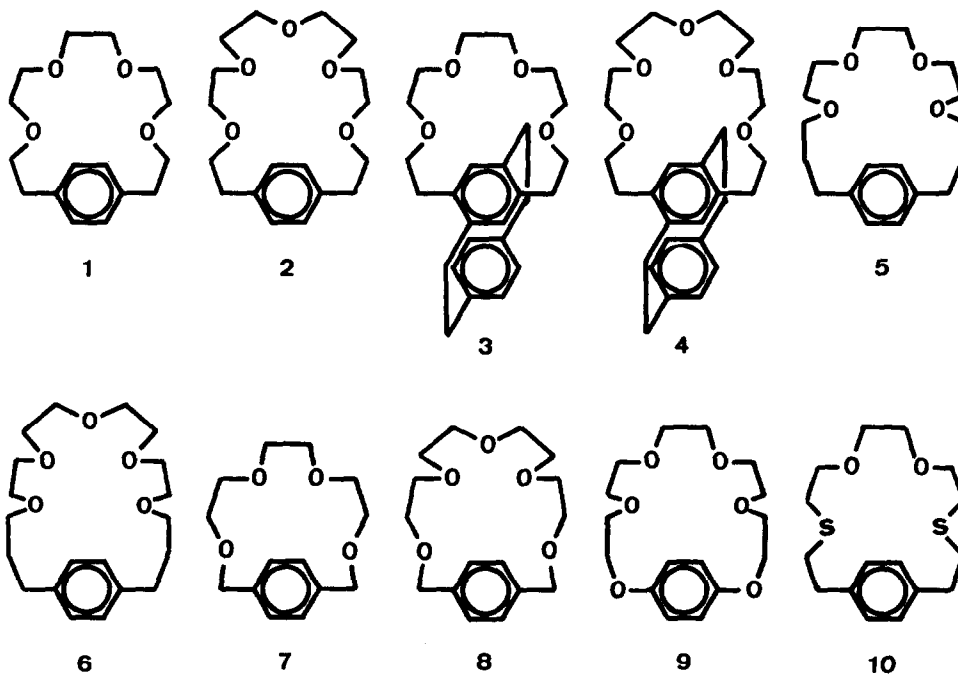


A SERIES OF CROWN ETHERS CONTAINING A π -DONOR SUBUNIT
IN THE MACROCYCLES

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Although there have been known many sorts of crown ethers possessing aromatic nuclei in their macrocycles,¹⁾ it has not been noted that the aromatic subunit serves as a π -donor for complexation with an alkali metal.²⁾ A crown compound containing para-substituted benzene in its macrocycle provides a possibility for such π -complexing. Here we wish to report on the syntheses of a series of para-phenylene crown ethers 1-10³⁾ and discuss their complexing properties.

Crown ethers 1-9 were synthesized by the Williamson reaction of the corresponding precursors 11-20⁴⁾ as summarized in Table 1. For example, 1 was obtained in 17% yield by treatment of para-phenylene diethanol 11 with sodium hydride in dry refluxing tetrahydrofuran under nitrogen, followed by slow addition of triethylene glycol ditosylate 16 in dry tetrahydrofuran. Dithia crown compound 10 was prepared by a conventional coupling method of 1,4-bis(2-mercaptoethyl)benzene 21 and 1,2-bis(2-chloroethoxy)ethane 22 in refluxing ethanol under high dilution



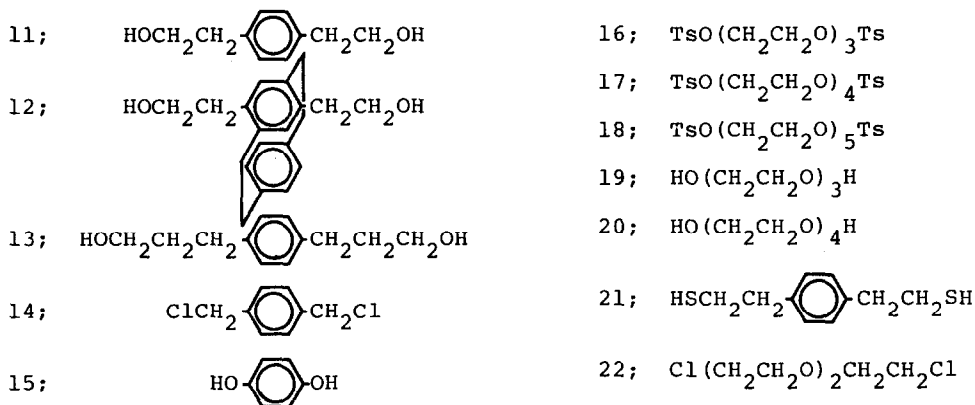


Table 1. Yields and Properties of Crown Ethers 1-10.

	Crown Ether	Reactants	Base	Yield(%)	m.p. (°C)
1	colorless oil	11+16	NaH	17.0	
2	colorless oil	11+17	t-BuOK	17.0	
3	colorless oil	12+16	NaH	46.0	
4	colorless fine crystals ^{a)}	12+17	NaH	25.0	94.0-94.5
5	colorless needles ^{a)}	13+16	NaH	2.9 ^{b)}	36.0-37.0
6	colorless oil	13+17	NaH	3.0 ^{b)}	
7	colorless plates ^{a)}	14+19	NaH	2.6 ^{b)} (lit., 4%) ^{c)}	56.0-56.5
8	colorless columns ^{a)}	14+20	NaH	10.0 (lit., 5%) ^{c)}	59.0-60.0
9	colorless oil	15+18	NaH	2.2 (lit., 2%) ^{d)}	
10	colorless prisms ^{a)}	21+22	KOH	51.0	55.5-56.0

a) Recrystallized from ether. b) Certain amounts of cyclic dimers were obtained: 10.6% for 6, 11.5% for 7, 2.7% for 8. c) Ref. 3a. d) Ref. 3b.

conditions. All the new crown compounds were characterized by elemental analyses, NMR,⁵⁾ and Mass spectroscopy or molecular weight measurements.

The yields of 1-4, which possess ethylene groups between the bridged heteroatom and the subring, are considerably higher than those of the other classes except 10. This implies a template effect in the cyclization reaction (see 23).⁶⁾ A strong complexing ability of this class of compounds was, in fact, realized by NMR study. Although the NMR spectra of the other classes had almost no change in the presence of one equivalent of alkali metal, crown ethers 1-4 exhibit significant shifts, indicating the incorporation of the alkali cation into the cavity of the macrocyclic ring. The data of 1 and 4 are given in Tables 2 and 3 for discussion. It may be pointed out that the downfield shifts of the aromatic protons are mainly due to a decrease in the π -electron density of the benzene ring when complexed. Interestingly the aromatic protons Ha and Hb of the outer benzene in 4 also show reasonable downfield shifts. This can be explained by a transannular π -electron

Table 2. Complexation effect on the nmr spectrum of 1.

	ArH(s)	β -CH ₂ (t)	γ -CH ₂ (s)	δ -CH ₂ (s)	α -CH ₂
Free	7.142	3.701	3.492	3.252	2.801
LiSCN	7.159(0.017)	3.725(0.024)	3.519(0.027)	3.321(0.069)	2.816(0.015)
NaSCN	7.277(0.135)	3.767(0.066)	3.551(0.059)	3.456(0.204)	2.862(0.061)
KSCN	7.341(0.199)	3.840(0.139)	3.568*(0.076)	3.500(0.248)	2.921(0.120)

δ ppm in CDCl₃, 100MHz; ()= δ (complex)- δ (free); * A₂B₂ multiplet.

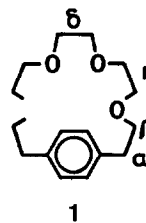
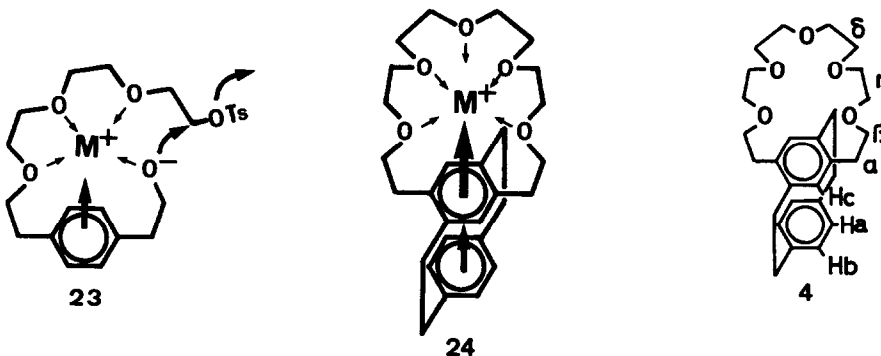


Table 3. Complexation effect on the nmr spectrum of 4.

	ArHa(dd)	ArHb(dd)	ArHc(s)	β -CH ₂ (t)	γ -CH ₂ (s)	δ -CH ₂ (A ₂ B ₂)
Free	6.643	6.389	6.095	3.573	3.490	3.346
LiSCN	6.644(0.001)	6.396(0.007)	6.120(0.025)	3.605(0.032)	3.497(0.007)	3.386(0.040)
NaSCN	6.653(0.010)	6.397(0.008)	6.157(0.062)	3.635(0.062)	3.505(0.015)	3.409(0.063)
KSCN	6.653(0.010)	6.411(0.022)	6.221(0.126)	3.696(0.123)	3.519(0.029)	3.468*(0.122)

δ ppm in CDCl₃, 100MHz; ()= δ (complex)- δ (free); * singlet; α -CH₂ and other benzylic CH₂: δ 3.11-2.43(m).



release from the outer benzene to the complexed inner benzene to enhance the π -complexing ability (see 24). This secondary effect probably contributes to much higher yields of 3 and 4 than 1 and 2.

The degree of complexation with crown ethers 1-10 was examined according to Gray's method using Zeise's salt $K[PtCl_3(C_2H_4)]$.⁷⁾ The results are shown in Table 4. The strong complexing abilities of 1-4 can be understood from the molecular model of a suitable conformation for complexation, in which all the oxygen atoms and the benzene can be oriented at almost equal distance toward the center of the cavity. On the other hand, the other crown compounds can not take any suitable conformations as described below. 1) In the complexes 5 and 6, the benzene ring and the incorporated metal are not close enough to interact 2) The cavity of 7 is too small to accommodate an alkaline metal cation. 3) In the cases of 8 and 9, all the oxygens and the benzene can not be oriented toward the center of the cavity at the same time. 4) Although dithia crown ether 10 should have essentially the same conformation as 1, it has rather a

weak complexing ability.⁸⁾ The difference is considered to result from the poor affinity of sulfur atom for hard alkali metal cations in contrast to oxygen atom.

Table 4. Complexation of crown ethers 1-10 with $K[PtCl_3(C_2H_4)]$ in $CDCl_3$.

crown ether	1	2	3	4	5	6	7	8	9	10
percentage of complexation	100	100	100	100	26	23	0	51	28	—*

* Compound 10 reacted with Zeise's salt.

References and Notes

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- 2) Recently, π -complexation of crown compounds was indicated in the following reports; V. K. Frensch and F. Vögtle, *Tetrahedron Lett.*, 2573 (1977); H. F. Beckford, R. M. King, and J. F. Stoddart, *ibid.*, 171 (1978).
- 3) Para-phenylene crown compounds 7-9 are known; a) R. T. Gray, D. N. Reinhoudt, C. J. Smit, and Ms. I. Veenstra, *Recueil*, 95, 258 (1976); b) R. C. Helgeson, J. M. Timko, and D. J. Cram, *J. Am. Chem. Soc.*, 96, 7380 (1974); R. C. Helgeson, T. L. Tarnowski, J. M. Timko, and D. J. Cram, *ibid.*, 99, 6411 (1977).
- 4) The syntheses of these precursors will be described elsewhere.
- 5) NMR data of new crown ethers (see Tables 2 and 3 for 1 and 4) (δ value in $CDCl_3$, 100MHz); 2, 7.171(s, 4H, ArH), 3.730(t, 4H, $ArCH_2CH_2$), 3.581(s, 8H, OCH_2CH_2O), 3.502(A_2B_2m , 8H, OCH_2CH_2O), 2.823(t, 4H, $ArCH_2$); 3, 6.626(A_2B_2dd , 2H, ArH), 6.382(A_2B_2dd , 2H, ArH), 6.078(s, 2H, ArH), 3.551(t, 4H, $ArCH_2CH_2$), 3.377(s, 8H, OCH_2CH_2O), 3.127(s, 4H, OCH_2CH_2O), 3.04-2.38(m, 12H, $ArCH_2$); 5, 7.152(s, 4H, ArH), 3.514(s, 4H, OCH_2CH_2O), 3.510(s, 8H, OCH_2CH_2O), 3.377(t, 4H, $ArCH_2CH_2CH_2$), 2.79-2.66(m, 4H, $ArCH_2$), 2.09-1.77(m, 4H, $ArCH_2CH_2CH_2$); 6, 7.164(s, 4H, ArH), 3.625(A_2B_2m , 8H, OCH_2CH_2O), 3.544(s, 8H, OCH_2CH_2O), 3.358(t, 4H, $ArCH_2CH_2CH_2$), 2.733(t, 4H, $ArCH_2$), 1.865(quin, 4H, $ArCH_2CH_2CH_2$); 10(60MHz), 7.16(s, 4H, ArH), 3.38(t, 4H, SCH_2CH_2O), 3.36(s, 4H, OCH_2CH_2O), 2.85(s, 8H, $ArCH_2CH_2S$), 2.17(t, 4H, SCH_2CH_2O).
- 6) R. N. Greene, *Tetrahedron Lett.*, 1793 (1972).
- 7) R. T. Gray and D. N. Reinhoudt, *Tetrahedron Lett.*, 2109 (1975).
- 8) A treatment of 10 with Zeise's salt did not permit an exact evaluation of complexation. The weak complexing ability of 10 was demonstrated by NMR shift experiments with alkali thiocyanate salts.

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