 5·24, Cl 8·76; found, C 62·36, H 5·28, Cl 8·73%.

1,5-Bis(hexadecyloxy)anthracene-9,10-dione (**15**). Hexadecyl alcohol (0·20 g, 0·825 mmol) in THF (5 ml) and NaH (60% 0·08 g, 2·0 mmol) in THF were stirred for 3 h under reflux. A solution **14** (0·29 g, 0·716 mmol) in THF (10 ml) was added dropwise. Work-up, followed by column chromatography (silica, CH_2Cl_2), yielded **15** (0·05 g, 10%) as a yellow solid: m.p. 98·0–98·5 °C. ^1H NMR: 0·85–1·75 [m, 62H, $(CH_2)_{14}CH_3$], 4·10 (m, 4H, OCH_2), 7·15–7·90 (m, 6H, ArH). Analysis: calculated for $C_{46}H_{72}O_4$, C 80·16, H 10·55; found, C 79·90, H 10·58%.

1-Hydroxy-5-(2-{2-[2-(2-methoxyethoxy)ethoxy] ethoxy}ethoxy)anthracene-9,10-dione (**16**). A mixture of **2** (1·85 g, 6·68 mmol), tetraethylene glycol monomethyl ether (3·0 g, 14·41 mmol) in THF (45 ml) and NaH (60%, 0·9 g, 22·5 mmol) in THF (5 ml) was stirred for 5 h. After work-up, column chromatography (silica, 2% MeOH–CH_2Cl_2) yielded **7** (3·4 g, 72%) **16** (0·3 g, 10%). Compound **16** was isolated as a yellow solid: m.p. 85·0–86·5 °C. ^1H NMR: 3·33 (s, 3H, OCH_3), 3·50–4·45 (m, 16H, OCH_2), 7·05–8·00 (m, 6H, ArH), 8·55 (s, 1H, OH). IR: 2900, 1680, 1640, 1590, 1450, 1265, 1130, 1100, 800, 700 cm^{-1}. Analysis: calculated for $C_{23}H_{26}O_8 \cdot \frac{1}{2}H_2O$, C 62·85, H 6·20; found, C 62·94, H 6·38%.

1-Hydroxy-5-heptadecyloxyanthracene-9,10-dione (**17**). 1-Heptadecanol (0·22 g, 0·86 mmol) and NaH (60%, 0·2 g, 5 mmol) in THF were stirred for 30 min and **16** (0·25 g, 0·557 mmol) was added slowly. After overnight reflux, the mixture was cooled and concentrated, the residue was dissolved in CH_2Cl_2 (50 ml), washed with H_2O (2 × 30 ml), dried ($MgSO_4$) and concentrated. Chromatotron chromatography (silica, 4 mm plate, 2% MeOH–CH_2Cl_2) gave **17** (0·19 g, 72%) as a yellow solid: m.p. 72·5–73·5 °C. ^1H NMR: 1·10–2·10 (m, 33H, CH_2CH_3), 4·13 (t, 2H, $ArOCH_2$), 7·05–7·95 (m, 6H, ArH), 8·40 (s, 1H, OH). IR: 2930, 2860, 1670, 1640, 1590, 1475, 1455, 1370, 1265, 785, 705 cm^{-1}. Analysis: calculated for $C_{31}H_{42}O_4$, C 77·77, H 8·86; found, C 78·08, H 8·86%.

1-Acetoxy-5-heptadecyloxyanthracene-9,10-dione (**18**). A solution of **17** (0·1 g, 0·25 mmol) in pyridine (5 ml) and acetic anhydride (2 ml) were refluxed for 15 h, cooled, CH_2Cl_2 (15 ml) was added and the mixture was washed successively with cold 3M HCl (2 × 15 ml) and H_2O until the washings were neutral and then concentrated *in vacuo*. Recrystallization from acetone gave **18** as a yellow solid (0·09 g, 70%): m.p. 120·0–121·5 °C. ^1H NMR: 0·80–1·65 (m, 33H, CH_2CH_3), 2·47 (s, 3H, $COCH_3$), 4·15 (t, 2H, $ArOCH_2$), 7·20–8·35 (m, 6H, ArH). IR (KBr): 2935, 2860, 1780, 1685, 1595, 1450, 1270, 1215, 1205, 710 cm^{-1}; Analysis: calculated for $C_{33}H_{44}O_5$, C 76·10, H 8·53, found, C 75·89, H 8·56%.

1,8-Bis(propyloxy)anthracene-9,10-dione (**19**). A mixture of propan-1-ol (0·18 ml, 2·42 mmol) and NaH (60%, 0·15 g, 3·75 mmol) in THF was stirred for 30 min and a solution of **6** (0·50 g, 0·94 mmol) was added, heated (reflux) for 4 h, cooled, concentrated and the residue was dissolved in CH_2Cl_2 and then washed with H_2O, dried over $MgSO_4$, filtered and concentrated. Chromatotron chromatography (silica, 4 mm plate, CH_2Cl_2) followed by recrystallization from absolute EtOH gave **19** (0·15 g, 49%) as a yellow solid: m.p. 137·0–139·0 °C. ^1H NMR 1·15 (t, 6H, CH_3), 1·95 (q, 4H, CH_2), 4·05 (t, 4H, CH_2O), 7·10–7·85 (m, 6H, ArH). Analysis: calculated for $C_{20}H_{20}O_4$, C 74·04, H 6·23; found, C 73·71, H 6·66%.

1,8-Bis(octyloxy)anthracene-9,10-dione (**20**). Octan-1-ol (0·37 ml, 2·35 mmol) and NaH (0·15 g, 3·75 mmol) in THF was added to **6** (0·48 g, 0·90 mmol). After reflux (4 h) the reaction mixture was worked up as described for **19** to give **20** (0·30 g, 72%) as a yellow solid: m.p. 105·0–106·0 °C. ^1H NMR: 0·85–2·10 (m, 30H, CH_2), 4·12 (t, 4H, OCH_2), 7·20–7·85 (m, 6H, ArH). ^{13}C NMR: 184·0, 159·0, 134·0, 133·5, 125·5, 120·0, 119·0, 70·0, 31·0, 29·5, 26·0, 22·5, 14·0 ppm. IR (KBr): 2940, 2870, 1685, 1600, 1450, 1320, 1300, 1230, 740 cm^{-1}. Analysis: calculated for $C_{30}H_{40}O_4$, C 77·53, H 8·69; found, C 77·37, H 8·77%.

1,8-Bis(hexadecyloxy)anthracene-9,10-dione (**21**). Hexadecan-1-ol (0·5 g, 2·06 mmol) in THF, NaH (100%, 0·6 g, 2·5 mmol) in THF and **5** (0·45 g, 0·85 mmol) in THF were heated for 4 h. After work-up and crystallization (absolute EtOH), **21** was obtained (0·50 g, 86%) as a yellow solid: m.p. 107·0–108·0 °C. ^1H NMR: 0·80–1·75 (m, 62H, CH_2), 4·10 (t, 4H, OCH_2), 7·15–7·85 (m, 6H, ArH). IR (KBr): 2940, 2875, 1690, 1600, 1320, 1225, 740 cm^{-1}. Analysis: calculated for $C_{46}H_{72}O_4$, C 80·16, H 10·55%; found, C 79·93, H 10·61%.

1,5-Bis(hexadecyloxy)anthracene-9,10-dione (**15**) and 1-hexadecyl-oxy-5-{2-[2-(2-methoxyethoxy)ethoxy] ethoxy}anthracene-9,10-dione (**22**). NaH (0·20 g, 5·00 mmol) in THF, hexadecan-1-ol (0·78 g, 3·22 mmol) and **5** (2·02 g, 3·79 mmol) in THF were heated under reflux for 1 h. The mixture was cooled, evaporated and the solid residue was dissolved in CH_2Cl_2 and washed with H_2O and concentrated. Column chromatography, followed by crystallization (EtOH), gave **15** (0·8 g,

36%) and monohexadecyloxy podand **22** (0·5 g, 25%). Compound **15**: m.p. 98·0–98·5 °C. ^{1}H NMR: 0·85–1·75 [m, 62H, $(CH_2)_{14}CH_3$], 4·10 (m, 4H, OCH2), 7·15–7·90 (m, 6H, ArH). Analysis: calculated for $C_{46}H_{72}O_4$ C 80·16, H 10·55; found, C 79·96, H 10·61%. Compound **22**: m.p. 79·0–80·0 °C. ^{1}H NMR: 0·8–2·2 (m, 31H, CH_2, CH_3) 3·35 (s, 3H, OCH_3), 3·5–4·45 (m, 14H, OCH_2), 7·1–8·0 (m, 6H, ArH). Analysis: calculated for $C_{37}H_{54}O_7$, C 72·74, H 8·93; found, C 72·69, H 8·95%.

1,5-Bis(decyloxy)anthracene-9,10-dione (**23**) *and 1-decyloxy-5-{2-[2-(2-methoxyethoxy)ethoxy] ethoxy} anthracene-9,10-dione* (**24**). NaH (0·2 g, 5·00 mmol) in THF, decan-1-ol (0·52 g, 3·28 mmol) and **5** (1·63 g, 3·06 mmol) were heated at 65 °C for 4 h. After work-up, **22**, **23** and **24** were isolated as yellow solids. Compound **23** was the major product (0·5 g, 31%): m.p. 93·0–94·0 °C. ^{1}H NMR: 0·8–1·6 (m, 38H, CH_2, CH_3), 4·0–4·3 (t, 4H, OCH_2), 7·1–8·0 (m, 6H, ArH). Analysis: calculated for $C_{34}H_{48}O_4$, C 78·40, H 9·31; found, C 77·66, H, 9·38%. Compound **24** was crystallized from EtOH (0·3 g, 19%): m.p. 60·0–61·0 °C. ^{1}H NMR: 0·8–2·2 (m, 19H, CH_2, CH_3), 3·35 (s, 3H, OCH_3), 3·5–4·5 (m, 14H, OCH_2), 7·7–8·0 (m, 6H, ArH). Analysis: calculated for $C_{31}H_{42}O_7$, C 70·68, 8·05; found, C 70·57, H 8·10%.

1,11-(1,8-Dioxyanthracene-9,10-dione)-3,6,9-trioxaundecane (**25**). 1,8-Dichloroanthraquinone (**3**) (4·22 g, 15·2 mmol) and tetraethylene glycol (3·18 g, 16·4 mmol) in THF (60 ml) were added slowly to NaH (1·9 g, 47·5 mmol) in THF (20 ml). The reaction mixture was heated for 3·5 h, concentrated and the residue was added to cold H_2O (100 ml), extracted with CH_2Cl_2 (200 ml then 100 ml), washed with brine (100 ml), dried over $MgSO_4$, filtered and concentrated. Column chromatography (silica, 5% MeOH–CH_2Cl_2), followed by crystallization from toluene, gave **25** (2·53 g, 42%) as a yellow solid: m.p. 154·5–155·5 °C. ^{1}H NMR: 3·85–4·32 (m, 16H, CH_2O), 7·10–7·88 (m, 6H, Ar). IR: 1675, 1590, 1450, 1420, 1390, 1355, 1125, 1075, 755 cm^{-1}. Analysis: calculated for $C_{22}H_{22}O_7$, C 66·32, H 5·57; found, C 66·21, H, 5·63%.

1,14-(1,8-Dioxyanthracene-9,10-dione)-3,6,9,12-tetraoxatetradecane (**26**). A mixture of **3** (1·73 g, 6·24 mmol), pentaethylene glycol (1·54 g, 6·46 mmol) in THF (30 ml) and NaH (0·91 g, 22·75 mmol) in THF (10 ml) was heated at reflux for 3·5 h, cooled, concentrated *in vacuo* and the residue was dissolved in H_2O (100 ml), extracted with CH_2Cl_2 (200 ml then 100 ml), washed with brine (100 ml), dried ($MgSO_4$) filtered and evaporated to give the crude solid, which was chromatographed (silica, 5% MeOH–CH_2Cl_2) and crystallized from EtOH to yield **26** (0·80 g, 30%) as a yellow: m.p. 125·0–126·0 °C. ^{1}H NMR: 3·71–4·40 (m, 20H, OCH_2), 7·12–7·88 (m, 6H, ArH). IR: 2900, 1675, 1595, 1350, 1275, 1135, 1070 cm^{-1}. Analysis: calculated for $C_{24}H_{26}O_8$, C 65·14, H 5·93; found, C 65·01, H 6·02%.

1,17-(1,8-Dioxyanthracene-9,10-dione)-3,6,9,12,15-pentaoxaheptadecane (**27**). To a suspension of KH (35% in oil, 3·0 g, 26·17 mmol) in dry THF was added slowly hexaethylene glycol (3·45 g, 12·22 mmol). The mixture was stirred for 30 min, a solution of **3** (2·74 g, 9·89 mmol) in THF (75 ml) was added and after reflux (3 h) the mixture was cooled, evaporated, H_2O (100 ml) and CH_2Cl_2 (200 ml) were added and the aqueous layer was extracted with CH_2Cl_2 (2 × 100 ml) and then concentrated. Column chromatography (silica, 5% MeOH–CH_2Cl_2), followed by crystallization from hexane, gave **27** (1·6 g, 35%) as a yellow solid: m.p. 101·5–102·5 °C. ^{1}H NMR: 3·60–4·40 (m, 24H, OCH_2), 7·15–7·90 (m, 6H, ArH). ^{13}C NMR: 183·9, 182·0, 158·5, 134·8, 133·6, 124·7, 119·7, 119·3, 71·5, 71·0, 70·5, 70·4, 69·5 ppm. IR (KBr): 2900, 1680, 1590, 1310, 1275, 1235 cm^{-1}. Analysis: calculated for $C_{26}H_{30}O_9$, C 64·18, H 6·22; found C 64·13, H 6·25%.

1-Morpholinoanthracene-9,10-dione (**28**). A solution of **1** (0·71 g, 2·93 mmol), morpholine (0·50 g, 5·74 mmol) and Na_2CO_3 (1·4 g) in MeCN was heated under reflux for 6 days. the reaction mixture was concentrated and the solid was dissolved in CH_2Cl_2, washed with H_2O and concentrated *in vacuo*. Column chromatography (silica, 2% MeOH–CH_2Cl_2), followed by recrystallization (CH_2Cl_2–hexane), gave **28** as a dark-red solid (0·26 g, 30%): m.p. 152·0–153·0 °C. ^{1}H NMR: 3·02 (t, 4H, NCH_2), 3·87 (t, 4H, OCH_2), 7·15–8·15 (m, 7H, ArH). IR: 3000–2840, 1670, 1650, 1595, 1430, 1365, 1315, 1270, 1260, 1230, 1110, 1000, 920, 700 cm^{-1}. Analysis: calculated for $C_{18}H_{15}NO_3$, C 73·70, H 5·16, N 4·78; found, C 73·61, H 5·17, N 4·68%.

1-Chloro-8-morpholinoanthracene-9,10-dione (**29**) and 1,8-bis(*morpholine*) *anthracene-9,10-dione* (**30**). A solution of 1,8-dichloroanthraquinone (1·03 g, 3·72 mmol), morpholine (1·96 g, 22·5 mmol) and sodium carbonate (3·61 g) in acetonitrile (40 ml) was heated to reflux for 6 days. After work-up as for **28**, Chromatotron chromatography (silica, 4 mm plate, 2% MeOH–CH_2Cl_2) gave **29** and **30**. Compound **29** was isolated as a purple solid (0·76 g, 62%): m.p. 174·0–175·0 °C. ^{1}H NMR: 3·20 (t, 4H, NCH_2), 3·96 (t, 4H, OCH_2), 7·15–8·20 (m, 6H, ArH). IR (KBr): 2960, 1680, 1590, 1310, 1240, 1230, 930 cm^{-1}. Analysis: calculated for $C_{18}H_{14}ClNO_3$, C 65·95, H 4·31, Cl 10·82; found, C 65·73, H 4·39, Cl 10·99%. Compound **30** was isolated as a purple solid (0·48 g, 34%): m.p. 212·0–213·0 °C. ^{1}H NMR: 3·15 (t, 8H, NCH_2), 3·97 (t, 8H, OCH_2), 7·20–7·90 (m, 6H, ArH). IR

(KBr): 3000–2800, 1665, 1635, 1585, 1420, 1360, 1300, 1235, 1200, 1100, 970, 900, 875, 730 cm^{-1}. Analysis: calculated for $C_{22}H_{22}N_2O_4$, C 69·82, H 5·87, N 7·40; found, C 69·67, H 5·92, N 7·29%.

1-Chloro-5-morpholinoanthracene-9,10-dione (**31**) and 1,5-bis(*morpholine*)*anthracene-9,10-dione* (**32**). A solution of **2** (2·99 g, 10·79 mmol), morpholine (7·0 ml, 80·27 mmol) and Na_2CO_3 (7·53 g) in CH_3CN (180 ml) was heated at reflux for 6 days. Work-up and column chromatography (silica, 2% MeOH–CH_2Cl_2) gave **31** and **32**. Compound **31** was isolated as a purple solid (1·87 g, 53%): m.p. 163·0–165·0 °C. ^1H NMR: 3·20 (t, 4H, NCH_2), 3·96 (t, 4H, OCH_2), 7·15–8·20 (m, 6H, ArH). IR: 3000, 1680, 1590, 1300, 1240, 1230, 925 cm^{-1}. Analysis: calculated for $C_{18}H_{14}ClNO_3$, C 65·95, H 4·31, Cl 10·82; found, C 66·02, H 4·35, Cl 10·79%. Compound **32** was isolated as a purple solid (1·86 g, 46%): m.p. 265·0–266·0 °C. ^1H NMR: 3·15 (t, 8H, NCH_2), 3·97 (t, 8H, OCH_2), 7·20–7·90 (m, 6H, ArH). IR: 3000, 1665, 1630, 1585, 1410, 1350, 1300, 1200, 1100, 970, 900, 875, 730 cm^{-1}. Analysis: calculated for $C_{22}H_{22}N_2O_4$, C 69·82, H 5·87, N 7·40; found, C 69·72, H 5·90, N 7·33%.

Bis(1-oxa-8-morpholinoanthracene-9,10-dione)-3,6-dioxacotane (**33**). Triethylene glycol (0·12 g, 0·80 mmol) was added to a suspension of NaH (0·09 g, 2·25 mmol) in THF. The mixture was stirred for 30 min and a solution of **29** (0·50 g, 1·53 mmol) dissolved in THF (15 ml) was added. After reflux (48 h) and work-up, crystallization from EtOAc gave **33** (0·77 g, 69%) as a purple solid: m.p. 166·0–167·0 °C. ^1H NMR: 3·05 (t, 8H, NCH_2), 3·80–4·35 (m, 20H, OCH_2), 7·00–7·85 (m, 12H, ArH). IR: 2860, 1680, 1590, 1305, 1270, 1110, 730 cm^{-1}. Analysis: calculated for $C_{42}H_{40}N_3O_{10}$, C 68·83, H 5·51, N 3·82; found, C 68·90, H 5·52, N 3·77%.

1-Chloro-8-(aza-15-crown-5)*anthracene-9,10-dione* (**35**) and 1,8-bis(*aza-15-crown-5*)*-anthracene-9,10-dione* (**36**). To a solution of aza-15-crown-5 (2·19 g, 9·98 mmol) in anhydrous diethyl ether (40 ml) was added *n*-butyllithium (1·6 M in hexane, 6 ml, 9·6 mmol). After 15 min, a solution of **3** (1·36 g, 4·91 mmol) in dry benzene (80 ml) was added. The mixture was stirred (20 min) and then heated at reflux for 1 h. The mixture was cooled, H_2O (50 ml) was added and the aqueous layer was extracted (CH_2Cl_2, 2 × 50 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo*. After column chromatography (silica, EtOAc, then 25% MeOH–CH_2Cl_2, then MeOH), **35** and **36** were isolated. Compound **35** was crystallized (EtOAc–hexane) to give a purple solid (0·21 g, 19%): m.p. 106·0–107·0 °C. ^1H NMR: 3·50–3·85 (m, 20H, NCH_2, OCH_2), 7·30–8·05 (m, 6H, ArH). IR (KBr): 2910, 1875, 1660, 1585, 1510, 1240, 1120, 1110, 720 cm^{-1}. Analysis: calculated for $C_{24}H_{26}ClNO_6$, C 62·27, H 5·71, N 3·05; found, C 62·55, H 5·75, N 2·99%. Compound **36** was isolated as viscous purple oil (0·10 g, 7%). ^1H NMR: 3·30–3·90 (m, 40H, NCH_2, OCH_2), 7·30–7·70 (m, 6H, ArH). Analysis: calculated for $C_{34}H_{46}N_2O_{10}$, C 63·52, H 7·23, N 4·36; found, C 62·96, H 7·35, N 4·09%.

1,8-Bis-(2-bromethoxy)anthraquinone (**37**). To a solution of 1,8-dihydroxyanthraquinone (5·0 g, 20·8 mmol) in anhydrous DMF (80 ml) was added Cs_2CO_3 (30 g, 92 mmol) while stirring during 10 min. A color change from orange to deep purple was observed. Dibromoethane (10 ml, 116 mmol) was then added and the mixture heated to 80 °C. After 3 h, the reaction mixture was cooled, filtered through a pad of Celite and the solvent removed *in vacuo*. Column chromatography (SiO_2, 0–4% MeOH–CH_2Cl_2) and crystallization from EtOAc afforded the dibromide (**37**) (3·2 g, 18%) as long orange needles: m.p. 153–154 °C. ^1H NMR: 3·76 (t, 4H, CH_2Br), 4·44 (t, 4H, $ArOCH_2$), 7·31 (d, 2H, Ar H-2 and H-7), 7·62 (t, 2H, Ar H-3 and H-6), 7·87 (d, 2H, Ar H-4 and H-5). Analysis: calculated for $C_{18}H_{14}Br_2O_2$, C 47·61, H 3·11; found, C 47·51, H 3·13%.

Anthraquinone-[2.2]-cryptand (**38**). A solution of 4,13-diaza-18-crown-6 (1·0 g, 3·8 mmol) in *n*-PrCN (50 ml) was added to a solution of the dibromide **37** (see above) (1·74 g, 3·8 mmol) in 350 ml of the solvent containing Na_2CO_3 (9·6 g, 91 mmol) and NaI (0·7 g, 4·7 mmol). The suspension was stirred and heated at 100 °C for 24 h, cooled, filtered and the solvent removed *in vacuo* to afford a green oil. Column chromatography (Al_2O_3, 0–1% MeOH–$CHCHl_3$) followed by recrystallization from absolute EtOH (20 ml) afforded **38** (1·1 g, 52%) as green crystals: m.p. 127–129 °C (turned brown). ^1H NMR: 3·05 (t, 8H, CH_2CH_2O), 3·72 (m, 8H, OCH_2CH_2N), 4·18 (t, 4H, $ArOCH_2$), 7·24 (d, 2H, Ar H-2 and H-7), 7·58 (t, 2H, Ar H-3 and H-6), 7·89 (d, 2H Ar H-4 and H-5). IR: 3440 (br), 2980, 2900, 2840, 1680, 1595, 1480, 1460, 1450, 1420, 1365, 1330, 1270, 1250, 1180, 1140, 1120, 1105 cm^{-1}. Analysis: calculated for $C_{30}H_{38}N_2O_8$, C 64·97, H 6·91, N 5·05; found, C 64·72, H 6·93, N 4·99%.

Crystal structure data for anthraquinone-[2.2]-cryptand (**38**). Crystals suitable for x-ray crystallographic analysis were obtained by slow evaporation of a solution containing **38** is absolute EtOH. Crystal structure data: $C_{30}H_{38}N_2O_8$, FW 554·7 g mol^{-1}, triclinic crystal system, space group $P\bar{1}$, $a = 8·6179(4)$ Å, $b = 11·2228(5)$ Å, $c = 15·3694(8)$ Å, $V = 138·5(1)$ $Å^3$; $d_c = 1·335$ g cm^3, Cu $K\beta$ radiation, graphite monochromator ($\mu = 7·57$ cm^{-1}), $R = 0·0172$ for 2843 unique observed reflections with $F > 6\Omega(F)$, measured

on an Enraf–Nonius CAD-4F (kappa geometry) x-ray spetrometer using $\Omega/2\theta$ scans, $2^\circ < 2\theta < 110^\circ$.

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