Synthesis and Characterization of Crowned 1,4-Benzoquinones as Ionophore-Dienophile (Redox) Combined Systems: Double Interaction with Catecholamines and Tryptamine

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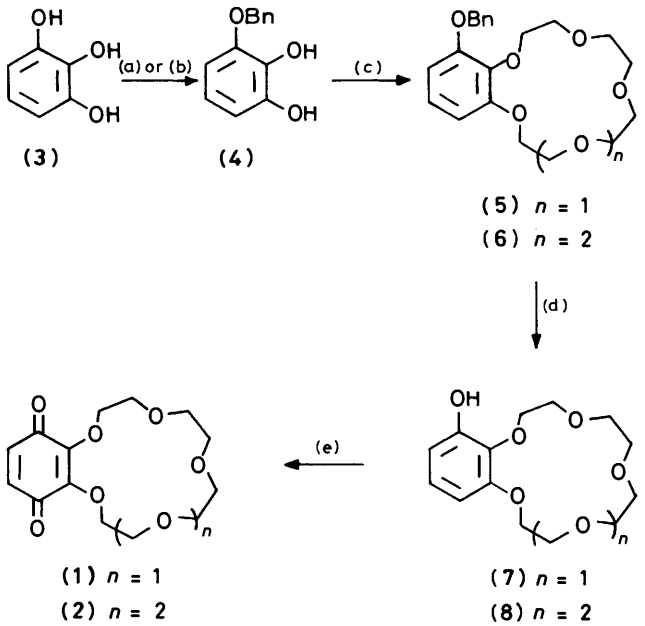
The crowned 1,4-benzoquinones (**1**) (15-crown-5) and (**2**) (18-crown-6) have been synthesized from pyrogallol (**3**) by: (1) the selective monobenzylation (**4**); (2) crown ether formation using a pyrocatechols (**5**) and (**6**); (3) debenzylation (**7**) and (**8**); and (4) oxidation to 1,4-benzoquinones. Both compounds (**1**) and (**2**) underwent smooth Diels–Alder reactions with cyclopentadiene (25 °C), thebaine (80 °C), and buta-1,3-diene (BF_3·Et_2O, 0 °C). The cyclopentadiene adducts (**11**) and (**12**) were photochemically transformed into the cage compounds (**13**) and (**14**), while the thebaine adducts (**15**) and (**16**) were smoothly converted into the hydroquinone derivatives (**17**) and (**18**) by silicic acid. The butadiene adducts (**19**) and (**20**) were transformed into the crowned naphthoquinones (**23**) and (**24**) in high yields. The redox potentials of these crowned quinones in the presence of alkali-metal ions were studied by cyclic voltammetry. The specific interaction between compound (**2**) and tryptamine, dopamine, and homoveratrylamine *via* ion-binding and charge-transfer complex formation was evidenced by u.v. spectroscopic studies.

In the highly specific enzyme catalysis of many biological processes, the co-operativity of subunits often plays an important role.[1] A number of model systems have been developed as enzyme mimics,[2] in which several functional groups, appropriately cited, co-operate in their specific reactions. Among them, crown ethers and related macrocyclic compounds have attracted great attention as artificial ionophores.[3] For example, these ion-complexing groups with other functional units such as chromophores,[4] redox systems,[5] charge-transfer complexation systems,[6] and aza crowns[7] have given rise to unique molecular systems, the functions of which are regularly modulated by noncovalent binding of specific ionic substrates (*i.e.*, modulators) as seen in allosteric enzymes.[8]

As a continuation of our studies on the design and preparation of multifunctional molecules,[9–11] we have investigated the synthesis, cycloadditions, and electrochemical behaviour of crowned benzoquinones such as (**1**) and (**2**) (Scheme 1) which can be regarded as ionophores bearing dienophilic as well as redox-active functions. The design was based on the idea that the ionophore function might be easily introduced into various dienic compounds *via* Diels–Alder reactions. Furthermore, a system containing an electron-acceptor group and a crown ether system might provide a new type of ditopic host molecule for amines bearing electron-donating aromatic rings such as dopamine and tryptamine and in which there is *double interaction via* ion-binding and charge-transfer complex formation. Herein we report the full details of this work[12] including cyclic voltammetric studies on the redox potentials of the crowned quinones prepared and u.v. spectral studies concerning the specific interaction of the biologically important pyrocatechol amines.



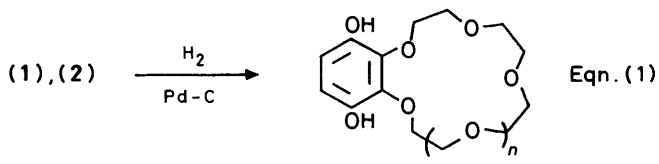
Scheme 1. (a) i, Borax, H_2O; ii, $PhCH_2Br$, NaOH; iii, H_2SO_4 (12%); (b)[12] i, $HC(OEt)_3$, Amberlyst, C_6H_6, slow distillation (65—75 °C) (67%); ii, $PhCH_2Cl$, NaOH, dioxane (80%); iii, TsOH, MeOH, H_2O (100%); (c) for (**5**), $ClCH_2(CH_2OCH_2)_3CH_2Cl$, NaOH, BuOH, 118 °C (64%); for (**6**), $TsOCH_2(CH_2OCH_2)_4CH_2OTs$, CsF, CH_3CN, 65 °C (30%); (d) for (**7**), H_2 (3 atm), Pd-black, EtOH (100%); for (**8**), H_2 (5 atm), 10% Pd–C, dioxane (96%); (e) Fremy's salt, for (**1**), pH 7 buffer, H_2O, acetone, for (**2**), CH_3CO_2Na, H_2O, benzene (30—50%)

Results and Discussion

Syntheses.—The crowned *p*-benzoquinones (**1**) (15-crown-5) and (**2**) (18-crown-6) were prepared from pyrogallol (**3**) by the routes as outlined in Scheme 1. The synthesis was based on (**1**) the selective protection (benzylation) of the 1-hydroxy group of (**3**); (2) crown ether formation using the pyrocatechol entity, (3) debenzylation; and (4) oxidation to 1,4-benzoquinones. Recently, Merz and co-workers[13] reported an independent synthesis of compounds (**1**) and (**2**) using a similar strategy except for the stepwise construction of the crown ether ring.†

† For the selective benzylation of (**3**), Merz's method[13] using the cyclic ortho ester of vicinal hydroxy groups seemed more practical than the previously reported one-pot reaction method.[12]

The crown *p*-benzoquinones thus obtained were deep-coloured crystalline compounds [(**1**), red needles, m.p. 121—123 °C (lit.,[13] 83—84 °C); (**2**), orange needles, m.p. 67.5 °C (lit.,[13] 65—66 °C)], which were smoothly hydrogenated to give the corresponding hydroquinones (**9**) and (**10**) as colourless crystalline compounds [equation (1)].



Eqn. (1)

(**9**) *n* = 1
(**10**) *n* = 2

The structures of these compounds were confirmed on the basis of spectroscopic data (see Experimental section) as well as chemical transformations (*vide infra*).

Diels–Alder Reactions.—First, in order to explore the utility of compounds (**1**) and (**2**) as dienophiles, Diels–Alder reactions with various dienic compounds were investigated. When compounds (**1**) and (**2**) were treated with cyclopentadiene in methylene dichloride at room temperature (30 min), the crystalline adducts (**11**) and (**12**) were obtained in 98 and 94% yields, respectively (Scheme 2). Structural assignments to these products was made on the basis of their mass [(**11**), M^+, *m/z* 364; (**12**), *m/z* 408], i.r. (1 650 cm^{-1}), and ^1H n.m.r. spectra [diagnostic signals for olefinic protons at δ 6.08 (2 H, small m)]. Their *endo* structure was confirmed by facile photochemical cage formation.[14,15] Thus, irradiation of compound (**11**) [or (**12**)] in chloroform with a 100-W high-pressure Hg lamp through a Pyrex filter gave a quantitative yield of the intramolecular [2 + 2] cycloaddition product (**13**) [or (**14**)]; $\nu_{max.}$(CO) 1 755 and 1 737 cm^{-1} (Scheme 2). The mass spectrum of compound (**13**) showed a relatively intense molecular ion peak at *m/z* 364 compared with that of (**11**) which was prone to retro Diels–Alder fragmentation.

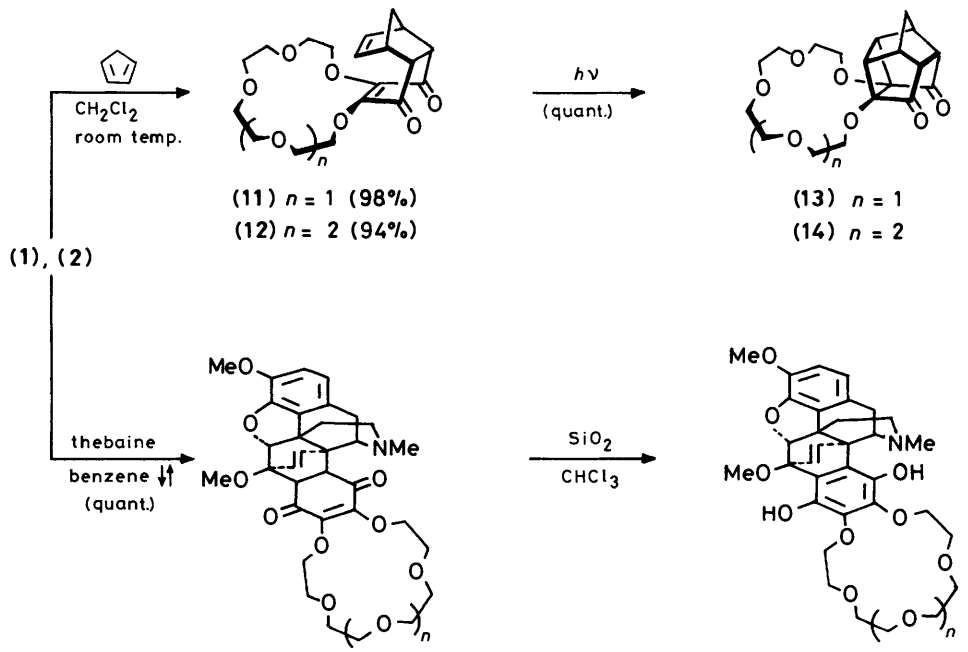
The reactions of compounds (**1**) and (**2**) with thebaine in refluxing benzene (3 h) resulted in smooth formation of the Diels–Alder adducts (**15**) and (**16**) ($\nu_{max.}$ 1 655 cm^{-1}) which, in turn, when stirred in chloroform with silicic acid or even on passage through a silica gel column, readily isomerized to give the hydroquinone derivatives[16,17] (**17**) (m.p. 193—195 °C) and (**18**) (m.p. 169—170 °C) in 82 and 98% overall yields, respectively (Scheme 2).

Compounds (**1**) and (**2**) also underwent Diels–Alder reactions with an acyclic diene such as buta-1,3-diene, and the adducts were conveniently converted into the crowned naphthoquinones (Scheme 3). Thus, reaction of compound (**1**) and an excess of buta-1,3-diene in methylene dichloride (0 °C) in the presence of BF_3·Et_2O (1 equiv.) afforded a quantitative yield of the 1:1 adduct (**19**): $\nu_{max.}$ 1 670 cm^{-1}; ^1H n.m.r. δ 2.3 (4 H, m), 3.1 (2 H, m), and 5.67 (2 H, t, *J* 1.5 Hz). Treatment of compound (**19**) with silica gel in chloroform in an open beaker resulted in aerial oxidation to give crystalline compound (**21**), m.p. 69—70 °C; $\nu_{max.}$ 1 650 cm^{-1}; δ 3.02 (4 H, d, *J* 1.2 Hz) and 5.78 (2 H, t, *J* 1.2 Hz). Dehydrogenation of compound (**21**) by dichlorodicyanobenzoquinone (DDQ) in benzene (80 °C) provided the crowned naphthoquinone (**23**) in 89% overall yield, m.p. 104.5—105.5 °C; $\nu_{max.}$ 1 650 and 1 600 cm^{-1}; δ 7.69 and 8.03 p.p.m. (4 H, AA′BB′-type m). Similarly, compound (**2**) was transformed into the 18-crown-6 derivative (**24**), m.p. 71.5—72.5 °C, in high yield *via* compounds (**20**) and (**22**) (Scheme 3).*

The above results indicated that compounds (**1**) and (**2**) can serve as a potent dienophile and hence provide a convenient way of introducing the crown ether entity into various dienic compounds *via* Diels–Alder reactions.

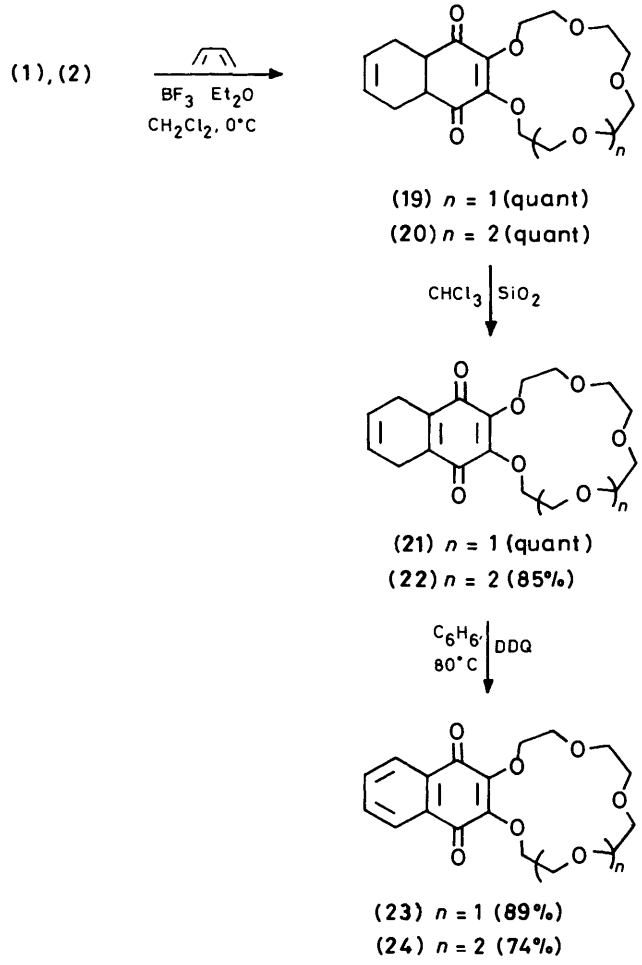
Electrochemistry.—In order to investigate the electrochemical properties of these ionophore-redox combined compounds, we

* Direct treatment of compounds (**19**) or (**20**) with DDQ in refluxing benzene afforded compounds (**23**) or (**24**) in much less satisfactory yields.



Scheme 2.

have undertaken cyclic voltammetric studies of the crowned quinones (**1**) and (**2**), the crowned naphthoquinones (**23**) and (**24**) as well as the cyclic 2,3-dialkoxy quinones* (**25**) and (**26**) as reference compounds for non-binding quinones.[18,19] The cyclic voltammograms of compound (**2**) in DMF containing 0.1M

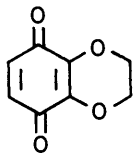


Scheme 3.

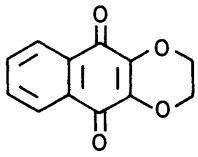
tetraethylammonium perchlorate (Et_4NClO_4; TEAP) as an electrolyte displayed a reversible redox couple at −0.57 V (*vs.* S.C.E.) (E_1) corresponding to the formation of the semiquinone radical (SQ^-) and a quasi-reversible redox couple at −1.29 V (E_2) corresponding to the formation of quinone-dianion (Q^{2-}). The redox potentials observed for other quinones under the same conditions (in DMF; 0.1M TEAP) are summarized in Table 1.

As Table 1 shows, the Q/SQ^- potentials (E_1) for these quinones became more negative in the order: 1,4-benzoquinone > (**1**) ≃ (**2**) > (**25**) > (**23**) ≃ (**24**) > (**26**), *i.e.*, the electron affinity decreases in this order. Hence, it is obvious that both a crown ether entity (or dialkoxy groups) and a fused aromatic ring make reduction of the quinones more difficult.

Furthermore, the electrochemical reactions of these ionophore-redox combined compounds seemed to be influenced by



(**25**)



(**26**)

ion complexation.[5b,20,21] Thus, replacement of TEAP as supporting electrolyte with $KClO_4$, $NaClO_4$, and $LiClO_4$ (each 0.1M) for compound (**1**) [or (**2**)] resulted in the observation of anodic shifts of Q/SQ^- (E_1) potential by +100 (+100), +100 (+90), and +60 (+60) mV, respectively,†‡ whereas the same replacement of electrolytes for 1,4-benzoquinone itself[22,23] caused E_1 potential shifts to a much smaller extent and even in the *reverse order* by < +5 (K^+), +20 (Na^+), and +40 mV (Li^+).§ It should be also noted that the magnitude of the potential shifts may reflect the degree of 'fit' of the metal ions in the crown cavities according to their sizes,[3] although the effects are relatively small. The crowned quinones (**23**) and (**24**) also showed cation-dependent E_1 potential shifts similar to those of compounds (**1**) and (**2**), while those of (**25**) and (**26**) were essentially the same as those of 1,4-benzoquinone.

From these results, it is concluded that the cation-dependent E_1 potential shifts observed for the crowned quinones (**1**) and (**2**) and (**23**) and (**24**) are consistent with complexation of the metal cations to the crown ether group, making the quinones easier to reduce.

Specific Interaction with Biologically Important Catecholamines.—Dopamine and related catecholamines play an important role in the central nervous systems as neurotransmitters.[24] These adrenergic agents possess the common structural feature that the amino group is bound to the electron-donating aromatic ring (*e.g.*, catechols and indoles) *via* a C-2 carbon chain. This structural characteristic of biologically important amines prompted us to investigate the interaction of the latter with the 18-crown quinone (**2**). Molecular model studies indicated that bifunctional amines (*e.g.* dopamine) possess inter-group distances suitable for 'double interaction' with compound (**2**): that is, *via* an ammonium ion-crown interaction (ion-binding) and charge-transfer (CT) complex formation between the aromatic ring and quinone group (see Figure 1).

In order to gain insight into this problem, we have studied the u.v. spectra of compound (**2**) as well as (**25**) as a reference compound both in the presence and the absence of HCl salts of various amines; the spectral changes caused by these additives are shown by difference u.v. spectra (Figure 2 and Table 2).

As Figure 2A shows, the u.v. spectrum of compound (**2**) in methanol (1.5×10^{-3}M) [$\lambda_{max.}$ 396 nm (ε 1 370)] was affected by added NH_4Cl (0.059M) to cause a slight hypsochromic shift ($\Delta\lambda_{max.} = -4$ nm) as well as a slight absorption decrease.¶

* In contrast to compounds (**1**) and (**2**), compound (**25**) was prepared by direct alkylation of compound (**3**), using 1,2-dibromoethane, without hydroxy group protection; the product was oxidised to the corresponding quinone, which was then converted into compound (**26**) *via* a Diels–Alder reaction with buta-1,3-diene (see Experimental section).

† Wolf and Cooper reported the similar cation-dependent E_1 potential shifts [+130 (K^+), +129 (Na^+), +50 mV (Li^+)] for the 2,6-crowned-1,4-benzoquinone derivative.[5b]

‡ From these potential shifts, electrochemical enhanced K^+-, Na^+-, and Li^+-binding for compound (**2**) were estimated as 50 times, 30 times, and 10 times, respectively, by the following equation $E_{complex} - E_{free} = -RT/nF[\ln (K_Q/K_{SQ})]$ where K is stability constant: D. A. Gustowski, L. Echegoyen, D. M. Goli, A. Kaifer, R. A. Shultz, and G. W. Gokel, *J. Am. Chem. Soc.*, 1984, **106**, 1633, and ref. 20.

§ Compounds (**1**) and (**2**) also showed cation-dependent SQ^-/Q^{2-} (E_2) potential shifts which were very similar to those of 1,4-benzoquinone itself and hence might derive largely from ion pairing.[22,23]

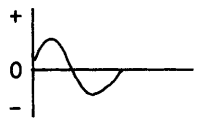
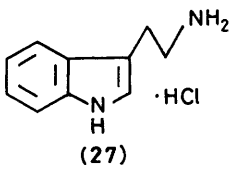
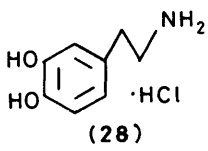
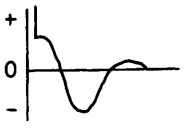
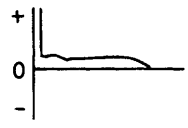
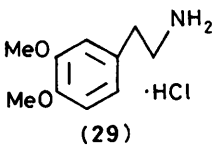
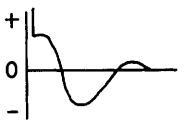
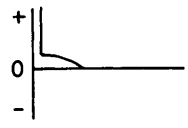
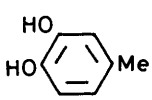
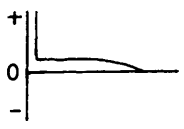
¶ Similar hypsochromic shifts ($\Delta\lambda_{max.} = -4$ to -6 nm) and a slight decrease in absorption were also observed upon addition of alkali-metal salts such as $MClO_4$ (M = Na, K, Li).

Table 1. The redox potentials (V) of quinoid compounds determined by cyclic voltammetry[a,b]

Compound	E_{1c}	E_{1a}	$E_{0.1}$	E_{2c}	E_{2a}	$E_{0.2}$
1,4-Benzoquinone	−0.540	−0.460	−0.50	−1.330	−1.235	−1.28
(1)	−0.630	−0.550	−0.59	−1.415	−1.325	−1.37
(2)	−0.600	−0.540	−0.57	−1.330	−1.255	−1.29
(25)	−0.660	−0.595	−0.63	−1.440	−1.370	−1.41
(23)	−0.810	−0.740	−0.78	−1.490	−1.415	−1.45
(24)	−0.810	−0.740	−0.78	−1.500	−1.420	−1.46
(26)	−0.880	−0.820	−0.85	−1.575	−1.505	−1.54

[a] Cyclic voltammograms were measured in DMF containing 0.1M Et_4NClO_4 at 100 mV s^{-1} (*vs.* S.C.E.). [b] The redox potentials ($E_{0,n}$) were taken as the average of anodic (E_{na}) and cathodic peak potentials (E_{nc}).

Table 2. The difference u.v. spectra of compounds (2) and (25) obtained after addition of additives[a]

Entry	Additive	Compound (2) Difference spectra ($\Delta\lambda_{max.}$/nm)[b]		Compound (25) Difference spectra ($\Delta\lambda_{max.}$/nm)[b]	
1	NH_4Cl		−3·6		0
2	 (27)		−6·2		−0·2
3	 (28)		−7·2		0
4	 (29)		−6·0		+3·0
5	 (30)		−2·2		−1·6

[a] All the difference spectra were taken between compound (2) (1.5mM) [or (25) (1.5mM)] alone and (2) [or (25)] in the presence of additives (*ca.* 50mM) in methanol at 25 °C. [b] $\Delta\lambda_{max.} = \lambda_{max.}$ [(2) or (25) alone] − $\lambda_{max.}$ [(2) or (25) in the presence of additive].

This can be attributed to the ammonium ion-crown interaction (ion-binding)[5c] since no such spectral change was observed for compound (25) upon addition of NH_4Cl (Table 2; entry 1). In contrast, the u.v. spectrum of compound (2) in the presence of tryptamine·HCl (27) showed, besides a similar hypsochromic shift, increases in absorption around at 320 and 520 nm; this leads to an apparently different pattern for the difference u.v. spectra [positive curve at the longer wavelength (Figure 2B)]. The u.v. spectrum of (25) showed only a slight increase in absorption with no noticeable shift upon addition of (27) (Table 2; entry 2).

Similarly, compounds (2) and (25) showed characteristically

different spectral changes upon addition of catecholamines such as dopamine·HCl (**28**) and homoveratrylamine·HCl (**29**) (Table 2; entries 3 and 4). Thus, upon addition of these ammonium salts, (**2**) exhibited a composite change of hypsochromatic shift and absorption increase, whereas (**25**) showed only a slight increase in absorption. The absorption increments apparently stem from the partial formation of a charge-transfer (CT) complex, since a similar change (absorption increase) was observed for both (**2**) and (**25**) upon addition of the catechol (**30**) (Table 2; entry 5) which is known as a class of compounds prone to CT-interaction with quinones.[25]

In this regard, it was generally observed that the absorption increments of compound (**2**) upon addition of the above additives were strengthened whilst the hypsochromic shifts were lessened by changing the solvent from methanol to DMF. This is in good accord with strengthening of the CT-interaction in more polar media and weakening of the ion-crown interaction.

Therefore, the characteristic spectral changes (hypsochromic shift + absorption increment) observed for (**2**) upon addition of (**27**)—(**29**) can be reasonably attributed to the simultaneous occurrence of ion-crown interaction and CT-complex formation (double interactions; see Figure 1). Interestingly, it is notable that these two reactions seem to influence each other positively in compound (**2**) since ion-binding by the crown group will tend to increase the electron affinity of the quinone moiety and, conversely, CT-complex formation (*i.e.* partial reduction of quinone) will tend to enhance the ion-binding ability of the crown group (see preceding section). These phenomena are reminiscent of the function of the positive effectors for the allosteric enzymes.

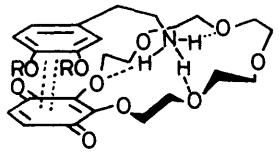


Figure 1. The schematic representation of 'double interaction' by CT-complex formation and ion-binding

The crowned naphthoquinone (**24**) showed similar spectral changes upon additions of NH_4Cl and compound (**28**), an indication of ion-crown interaction but no CT-complex formation between (**24**) and (**28**). These results suggested that the CT-interaction between (**24**) and (**28**) is much less favourable than between (**2**) and (**28**); this is consistent with the observations of the remarkably decreased electron affinity of (**24**) compared with that of (**2**) (*vide supra*).

In conclusion, the utility of crowned benzoquinones (**1**) and (**2**) as the ionophore-dienophile (redox) combined system has been demonstrated in the cycloadditions, electrochemical reactions, and specific interactions with catecholamines. Compounds (**1**) and (**2**) proved to be useful dienophiles for the introduction of the crown ether function into various dienes *via* Diels–Alder reactions: the crowned naphthoquinones (**23**) and (**24**) were so prepared. In such combined crown-quinone systems, the redox reaction and crown-ion interaction are nicely coupled; *i.e.*, the ion-binding by crown group makes the quinone easier to reduce and *vice versa*. This co-operativity of the two functional groups was utilized for the 'double interaction' between compound (**2**) and some amines bearing an electron-rich aromatic ring (*e.g.* dopamine and tryptamine) *via* ion-binding and CT-complex formation. Since this kind of interaction specifically occurred with these biologically important amines, compound (**2**) may serve as their receptor mimic.*

* Such a double interaction seemed not to occur between (**2**) and related amino acids, since the u.v. spectra of (**2**) in the presence of tyrosine·HCl or GABA·HCl (γ-aminobutyric acid) showed only a slight hypsochromic shift due to ammonium ion-crown interaction.

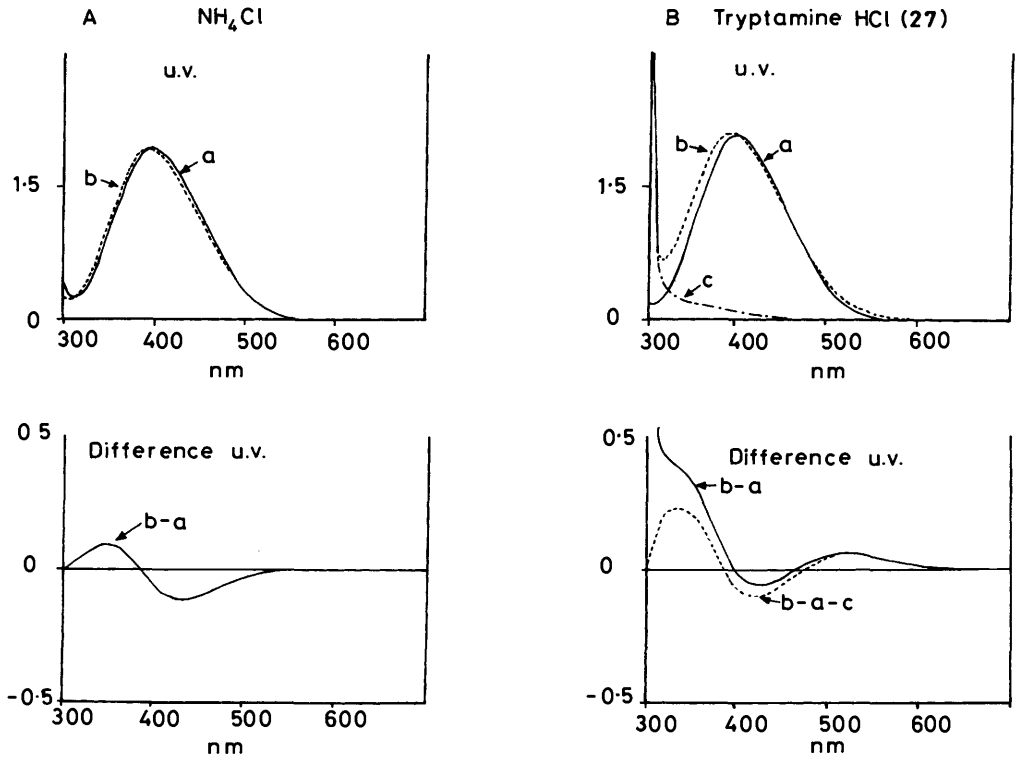


Figure 2. The u.v. absorption spectra (top) and differential absorption spectra (bottom) of compound (**2**) (1.5mM) in methanol obtained after addition of additives: A; (a) (**2**) alone, (b) (**2**) + NH_4Cl (59mM). B; (a) (**2**) alone, (b) (**2**) + (**27**) (48mM), (c) (**27**) (48mM) alone

Experimental

The m.p.s were measured with Yanagimoto micro melting point apparatus and are uncorrected. ^{1}H N.m.r. spectra were taken with a JEOL PS-100 or Hitachi R-600 spectrometer with tetramethylsilane as an internal standard; chemical shifts are expressed in δ values. I.r. spectra were taken with a JASCO IR A-100 infrared spectrophotometer. U.v. spectra were determined with a Shimadzu UV-260 spectrophotometer. Mass spectra were determined on a JEOL-D300 equipped with a JMA 3100/3500 at an ionization voltage of 70 eV. Elemental analyses were performed on Yanagimoto MT2 BHN recorder. Column chromatography was performed by using Merck Kieselgel 60 (70—200 mesh) as the stationary phase.

3-Benzyloxypyrocatechol (**4**).—This is a modification of the procedure for monomethylation reported by Scheline.[26] Pyrogallol (1.26 g, 10 mmol) and a solution of sodium hydroxide (3 g) in water (11 ml) were added to 5% aqueous borax (180 ml). Benzyl bromide (1.2 ml, 10 mmol) was then added dropwise with vigorous stirring at room temperature to this mixture. After being stirred for 30 min the mixture was heated under reflux for 10 h. After cooling, the mixture was acidified and extracted with ethyl acetate (4 × 50 ml). The combined organic layers were dried (Na_2SO_4) and evaporated under reduced pressure. The crude product was chromatographed on a silica gel column with chloroform–methanol (50:1) to give the title compound (**4**) (262 mg, 12%) as a yellow oil: $\delta_H(CDCl_3)$ 5.09 (2 H, s), 5.35, 5.48 (each 1 H, br s, D_2O exchange, OH), 6.4—6.8 (3 H, m), and 7.40 (5 H, m); $\nu_{max.}$(neat) 3 325 (OH) and 1 600 cm^{-1}.

Compound (**4**) was also prepared from pyrogallol in high yields according to the method of Merz and co-workers.[13]

1-Benzyloxy-6,7,9,10,12,13,15,16-octahydro-5,8,11,14,17-pentaoxabenzocyclopentadecene (*3′-Benzyloxybenzo-15-crown-5*) (**5**).—A mixture of compound (**4**) (863 mg, 4 mmol) and 12,13-dichloro-1,4,7,10-tetraoxatetradecane (1.1 g, 4 mmol)[27] in butanol (6 ml), and sodium hydroxide (0.34 g, 8.5 mmol) in water (10 ml) was refluxed at 118 °C under nitrogen with mechanical stirring. After 10 h the solution was cooled to room temperature and acidified with concentrated HCl. The resulting precipitate was filtered off and washed well with methanol. The filtrate was evaporated under reduced pressure and the residue was dissolved in chloroform. The solution was then washed with brine, dried (Na_2SO_4) and evaporated and the residue chromatographed on a silica gel column with chloroform–methanol (50:1) as eluant to give the title compound (**5**) (962 mg, 64%) as a brown oil: $\delta_H(CDCl_3)$ 3.5—4.3 (16 H, m), 5.10 (2 H, s), 6.4—7.1 (3 H, m), and 7.38 (5 H, s); $\nu_{max.}(CHCl_3)$ 3 000, 2 925, 2 875, and 1 595 cm^{-1}; *m/z* 374 (M^+, 23), 242 (27), and 91 (100).

1-Benzyloxy-6,7,9,10,12,13,15,16,18,19-Decahydro-5,8,11,14,17,20-hexaoxabenzocyclo-octadecene (*3′-Benzyloxybenzo-18-crown-6*) (**6**).—Anhydrous caesium fluoride[28] (7.6 g, 50 mmol) was added to a stirred solution of (**4**) (2.18 g, 10 mmol) in dry acetonitrile (160 ml) under nitrogen. The mixture was vigorously stirred for 1 h, after which a solution of pentaethyleneglycol ditosylate[29] (5.46 g, 10 mmol) in acetonitrile (70 ml) was added dropwise; the mixture was then heated at 65 °C for 24 h. The precipitate was filtered off and the filtrate evaporated under the reduced pressure to give a residue which was chromatographed on a silica gel column with ethyl acetate as eluant to provide the title compound (**6**) (1.3 g, 30%) as yellow oil: $\delta_H(CDCl_3)$ 3.4—4.3 (20 H, m), 5.11 (2 H, s), 6.3—7.0 (3 H, m), and 7.37 (5 H, s); $\nu_{max.}(CHCl_3)$ 3 000, 2 870, and 1 595 cm^{-1}; *m/z* 418 (M^+, 15), 242 (47), 152 (69), and 91 (100).

6,7,9,10,12,13,15,16-Octahydro-5,8,11,14,17-pentaoxabenzocyclopentadecen-1-ol (*3′-Hydroxybenzo-15-crown-5*) (**7**).—A mixture of compound (**5**) (960 mg, 2.6 mmol) and Pd black (90 mg) in ethanol (4 ml) was stirred under an atmosphere of hydrogen for 3 days. The catalyst was filtered off and the solvent evaporated under reduced pressure to give the title compound (**7**) (730 mg, 100%) as an oil which was used for the next reaction without further purification: $\delta_H(CDCl_3)$ 3.6—4.4 (16 H, m), 4.3 (1 H, br s, D_2O exchange, OH), and 6.7—7.1 (3 H, m); $\nu_{max.}(CHCl_3)$ 3 530 (OH), 3 000, 2 925, 2 870, and 1 600 cm^{-1}.

6,7,9,10,12,13,15,16,18,19-Decahydro-5,8,11,14,17,20-hexaoxabenzocyclo-octadecen-1-ol (*3′-Hydroxybenzo-18-crown-6*) (**8**).—A mixture of compound (**6**) (1.01 g, 2.42 mmol) and 10% Pd–C (100 mg) in dioxane (5 ml) was stirred under hydrogen (5 atm) for 1 week. The catalyst was filtered off and the solvent evaporated to give compound (**8**) (0.76 g, 96%) as a pale yellow oil: $\delta_H(CDCl_3)$ 3.58 (4 H, s), 3.65—3.75 (8 H, m), 3.8—4.1 (4 H, m), 4.1—4.4 (4 H, m), and 6.3—7.0 (3 H, m); $\nu_{max.}$(neat) 3 400 (OH), 2 900, 2 850, and 1 585 cm^{-1}.

6,7,9,10,12,13,15,16-Octahydro-5,8,11,14,17-pentaoxabenzocyclopentadecene-1,4-quinone (*2,3-Benzoquino[15]crown-5*) (**1**).—Fremy's salt[30] (1.05 g, 3.9 mmol) dissolved in pH 7 phosphate buffer (11 ml) and water (33 ml) was added to a stirred solution of compound (**7**) (203 mg, 0.7 mmol) in acetone (8 ml) at 0 °C. After the mixture had been stirred for 45 min it was extracted with chloroform (3 × 50 ml). The combined extracts were dried (Na_2SO_4) and concentrated under reduced pressure to provide a residue which was chromatographed on a silica gel column with chloroform–methanol (50:1) as eluant to give the title compound (**1**) (107 mg, 50%) as red needles, m.p. 121—123 °C (from dichloromethane–ether) (lit.,[13] m.p. 83—84 °C); $\delta_H(CDCl_3)$ 3.67 (8 H, s), 3.84 and 4.51 (8 H, AA′BB′ type, *J* 6.0, 4.2 Hz), and 6.58 (2 H, s); $\nu_{max.}(CHCl_3)$ 3 000, 2 870, and 1 650 cm^{-1} (quinone); *m/z* 298 (M^+, 44), 270 (23), 166 (100), and 138 (70); $\lambda_{max.}$(MeCN) 251 (ε 12 600) and 399 nm (1 390) (Found: C, 56.45; H, 5.95. Calc. for $C_{14}H_{18}O_7$: C, 56.37; H, 6.08%).

6,7,9,10,12,13,15,16,18,19-Decahydro-5,8,11,14,17,20-hexaoxabenzocyclo-octadecene-1,4-quinone (*2,3-Benzoquino[18]crown-6*) (**2**).—*Method A.* Fremy's salt (3.8 g, 14 mmol) was added to a stirred suspension of compound (**8**) (765 mg, 2.3 mmol) in benzene (30 ml) and 5% aqueous sodium acetate (280 ml). After the mixture had been stirred at room temperature for 15 min, it was extracted with benzene (3 × 70 ml). The combined organic layers were dried (Na_2SO_4) and concentrated under reduced pressure and the residue was chromatographed on a silica gel column with chloroform–methanol (30:1) as eluant to give the title compound (**2**) (467 mg, 58%) as orange needles, m.p. 67.5—68.5 °C (from ethyl acetate–hexane) (lit.,[13] m.p. 65—66 °C); $\delta_H(CDCl_3)$ 3.65 (4 H, s), 3.69 (8 H, s), 3.84, 4.50 (8 H, AA′BB′ type, *J* 5.4, 3.6 Hz), and 6.58 (2 H, s); $\nu_{max.}(CHCl_3)$ 3 005, 2 870, 1 655, and 1 585 cm^{-1}; *m/z* 342 (M^+, 10), 166 (100), and 138 (67); $\lambda_{max.}$(MeCN) 251 (ε 12 110) and 398 nm (1 330).

Method B.[31] A solution of $NaNO_2$ (0.84 g, 12 mmol) in water (10 ml) was added slowly to a stirred suspension of sulphanilic acid (2.1 g, 12 mmol) and concentrated HCl (2.1 ml) in water (20 ml) at 0 °C. After the mixture had been stirred for 1 h at 0 °C it was added over 1 h to a pre-cooled mixture of compound (**8**) (2.67 g, 8.1 mmol) and NaOH (1.67 g) in water (10 ml). After being set aside overnight at room temperature, the mixture was chilled in ice, acidified with HCl, and then tin(II) chloride (4.4 g) was added. The mixture was heated on a steam-bath at 60 °C for 30 min and then filtered. The filtrate was concentrated under reduced pressure and the residual oil was dissolved in a cold

mixture of 6M H_2SO_4 (5.7 ml) and ice–water (85 ml). A cold mixture of 10% aqueous sodium dichromate (33 ml) and 6M H_2SO_4 (8.8 ml) was added to this mixture. After 5 min the aqueous solution was extracted repeatedly with chloroform (5 × 70 ml) and the combined extracts were dried (Na_2SO_4) and concentrated under reduced pressure. The residue was chromatographed on a silica gel column with chloroform–methanol as eluant to give compound (**2**) (966 mg, 44%) as orange needles.

6,7,9,10,12,13,15,16-*Octahydro*-5,8,11,14,17-*pentaoxabenzocyclopentadecene*-1,4-*diol* (o,o′-*Dihydroxybenzo*[15]*crown*-5) (**9**).—A mixture of compound (**1**) (17 mg, 0.057 mmol) and 5% Pd–C (2 mg) in ethanol (3 ml) was stirred under an atmosphere of hydrogen for 1 h. During this time the red solution became colourless. The catalyst was filtered off and the filtrate evaporated to give the title compound (**9**) (16 mg, 93%) as colourless crystals, m.p. 130—131 °C (lit.,[13] m.p. 132 °C); $\delta_H(CDCl_3)$ 3.73 (8 H, s), 3.9—4.1 (4 H, m), 4.1—4.3 (4 H, m), and 6.58 (2 H, s); $\nu_{max.}$(KBr) 3 230, 2 855, and 1 490 cm^{-1}; *m/z* 300 (M^+, 22), 212 (19), 168 (100), and 153 (31).

6,7,9,10,12,13,15,16,18,19-*Decahydro*-5,8,11,14,17,20-*hexaoxabenzocyclo-octadecene*-1,4-*diol* (o,o′-*Dihydroxybenzo*[18]*crown*-6) (**10**).—Compound (**2**) (463 mg, 1.35 mmol) was hydrogenated under conditions similar to those above. Chromatography of the crude product on a silica gel column with chloroform–methanol gave pure title compound (**10**) (247 mg, 53%) as colourless needles, m.p. 111.5—112.5 °C (from dichloromethane–ether (lit.,[13] m.p, 110—111 °C); $\delta_H(CDCl_3)$ 3.65 (4 H, s), 3.71 (8 H, br s, 3.88, 4.31 (8 H, AA′BB′ type m), 5.80 (2 H, s 2 H, D_2O exchange, OH), and 6.59 (2 H, s); $\nu_{max.}(CHCl_3)$ 3 350 (OH), 2 975, 2 850, and 1 480 cm^{-1}; *m/z* 344 (M^+, 21), 168 (100), 166 (65), and 138 (42).

Cycloadditions of Compounds (**1**) *and* (**2**) *with Cyclopentadiene*.—Cyclopentadiene (0.034 ml, 0.43 mmol) was added dropwise to a stirred solution of (**1**) (128 mg, 0.43 mmol) in dichloromethane (5 ml) at room temperature. After 40 min the solvent was removed under reduced pressure and the residue was chromatographed on a silica gel column with chloroform–methanol (50:1) as eluant to give compound (**11**) (152 mg, 98%) as light brown crystals, m.p. 86—87.5 °C (from ether); $\delta_H(CDCl_3)$ 1.39 (1 H, dm, *J* 9 Hz), 1.56 (1 H, dm, *J* 9 Hz), 3.16—3.24 (2 H, m), 3.40—3.56 (2 H, m), 3.6—3.8 (12 H, m), 4.2—4.6 (4 H, m), and 6.08 (2 H, m); $\nu_{max.}(CHCl_3)$ 3 000, 2 860, and 1 650 cm^{-1}; *m/z* 364 (M^+, 8), 298 (28), 168 (39), 167 (27), 166 (39), and 66 (100) (Found: C, 62.6; H, 6.65. $C_{19}H_{24}O_7$ requires C, 62.63; H, 6.64%).

The reaction of compound (**2**) (79 mg, 0.23 mmol) and cyclopentadiene (0.019 mg, 0.23 mmol) under conditions similar to those described above gave compound (**12**) (100 mg, 94%) as light brown crystals, m.p. 46.5—47.5 °C (from dichloromethane–ether); $\delta_H(CDCl_3)$ 1.40 (1 H, dm, *J* 9 Hz), 1.55 (1 H, dm, *J* 9 Hz), 3.10—3.25 (2 H, m), 3.40—3.55 (2 H, m), 3.55—3.70 (12 H, m), 3.78 and 4.39 (8 H, AA′BB′ type, *J* 6.0, 3.6 Hz), and 6.07 (2 H, m); $\nu_{max.}(CHCl_3)$ 2 980, 2 850, 1 645, and 1 570 cm^{-1}; *m/z* 408 (M^+, 0.4), 166 (11), 138 (11), and 66 (100) (Found: C, 61.9; H, 6.9. $C_{21}H_{28}O_8$ requires C, 61.75; H, 6.9%).

Photochemical [2 + 2] *Cycloaddition of the Adducts* (**11**) *and* (**12**).—A solution of compound (**11**) (12.5 mg, 0.034 mmol) in chloroform (0.5 ml) was irradiated with a 400 W high-pressure mercury lamp through a Pyrex filter at room temperature under argon. The reaction was monitored by thin-layer chromatography (t.l.c.). After complete disappearance of (**11**) (3 h) the solution was evaporated under reduced pressure to give compound (**13**) (12.5 mg, 100%) as a pale yellow oil $\delta_H(CDCl_3)$ 1.9—2.1 (2 H, m), 2.55—2.75 (2 H, m), 2.80—3.05 (2 H, m), 3.1—3.45 (2 H, m), and 3.6—4.4 (16 H, m); $\nu_{max.}(CHCl_3)$ 2 990, 2 925, 2 860, 1 755, and 1 737 cm^{-1}; *m/z* 364 (M^+, 47), 233 (38), 232 (79), and 136 (100).

A solution of compound (**12**) (72 mg, 0.18 mmol) was irradiated under similar conditions to those described above give (**14**) (72 mg, 100%) as a pale yellow oil, $\delta_H(CDCl_3)$ 1.9—2.1 (2 H, m), 2.55—2.75 (2 H, m, 2.8—3.05 (2 H, m), 3.2—3.4 (2 H, m), and 3.6—4.3 (20 H, m); $\nu_{max.}(CHCl_3)$ 3 000, 2 940, 2 870, 1 760, and 1 745 cm^{-1}; *m/z* 408 (M^+, 8), 232 (24), 136 (24), 89 (25), and 45 (100).

Cycloaddition of Compounds (**1**) *and* (**2**) *with Thebaine*.—A mixture of compound (**1**) (24.7 mg, 0.083 mmol) and thebaine (25.8 mg, 0.083 mmol) in benzene (5 ml) was refluxed for 2 h. The solvent was removed under reduced pressure to give compound (**15**) (50.5 mg, 100%) as yellow oil, $\delta_H(CDCl_3)$ 2.44 (3 H, s), 3.62 (3 H, s), 3.79 (3 H, s), 4.69 (1 H, d, *J* 1 Hz), 5.37 (1 H, d, *J* Hz), 5.79 (1 H, dd, *J* 8, 1 Hz), 6.51 (1 H, d, *J* 8 Hz), and 6.64 (1 H, d, *J* 8 Hz); $\nu_{max.}(CHCl_3)$ 3 000, 2 945, 2 910, 2 805, and 1 655 cm^{-1}.

A similar reaction of (**2**) (110 mg, 0.32 mmol) and thebaine (100 mg, 0.32 mmol) gave compound (**16**) (210 mg, 100%) as yellow foam, $\delta_H(CDCl_3)$ 2.45 (3 H, s), 3.64 (3 H, s), 3.80 (3 H, s), 4.71 (1 H, d, *J* 1 Hz), 5.36 (1 H, d, *J* 8 Hz), 5.82 (1 H, dd, *J* 8, 1 Hz), 6.35 (1 H, d, *J* 8 Hz), and 6.65 (1 H, d, *J* 8 Hz); $\nu_{max.}(CHCl_3)$ 3 000, 2 920, 2 900, 2 860, 1 655, and 1 590 cm^{-1}; *m/z* 653 (M^+, 70), 435 (100), 259 (34), and 216 (38).

Isomerization of the Adducts (**15**) *and* (**16**).—A mixture of compound (**15**) (65 mg, 0.11 mmol) and silica gel (3 g) in chloroform (15 ml) was stirred vigorously at room temperature for 1 h. The silica gel was then filtered off and washed well with chloroform. The combined filtrate and washings were evaporated to dryness under the reduced pressure and the residual solid recrystallized from dichloromethane–ether to give (**17**) (53.5 mg, 82%) as colourless needles, m.p. 193.5—195 °C; $\delta_H(CDCl_3)$ 2.58 (3 H, s), 3.75 (8 H, s), 3.8—4.5 (4 H, m), 3.83 (3 H, s), 3.92 (3 H, s), 4.14—4.38 (4 H, m), 4.66 (1 H, d, *J* 1 Hz), 5.73 (1 H, d, *J* 8 Hz), 6.42 (1 H, dd, *J* 8, 1 Hz), 6.61 (1 H, d, *J* 8 Hz), 6.70 (1 H, d, *J* 8 Hz), and 9.03 (1 H, s, D_2O exchange, OH); $\nu_{max.}(CHCl_3)$ 3 320, 2 990, and 2 850 cm^{-1}; *m/z* 609 (M^+, 78), 391 (100), 259 (31), and 230 (42) (Found: C, 64.45; N, 2.25; H, 6.4. $C_{33}H_{39}NO_{10}\cdot\frac{1}{3}H_2O$ requires C, 64.39; N, 2.28; H, 6.49%).

A similar SiO_2 treatment of compound (**16**) (210 mg, 0.32 mmol) gave (**17**) (213.8 mg, 98%) as colourless needles, m.p. 169.5—170.0 °C (from dichloromethane–ether); $\delta_H(CHCl_3)$ 2.57 (3 H, s), 3.64 (4 H, s), 3.67 (8 H, s), 3.8—4.1 (4 H, m), 3.83 (3 H, s), 3.91 (3 H, s), 4.1—4.3 (4 H, m), 4.64 (1 H, d, *J* 1 Hz), 5.73 (1 H, d, *J* 8 Hz), 6.39 (1 H, dd, *J* 8, 1 Hz), 6.56 (1 H, d, *J* 8 Hz), 6.70 (1 H, d, *J* 8 Hz), 9.0 (1 H, s, D_2O exchange, OH), and 13.0 (1 H, br s, D_2O exchange, OH); $\nu_{max.}(CHCl_3)$ 3 325, 3 000, 2 950, 2 860, and 1 500 cm^{-1}; *m/z* 653 (M^+, 38), 435 (80), 89 (53), and 45 (100) (Found: C, 64.15; H, 6.65; N, 2.1. $C_{35}H_{43}NO_{11}$ requires C, 64.31; H, 6.63; N, 2.14%).

7,8,10,11,13,14,16,17-*Octahydro*-6,9,12,15,18-*pentaoxacyclopentadeca*[b]*naphthalene*-5,19-*quinone* (2,3-*Naphthoquino*[15]-*crown*-5) (**23**).—$BF_3\cdot Et_2O$ (0.04 ml, 0.34 mmol) was added to a stirred solution of (**1**) (100 mg, 0.34 mmol) in dry dichloromethane (5 ml) at 0 °C under argon. After 30 min buta-1,3-diene was bubbled through the mixture for 5 min which was then stirred at 0 °C for 2 h. After this, water (5 ml) was added and the organic layer was extracted with dichloromethane (3 × 15 ml). The extracts were dried (Na_2SO_4) and evaporated under reduced pressure to give compound (**19**) (118 mg, 100%) as orange oil, $\delta_H(CDCl_3)$ 2.15—2.50 (4 H, m), 3.0—3.3 (2 H, m), 3.6—3.7 (8 H, m), 3.81,

4.48 (8 H, AA'BB' type, *J* 6.0, 3.6 Hz), and 5.67 (2 H, t, *J* 1.5 Hz); $\nu_{max.}$($CHCl_3$) 3 000, 2 925, 2 870, 1 670, and 1 580 cm^{-1}.

A mixture of compound (**19**) (118 mg, 0.34 mmol) and silica gel (2 g) in chloroform (10 ml) was stirred vigorously in an open beaker for 1.5 h. The silica gel was then filtered off and the filtrate evaporated under reduced pressure to give compound (**21**) (117 mg, 100%) as orange needles, m.p. 68.5—70.0 °C (from dichloromethane–ether–hexane); δ_H($CDCl_3$) 3.02 (4 H, d, *J* 1.2 Hz), 3.6—3.7 (8 H, m), 3.8, 4.5 (8 H, AA'BB' type, *J* 5.4, 4.2 Hz), and 5.78 (2 H, t, *J* 1.2 Hz); $\nu_{max.}$($CHCl_3$) 2 925, 2 860, 1 650, and 1 605 cm^{-1}.

A solution of compound (**21**) (117 mg, 0.34 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (153 mg, 0.67 mmol) in dry benzene (35 ml) was refluxed for 3 h under argon. The resulting precipitate was filtered off and the filtrate concentrated under reduced pressure. The residue was chromatographed on a silica gel column with chloroform–methanol (50:1) as eluant to give the title compound (**23**) (104.1 mg, 89%) as orange needles, m.p. 104.5—105.5 °C (from dichloromethane–ether); δ_H($CDCl_3$) 3.56—3.75 (8 H, m), 3.88, 4.60 (8 H, AA'BB' type, *J* 6.0, 3.6 Hz), and 7.69, and 8.03 (4 H, AA'BB' type m); $\nu_{max.}$($CHCl_3$) 3 000, 1 860, 1 650, and 1 600 cm^{-1}; *m/z* 348 (M^+, 55), 216 (84), 132 (41), and 104 (100); $\lambda_{max.}$(MeCN) 330 (ε 2 690), and 391 nm (1 310) (Found: C, 62.0; H, 5.8. $C_{18}H_{20}O_7$ requires C, 62.06; H, 5.79%).

7,8,10,11,13,14,16,17,19,20-*Decahydro*-6,9,12,15,18,21-*hexaoxacyclo-octadeca*[b]*naphthalene*-5,22-*quinone* (2,3-*Naphthoquino*[18]*crown*-6) (**24**).—A similar BF_3•Et_2O-catalyzed reaction of compound (**2**) (500 mg, 1.46 mmol) and buta-1,3-diene (excess) afforded (**20**) (579 mg, 100%) as an orange oil, δ_H($CDCl_3$) 2.1—2.5 (4 H, m), 2.9—3.3 (2 H, m), 3.5—3.7 (12 H, m), 3.81 and 4.46 (8 H, AA'BB' type, *J* 6.0, 3.6 Hz), and 5.68 (2 H, t, *J* 1.2 Hz); $\nu_{max.}$($CHCl_3$) 2 900, 1 670, and 1 580 cm^{-1}.

Treatment of compound (**20**) (579 mg, 1.46 mmol) with silica gel as described above gave compound (**22**) (489 mg, 85%) as orange needles, m.p. 83—84 °C (from dichloromethane–ether); δ_H($CDCl_3$) 3.03 (4 H, d, *J* 1.2 Hz), 3.5—3.7 (12 H, m), 3.83 and 4.47 (8 Hz, AA'BB' type, *J* 5.4, 3.6 Hz), and 5.79 (2 H, t, *J* 1.2 Hz); $\nu_{max.}$($CHCl_3$) 2 870, 1 645, and 1 605 cm^{-1}.

The dehydrogenation of compound (**22**) (489 mg, 1.24 mmol) by DDQ as described above gave the title compound (**24**) (359 mg, 74%) as yellow needles, m.p. 71.5—72.5 °C (from ethyl acetate–hexane); δ_H($CDCl_3$) 3.6—3.75 (12 H, m), 3.87, 4.59 (8 H, AA'BB' type, *J* 6.0, 3.6 Hz), and 7.66 and 8.04 (4 H, AA'BB' type m); $\nu_{max.}$($CHCl_3$) 2 980, 2 850, 1 645, and 1 590 cm^{-1}; *m/z* 392 (M^+, 23), 216 (85), 104 (70), and 73 (100); $\lambda_{max.}$(MeCN) 329 (ε 2 940) and 383 nm (1 390) (Found: C, 61.25; H, 6.15. $C_{20}H_{24}O_8$ requires C, 61.22; H, 6.16%).

2,3-*Dihydro*-1,4-*benzodioxine*-5,6-*quinone* (**25**).—Sodium hydroxide (1.6 g, 40 mmol) in water (10 ml) was added to a stirred mixture of pyrogallol (2.52 g, 20 mmol) and dibromoethane (3.75 g, 20 mmol) in *N*,*N*-dimethylformamide (20 ml). The solution was refluxed for 9 h and then acidified with 10% HCl. The organic layer was extracted with benzene (3 × 50 ml), and the extract dried (Na_2SO_4), and evaporated under reduced pressure. The residue was chromatographed on a silica gel column with ethyl acetate–hexane (1:2) to give 2,3-dihydro-1,4-benzodioxin-5-ol (797 mg, 32%) as a colourless oil, δ_H($CDCl_3$) 4.24 (4 H, s), 5.55 (1 H, br s, D_2O exchange, OH), and 6.30—6.92 (3 H, m); $\nu_{max.}$(neat) 3 425 and 1 600 cm^{-1}.

This product (950 mg, 6.3 mmol) was oxidized in a similar way to that described for compounds (**1**) and (**2**) (method B) to give the title compound (**25**) (375 mg, 36%) as red needles, m.p. 158—159.5 °C (from ethyl acetate–hexane); δ_H($CDCl_3$) 4.35 (4 H, s) and 6.60 (2 H, s); $\nu_{max.}$($CHCl_3$) 3 020, 1 660, 1 640, and 1 590 cm^{-1}; *m/z* 166 (M^+, 100), 82 (31), and 54 (27).

2,3-*Dihydronaphtho*[2,3-b]-p-*dioxine*-5,10-*quinone* (**26**).—BF_3•Et_2O (0.26 ml, 2.1 mmol) was added to a solution of compound (**25**) (350 mg, 2.1 mmol) in dry dichloromethane (20 ml) at −30 °C under argon. The solution was stirred at −30 °C for 30 min and then buta-1,3-diene was bubbled through it for 5 min. After being stirred for 25 min, the mixture was diluted with water (10 ml) and extracted with dichloromethane. The dried (Na_2SO_4) extract was evaporated under reduced pressure to give 2,3,5a,6,9,9a,-hexahydronaphtho[2,3-*b*]-*p*-dioxine-5,10-quinone (433 mg, 93%) as colourless crystals, m.p. 142—152 °C (decomp.) (from dichloromethane–ether); δ_H($CDCl_3$) 2.2—2.55 (4 H, m), 3.0—3.35 (2 H, m), 4.32 (4 H, s), and 5.69 (2 H, t, *J* 1.2 Hz); $\nu_{max.}$($CHCl_3$) 3 005, 2 940, 2 880, 2 840, 1 670, and 1 605 cm^{-1}.

This product (405 mg, 1.8 mmol)was dehydrogenated in a similar manner to that described for compound (**21**) to give 2,3,6,9-tetrahydronaphtho[2,3-*b*]-*p*-dioxine-*p*-quinone (401 mg, 100%) as red needles, m.p. 150 °C (decomp.) (from dichloromethane–ether); δ_H($CDCl_3$) 3.06 (4 H, d, *J* 1.2 Hz), 4.33 (4 H, s), and 5.80 (2 H, t, *J* 1.2 Hz); $\nu_{max.}$($CHCl_3$) 1 650 and 1 610 cm^{-1}.

The above product (423 mg, 1.9 mmol) was treated with DDQ under similar conditions to those described for compounds (**23**) and (**24**) to give the title compound (**26**) (291 mg, 70%) as orange crystals, m.p. 278.5—279.5 °C (from dichloromethane–ether); δ_H($CDCl_3$) 4.42 (4 H, s), 7.73 and 8.08 (4 H, AA'BB' type m); $\nu_{max.}$(KBr) 1 655, 1 610, and 1 575 cm^{-1}; *m/z* 216 (M^+, 100), 132 (29), 104 (80), and 76 (13) (Found: C, 66.4; H, 3.8. $C_{12}H_8O_4$ requires C, 66.67; H, 3.73%).

Electrochemistry.—Cyclic voltammetry was performed with a Yanagimoto AC DC Cyclic Polalograph P-900. Glassy carbon was used as the working electrode and a Pt wire as the counterelectrode. E_0 Values are reported *vs.* a saturated aqueous calomel electrode (S.C.E.). Solutions were purged with nitrogen for 10 min prior to scanning and maintained under a nitrogen atmosphere during scanning. Unless otherwise noted, all voltammograms were obtained in DMF containing 0.1M Et_4NClO_4 as a supporting electrolyte at a scan rate of 100 mV s^{-1}. The redox potentials of quinones were essentially independent (±10 mV) of concentrations (1.1×10^{-3}—2.9×10^{-4}M) and scan rates (80—500 mV s^{-1}. Several measurements were taken at each run and the average value was used (Table 1).

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