

One-step Synthesis and Cation-dependent Redox Properties of New 'Quinonoid Macrocycles' Bearing Ion-binding Polyether Moieties

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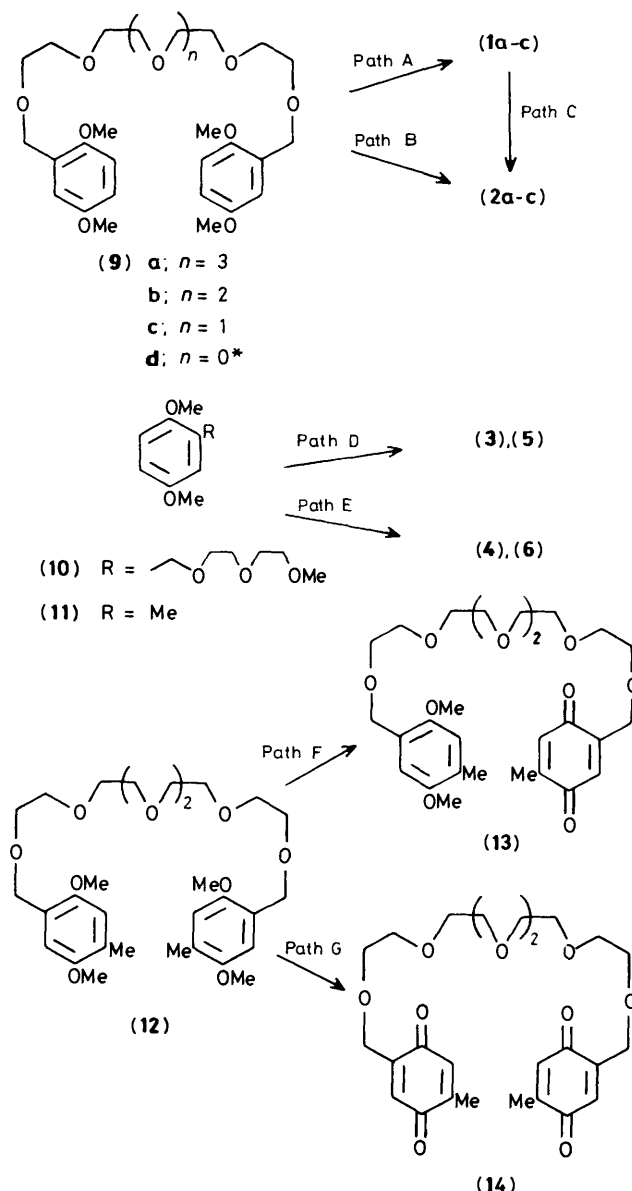
A one-step synthesis of novel macrocyclic quinonoid compounds bearing ion-binding polyether moieties, 'quinonoid macrocycles,' has been developed. By using an oxidative C–C coupling reaction as the ring-closure step, acyclic polyether precursors bearing hydroquinone dimethyl ether groups on both terminals were readily converted into new quinonoid macrocycles. The macrocycles obtained show characteristic cation-dependent redox properties very different from those of common quinonoid compounds. Since electrochemically reduced quinonoid macrocycles bind Li⁺ and other alkali metal cations more strongly than their neutral forms, their redox properties were effectively modified by adding these metal cations.

Macrocyclic crown ethers bearing electrochemically active groups have recently attracted considerable attention. When quinone,¹ nitrobenzene,² and other reducible groups³ are attached to the ion-binding crown ethers, a new type of host-guest complex is formed under electrochemically reduced conditions. In these complexes, the reduced radical species act as more effective ligating donors than their neutral forms and provide further co-ordination to the guest cations trapped in the crown ether rings. Since such cation-co-ordinating radicals can be stabilized, their redox properties are largely influenced by the nature of guest metal cation, and can be effectively coupled with host-guest complexes of crown ether moieties.

Here we report a one-step synthesis and the unique electrochemical properties of a new series of macrocyclic quinonoid compounds bearing polyether rings, 'quinonoid macrocycles.'⁴ By applying oxidative C–C coupling cyclization, we have successfully prepared a variety of quinonoid macrocycles without high dilution conditions, template techniques, and other complicated procedures. Cyclic voltammetric studies clearly indicate that the quinonoid macrocycles obtained bind Li⁺ and other guest metal cations much more strongly upon electrochemical reduction, and their electrochemistry was markedly influenced by the addition of these metal cations. Since similar cation-dependent electrochemical properties were not observed with common quinonoid compounds, molecular combination of an electrochemically active quinonoid function and a polyether ring provides a characteristic redox reaction system. It is well-known that naturally-occurring and synthetic quinonoid compounds play important roles in photochemistry, biochemistry, physiology, and electrochemistry,⁵ and the 'quinonoid macrocycles' described herein offer further possibilities in controlling various quinonoid functions *via* host-guest chemistry.

Results and Discussion

Synthesis of Quinonoid Macrocycles by an Oxidative C–C Coupling Cyclization.—Three different types of quinonoid compounds were prepared for this study (Figure 1): the macrocycles (1) and (2); the polyethers (3) and (4); and the simple quinonoid compounds (5) and (6). As a new synthetic approach to the macrocycles (1) and (2), we used an oxidative C–C coupling reaction to bring about ring-closure step of acyclic precursors (9) (see the Scheme). By treatment with a Ce(IV) salt, the terminal hydroquinone dimethyl ether groups of the precursors (9) were readily coupled intramolecularly to give the cyclic oxidized products (1) and (2). Previously



Scheme 1. C–C Coupling cyclization and related reactions *via* Ce(IV) oxidation

* Compound (9d) did not give cyclic products by Ce(IV) oxidation.

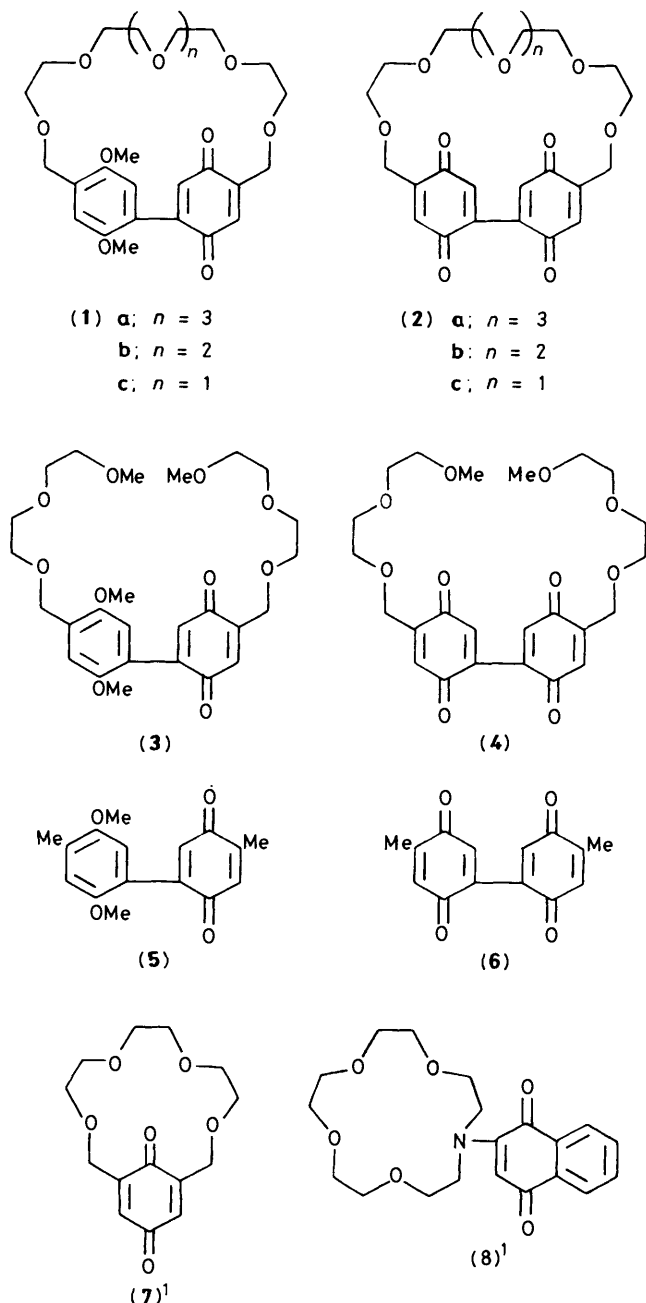


Figure 1. Structures of quinonoid macrocycles and related compounds

reported studies on macrocyclic polyether syntheses have focussed on C–O cyclization reactions,⁶ but we found that the C–C cyclization is a simple and useful synthetic method for functionalized macrocycles.⁷

Typically, to a stirred solution of the oligoethylene glycol precursor (**9a**) (3 mmol) in MeCN (20 ml), was added dropwise aqueous ammonium cerium nitrate (5.9 mmol in 20 ml water) at room temperature. Stirring was continued for 30 min after which time the reaction mixture was extracted with CHCl₃. The extract was dried (MgSO₄), evaporated, and chromatographed on silica gel eluting with EtOAc. The pure compound (**1a**) was obtained by crystallization from hexane–CCl₄ (24% yield). Compound (**2a**) was synthesized by two different reaction paths B and C (see the Scheme) and both paths gave same coupled

product. Reaction conditions and isolated yields for a variety of ring-containing compounds are summarized in Table 1.

Table 1 shows that our oxidative C–C coupling cyclization is an effective synthesis of reasonably large ring macrocycles. The quinonoid macrocycles (**1a–c**) and (**2a–c**), in which there are 23–29-membered ring systems, were easily prepared from acyclic precursors (**9a–c**) via Ce(IV) oxidation. On the other hand, the precursors (**9d**) and (**12**), having short polyether chains and substituents attached to the phenyl rings, gave none of the cyclized products; only unidentified materials and acyclic oxidized products (**13**) and (**14**) (paths F and G). Since ¹H n.m.r. spectra of the macrocycles (**1**) and (**2**) (see the Experimental section) indicated that intramolecular C–C coupling had occurred at the 4'-position of the phenyl rings of the precursor (**9**), and that polyether chain-length and the position of the substituents on the precursors are limited in this cyclization. High dilution conditions were also attempted, but total yields of the macrocycles did not depend on the concentrations of the precursor and oxidant. It seems probable, that rapid intramolecular radical coupling is occurring.

The simple hydroquinone dimethyl ether derivatives (**10**) and (**11**) were similarly oxidized to yield intermolecular C–C coupling products (**3**)–(**6**) under similar conditions (paths D and E),⁸ and same coupling patterns of the products were established both in the intra- and inter-molecular reactions. Although high dilution conditions, template reactions, and other synthetic strategies have been developed,⁶ the route described here offers new possibilities for the synthesis of various crown ethers, cyclophanes, and related macrocycles containing aromatic amines, alcohols, and other oxidative residues.

Cation-binding Properties of Neutral Quinonoid Macrocycles.—Macrocyclic crown ethers bearing quinone moieties have been prepared and characterized by several researchers,¹ some of which showed large visible spectral changes induced by cation-bindings.⁹ Since our quinonoid macrocycles (**1**) and (**2**) also showed absorption bands characteristic of quinonoid moieties in the visible region, the cation-binding properties of their neutral forms were investigated by spectroscopic methods.

For example, the addition of NaClO₄ and KClO₄ salts to a MeCN solution of quinonoid macrocycle (**1c**) enhanced the intensity of the characteristic absorption band centred at 430–440 nm,* whilst no appreciable change was detected in the presence of LiClO₄ (Figure 2). The absorption intensities were found to increase with increased amounts of NaClO₄ and KClO₄ as shown in Figure 3, but the deviations were too small to be quantitatively analysed. Similar spectral changes were observed in the other quinonoid macrocycles (**1a**), (**1b**), and (**2a–c**). Hence, the neutral quinonoid macrocycles seemed to form selective but loose complexes with Na⁺ and K⁺ ions. CPK molecular models of the macrocycles (**1**) and (**2**) strongly indicate that for elongated polyether rings it is difficult to form the spherical cavity needed to accommodate guest metal cations, as observed with usual crown ethers, and that only a few polyether oxygen atoms can simultaneously bind the guest metal cations to the quinonoid moieties.

Electrochemical Properties of Quinonoid Macrocycles.—Electrochemical properties of the quinonoid macrocycles (**1**) and (**2**) were studied by cyclic voltammetric techniques and compared with those of the common quinonoid compounds (**3**)–(**6**). Misumi, Vögtle, and other investigators have reported

* Quinonoid macrocycles (**1**) showed somewhat different spectral profiles under more concentrated conditions (>0.5 mM). A shoulder on the shorter wavelength side of the main absorption band was observed.

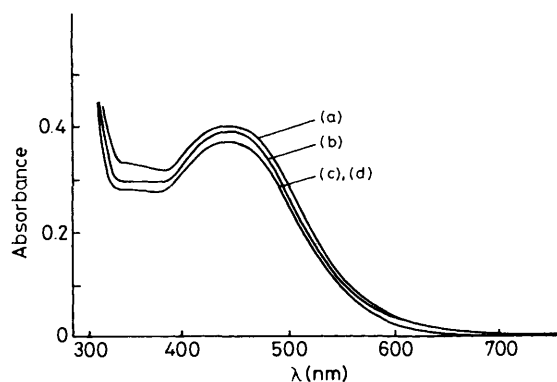


Figure 2. Spectral changes of quinonoid macrocycle (1c) in the presence of (a) KClO_4 , (b) NaClO_4 , (c) LiClO_4 , and (d) in the absence of guest salt; quinonoid macrocycle (1c) 0.3 mM; guest salt, 9.0 mM in MeCN

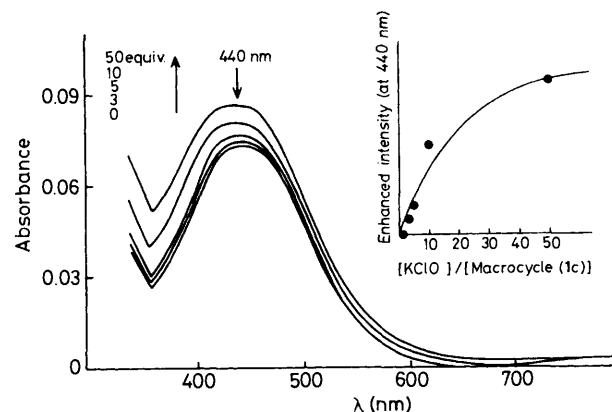


Figure 3. Spectral changes of quinonoid macrocycle (1c) in the presence of KClO_4 . Quinonoid macrocycle (1c): 0.08 mM; KClO_4 : 0, 0.24, 0.40, 0.80, and 4.0 mM in MeCN

Table 1. Oxidative C–C coupling cyclization and related reactions^a

Precursor	mmol	MeCN (ml)	Ce(IV) (mmol)	Water (ml)	Product	Isolated yield (%)	Path
(9a)	3.0	20	5.9	20	(1a)	24	A
(9b)	0.93	200	1.9	200	(1b)	10	A
	0.93	40	1.9	40		20	A
	2.0	40	4.1	40		25	A
	3.9	40	8.4	40		29	A
(9c)	0.86	40	1.8	40	(1c)	30	A
(9a)	1.0	40	6.8	20	(2a)	37	B
(9b)	2.0	40	2.0	40	(2b)	40	B
(9c)	0.86	40	6.2	40	(2c)	22	B
(1a)	0.22	40	1.3	40	(2a)	43	C
(1b)	0.28	40	1.8	40	(2b)	36	C
(1c)	0.55	40	3.6	40	(2c)	35	C
(10)	4.0	80	4.0	20	(3)	18	D
(10)	3.7	40	3.7	40	(3)	35	D
(11)	3.3	5	3.2	10	(5)	38	D
(10)	3.7	60	11	40	(4)	7	E
	4.6	10	14	20		14	E
(11)	3.3	5	9.7	10	(6)	75	E
(12)	1.0	40	2.2	40	(13)	23	F
(12)	1.2	60	8.2	40	(14)	42	G

^a Reaction conditions: see text. ^b Determined by means of ^1H n.m.r. spectroscopy in this case.

crown ether derivatives containing quinonoid groups of types (7) and (8).¹ Their electrochemical and e.s.r. spectroscopic studies have revealed that reduced benzo- and naphtho-quinone anion radicals strongly interact with some guest metal cations. The macrocycles (1) and (2) have unique electrochemically active quinonoid groups in the polyether ring systems, and since their reduced forms may provide more effective ligation sites for metal cations than the neutral forms, their redox properties were expected to be influenced by the addition of guest metal cations.

The macrocycle (1b) showed a typical cyclic voltammogram at potentials similar to those observed with the simple quinonoid compound (5) (Figure 4). Addition of alkali metal salts to a MeCN solution of the macrocycle (1b) caused characteristic anodic shifts in the reduction peak potentials, indicating that the electrochemically reduced macrocycle (1b)

bound alkali metal cations more strongly than its neutral form and was stabilized by metal co-ordinations. Among the metal cations examined, Li^+ induced larger anodic shifts (260 mV) than Na^+ (80 mV), and K^+ (30 mV) ions. The macrocycles (1a and c) showed similar cation-dependent redox reactions, and the shifts measured in their reduction potentials were found to be larger than those of the corresponding simple quinonoid compound (5) (Table 2). Thus, the introduction of macrocyclic polyether structures greatly enhances the cation-effects on the electrochemistry of quinonoid moieties.

The reduction peak potentials of the quinonoid macrocycles (1a–c) shifted 'continuously' as the guest cation concentrations were increased. Typical examples are shown in Figure 5. This indicates that the reduced quinonoid macrocycle (1c) forms a somewhat dynamic complex with the guest Li^+ ion. Plots of induced shifts vs mole ratio of Li^+ ion added to (1c) showed a

Table 2. Reduction potentials of quinonoid macrocycles (1) and related compounds (3) and (5)^a

Quinonoid compound	Original reduction potential (V)	MClO ₄ :Quinonoid (mol:mol)	Reduction potential in the presence of MClO ₄ (V)		
			M ⁺ = Li ⁺	Na ⁺	K ⁺
(1a)	-1.05	7	-0.85	-0.97	-1.01
		30	-0.80	-0.93	<i>b</i>
(1b)	-1.06	7	-0.84	-0.99	-1.03
		30	-0.80	-0.98	<i>b</i>
(1c)	-1.06	7	-0.86	-1.01	-1.04
		30	-0.83	-0.96	<i>b</i>
(3)	-1.08	7	-0.91	-1.02	-1.06
		30	-0.86	-0.98	<i>b</i>
(5)	-1.08	7	-0.99	-1.07	-1.08
		30	-0.95	-1.05	<i>b</i>

^a Detailed conditions: see Figure 4. ^b Not measured.

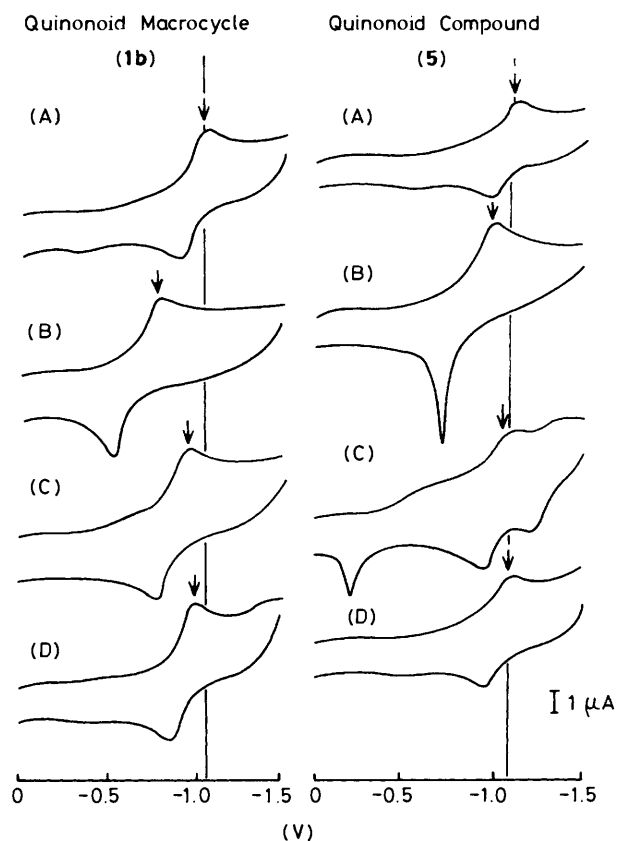


Figure 4. Cyclic voltammograms of quinonoid macrocycle (1b) and quinonoid compound (5) (A) in the absence of any salt; (B) in the presence of LiClO₄; (C) in the presence of NaClO₄; and (D) in the presence of KClO₄. Arrows indicate the first reduction peaks. 30 equiv. of MClO₄ was added to a 0.3mM solution of the quinonoid compound, except for KClO₄ (7 equiv.).* When 7 equiv. of LiClO₄ was added, the reduction potential of (1b) shifted anodically by 220 mV

* Since KClO₄ salt is sparingly soluble in MeCN, some complications arose in the K⁺ cation-binding systems.

clear break point at the mole ratio of 1:1 or 2:1, for which a stoichiometric complexation between macrocycle and guest cation is postulated. Although the macrocycles we describe form loose and non-stoichiometric complexes in their neutral forms, their cation-binding abilities are effectively enhanced upon electrochemical reduction.

Quinonoid compound (3) in which there are ion-binding

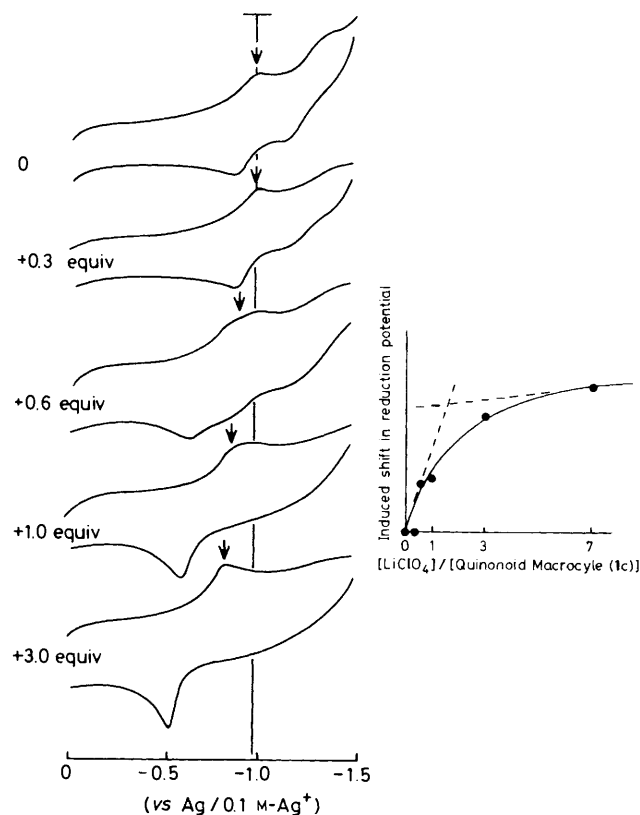


Figure 5. Li⁺ Cation-induced changes in cyclic voltammograms of the quinonoid macrocycle (1c)

linear polyether chains showed an interesting cation-dependent electrochemical reaction. The cation-induced shifts in the reduction potentials were found to be intermediate between those of the macrocycles (1) and those of compound (5) (220 mV for Li⁺; 100 mV for Na⁺; and 20 mV for K⁺). These observations clearly demonstrate that both acyclic and cyclic polyether structures can promote cation-binding and subsequent stabilization of reduced quinonoid moieties of this type.

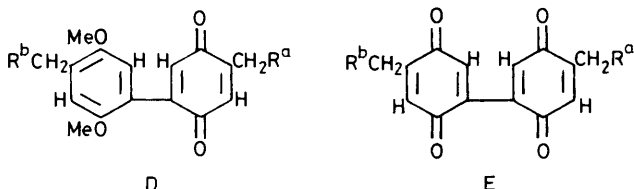
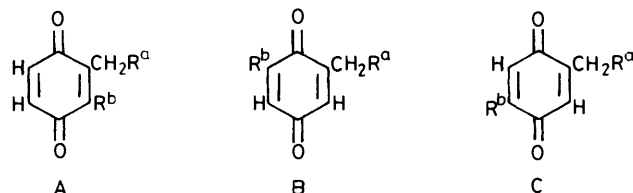
The macrocycles (2a–c) bearing reducible diquinone groups exhibited parallel electrochemical behaviour to that of the macrocycles (1a–c) (Table 3). Their reduction peak potentials were found to be largely shifted in the presence of Li⁺ ion, while Na⁺ and K⁺ ions induced small shifts. Table 3 also shows that the macrocycles (2a–c) produced cation-induced shifts larger than the corresponding quinonoid compound (6), but smaller

Table 3. Reduction potentials of quinonoid macrocycles (2) and related compounds (4) and (6)^a

Quinonoid compound	Original reduction potential (V)	MClO ₄ :Quinonoid (mol:mol)	Reduction potential in the presence of MClO ₄ (V)		
			M ⁺ = Li ⁺	Na ⁺	K ⁺
(2a)	-0.89	30	-0.76	-0.79	(-0.86) ^b
(2b)	-0.90	30	-0.75	-0.82	(-0.85) ^b
(2c)	-0.85	30	-0.76	-0.80	(-0.83) ^b
(4)	-0.90	30	-0.79	-0.83	(-0.89) ^b
(6)	-0.90	30	-0.78	-0.88	(-0.90) ^b

^a Detailed conditions: see in Figure 4. ^b In these cases, MClO₄:Quinonoid is 10 mol:mol.

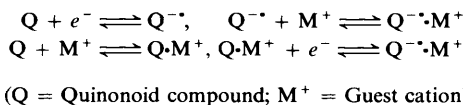
than the macrocycles (1a—c). When the electron density increases upon electrochemical reduction, it becomes less localized on the diquinone moieties of the compounds (2), (4), and (6) than on those of compounds (1), (3), and (5). Hence, ion-radical pairing interaction between the reduced quinonoid radical and the guest metal cation may be weaker in the former system than in the latter. In other words, the nature of electrochemically active group incorporated in the macrocyclic polyether ring determines the cation-dependence of its redox reaction.

**Figure 6.**

Electrochemical Cation-binding Enhancement of Quinonoid Macrocycles.—As mentioned above, the cation-binding abilities of the quinonoid macrocycles (1) and (2) were enhanced by electrochemical reduction, and their enhancements (K_1/K_2) were calculated from the observed shifts in reduction potentials (ΔE)^{*} [$\Delta E = (RT/nF) \ln(K_1/K_2)$], where K_1 and K_2 are stability constants for the guest metal cation of the reduced and neutral ligands. Table 4 summarizes the calculated electrochemical cation-binding enhancements for all the quinonoid compounds.

The quinonoid macrocycles (1) and (2) showed larger cation-induced shifts in their reduction potentials and higher electrochemically enhanced cation-binding abilities than the corresponding simple quinonoid compounds (3)—(6). In

^{*} $\Delta E = E_c - E_f$, where E_c and E_f represent the observed potentials in the presence and absence of guest cations. In this calculation, four cyclic processes were assumed.

**Table 4.** Electrochemical cation-binding enhancement of quinonoid macrocycles and related compounds

Quinonoid compd	Cation-binding enhancement (K_1/K_2) ^a		
	Cation: Li ⁺	Na ⁺	K ⁺
(1a)	17 000	110	4.7
(1b)	25 000	23	3.2
(1c)	7 800	49	2.2
(3)	5 300	49	2.2
(5)	160	3.2	1.0
(2a)	160	49	3.2
(2b)	340	23	7.0
(2c)	33	7.0	2.2
(4)	73	15	1.5
(6)	110	2.2	1.0

^a Calculated from the reduction peak potentials shown in Tables 2 and 3 (see text).

particular, electrochemical enhancements for the macrocycle (1b) were estimated as factors of 25 000 for Li⁺, 23 for Na⁺, and 3 for K⁺, while those of simple quinonoid compound (5) were only 160-fold for Li⁺, 3 for Na⁺, and 1 for K⁺ ions. These calculated cation-binding enhancements decreased from Li⁺ to K⁺ in all cases. This is also the order of decreasing charge-to-size ratio of alkali metal cations, and suggests that ion-pairing between the guest metal cation and reduced quinonoid group is essential, as well as the ion-binding of the polyether ring.

Although we have confirmed that the polyether structures of quinonoid macrocycles (1) and (2) weakly interacted with these metal cations, it is possible that they could wrap around the guest metal cations fixed with electrochemically reduced quinonoid anion radicals. Therefore, further combinations of ion-binding groups and electrochemically active groups could lead to the design of new host compounds showing redox-coupled functionalities.

Experimental

Synthesis of Quinonoid Compounds.—The quinonoid compounds (1)—(6), (13), and (14) were prepared by oxidation of the corresponding precursors (9)—(12) (10), (11), and (12) as described in text. The precursors were obtained from 2,5-dimethoxybenzyl alcohol derivatives and corresponding toluene-*p*-sulphonates in the presence of NaH as previously reported¹⁰ and showed satisfactory mass, ¹H n.m.r. and i.r. spectral data. Physical properties, spectral profiles, and elemental analysis data of the newly obtained quinonoid macrocycles and related compounds are given below.

Macrocycle (1a): red crystals, m.p. 119—121 °C (Found: C, 61.1; H, 7.0. C₂₈H₃₈O₁₁ requires C, 60.85; H, 6.9%); δ_H (CDCl₃; 400 MHz), 3.73—3.81 (24 H, m, CH₂CH₂O), 3.75 (3 H, s, OMe),

3.78 (3 H, s, OMe), 4.45 (2 H, d, J 2.1 Hz, quinone-CH₂), 4.61 (2 H, s, PhCH₂), 6.67 (1 H, s, ring-H[†]), 6.78 (1 H, s, ring-H), 6.93 (1 H, t, J 2.1 Hz, quinone-H), and 7.12 (1 H, s, ring-H); ν_{\max} . (KBr) 1 660 cm⁻¹; m/z 550 (M^+).

Macrocycle (1b): red crystals, m.p. 124–126 °C (Found: C, 61.5; H, 6.8. C₂₆H₃₄O₁₀ requires C, 61.65; H, 6.8%); δ_{H} (CDCl₃; 400 MHz) 3.36–3.73 (20 H, m, CH₂CH₂O), 3.77 (3 H, s, OMe), 3.80 (3 H, s, OMe), 4.47 (2 H, d, J 1.5 Hz, quinone-CH₂), 4.63 (2 H, s, PhCH₂), 6.69 (1 H, s, ring-H), 6.77 (1 H, s, ring-H), 7.18 (1 H, s, ring-H), and 7.22 (1 H, t, J 1.6 Hz, quinone-H); ν_{\max} . (KBr) 1 660 cm⁻¹; m/z 506 (M^+).

Macrocycle (1c): red crystals, m.p. 116 °C (Found: C, 62.0; H, 6.65. C₂₄H₃₀O₉ requires C, 62.0; H, 6.5%); δ_{H} (CDCl₃; 400 MHz) 2.94–3.70 (16 H, m, CH₂CH₂O), 3.80 (3 H, s, OMe), 3.83 (3 H, s, OMe), 4.42 (2 H, br s, quinone-CH₂), 4.62 (2 H, s, PhCH₂), 6.84 (1 H, s, ring-H), 6.89 (1 H, t, J 1.2 Hz, quinone-H), 6.96 (1 H, s, ring-H), and 7.10 (1 H, s, ring-H); ν_{\max} . (KBr) 1 660 cm⁻¹; m/z 462 (M^+).

Macrocycle (2a): yellow crystals, m.p. 115–116 °C (Found: C, 59.9; H, 6.2. C₂₆H₃₂O₁₁ requires C, 60.0; H, 6.2%); δ_{H} (CDCl₃; 400 MHz) 3.62–3.73 (24 H, m, CH₂CH₂O), 4.46 (4 H, d, J 1.8 Hz, quinone-CH₂), 6.74 (2 H, s, quinone-H), and 7.24 (2 H, t, J 2.1 Hz, quinone-H); ν_{\max} . (KBr) 1 660 cm⁻¹; m/z 520 (M^+).

Macrocycle (2b): yellow crystals, m.p. 128–132 °C (Found: C, 60.55; H, 5.9. C₂₄H₂₈O₁₀ requires C, 60.5; H, 5.9%); δ_{H} (CDCl₃; 400 MHz) 3.57–3.72 (20 H, m, CH₂CH₂O), 4.45 (4 H, d, J 2.1 Hz, quinone-CH₂), 6.73 (2 H, s, quinone-H), and 7.44 (2 H, t, J 2.0 Hz, ring-H); ν_{\max} . (KBr) 1 660 cm⁻¹; m/z 476 (M^+).

Macrocycle (2c): yellow crystals, m.p. 126–127 °C (Found: C, 60.8; H, 5.8. C₂₂H₂₄O₉ requires C, 60.8; H, 5.6%); δ_{H} (CDCl₃; 400 MHz) 3.31–3.69 (16 H, m, CH₂CH₂O), 4.41 (4 H, br s, quinone-CH₂), 6.93 (2 H, t, J 1.2 Hz, quinone-H), and 6.99 (2 H, s, quinone-H); ν_{\max} . (KBr) 1 660 cm⁻¹; m/z 432 (M^+).

Compound (3): red oil (Found: C, 61.7; H, 7.3. C₂₆H₃₆O₁₀ requires C, 61.4; H, 7.1%); δ_{H} (CDCl₃; 400 MHz) 3.38 (3 H, s, OMe), 3.39 (3 H, s, OMe), 3.54–3.82 (22 H, m, OMe), CH₂CH₂O), 4.47 (2 H, d, J 2.1 Hz, quinone-CH₂), 4.64 (2 H, s, PhCH₂), 6.66 (1 H, s, ring-H), 6.74 (1 H, s, ring-H), 7.20 (1 H, t, J 2.0 Hz, quinone-H), and 7.26 (1 H, s, ring-H); ν_{\max} . (neat) 1 660 cm⁻¹; m/z 508 (M^+).

Compound (4): yellow crystals, m.p. 100–102 °C (Found: C, 60.1; H, 6.25. C₂₄H₃₀O₁₀ requires C, 60.2; H, 6.3%); δ_{H} (CDCl₃; 400 MHz) 3.39 (6 H, s, OMe), 3.55–3.75 (16 H, m, CH₂CH₂O), 4.45 (4 H, d, J 2.1 Hz, quinone-CH₂), 6.79 (2 H, s, quinone-H), and 6.97 (2 H, t, J 2.1 Hz, quinone-H); ν_{\max} . (KBr) 1 640 cm⁻¹; m/z 478 (M^+).

Compound (5): dark violet crystals, m.p. 160 °C (lit.,¹¹ m.p. 153 °C) (Found: C, 70.45; H, 5.96. C₁₆H₁₆O₄ requires C, 70.57; H, 5.92%); δ_{H} (CDCl₃; 400 MHz) 2.09 (3 H, d, J 1.5 Hz, quinone-Me), 2.25 (3 H, s, PhCH₂), 3.72 (3 H, s, OMe), 3.78 (3 H, s, OMe), 6.63 (1 H, s, ring-H), 6.68 (1 H, q, J 1.5 Hz, quinone-H), 6.78 (1 H, s, ring-H), and 6.80 (1 H, s, ring-H); ν_{\max} . (KBr) 1 650 cm⁻¹; m/z 272 (M^+).

Compound (6): yellow crystals, m.p. 181–183 °C (lit.,¹² m.p. 178.5–179.5 °C) (Found: C, 69.16; H, 4.09. C₁₄H₁₀O₄ requires C, 69.42; H, 4.16%); δ_{H} (CDCl₃; 400 MHz) 2.10 (6 H, d, J 1.5 Hz, quinone-Me), 6.70 (2 H, q, J 1.5 Hz, quinone-H), and 6.81 (2 H, s, quinone-H); ν_{\max} . (KBr) 1 640 cm⁻¹; m/z 242 (M^+).

Ce(IV) oxidation of dimethoxybenzene derivatives may give several positional isomers, but we assigned the coupling patterns of the isolated products (1)–(6) on the basis of 400 MHz ¹H n.m.r. spectral data, as the two ring protons of quinone compounds of type A and B are known to show pseudo-ortho and pseudo-meta couplings (Figure 6), generally of 9–10 Hz

and 2–3 Hz.¹³ Since we observed no-coupling of two ring protons for the compounds (1)–(6), they were deduced to have the quinone-structure type C. Similarly, we did not observe ortho- and meta-couplings of the two aromatic protons of the compounds (1), (3), and (5). Therefore, the present C–C coupling reaction yielded the quinonoid compounds of type D and E. Such coupling patterns have also been reported in the AgO oxidation of dimethoxybenzenes.¹⁴

Compound (13): orange oil (Found: C, 62.8; H, 7.7. C₂₈H₄₀O₁₀ requires C, 62.7; H, 7.5%); δ_{H} (CDCl₃; 100 MHz) 2.02 (3 H, d, J 2 Hz, quinone-Me), 2.20 (3 H, s, Me), 3.62–3.74 (20 H, m, CH₂CH₂O), 3.77 (3 H, s, OMe), 3.81 (3 H, s, OMe), 4.39 (2 H, d, J 2 Hz, quinone-CH₂), 4.57 (2 H, s, PhCH₂), 6.56 (1 H, q, J 2 Hz, quinone-H), 6.69 (1 H, s, ArH), 6.86 (1 H, t, J 2 Hz, quinone-H), and 6.94 (1 H, s, ArH); ν_{\max} . (neat) 1 650 cm⁻¹; m/z 536 (M^+).

Compound (14): yellow crystals, m.p. 67–69 °C (Found: C, 61.4; H, 6.6. C₂₆H₃₄O₁₀ requires C, 61.65; H, 6.8%); δ_{H} (CDCl₃; 100 MHz) 2.02 (6 H, d, J 2 Hz, quinone-Me), 3.62–3.70 (20 H, m, CH₂CH₂O), 4.38 (4 H, d, J 2 Hz, quinone-CH₂), 6.55 (2 H, q, J 2 Hz, quinone-H), and 6.84 (2 H, t, J 2 Hz, quinone-H); ν_{\max} . (KBr) 1 640 cm⁻¹; m/z 506 (M^+).

Other reagents employed were commercially available and used after the usual purification procedures.

Cyclic Voltammetry Experiments.—Electrochemical measurements were conducted under N₂ in 0.1M Et₄NClO₄ in MeCN. The MeCN was distilled over CaH₂ under a dry N₂ atmosphere and allowed to stand over 4A molecular sieves prior to use. Alkali metal perchlorates were dried *in vacuo* over 130 °C for 5 h. A standard H-cell, glassy carbon working electrode, and a platinum wire counter-electrode were used. All the cyclic voltammograms were recorded at room temperature under single sweep conditions (scan rate: 100 mV s⁻¹), and peak potentials were obtained *vs* Ag–1M-AgClO₄ in MeCN unless otherwise stated. It was necessary to repeatedly polish the electrode during the experiments, because the quinonoid compounds were frequently adsorbed onto the electrode surface.

References

- 1 K. Sugihara, H. Kamiya, M. Yamaguchi, T. Kaneda, and S. Misumi, *Tetrahedron Lett.*, 1981, **22**, 1619; R. E. Wolf and S. R. Cooper, *J. Am. Chem. Soc.*, 1984, **106**, 4646; H. Bock, B. Hierholzer, F. Vögtle, and G. Hollmann, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 57.
- 2 D. A. Gustowski, L. Echegoyen, D. M. Goli, A. Kaifer, R. A. Schultz, and G. W. Gokel, *J. Am. Chem. Soc.*, 1984, **106**, 1633.
- 3 S. Shinkai, Y. Ishikawa, H. Shinkai, T. Tsuno, H. Makishima, K. Ueda, and O. Manabe, *J. Am. Chem. Soc.*, 1984, **106**, 1801.
- 4 Preliminary communication: K. Maruyama, H. Sohmiya, and H. Tsukube, *Tetrahedron Lett.*, 1985, **26**, 3583.
- 5 'Chemistry of Quinonoid Compounds,' ed. S. Patai, Wiley, New York, 1974.
- 6 G. W. Gokel and S. H. Korzeniowski, 'Macrocyclic Polyether Syntheses,' Springer-Verlag, Berlin, 1982.
- 7 Other synthetic examples of related macrocycles *via* oxidations: L. Rossa and F. Vögtle, 'Topics in Current Chemistry,' ed. F. Vögtle, Springer-Verlag, Berlin, 1983, vol. 113, p. 72.
- 8 P. Jacob, III, P. S. Callery, A. T. Shulgin, and N. Castagonoli, Jr., *J. Org. Chem.*, 1976, **41**, 3627.
- 9 H. Lohr and F. Vögtle, *Acc. Chem. Res.*, 1985, **18**, 65.
- 10 J. Rebeck, Jr., and R. V. Wattlely, *J. Am. Chem. Soc.*, 1980, **102**, 4853.
- 11 T. Posternak, W. Alcalay, R. Luzzati, and A. Tardent, *Helv. Chim. Acta.*, 1948, **31**, 525.
- 12 Y. H. C. Giza, K. A. Kun, and H. G. Cassidy, *J. Org. Chem.*, 1962, **27**, 679.
- 13 Ref. 5, p. 165.
- 14 D. V. Rao, H. Ulrich, and A. A. R. Sayigh, *J. Org. Chem.*, 1975, **40**, 2548.

† Unfortunately, it proved difficult to assign the signals of quinone and aromatic hydrogen atoms.