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Synthesis, Structures, and Complexing Abilities of Corands Based on 2-Methoxyresorcinol

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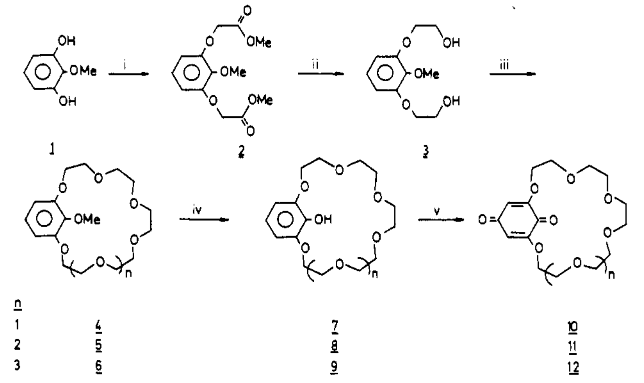
A series of 13 new crown ethers (corands) that bear one or two inward-facing methoxyl groups are synthesized from 2-methoxyresorcinol, and crystal structures of two anisole corands and one bisanisole corand are determined. Demethylation of anisole corands with lithium aluminum hydride affords the corresponding corand phenols, which produce corand quinones upon oxidation by Fremy's salt. Complexing abilities of the new corand anisoles, phenols, and quinones for sodium, potassium, and rubidium cations in methanol are assessed by potentiometry, and the electrochemical behavior of the corand quinones and a corand bisquinone is also investigated.

Crown ethers (corands[1]) based on the 1,3-xylyl subunit with various substituents at the intraannular 2-position have been the subject of several recent investigations.[2-9] Cram and co-workers studied a series of corands that possessed one or two intraannular methoxyl groups.[2,3] Corands with inward-facing phenolic units have been investigated extensively by Ferguson and McKervey and co-workers.[4] Other 1,3-xylyl-based corands with intraannular carboxyl,[5,6] methoxycarbonyl,[3,5,6] hydroxyl,[7] nitrile,[6] and sulfino[9] groups have been reported. Corand quinones[8] have also been synthesized from the corand phenols. A common structural feature of these macrocyclic compounds is attachment of polyether chain oxygens to benzylic methylene groups at the 1- and 3-positions of the aromatic ring.

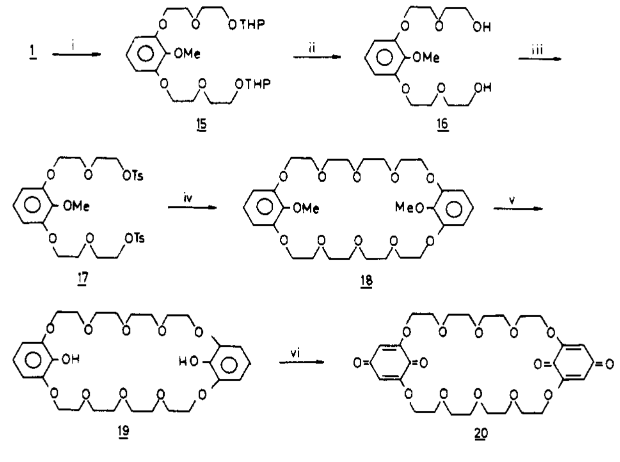
In contrast to the 1,3-xylyl-based corands, structurally related compounds in which the polyether chain oxygens are bonded directly to the aromatic subunit have received much less attention.[10] We now report the synthesis of 13 new corand anisoles, phenols, and quinones derived from 2-methoxyresorcinol. The influence of structural variation within the corands upon complexation of sodium, potassium, and rubidium cations in methanol is probed by potentiometry. In addition, crystal structures of two new anisole corands and one bisanisole corand are provided, and the electrochemistry of the novel corand quinones and a corand bisquinone is investigated.

Scheme I[a]



[a] (i) $BrCH_2CO_2Me$, K_2CO_3 in acetone; (ii) LAH in THF; (iii) $TsOCH_2(CH_2OCH_2)_nCH_2OTs$, t-BuOK in THF; (iv) LAH in THF; (v) $K_2S_2O_6NO$ in benzene.

Scheme II[a]



[a] (i) $ClCH_2CH_2OCH_2CH_2OTHP$, NaOH in 1-butanol; (ii) HCl in CH_2Cl_2-MeOH; (iii) TsCl in pyridine; (iv) 16, t-BuOK in THF; (v) LAH in THF; (vi) $K_2S_2O_6NO$ in aqueous acetone.

Results and Discussion

Synthesis. Anisole corands 4–6 were prepared by the reaction sequence outlined in Scheme I. Reaction of 2-methoxyresorcinol (1) with methyl bromoacetate and

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(1) For contemporary nomenclature of macrocyclic polyethers, see: Cram, D. J. *Angew. Chem.* **1986**, *25*, 1039–1057.

(2) Koenig, K. E.; Lein, G. H.; Stuckler, P.; Kaneda, T.; Cram, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 3553–3556.

(3) Koenig, K. E.; Helgeson, R. C.; Cram, D. J. *J. Am. Chem. Soc.* **1976**, *98*, 4018–4020.

(4) Browne, C. M.; Ferguson, G.; McKervey, M. A.; Mulholland, D. L.; O'Connor, T.; Parvez, M. *J. Am. Chem. Soc.* **1985**, *107*, 2703–2713.

(5) Bell, T. W.; Cheng, P. G.; Newcomb, M.; Cram, D. J. *J. Am. Chem. Soc.* **1982**, *104*, 5185–5188.

(6) Newcomb, M.; Moore, S. S.; Cram, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 6405–6410.

(7) Van der Leij, M.; Oosterink, H. J.; Hall, R. H.; Reinhoudt, D. N. *Tetrahedron* **1981**, *37*, 3661–3666.

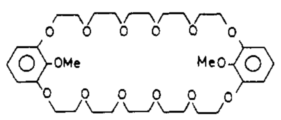
(8) Sugihara, K.; Kamiyama, H.; Yamaguchi, M.; Kaneda, T.; Misumi, S. *Tetrahedron Lett.* **1981**, *22*, 1619–1622.

(9) Skowronska-Ptasinka, M.; Telleman, P.; Aarts, V. M. L. J.; Grootenhuis, P. D. J.; van Eerden, J.; Harkema, S.; Reinhoudt, D. N. *Tetrahedron Lett.* **1987**, *28*, 1937–1940.

(10) Richards, T. P.; Hamilton, A. D. *J. Chem. Soc., Chem. Commun.* **1985**, 1198–1199.

0022-3263/89/1954-0861$01.50/0

anhydrous K_2CO_3 in acetone afforded the corresponding diester **2** in 95% yield. Reduction of **2** with lithium aluminum hydride (LAH) in THF provided a 73% yield of diol **3**. Treatment of **3** with t-BuOK followed by cyclization with the appropriate ditosylate produced anisole corands **4–6** in yields of 6, 35, and 26%, respectively. In the synthesis of anisole corand **4**, a 38-membered dimer **13** was also isolated in 11% yield from the reaction mixture.



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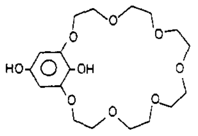
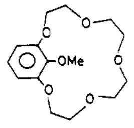


14

Demethylation of anisole corands **4–6** was accomplished by refluxing with LAH in THF,[11] which gave corand phenols **7–9** in yields of 82, 81, and 86%, respectively. Oxidation with Fremy's salt[12] transformed these corand phenols into the corresponding corand quinones **10–12** in yields of 84, 92, and 96%, respectively. Reduction of corand quinone **11** with sodium dithionite gave a 92% yield of the corand hydroquinone **14**.

Bisanisole, bisphenol, and bisquinone corands **18–20** were synthesized according to Scheme II. Reaction of 2-methoxyresorcinol with NaOH and the tetrahydropyranyl ether of diethylene glycol monochlorohydrin[13] produced **15** in 93% yield. Acid-catalyzed deprotection of **15** afforded a 90% yield of diol **16**, which was transformed into ditosylate **17** in 96% yield. Cyclization of **16** and **17** in the presence of t-BuOK in THF gave a 24% yield of the 32-membered bisanisole corand **18**. Reaction of **18** with LAH in THF afforded a 61% yield of corand bisphenol **19**. This result was somewhat surprising since other workers have reported[14] exclusive and quantitative monodemethylation of a tetramethoxy-substituted spherand using LAH in benzene. Corand bisphenol **19** formed a solid monohydrate, which released water upon heating under vacuum to become an extremely hygroscopic liquid. When exposed to moist air, anhydrous **19** was transformed into the hydrate. Oxidation of **19** with Fremy's salt in aqueous acetone produced corand bisquinone **20** in 80% yield.

Attempted in situ monotosylation and intramolecular ring closure[15] of diol **16** to produce anisole corand **21** gave a complex mixture from which the desired product could not be isolated. Examination of CPK molecular models reveals that serious steric interactions in **21** can be reduced only when the plane of the anisole group is twisted away from that of the polyether oxygens. Since ditosylate **17** and the bisanisole corand **18** were identified in the reaction mixture, it appears that steric factors preclude formation of anisole corand **21**.



21

Table I. Stability Constants[a] for Complexation of NaCl, KCl, and RbCl by Corands 4–13 and 18 in Methanol at 25 °C

compound		log K_s		
number	corand	Na^+	K^+	Rb^+
4	anisole	2.35	3.0	2.5
5	anisole	2.5	3.6	3.2
6	anisole	2.7	3.5	3.2
7	phenol	2.8	3.0	2.8
8	phenol	3.5	4.5	3.6
9	phenol	2.4	3.5	3.3
10	quinone	NB[b]	NB	NB
11	quinone	2.7	3.4	3.0
12	quinone	2.15	3.15	3.1
13	bisanisole	2.7	3.5	3.1
18	bisanisole	1.9	2.7	2.8
22[c]		2.5	3.6	
23[c]		2.4	3.2	
24[c]		1.8	2.7	

[a] Determined by potentiometry using ion-selective electrodes. [b] No binding was detected. [c] Reference 8.

Corand phenols based on the 1,3-xylyl subunit have been shown to undergo smooth para nitration when treated with aqueous $NaNO_2$–HNO_3.[4] When this mild nitration reaction was attempted with corand phenol **8**, only tars and a small amount of unidentified, red byproduct were formed. Reaction of *p*-nitrobenzenediazonium ion with corand phenol **8** resulted in a complicated mixture of products and tars. This result contrasts with the facile synthesis of chromogenic corand azophenols from 1,3-xylyl-based corand phenols.[16]

Structures of all new compounds were verified by nuclear magnetic resonance (^1H NMR and ^{13}C NMR) and infrared (IR) spectroscopy, mass spectrometry (MS), and elemental analysis.

Spectral Properties. The ^1H NMR spectral absorptions for the methylene protons in the polyether units of anisole corands **4** and **5** exhibit interesting differences from those for **6**, **13**, and **18**. A 1.1 ppm wide multiplet for the 19-membered cycle **4** decreased to 1.0 ppm in the 22-membered ring compound **5** and was only 0.8 ppm wide in the larger ring corands **6**, **13**, and **18**. Examination of CPK molecular models suggests that steric factors should retard ring inversion of **4** and **5** compared with that for **6**, **13**, and **18**.

The ^1H NMR spectra of diester **2**, diol **3**, anisole corands **4–6**, and bisanisole corand **13** displayed a characteristic seven-line multiplet for the aromatic protons at 6.45–7.15 ppm. Transformation of the anisole corands into the corresponding corand phenols collapsed this multiplet into a sharp singlet for which the chemical shift varied slightly with ring size (6.75, 6.70, 6.67, and 6.61 ppm for **7**, **8**, **9**, and **19**, respectively). Similar ring size dependence was noted for the vinylic proton singlets in the ^1H NMR spectra of corand quinones **10–12** and bisquinone **20** (6.00, 5.93, 5.88, and 5.86 ppm, respectively).

IR spectra of the corand quinones **10–12** and bisquinone **20** exhibited two carbonyl group absorptions at 1695 and 1645 cm^{-1}. By comparison with the IR spectra of *p*-benzoquinone and 2,6-dimethoxy-*p*-benzoquinone, the former absorption is assigned to the intraannular carbonyl group and the latter band to the outward-facing carbonyl function.

Alkali Metal Cation Binding and pK_a Determinations. Stability constants (K_s) for association of corands **4–13** and **18** with sodium, potassium, and rubidium ions in MeOH at 25 °C were measured potentiometrically with

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(11) Czech, A.; Czech, B. P.; Desai, D. H.; Hallman, J. L.; Phillips, J. B.; Bartsch, R. A. *J. Heterocycl. Chem.* **1986**, *23*, 1355–1358.

(12) Zimmer, H.; Lankin, D. C.; Horgan, S. W. *Chem. Rev.* **1971**, *71*, 229–246.

(13) Kyba, E. P.; Helgeson, R. C.; Madan, K.; Gokel, G. W.; Tarnowski, T. L.; Moore, S. S.; Cram, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 2564–2571.

(14) Kaneda, T.; Umeda, S.; Tanigawa, H.; Misumi, S. *J. Am. Chem. Soc.* **1985**, *107*, 4802–4803.

(15) Kuo, P. L.; Miki, M.; Okahara, M. *J. Chem. Soc., Chem. Commun.* **1978**, 504–505.

(16) Kitazawa, S.; Kimura, K.; Shono, T. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3253–3257.

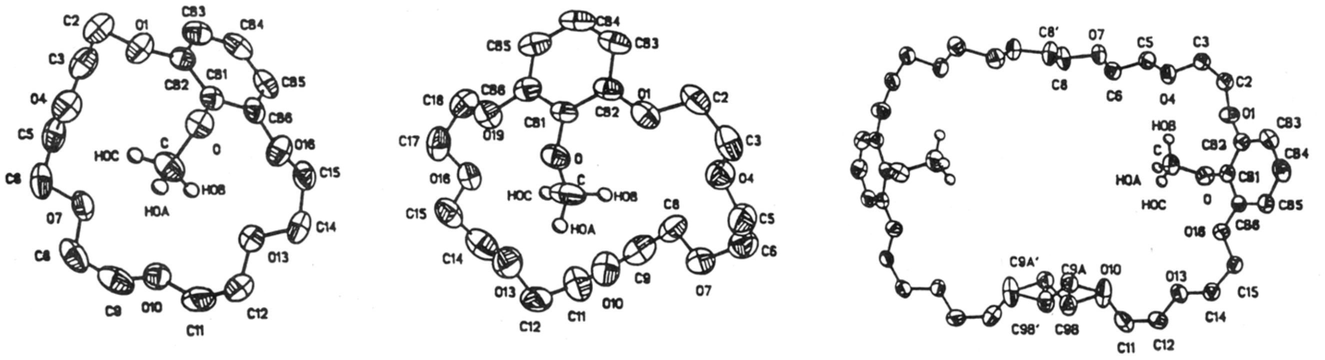


Figure 1. Computer drawings of anisole corands 4 and 5 and bisanisole corand 13 with the numbering systems identified. Hydrogens of all three compounds with exception of the methyl hydrogens and the disordered atoms of 5 are omitted from the drawings. Thermal ellipsoids are drawn at the 50% probability levels.

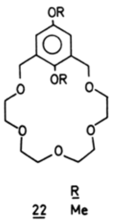
Table II. Acidities[a] of Phenolic Compounds in Water at 25 °C

compound	pK_a	compound	pK_a
7	10.9	9	10.7
8	10.8	2,6-dimethoxyphenol	10.2

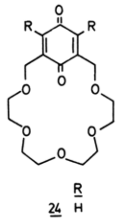
[a] Reproducibility is ±4% of the listed pK_a value.

ion-selective electrodes[17,18] and are summarized in Table I. Except with **10** for which the metal ion binding was too weak to measure, stability constants for association of potassium ion with the corand anisoles, phenols, and quinones were uniformly higher than for sodium and rubidium ions.

The 19-membered ring corands **4**, **7**, and **10** bear a structural similarity to the 1,3-xylyl-based, 18-membered ring corands **22–24**. Reported stability constants for complexation of sodium and potassium ions by **22–24** in MeOH[8] are also recorded in Table I. For all three macrocyclic ligands, stability constants for association with potassium ion are again larger than those with sodium ion. Although the stability constants for association of sodium and potassium ions with **4** vs **22** and **7** vs **23** were of similar magnitude, the cation binding by the 1,3-xylyl-based corand quinone **24** is decidedly stronger than with corand quinone **10**.



	R
22	Me
23	H



	R
24	H
25	Me

The 38-membered bisanisole corand **13** complexed sodium, potassium, and rubidium ions more strongly than did the 32-membered bisanisole corand **18**. Although **13** exhibited a clear preference for potassium ion complexation, **18** complexed potassium and rubidium ions equally well.

For corand phenols **7–9** and a reference compound, 2,6-dimethoxyphenol, pK_a values were determined in water and are listed in Table II. The relatively large differences between the pK_a values for the corand phenols **7–9** and 2,6-dimethoxyphenol indicates that hydrogen bonding between the phenolic hydroxyl group and the polyether oxygens is more pronounced than was observed with 1,3-xylyl-based corand phenols.[4] In agreement with the data obtained for the 1,3-xylyl-based corand phenols,[4] macrocyclic compounds **7–9** exhibit only a slight influence of ring size on acidity.

Table III. (C)H•••O Distances[a] Less Than 2.70 Å

C	H	O	H···O, Å	(C)H···O, deg
		4		
C	HOB	O16	2.68	108
C	HOC	O4	2.67	164
C	HOC	O7	2.58	128
		5		
none				
		13		
C	HOB	O4	2.58	161
C	HOB	O1	2.57	106

[a] Uncertainties could not be calculated since the C–H bond distance was fixed at 1.08 Å in all calculations.

Solid-State Structures of Anisole and Bisanisole Corands. Computer drawings with atom labels for the solid state structures of anisole corands **4** and **5** and bisanisole corand **13** are shown in Figure 1. Tables of positional and thermal parameters for the atoms in compounds **4**, **5**, and **13** and bond lengths are provided as supplementary material.

The rigid aromatic group or groups in each macrocycle causes the cavity to be open similar to the conformation that would be anticipated when the macrocycle complexes a metal cation. The plane of the aromatic ring(s) makes angles of 63.6°, 49.1°, and 54.4° with the least-squares plane of the ring oxygens in **4**, **5**, and **13**, respectively. As expected, the three oxygen atoms bonded directly to each benzene ring lie in the plane of the aromatic unit. Carbon atoms of the adjacent methylene groups do not deviate by more than 0.6 Å from the plane of the aromatic ring. However, the carbon atoms of the methoxyl groups deviate from the plane of the aromatic unit by 1.1307, 1.0992, and 1.1438 Å in **4**, **5**, and **13**, respectively. In all three compounds, the methyl group carbon atom is bent toward the polyether ring (see Figure 1). This is surprising since there would be less steric interaction if the methyl group were directed away from the macrocyclic ring. As a result of this conformation, the nonbonding electron pairs of the methoxyl group oxygen point away from the cavity and would not be available for interaction of a cation complexed within the cavity without a 180° rotation about the CB1-O bond.

In an effort to rationalize this unusual positioning of the methyl group(s) in **4**, **5**, and **13**, all intramolecular (C)H···O distances involving methyl group hydrogens were examined

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[17] Frensdorff, H. K. *J. Am. Chem. Soc.* **1971**, *93*, 600–606.

[18] This treatment does not take into account the proton–cation exchange reaction LH + M$^+$ $\rightleftharpoons$ LM + H$^+$ for the corand phenols and bisphenol. However exclusion of this possibility seems reasonably in view of the large difference between the pK_a's of the corand phenols (vide infra) and the "pH" of methanol in which the stability constants were determined.

Table IV. Cyclic Voltammetric Data for Quinone/Semiquinone Anion Radical Couples[a]

	0.1 M TBAP		0.1 M $KBPh_4$	
quinone	$E_{1/2}$, V	ΔE_p, mV	$E_{1/2}$, V	ΔE_p, mV
BQ[b]	-0.48	100		
DMBQ[c]	-0.69	100	-0.60	90
10	-0.72	220		
11	-0.70	180	-0.40	110
12	-0.70	180		
20	-0.69	110	-0.40	90

[a] 25.0 °C, $E_{1/2}$ (quinone/semiquinone anion radical) expressed relative to NHE (HEF standard). Uncertainty estimated at ±0.01 V. [b] 1,4-Benzoquinone. [c] 2,6-Dimethoxy-1,4-benzoquinone.

to see if any were shorter than 2.7 Å, the sum of the van der Waals radii of (C)H and O,[19] which would suggest hydrogen bonding. All such interactions are listed in Table III. For these calculations, the C–H bond length was considered to be 1.08 Å. There are three short distances for anisole corand **4** and two for bisanisole corand **13**. Although there are no short distances in **5**, three HOC····O and one HOB····O distances (see Figure 1 for designations) less than 2.95 Å are observed. These results indicate that there are attractive forces that bend the methyl group toward the interior of the polyether ring, but that the interactions are weak and would not produce a significant energy barrier to rotation about the CB1-0 bond.

The bond lengths are normal with the exception of bonds involving the disordered atoms in **5** and **13** and C11-C12 in **4**. Omitting these bond distances, the average $O–CH_2$ bond, excluding the oxygens bonded to the aromatic unit, and $H_2C–CH_2$ bond lengths in the polyether rings are 1.411 (6) Å and 1.484 (11) Å, respectively. The average $C_{benzene}–O$ bond distance is 1.365 (7) Å, while the average $ArO–CH_2$ bond length is 1.432 (5) Å. The average $O–CH_3$ bond distance is 1.426 (6) Å.

Bond and torsion angles are provided as supplementary material. Angles for the polyether ring atoms have expected values except for those atoms involved in disorder. The torsion angles reflect the strain created by the presence of the aromatic groups in the rings. Values near 180° are found for most C–O–C–C torsion angles, while most O–C–C–O torsion angles are close to 60°. However, in each compound there are torsion angles that differ appreciably from these low-energy values. A few such values are C11–C12–O13–C14, 118.0 (5)°, and O13–C14–C15–O16, 74.0 (4)° in **4**; O10–C11–C12–O13, 80.1 (8)°, O10–C11A–C12A–O13, -84.3 (9)°, and C11–C12–O13–C14, 85.0 (8)° in **5**; and C5–C6–O7–C8, 159.4 (2)°, C6–O7–C8–C8′, 156.0 (1)°, C9B–C9A′–O10′–C11′–C11′, -92.1 (4)°, and C9B–O10–C11–C12, 164.3 (3)° in **13**. Most of these angles involve atoms that are disordered. Such higher energy torsion angles have been found in other cyclic polyether molecules that contain benzo groups.[20]

Electrochemical Behavior of Corand Quinones and Bisquinones. Cyclic voltammograms of corand quinones **10–12** and the corand bisquinone **20** in acetonitrile solutions that contained 0.1 M Bu_4NClO_4 (TBAP) exhibited quasi-reversible quinone/semiquinone anion radical reduction waves in the interval of -0.4 to -0.8 V vs NHE. Scanning to very negative potentials gave further increases in cathodic current commencing at about -1.6 V vs NHE, but semiquinone anion radical/hydroquinone dianion waves could not be resolved from the background current due to the solvent at such negative potentials. Half-wave potentials and anodic-to-cathodic peak current separations (ΔE_p) observed for one-electron reductions of the corand quinones are compared in Table IV with analogous parameters for 1,4-benzoquinone (BQ) and 2,6-dimethoxy-1,4-benzoquinone (DMBQ). Large peak-to-peak separations of 100–220 mV (50 mV/s sweep rate), indicative of slow heterogeneous electron transfer kinetics, greatly exceed the value of 59 mV expected for fully reversible one-electron reduction waves. Nevertheless, $E_{1/2}$ values were shown to be independent of sweep rate in the interval of 50–400 mV/s, and the ratio of cathodic to anodic peak current[21] was consistently within experimental error of 1.0, demonstrating the stability of benzoquinone reduction products to disproportionation or decomposition on the electrochemical time scale. No new electroactive species were revealed in the second and subsequent sweeps of steady-state voltammograms. Nearly identical voltammograms were obtained with glassy carbon and platinum working electrodes.

Considering reductions conducted in acetonitrile solutions that contained 0.1 M TBAP, the 0.21 V negative shift in the $E_{1/2}$ value for DMBQ relative to that of BQ is as expected from the inductive effects of the two electron-releasing methoxy substituents. Half-wave potentials for all three corand quinones and the corand bisquinone are nearly the same as that for the reference compound, DMBQ. Only a slight trend toward more positive potentials with increasing corand ring size is apparent.

The $E_{1/2}$ values for corand quinone **11** and corand bisquinone **20** exhibited pronounced anodic shifts on the order of 0.30 V when the TBAP supporting electrolyte was replaced by 0.1 M $KBPh_4$. Thus, both **11** and **20** were reduced with a value of $E_{1/2}$ = -0.40 V vs NHE in the presence of 0.1 M $KBPh_4$, which implies that potassium ion strongly stabilizes the semiquinone products. Potassium ion also promotes heterogeneous electron transfer rates, since ΔE_p decreases of 20 and 70 mV for **11** and **20**, respectively, were observed relative to voltammograms generated in 0.1 M TBAP. Assuming that the 0.09 V positive shift in $E_{1/2}$ observed for DMBQ may be attributed to electrostatic interactions (ion pairing), the perturbation in potential owing to potassium ion coordinated within the corand cavity of quinone **11** may be estimated as +0.21 V. Expressed as a free energy change, this increment of 0.21 V corresponds to a 4.8 kcal/mol stabilization of the semiquinone anion radical through interactions of potassium ion with the corand oxygen atoms and the increased negative charge residing on the intraannular quinone oxygen. Similarity of the potassium ion effects on the electrochemical behaviors of quinone **11** and bisquinone **20** shows that there is no special stabilization of the polyether-ligated cation in the larger bisquinone crown cavity or potassium ion-mediated redox interaction between the two quinonoid moieties of **20**. Thus the bisquinone behaves electrochemically as two independent redox centers with the characteristics of the monoquinone **11**.

If one assumes that essentially all of the corand quinone **11** present in 0.1 M $KBPh_4$ is complexed by potassium ion, as is reasonable considering the log K_s value of 3.4 in MeOH, the cation-induced positive shift in $E_{1/2}$ may be quantitatively related[22] (eq 1) to the ratio of stability constants for potassium complexes with the semiquinone anion radical (K_s^r) and quinone (K_s) forms of the ligand. On this basis, a K_s^r/K_s ratio of 1.2×10^5 is calculated for

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(19) Taylor, R.; Kennard, G. *J. Am. Chem. Soc.* **1982**, *104*, 5063–5072.

(20) Bright, D.; Truter, M. R. *J. Chem. Soc. B* **1970**, 1544–1550 and others.

(21) Johnston, R. J.; Holwerda, R. A. *Inorg. Chem.* **1985**, *24*, 153–159.

(22) Wolf, R. E., Jr.; Cooper, S. R. *J. Am. Chem. Soc.* **1984**, *106*, 4646–4647.

$$\Delta E_{1/2} = E_{1/2}(\text{complex}) - E_{1/2}(\text{quinone}) \approx (RT/nF)\ \ln\ (K_s^r/K_s) \quad (1)$$

quinone **11**. After correction for the influence of potassium ion on $\Delta E_{1/2}$ for the acyclic model compound DMBQ (+0.09 V), a revised K_s^r/K_s ratio of 3×10^3 is calculated, which reflects the specific effect of polyether-bound potassium ion on the relative stabilities of the quinone and semiquinone oxidation states.

Although enhancements in cation binding to crown ether and lariat ether quinone compounds coupled with one-electron reduction have been reported previously,[22,23] the relative stabilization by potassium ion of the corand semiquinone derived from **11** is the largest observed to date for that alkali metal cation. Thus, Wolf and Cooper[22] reported 120- and 130-mV anodic shifts in the quinone/semiquinone anion radical reduction potentials for sodium and potassium ion complexes, respectively, of the corand quinone **25**, which corresponds to binding constant enhancements of 10^2 (uncorrected for ion pairing). Apparently the larger ring and electron-donating quinonoid alkoxy substituents of **11** contribute significantly to enhanced potassium ion binding by the semiquinone anion radical form.

Maruyama and co-workers[23] found that the presence of either cyclic or acyclic polyether units promoted cation binding to reduced quinone species. Both corand quinone and bisquinone compounds with large polyether units exhibited extremely poor alkali metal cation affinities. However, lithium cation binding enhancements on the order of 2×10^4 were found for several of the corresponding semiquinone anion radicals. Cation binding enhancements followed the sequence lithium ≫ sodium > potassium ion, such that the semiquinone anion radical/quinone binding ratios for sodium and potassium ions once again were very modest ($1-10^2$).

The exceptional stimulation of potassium ion binding associated with the reduction of **11** suggests that such compounds could be used to complex and transport potassium ion with redox control of ion uptake and release.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary apparatus and are uncorrected. IR spectra were obtained with a Perkin-Elmer 267 spectrophotometer. ^{1}H NMR spectra were measured with a Varian EM 360A spectrometer, ^{13}C NMR spectra were recorded on a JEOL FT 90Q spectrometer, and chemical shifts are reported in parts per million (δ) downfield from tetramethylsilane. Mass spectra were measured with a Hewlett-Packard Model 5982A spectrometer. Elemental analysis was performed by Galbraith Laboratories of Knoxville, TN.

Materials. Unless specified otherwise, reagent grade reactants and solvents were used as received from chemical suppliers. Acetone was stored over anhydrous K_2CO_3. Tetrahydrofuran was dried over molecular sieves (4-Å). Ditosylates of triethylene, tetraethylene, and pentaethylene glycols were prepared by the standard method.[13] The tetrahydropyranyl ether of 2-(2′-chloroethoxy)ethanol was prepared by adaptation of a literature procedure.[13]

1,3-Bis[(methoxycarbonyl)methoxy]-2-methoxybenzene (2). To a stirred mixture of anhydrous K_2CO_3 (30 g) and methyl bromoacetate (30.5 g, 0.20 mol) in 400 mL of acetone was added dropwise under nitrogen a solution of 2-methoxyresorcinol in 100 mL of acetone, and the mixture was refluxed for 30 h. Filtration and evaporation of the filtrate gave a residue, which was purified by column chromatography on silica gel with CH_2Cl_2–CH_3OH (50:1) as eluent to give 19.3 g (95%) of **2** as a colorless, viscous liquid, which solidified during storage. An analytical sample was recrystallized from benzene–hexane: mp 70–72 °C; IR (deposit on NaCl) 1760 (C=O), 1120 (C—O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.80 (s, 6 H), 3.97 (s, 3 H), 4.75 (s, 4 H), 6.45–7.10 (m, 3 H). Anal. Calcd for $C_{13}H_{16}O_7$: C, 54.93; H, 5.67. Found: C, 54.82; H, 5.55.

1,3-Bis(2-hydroxyethoxy)-2-methoxybenzene (3). Diester **2** (16.0 g, 0.056 mol) in 120 mL of THF was added dropwise to a suspension of $LiAlH_4$ (3.2 g, 0.084 mol) in 280 mL of THF. After the mixture was stirred for 2 h at room temperature, 100 mL of 10% H_2SO_4 was added, and the mixture was stirred overnight at room temperature. After addition of NaCl, the THF layer was separated. The solvent was removed in vacuo, and the crude product was repeatedly recrystallized from EtOAc to afford 9.4 g (73%) of **3** as white crystals: mp 88.5–90.5 °C; IR (deposit on NaCl) 3440 (O–H), 1110 (C–O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.8–4.25 (m, 13 H), 6.45–7.15 (m, 3 H). Anal. Calcd for $C_{11}H_{16}O_5$: C, 57.89; H, 7.07. Found: C, 57.91; H, 6.87.

General Procedure for the Synthesis of Anisole Corands 4–6. To a solution of diol **3** (3.42 g, 0.015 mol) in 225 mL of THF under argon was added t-BuOK (3.70 g, 0.033 mol), the mixture was stirred for 1 h at room temperature, and then the appropriate polyethylene glycol ditosylate (15 mmol) dissolved in 110 mL of THF was added dropwise. The reaction mixture was stirred at room temperature overnight and refluxed for 72 h. The solvent was removed in vacuo, and $CHCl_3$ and H_2O (100 mL of each) were added to the residue. The aqueous layer was made acidic with 6 N HCl, the organic layer was separated and the aqueous layer was extracted twice with $CHCl_3$. The combined organic layers were dried ($MgSO_4$), and the solvent was evaporated in vacuo. Column chromatography followed by recrystallization produced pure products.

4: 6.4% yield after chromatography on alumina with EtOAc–petroleum ether (3:1 → 1:1) as eluent and recrystallization from benzene–heptane (1:1); white crystals with mp 73–74 °C; IR (deposit on NaCl) 1105 (C–O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.41 (s, 4 H), 3.5–3.9 (m, 12 H), 3.95 (s, 3 H), 4.2–4.45 (m, 4 H), 6.5–7.1 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 61.0, 68.8, 69.8, 70.5, 71.0, 108.5, 122.7, 152.9; MS, *m/e* 342 (M$^+$). Anal. Calcd for $C_{17}H_{26}O_7$: C, 59.64; H, 7.65. Found: C, 59.77; H, 7.58.

13: 11.5% yield was eluted from the column as the second band in the preparation of **4**; white crystals with mp 78.5–80.5 °C; IR (deposit on NaCl) 1105 (C–O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.5–4.0 (m, 32 H), 3.85 (s, 6 H), 4.0–4.3 (m, 8 H), 6.45–7.1 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 60.7, 69.1, 69.8, 70.7, 70.9, 108.0, 123.3, 152.9; MS, *m/e* 684 (M$^+$). Anal. Calcd for $C_{34}H_{52}O_{14}$: C, 59.64; H, 7.65. Found: C, 59.79; H, 7.69.

5: 35% yield after column chromatography on silica gel with CH_2Cl_2–MeOH (30:1) as eluent and on alumina with EtOAc–petroleum ether (3:1) as eluent; white crystals with mp 72–74 °C after recrystallization from benzene–heptane (1:1); IR (deposit on NaCl) 1100 (C–O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.4–4.05 (m, 20 H), 3.98 (s, 3 H), 4.1–4.4 (m, 4 H), 6.5–7.1 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 61.3, 69.0, 69.6, 70.6, 70.8, 71.0, 107.7, 123.0, 153.0; MS, *m/e* 386 (M$^+$). Anal. Calcd for $C_{19}H_{30}O_8$: C, 59.05; H, 7.82. Found: C, 59.24; H, 7.69.

6: 26% yield after careful chromatography on alumina with EtOAc–petroleum ether (3:1) as eluent; colorless oil; ^{1}H NMR ($CDCl_3$) δ 3.5–4.05 (m, 24 H), 3.92 (s, 3 H), 4.05–4.3 (m, 4 H), 6.5–7.15 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 60.9, 69.2, 69.8, 70.8, 71.1, 107.7, 123.2, 153.0; MS, *m/e* 430 (M$^+$). Anal. Calcd for $C_{21}H_{34}O_9 \cdot 0.25H_2O$: C, 57.98; H, 7.99. Found: C, 57.96; H, 8.14.

General Procedure for the Synthesis of Corand Phenols 7–9. A solution of the anisole corand (3.5 mmol) in 20 mL of THF was added to a suspension of $LiAlH_4$ (27 mmol) in 50 mL of THF, and the mixture was refluxed for 20 h. After the mixture was cooled to 0 °C, 10% H_2SO_4 (30 mL) was added, and the mixture was stirred overnight at room temperature. Extraction with $CHCl_3$ (2 × 25 mL), drying ($MgSO_4$), and evaporation of the solvent in vacuo gave the crude product, which was purified by careful column chromatography an alumina with EtOAc–MeOH (50:1 → 20:1) as eluent.

7: 82% yield; white crystals with mp 57–58 °C; IR (deposit on NaCl) 3420 (O–H), 1030–1140 (C–O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.5–3.9 (m, 16 H), 4.1–4.3 (m, 4 H), 6.75 (s, 3 H), 7.31 (br s, 1 H). Anal. Calcd for $C_{16}H_{24}O_7$: C, 58.53; H, 7.37. Found: C, 58.89; H, 7.44.

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[23] Maruyama, K.; Sohmiya, H.; Tsukube, H. *J. Chem. Soc., Perkin Trans. 1* **1986**, 2069–2074.

8: 81% yield; colorless oil; IR (neat) 3300–3550 (O–H), 1095 (C–O) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.65–3.95 (m, 20 H), 4.05–4.3 (m, 4 H), 6.70 (s, 3 H), 7.07 (s, 1 H). Anal. Calcd for $C_{18}H_{28}O_8$: C, 58.05; H, 7.58. Found: C, 57.82; H, 7.74.

9: 86% yield; colorless oil; IR (neat) 3510, 3190 (O–H), 1100 (C–O) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.6–4.0 (m, 28 H), 4.05–4.35 (m, 4 H), 6.67 (s, 3 H), 7.20 (br s, 1 H). Anal. Calcd for $C_{20}H_{32}O_9 \cdot 1.5H_2O$: C, 54.17; H, 7.95. Found: C, 54.15; H, 7.75.

General Procedure for the Synthesis of Corand Quinones 10–12. To a vigorously stirred solution of the corand phenol (15.6 mmol) in benzene (22 mL) was added 210 mL of 5% aqueous sodium acetate followed by potassium nitrosodisulfonate (9.95 mmol). Stirring was continued for 2 h at room temperature, and benzene (100 mL) was added. The organic layer was separated, and the water layer was reextracted several times with CH$_2$Cl$_2$. The combined organic layers were dried (MgSO$_4$), and the solvent was evaporated in vacuo to give the crude product, which was purified by flash chromatography on silica gel with CH$_2$Cl$_2$–CH$_3$OH (20:1) as eluent to afford the pure corand quinone.

10: 84% yield; yellow crystals with mp 98–99 °C; IR (deposit on NaCl) 3070 (C=C), 1695, 1645 (C=O), 1620, 1595 (C=C), 1100 (C—O) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.35–4.0 (m, 16 H), 4.15–4.4 (m, 4 H), 6.00 (s, 2 H). Anal. Calcd for $C_{16}H_{22}O_8$: C, 56.14; H, 6.48. Found: C, 56.18; H, 6.28.

11: 92% yield; yellow crystals with mp 91–92 °C; IR (deposit on NaCl) 3070 (C=C), 1690, 1640 (C=O), 1620, 1595 (C=C), 1090–1130 (C—O) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.5–4.3 (m, 24 H), 5.93 (s, 2 H). Anal. Calcd for $C_{18}H_{26}O_9$: C, 55.95; H, 6.78. Found: C, 55.90; H, 7.00.

12: 96% yield; yellow oil; IR (neat) 3070 (C=C), 1700, 1645 (C=O), 1595 (C=C), 1100 (C—O) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.55–4.2 (m, 28 H), 5.88 (s, 2 H). Anal. Calcd for $C_{20}H_{30}O_{10} \cdot 0.25H_2O$: C, 55.23; H, 7.07. Found: C, 55.24; H, 6.93.

Preparation of Corand Hydroquinone 14. A heterogenous mixture of corand quinone **11** (0.30 g, 0.78 mmol) dissolved in 15 mL of CHCl$_3$ and a saturated aqueous solution of sodium dithionite (20 mL) was stirred vigorously at room temperature for 2 h. The colorless organic layer was separated and dried (MgSO$_4$), and the solvent was removed in vacuo. The residue was immediately purified by flash chromatography on silica gel with nitrogen to pressurize the column and CH$_2$Cl$_2$–MeOH (10:1) as eluent. The product was isolated as an amorphous white solid (0.275 g, 92%): mp 68–70 °C; IR (neat) 3350 (O–H), 1110 (C–O) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.3–4.2 (m, 24 H), 6.20 (s, 2 H), 6.70 (br s, 2 H); MS, *m/e* 388 (M$^+$). Anal. Calcd for $C_{18}H_{28}O_9 \cdot H_2O$: C, 53.19; H, 6.94. Found: C, 53.53; H, 7.28.

Preparation of Bis(tetrahydropyranyl ether) 15. By use of the literature procedure, **15** was prepared in 93% yield.[13] An analytical sample was obtained by column chromatography on silica gel with EtOAc–petroleum ether (2:1) as eluent: colorless liquid; IR (neat) 1120 (C–O) cm^{-1}; ^{1}H NMR (CHCl$_3$) δ 1.3–1.9 (m, 12 H), 3.35–4.3 (m, 23 H) 4.60 (br s, 2 H), 6.5–7.05 (m, 3 H). Anal. Calcd for $C_{25}H_{40}O_9$: C, 61.97; H, 8.32. Found: C, 61.72; H, 8.20.

Preparation of Diol 16. Bis(tetrahydropyranyl ether) **15** was deprotected by stirring with concentrated aqueous HCl in CH$_2$Cl$_2$–MeOH to produce diol **16** in 90% yield. An analytical sample was purified by column chromatography on silica gel with EtOAc–MeOH (10:1) as eluent: colorless liquid; IR (neat) 3405 (O–H), 1100 (C–O) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.05 (br s, 2 H), 3.55–4.3 (m, 19 H), 6.5–7.05 (m, 3 H). Anal. Calcd for $C_{15}H_{24}O_7 \cdot 0.25H_2O$: C, 56.15; H, 7.70. Found: C, 55.98; H, 7.70.

Preparation of Ditosylate 17. Reaction of diol **16** with *p*-toluenesulfonyl chloride in pyridine converted diol **16** into ditosylate **17** in 96% yield. An analytical sample was purified by flash chromatography on silica gel with CH$_2$Cl$_2$–EtOH (50:1) as eluent: colorless oil; IR (neat) 1355, 1190, and 1175 (S=O), 1095 (C—O) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.40 (s, 6 H), 3.6–4.3 (m, 19 H), 6.4–7.05 (m, 3 H), 7.55 (AB q, 8 H). Anal. Calcd for $C_{29}H_{36}S_2O_{11}$: C, 55.76; H, 5.81. Found: C, 56.13; H, 5.76.

Preparation of Bisanisole Corand 18. To a solution of diol **16** (1.58 g, 5.0 mmol) in THF (75 mL) was added t-BuOK (1.23 g, 11.0 mmol), and the solution was stirred under argon for 1 h. A solution of ditosylate **17** (3.12 g, 5.0 mmol) in 37 mL of THF was added, and the mixture was stirred at room temperature for 5 days and then refluxed for 36 h. The solvent was evaporated in vacuo, and the residue was partitioned between CH$_2$Cl$_2$ (100 mL) and water (100 mL). The organic layer was dried (MgSO$_4$) and evaporated in vacuo. The residue was purified by column chromatography on alumina with EtOAc–petroleum ether (2:1) as eluent to produce 0.71 g (24%) of **18** as a white solid: mp 56–58 °C; IR (deposit on NaCl) 1105 (C–O) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.5–4.3 (m, 38 H), 6.4–7.05 (m, 6 H); MS, *m/e* 596.05 (M$^+$). Anal. Calcd for $C_{30}H_{44}O_{12}$: C, 60.39; H, 7.43. Found: C, 60.51; H, 7.52.

Preparation of Corand Bisphenol 19. To a solution of **18** (0.54 g, 0.91 mmol) in THF (15 mL) was added 0.30 g (7.9 mmol) of LiAlH$_4$. The mixture was refluxed for 20 h and cooled to 0 °C, and aqueous 15% NaOH was added dropwise. The solid material was filtered and washed several times with hot THF. The combined filtrate and washings were evaporated under vacuum, and the residue was chromatographed on an alumina column with EtOAc–MeOH (20:1 → 5:1) as eluent to give 0.31 g (61%) of **19** as white crystals: mp 91–93 °C (from ether–pentane); IR (deposit on NaCl) 3500–3200 (O–H), 1100 (C–O) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.5–4.3 (m, 34 H), 6.61 (s, 6 H). Anal. Calcd for $C_{28}H_{40}O_{12} \cdot H_2O$: C, 57.33; H, 7.21. Found: C, 57.33; H, 7.20.

Preparation of Corand Bisquinone 20. Corand bisphenol **19** (0.100 g, 0.175 mmol) was oxidized with potassium nitrosodisulfonate (0.57 g, 2.1 mmol) in an acetone–5% aqueous sodium acetate mixture by an adaptation of a literature procedure.[8] Column chromatography on silica gel with CH$_2$Cl$_2$–MeOH (20:1) afforded 0.086 g (83%) of **20** as a yellow solid: mp 177–179 °C dec; IR (deposit on NaCl) 3060 (C=C), 1695, 1645 (C=O), 1082 (C—O) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.4–4.2 (m, 32 H), 5.86 (s, 4 H). Anal. Calcd for $C_{28}H_{36}O_{14} \cdot 0.5H_2O$: C, 55.53; H, 6.16. Found: C, 55.68; H, 6.14.

Attempted Preparation of Anisole Corand 21. To a suspension of powdered sodium hydroxide (0.48 g, 12.0 mmol) in dioxane (15 mL) at 60 °C under argon was added a solution of diol **16** (0.95 g, 3.0 mmol) and *p*-toluenesulfonyl chloride (0.57 g, 3.0 mmol) in 9 mL of dioxane over an 8-h period, and the mixture was heated for 20 h at 60 °C. The solvent was removed in vacuo, and the crude product was subjected to column chromatography. Small quantities of ditosylate **17** and corand **18** were isolated and identified by comparison with the authentic samples.

Determination of Stability Constants. The stability constants were determined for complexation of NaCl, KCl, and RbCl by corand ligands in anhydrous methanol at 25 ± 0.5 °C by the Frensdorff method.[16] A monovalent cation Corning 476220 electrode was used for potassium and rubidium, and a Corning 476210 electrode for sodium. Emf changes were determined with a Corning Model 101 digital electrometer. The experimental error was ±1.5% in log K_s.

Measurement of pK_a Values. Determination of pK_a values was performed in water at 25 ± 0.5 °C according to the published method[24] with an Orion Model 601A digital ionalyzer.

Crystal Growth, Crystal Data, Structure Solutions, and Refinement. Crystals of **4**, **5**, and **13** suitable for X-ray structure studies were prepared by seeding 1:1 benzene–heptane solutions of the compounds and allowing the solvent to evaporate slowly. The three compounds formed clear, colorless, platelike crystals.

Crystal and intensity data were obtained with a Nicolet R3 automated diffractometer, which utilized Mo Kα radiation (λ = 0.710 73 Å). Lattice parameters for the three compounds and their respective orientation matrices were calculated by a least-squares refinement of the angular setting of several carefully centered reflections. Crystal data and experimental procedures are summarized in Table V. Intensity data for each compound were obtained using a variable scan speed θ–2θ procedure. The presence of the aromatic groups in the macrocycles caused strain in the polyether rings with resulting large vibrational motion and/or minor disorder. This at least partially accounts for the large number of unobserved data in the small ring compounds **4** and **5**.

Trial structures of all three compounds were obtained by direct methods. All non-hydrogen atoms of each compound were located in their respective E maps. Molecule **13** was found to contain a crystallographic 2-fold axis, which bisects the C8–C8′ and C9–C9′ bonds (see Figure 1). During the refinement process, it was apparent that there were disordered atoms in **5** and **13**, and in

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(24) Albert, A.; Serjeant, E. P. *Determination of Ionization Constants*; Chapman and Hall: New York, 1984; Chapter 2.

Table V. Summary of Data Collection and Processing Parameters

	4	5	13[a]
formula	$C_{17}H_{26}O_7$	$C_{19}H_{30}O_8$	$C_{34}H_{52}O_{14}$
formula weight	342.4	386.4	684.8
$F(000)$	736	1664	1472
crystal size, mm	0.4 × 0.4 × 0.35	0.4 × 0.5 × 0.35	0.55 × 0.50 × 0.09
space group	$P2_1/n$	$Pbca$	$C2/c$
number and range of data	25, 6.3 < 2θ < 29.2	17, 10.7 < 2θ < 23.4	16, 16.0 < 2θ < 25.0
a, Å	12.277 (5)	13.275 (3)	14.735 (12)
b, Å	8.788 (3)	16.277 (4)	14.016 (13)
c, Å	16.626 (6)	18.926 (5)	17.187 (11)
β, deg	94.70 (3)	90	98.16 (6)
V, Å^3	1787 (1)	4089 (1)	3514 (4)
Z	4	8	4
d_c, g/cm^3	1.27	1.26	1.29
μ, cm^{-1}	0.91	0.91	0.94
$\sin \theta/\gamma$	0.59	0.50	0.54
observed data	1967	1807	2073
unobserved data	1911	1225	274
criteria for unobsd data	$F < 3\sigma(F)$	$F < 3\sigma(F)$	$F < 2.5\sigma(F)$
R_m	0.017		0.029
R	0.068	0.072	0.046
R_w	0.073	0.064	0.041
data/parameter	9.4	7.3	9.5
goodness of fit	1.42	1.62	1.88
scan rate limits, deg/min	3–30	3–30	4–30
max and min peaks in Δ map e Å^{-3}	0.29, −0.26	0.23, −0.20	0.27, −0.17

[a] Four octants of data were collected for **13**, which were later merged.

both molecules the disorder was at least partially resolved. The large thermal motion of C11 and C12 in **4** and an abnormally short C11–C12 [1.439 (8) Å] bond also indicated that there was also disorder in **4**, but it could not be resolved. During the refinement process, the benzene unit in each molecule was refined as a rigid body with C–C bonds of 1.395 Å and C–C–C angles of 120°. The methyl group in each compound was also refined as a rigid body. Positions for most hydrogens were calculated by use of geometrical conditions, though many hydrogens were apparent in difference maps. Positions for hydrogen atoms bonded to disordered carbons were either located in difference maps or calculated with the atoms of only one site being included in the calculations. Hydrogens were allowed to ride on the atoms to which they were bonded, and their isotropic thermal parameters were set equal to 1.2 times the initial equivalent isotropic parameter of the bonded carbon and were not refined. Weights based and counting statistics were applied to the data during the refinement process, and an emperical extinction correction was applied to each data set. Scattering factors were taken from *The International Tables for X-ray Crystallography*.[25] All computer programs used in solution, refining, and displaying these structures are contained in the SHELXTL[26] program package supplied by Nicolet.

Electrochemical Measurements. Cyclic voltammograms of solutions thermostated at 25.0 ± 0.1 °C were generated with a Bioanalytical Systems CV-1B apparatus, and output was obtained from a Hewlett-Packard 7004 X-Y recorder. A three-electrode configuration was used, composed of platinum button working and auxiliary electrodes coupled with an aqueous saturated calomel reference minielectrode (Sargent-Welch) immersed in 0.1 M $NaNO_3$. The working and reference electrode compartments were connected through sintered glass spacers to a central compartment containing 0.1 M Bu_4NClO_4 (TBAP) in acetonitrile. Voltammograms were obtained of acetonitrile solutions, which contained 1.0 mM electroactive solute and 0.1 TBAP and $KBPh_4$. The capped working electrode compartment was purged for 45 min with acetonitrile-saturated nitrogen prior to the measurement of cyclic voltammograms, and the nitrogen flow was continued over the top of quinone solutions throughout the electrochemical measurements in order to maintain oxygen-free conditions. Half-wave quinone/semiquinone reduction potentials ($E_{1/2}$) were calculated from quasi-reversible voltammograms as the average of cathodic and anodic peak potentials at a sweep rate of 50 mV/s. The reference electrode potential was calibrated against (hydroxyethyl)ferrocene[27] in order to express $E_{1/2}$ values relative to the normal hydrogen electrode (NHE) and to compensate for small day-to-day variations in cell IR drop and $E°$ (SCE).

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Registry No. **2**, 118356-71-1; **3**, 118356-72-2; **4**, 118356-73-3; **5**, 118356-74-4; **6**, 118356-75-5; **7**, 118356-76-6; **8**, 118356-77-7; **9**, 118356-78-8; **10**, 118356-79-9; **11**, 118356-80-2; **12**, 118356-81-3; **13**, 118356-82-4; **14**, 118356-83-5; **15**, 118356-84-6; **16**, 118356-85-7; **17**, 118356-86-8; **18**, 118356-87-9; **19**, 118356-88-0; **21**, 118356-89-1; **22**, 78840-05-8; **23**, 78840-09-2; 2-methoxyresorcinol, 29267-67-2; methyl bromoacetate, 96-32-2.

Supplementary Material Available: Tables of positional and thermal parameters for all atoms and bond lengths for crystal structures of **4**, **5**, and **13**, as well as bond and torsion angles in the polyether rings of **4**, **5**, and **13**, excluding any angle that involves two benzene atoms (13 pages). Ordering information is given on any current masthead page.

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(25) *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynock Press: Birmingham, England, 1974; Vol. 4, p 99.

(26) Sheldrick, G. M. *SHELXTL. An Integrated System for Solving, Refining and Displaying Structures from Diffraction Data*, 4th revision; University of Göttingen: Federal Republic of Germany, 1983.

(27) Baek, H. K.; Holwerda, R. A. *Inorg. Chem.* **1983**, *22*, 3452–3456.