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Bis- and Oligo(benzocrown ether)s

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Contents

1. Introduction

Since Pedersen reported the synthesis and complexing properties of the crown ethers,[1] there has been increasing interest in the crown compounds as complexing agents for various cations and anions.[2] These complexing agents have found application in many areas.[3] Different kinds of crown ligands have been synthesized in order to find molecules with superior properties and proper application in various areas, including the lariat ethers,[4] bis(crown ether)s,[5] azacrown ethers,[6] molecular threads,[7] cryptands,[8] macropolycyclic polyethers,[9] and other preorganized macromolecules.[10]

Smid and co-workers[11,12] first reported sandwich-type complexes of crown ethers with metal cations. They connected two crown units together to provide bis(crown ether)s which had attractive cation-binding properties. Since then, an extensive number of bis(crown ether)s have been synthesized. They have applications in various areas especially in ion-selective electrodes.[3h,13-19] By the cooperative action of two adjacent crown units, bis(crown ether) derivatives tend to form stronger complexes with particular metal ions than the corresponding monocrown ethers. Cooperativity of the two crown units in bis(crown ether)s has been observed in their binuclear complexes.[20] Photoresponsive[21-23] and cyanine dye-containing[24-26] bis(crown ether) derivatives were also studied. Diloop[27] and spiro[28,29] bis(crown ether)s have been prepared to study their particular properties. Tris(crown ether)s,[30,31] porphyrin- and phthalocyanine-bridged[32,33] tetrakis(crown ether)s, and higher oligomers[34] have also been synthesized for certain applications.

The applications of bis(crown ether)s in ion-selective electrodes have been briefly reviewed by several authors,[3h,14-19] and the syntheses of bis(crown ether)s have been briefly described in other reviews.[5,6,35-38] However, no comprehensive review for bis- and oligo(crown ether)s has been published. From time to time, the same research results have been reported in two or more laboratories, especially where results are published in different countries and languages. Therefore, it is appropiate to review this area of crown ether chemistry. In this review, particular effort has been made to include literature from the People's Republic of China, Japan, Europe, and the former USSR. Nearly 300 references in this review were obtained from over 100 different journals, patents, and books.

This review covers the synthesis of all bis- and oligo(benzocrown ether) derivatives, including various bis(benzocrown ether)s, tris-, tetrakis-, and octakis(benzocrown ether)s up to early 1993. A listing of these bis- and oligo(benzocrown ether)s and a brief report on some of their properties are also included. We have also included the porphyrin- and phthalocyanine-bridged oligo(benzocrown ether) derivatives, but multiporphyrins and phthalocyanines are not included. Aliphatic and nitrogen-containing bis- and oligo(crown ether)s without aromatic rings, bis-paracyclophanes, cyclodextrin-containing crown ethers, macrotricyclic quaternary ammonium salts connected with ethers or their dimers, crowned arborols, and polymer-containing crown units are not part of this review.

Two benzocrown units connected together by various bridges or chains form the bis(benzocrown ether) derivatives. Different benzocrown units give different kinds of bis(benzocrown ether)s, including bis(benzo-12-crown-4), bis(benzo-15-crown-5), bis(benzo-18-crown-6), and bis(benzo-21-crown-7) derivatives. Since benzo-15-crown-5 is cheap and easily made, the bis(benzo-15-crown-5) derivatives are the more numereous of the bis(benzocrown ether)s. The 4′-position of the benzene ring of the benzocrown ethers is the most reactive position for electrophilic aromatic substitution, therefore, most derivatives are connected at the 4′-position forming bis(4′-benzocrown ether) derivatives. The "4′" will be omitted in most situations. Bis(benzocrown ether)s can be classified as symmetric and asymmetric. The former contains two identical crown moieties with

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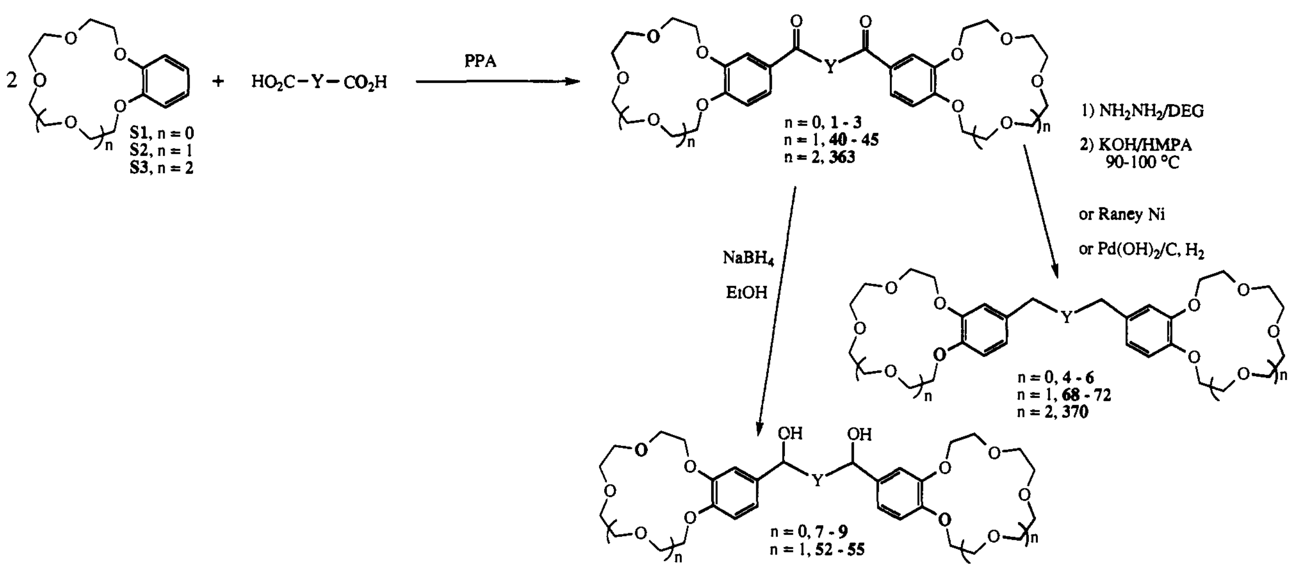
symmetric or asymmetric bridges, while the latter contains two different crown moieties with symmetric or asymmetric bridges. Sections 2–5 describe symmetric bis(benzocrown ether)s and the asymmetric ones will be discussed in section 6.

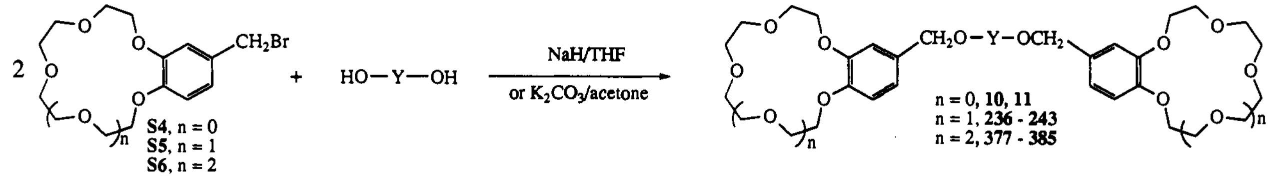
2. Bis(benzo-12-crown-4) Derivatives

Bis(crown ether)s with benzo-12-crown-4 moieties form stable sandwich complexes with Na^+. Some of them were used to prepare sodium ion-selective elec-

Scheme 1. Procedure A[39,59–61,80]



Scheme 2. Procedure B[42,118,153,155,156]



trodes and they exhibit good Na^+ selectivities. Ion-selective electrodes with high selectivities for certain metal cations have been the goal of many scientists. In this regard, new ligands have been developed by changing the rigidity, length, and bond type of the connecting organic moiety in bis(benzo-12-crown-4) derivatives (see Table 1).

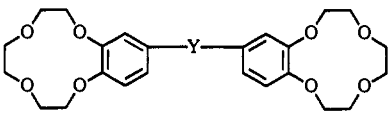
Huang and co-workers[39] reported the synthesis of a series of bis(benzo-12-crown-4) derivatives containing alkanedioyl, polymethylene, and α,α'-dihydroxypolymethylene bridges (Scheme 1, procedure A). Acylation of alkanedioic acids [$HO_2C(CH_2)_mCO_2H$, $m = 6, 7, 8$] onto benzo-12-crown-4 (**S1**) using polyphosphoric acid (PPA) as a catalyst gave alkanedioyl-bridged bis(benzo-12-crown-4)s **1–3**. The corresponding polymethylene- and α,α'-dihydroxypolymethylene-bridged bis(benzocrown ether)s (**4–6**, **7–9**, respectively) were obtained from **1–3** by the modified Huang Minlon reduction and by reduction with $NaBH_4$ in ethanol, respectively. These are very simple methods for the preparation of these types of bis(benzocrown ether)s and the modified Huang Minlon reduction was first used in crown ether chemistry. Sodium ion-selective electrodes were prepared on the basis of biscrowns **1–6** as the neutral carriers.[40] The relationship between the structure of the bis(crown ether)s and solution pH, type of plasticizers, and electrode performance were investigated. Sodium ion-selective electrodes were also prepared by coating a carbon rod with an NaCl-saturated THF solution containing biscrown **4**.[41] This electrode required no internal reference electrode. This is a convenient and low-cost method to prepare a sodium ion-selective electrode.

Bis(benzo-12-crown-4)s **10** and **11** with ethereal linkages were reported by Wong and co-worker (Scheme 2, procedure B).[42] 4′-(Bromomethyl)benzo-12-crown-4 (**S4**), obtained from the corresponding methyl derivative, was reacted with the appropriate oligoethylene glycols in THF using sodium hydride as the base to give bis(benzo-12-crown-4) derivatives **10** and **11**. Complexation between alkali metal picrate salts and these bis(crown ether)s was investigated by UV–visible spectroscopy.[43] Because of the small ring size of the benzo-12-crown-4 moiety, Na^+ and K^+ ions could not be wrapped completely by these bis(crown ether)s. Therefore, bis(crown ether)s **10** and **11** form V-shaped sandwich complexes (metal ion/crown unit: 1/2) with Na^+ and K^+ ions. The extraction efficiencies from an aqueous phase into chloroform by **10** and **11** are much greater than those by the corresponding monomeric crown ethers.

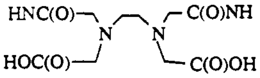
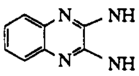
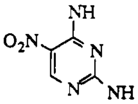
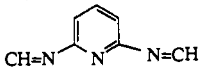
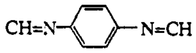
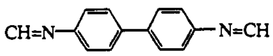
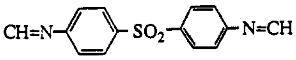
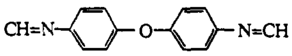
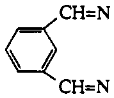
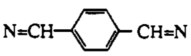
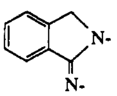
Photoresponsive azobis(benzo-12-crown-4) (**12**) was synthesized by a self-condensation reduction of two molecules of 4′-nitrobenzo-12-crown-4 (**S7**) using powdered zinc and potassium hydroxide as the catalyst (Scheme 3, procedure C).[22] However, the corresponding photoresponsive azoxybis(benzocrown ether) (**13**) was obtained by using powdered zinc as the catalyst in the presence of an electron-transfer agent (a polymer containing benzylpyridinium chloride) (Scheme 3, procedure D).[44] The photoisomerization and thermal isomerization of these biscrowns were studied.[22,23,44]

Amide-containing bis(benzo-12-crown-4) derivatives **14–16** (see Table 1) were synthesized by acylation of 4′-aminobenzo-12-crown-4 (**S10**), obtained by the reduction of **S7**, with the appropriate diacid dichlorides (Scheme 4, procedure E)[45,46] or EDTA dianhydride (procedure F).[47] Solvent extraction of alkali metal picrates with bis(crown ether) **14** was studied.[45] With two carboxyl groups on the bridge, biscrown **16** is water soluble, therefore its complexing properties can be studied in water. Quinoxaline- and pyrimidine-bridged

Table 1. Bis(benzo-12-crown-4) Derivatives

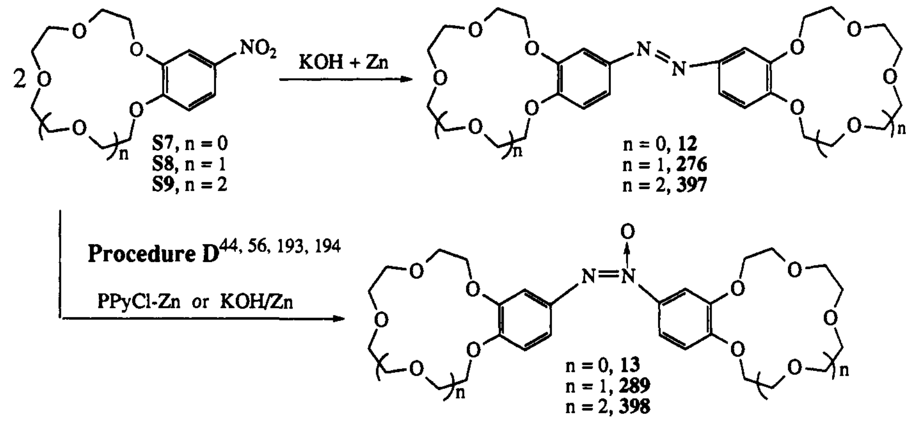


1 - 35

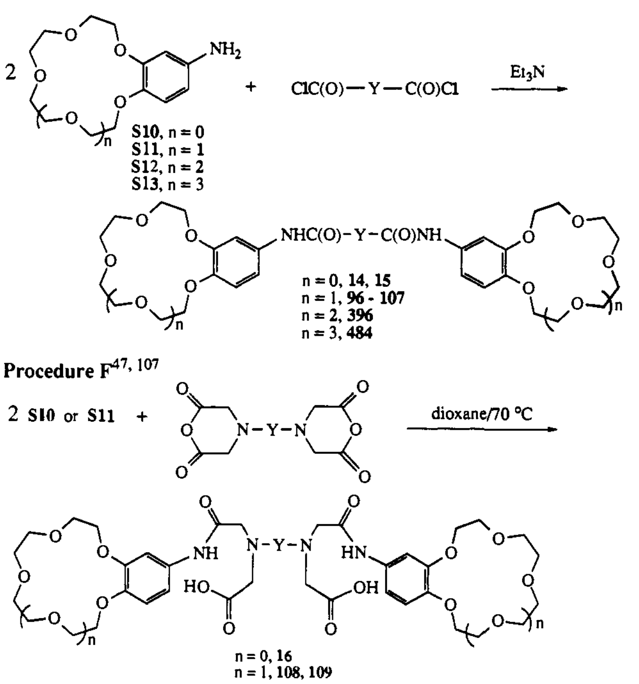
no.	remarks (Y =)	mp, °C	yield, %	procedure	ref.
1	$C(O)(CH_2)_6C(O)$	113–113.5	65	A	39
2	$C(O)(CH_2)_7C(O)$	81–81.5	55	A	39
3	$C(O)(CH_2)_8C(O)$	89–90	60	A	39
4	$CH_2(CH_2)_6CH_2$	79	85	A	39
5	$CH_2(CH_2)_7CH_2$	61	80	A	39
6	$CH_2(CH_2)_8CH_2$	80	83	A	39
7	$CH(OH)(CH_2)_6CH(OH)$	120–121	90	A	39
8	$CH(OH)(CH_2)_7CH(OH)$	88–89	88	A	39
9	$CH(OH)(CH_2)_8CH(OH)$	70	80	A	39
10	$CH_2O(CH_2CH_2O)_2CH_2$	oil	20	B	42
11	$CH_2O(CH_2CH_2O)_3CH_2$	oil	25	B	42
12	$N{=}N$	149–150	10.9[a]	C	22
13	$N{=}N(O)$	118–120	58	D	44
14	$NHC(O)(CH_2)_3C(O)NH$	170–171		E	45
15				E	46
16		139–140.5	30.1[a]	F	47
17		136–137	45	G	48
18		165–167	64	G	49
19	$CH{=}N(CH_2)_3N{=}CH$	113		H	50
20	$CH{=}N(CH_2)_4N{=}CH$	108		H	50
21	$CH{=}N(CH_2)_5N{=}CH$	111		H	50
22	$CH{=}N(CH_2)_6N{=}CH$	103		H	50
23	$CH{=}N(CH_2)_7N{=}CH$	69		H	50
24	$CH{=}N(CH_2)_6N{=}CH$	92		H	50
25	$CH{=}N(CH_2)_9N{=}CH$	78		H	50
26	$CH{=}N(CH_2)_{10}N{=}CH$	95		H	50
27	$CH{=}N(CH_2)_{12}N{=}CH$	84		H	50
28		230–232	66	H	51
29		229–231	90	H	51
30		278–280	90	H	51
31		124–126	81	H	51
32		145–146	62	H	51
33		120–121	40	I	52
34		194–195	80.2	I	52
35		115–117	31	I	52
36	$C\equiv C$	115–117	77	J	53
37	CH_2CH_2	113.1–115.1	81	J	53
38	$CH{=}N$	194–197	40	K	54

[a] Overall yield.

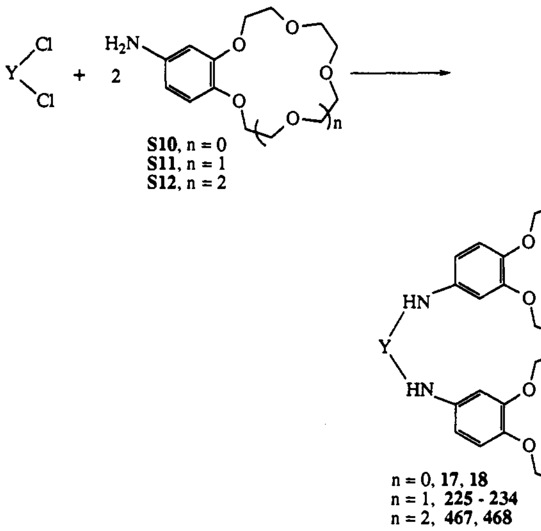
Scheme 3. Procedures C[21,22,180–182] and D[44,56,193,194]



Scheme 4. Procedures E[45,46,101–105,213,214] and F[47,107]



Scheme 5. Procedure G[48,49,142–147,224]



bis(benzo-12-crown-4)s 17 and 18 were synthesized by the reaction of S10 with 2,3-dichloroquinoxaline and 2,4-dichloro-5-nitropyrimidine (Scheme 5, procedure G).[48,49] Conductance studies showed that 17 formed a sandwich complex with Na^+ ions.[48] Its extraction properties were also studied.

Schiff base-containing bis(benzo-12-crown-4) derivatives 19–32 (Table 1) were synthesized by the condensation of 4′-formylbenzo-12-crown-4 (S14) with the corresponding α,ω-diaminoalkanes[50] or appropriate aromatic diamines[51] (Scheme 6, procedure H). The interaction of biscrowns 19–27 with alkali metal cations was investigated by a spectroscopic technique and by solvent extraction.[50] Biscrowns 28–32 were reported to be useful for the preparation of ion-selective electrodes and as drug intermediates.[51] Wang and coworkers[52] reported the synthesis of another series of Schiff base-containing bis(benzo-12-crown-4) derivatives (33–35) (Scheme 6, procedure I). Biscrowns 33 and 34 were synthesized by the treatment of 4′-aminobenzo-12-crown-4 (S10) with *m*-phthalic dialdehyde and terephthalic dialdehyde, respectively. Biscrowns 35 and 286 (Table 8) were obtained by the condensation of *o*-phthalic dialdehyde with S10 and 4′-aminobenzo-15-crown-5 (S11), respectively.[52] Sodium ion-selective electrodes based on bis(crown ether)s 33–35 were studied, and the potentiometric selectivity coefficients for the alkali and alkaline earth metal cations were measured.

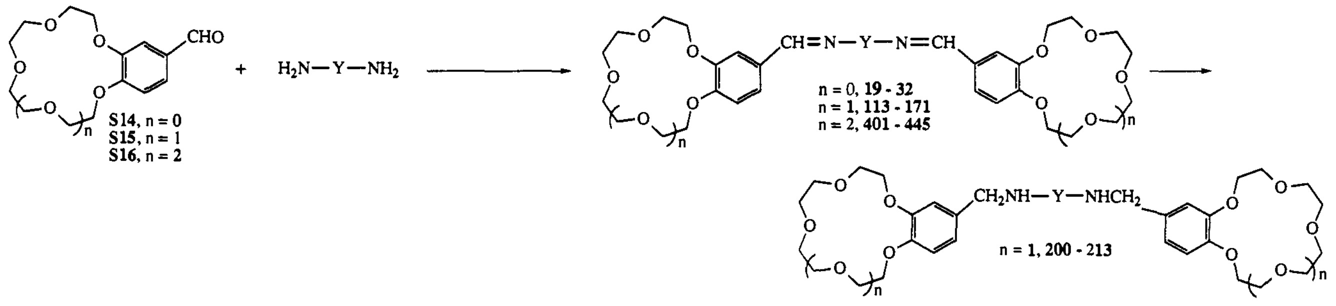
All of the methods described above can only be used for the preparation of symmetric bis(benzocrown ether)s which contain two identical crown moieties. The following two methods can be used to prepare either symmetric or asymmetric bis(benzocrown ether)s (see section 6). 4′-Iodobenzo-12-crown-4 (S17) was treated with 4′-acetylenylbenzo-12-crown-4 (S21) using CuI/$(Ph_3P)_2PdCl_2$ as the catalyst to give bis(benzo-12-crown-4-yl)acetylene (36) which was then reduced to bis(benzo-12-crown-4-yl)ethane (37) (Scheme 7, procedure J).[53] Bis(benzocrown ether) 38 was synthesized by the condensation of 4′-aminobenzo-12-crown-4 (S10) and 4′-formylbenzo-12-crown-4 (S14) (Scheme 8, procedure K).[54]

3. Bis(benzo-15-crown-5) Derivatives

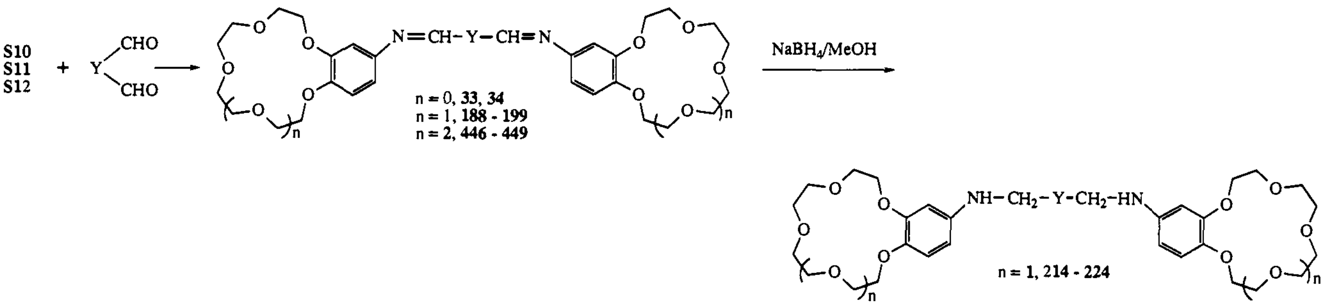
Bis(benzo-15-crown-5) derivatives are the biscrowns containing two identical benzo-15-crown-5 moieties with symmetric or asymmetric bridges. As mentioned above, bis(benzo-15-crown-5) derivatives have been synthesized containing various bridges including ketone-, alcohol-, alkene-, alkyne-, and polymethylene-contain-

Scheme 6. Procedures H[50,51,114-124,140] and I[52,134-136,141,226]

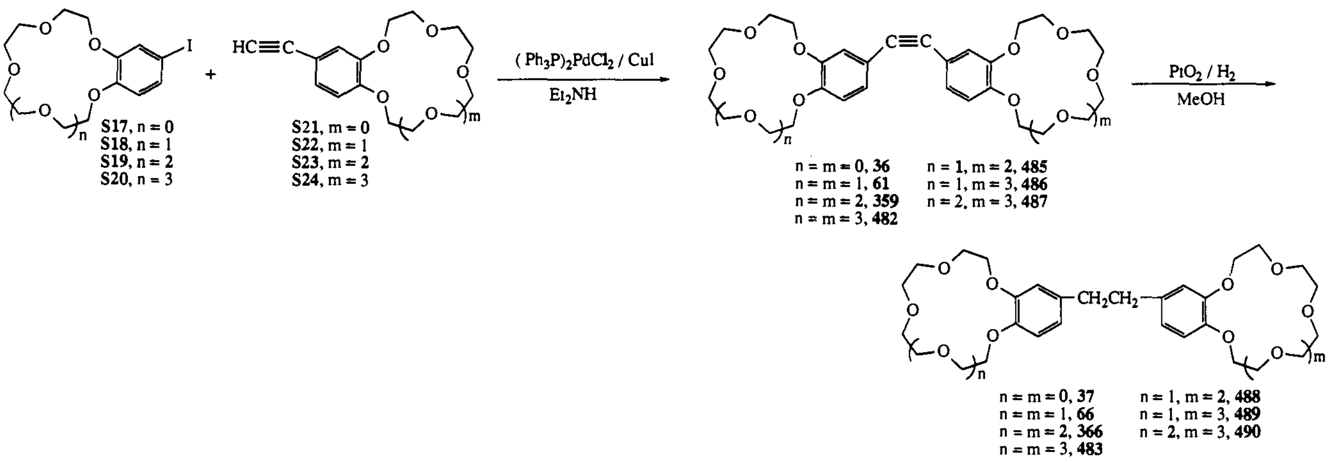
Procedure H[50, 51, 114-124, 140]



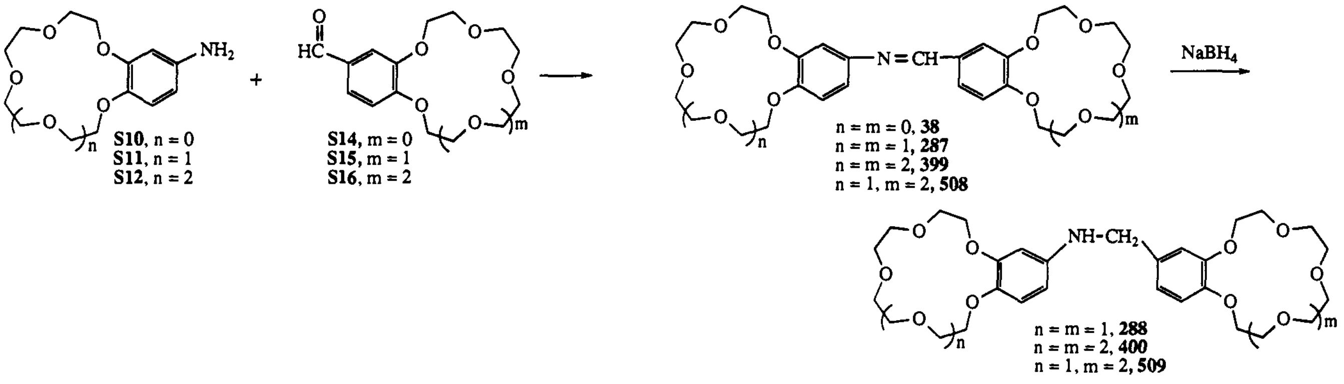
Procedure I[52, 134-136, 141, 226]



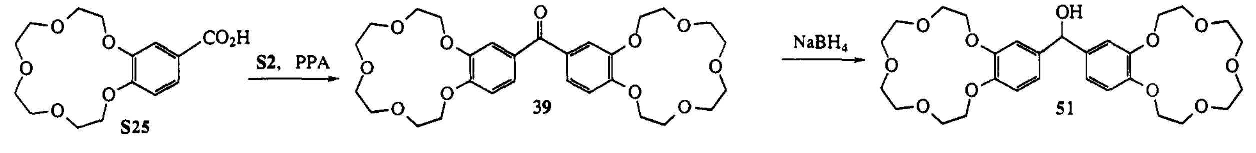
Scheme 7. Procedure J[53,80]



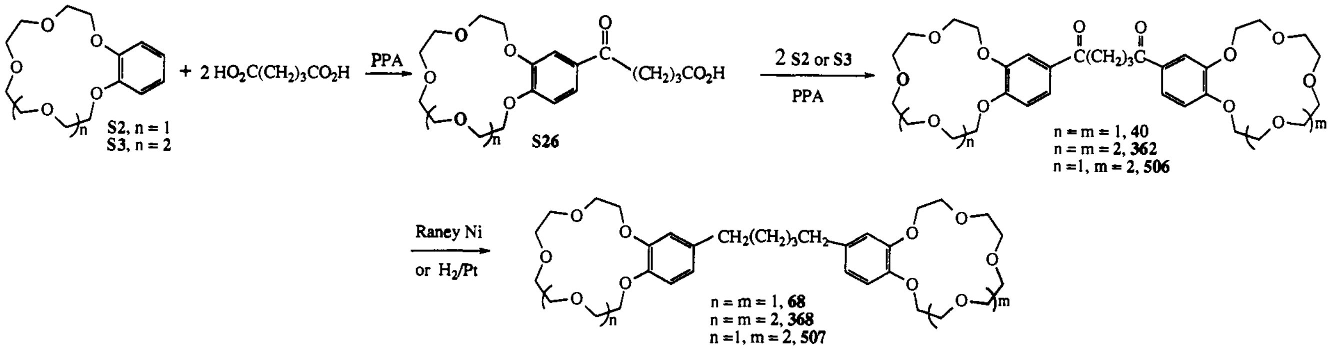
Scheme 8. Procedure K[54,56,223]



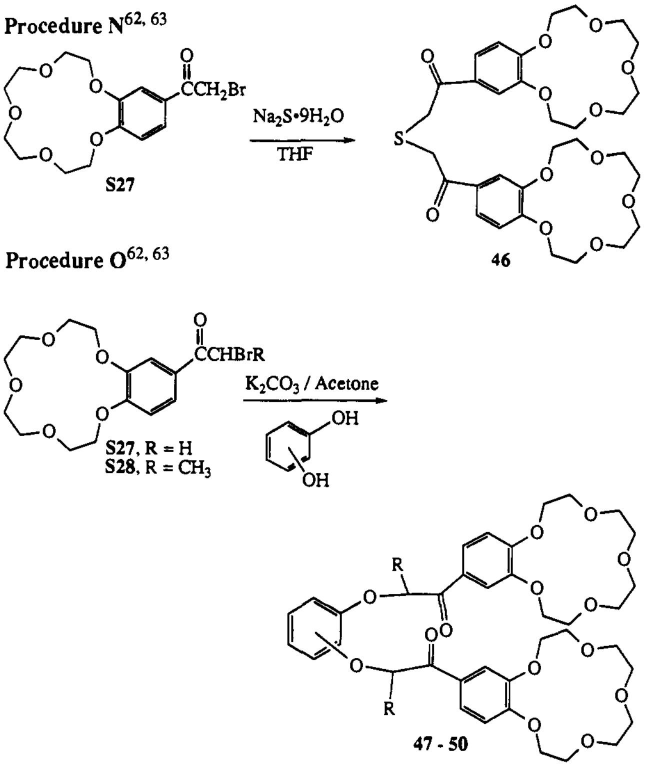
Scheme 9. Procedure L[55-58]



Scheme 10. Procedure M[60]



Scheme 11. Procedures N[62,63] and O[62,63]



ing bridges (Table 2); ester-, keto ester-, and amide-containing bridges (Table 3); Schiff base-containing bridges (Table 4); diamine-containing bridges (Table 5); ether-containing bridges (Table 6); and miscellaneous bridges (Table 7). Bis(benzo-15-crown-5) derivatives containing asymmetric bridges and other substituents on benzene rings are listed in Tables 8 and 9, respectively.

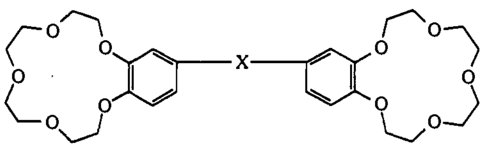
Bis(benzo-15-crown-5)-containing ketone **39** was synthesized by acylation of benzo-15-crown-5 (**S2**) with 4′-carboxybenzo-15-crown-5 (**S25**) using polyphosphoric acid (PPA) (Scheme 9, procedure L).[55-58] The reduction of **39** by $NaBH_4$ gave bis(benzo-15-crown-5)carbinol (**51**).[58] Biscrown **39** formed a complex with Na^+.[55] Sodium ion-selective electrodes prepared from **39** and the photophysical behavior of **39** were studied.[56,57]

Diketo-containing bis(benzo-15-crown-5) derivatives **40–45** were synthesized by the treatment of **S2** with the appropriate dicarboxylic acids (Scheme 1, procedure A).[59-61] Another method for the preparation of **40** was reported (Scheme 10, procedure M).[60] Benzo-15-crown-5 (**S2**) was reacted with an excess of glutaric acid to give **S26** which was then reacted with an excess of **S2** to give diketo-containing biscrown **40**. This method can be used for the preparation of symmetric and asymmetric bis(benzocrown ether)s. However, for the preparation of symmetric bis(benzocrown ether)s, procedure A is the best method. Using glutaric anhydride instead of glutaric acid in the preparation of **S26** could improve the yield and aid in the purification of the product.

Reduction of diketo-containing bis(benzocrown ether)s **40** and **42–44** by $NaBH_4$ produced the corresponding *α,α′*-dihydroxypolymethylene-containing bis(benzocrown ether)s **52–55** (Scheme 1, procedure A).[59] Diketo-containing bis(benzocrown ether)s **40** and **42–45** were also reduced to the corresponding polymethylene-bridged bis(benzocrown ether)s **68–72** by Raney Ni or by hydrogenation with $Pd(OH)_2/C$ as the catalyst.[59,60] The hydrogenation method gave higher yields than Raney Ni (Scheme 1, Table 2). Wu and co-workers[62,63] chose 4′-(*α*-bromoalkanoyl)benzo-15-crown-5 (**S27** and **S28**) as starting materials for the preparation of diketo-containing bis(benzocrown ether)s (Scheme 11). Biscrown **46** was synthesized by coupling (bromoacetyl)benzocrown ether **S27** with Na_2S (Scheme 11, procedure N).[62,63] The aromatic ring-containing bridged bis(benzocrown ether)s **47–50** were prepared by the reaction of (bromoacyl)crown ether **S27** or **S28** with catechol, resorcinol, or hydroquinone using K_2CO_3 as the base and starting crown ether as the phase-transfer catalyst (Scheme 11, procedure N).[62,63]

Complexation between bis(crown ether)s **40**, **42–44**, **52–55**, and **68–71** and alkali metal picrates was studied by optical spectrometry.[64] The results indicated that all of these biscrowns formed sandwich complexes with K^+, Rb^+, and Cs^+. The order of the complexing ability of the biscrowns and the alkali cations are alcohol-bridged > alkane-bridged > ketone-bridged biscrowns and $K^+ > Rb^+ > Cs^+$, respectively. The complexation properties of octanedioyl-bridged bis(benzo-15-crown-5) (**42**) and octamethylenyl-bridged bis(benzo-15-crown-5) (**69**) with rare earth elements (Nd^{3+}, Eu^{3+}, Eu^{2+}, Dy^{3+}, Er^{3+}, and Yb^{3+}) were studied.[65-67] Potassium ion-selective PVC membrane electrodes based on biscrowns **40**, **42–44**, **52–55**, and **68–71** were prepared and their characteristics were investigated.[68-70] The response performance of the electrodes indicated that alkane- and ketone-bridged biscrowns with long carbon connecting chains are acceptable as the neutral carrier for K^+-selective electrodes. Tl^+ and K^+ ion-selective electrodes were developed by coating PVC membranes containing biscrowns **68** and **69**, respectively, on graphite rods.[71,72] Selectivity coefficients of ion-selec-

Table 2. Bis(benzo-15-crown-5) Derivatives Containing Ketonic, Alcoholic, Alkenyl, Alkynyl, and Alkanyl Bridges



39 - 72

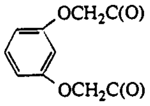
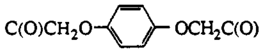
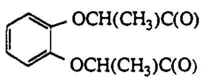
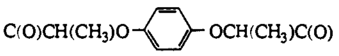
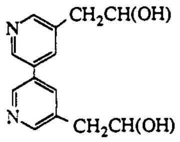
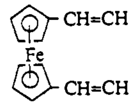
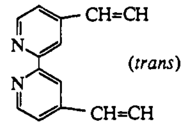
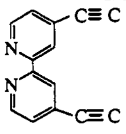
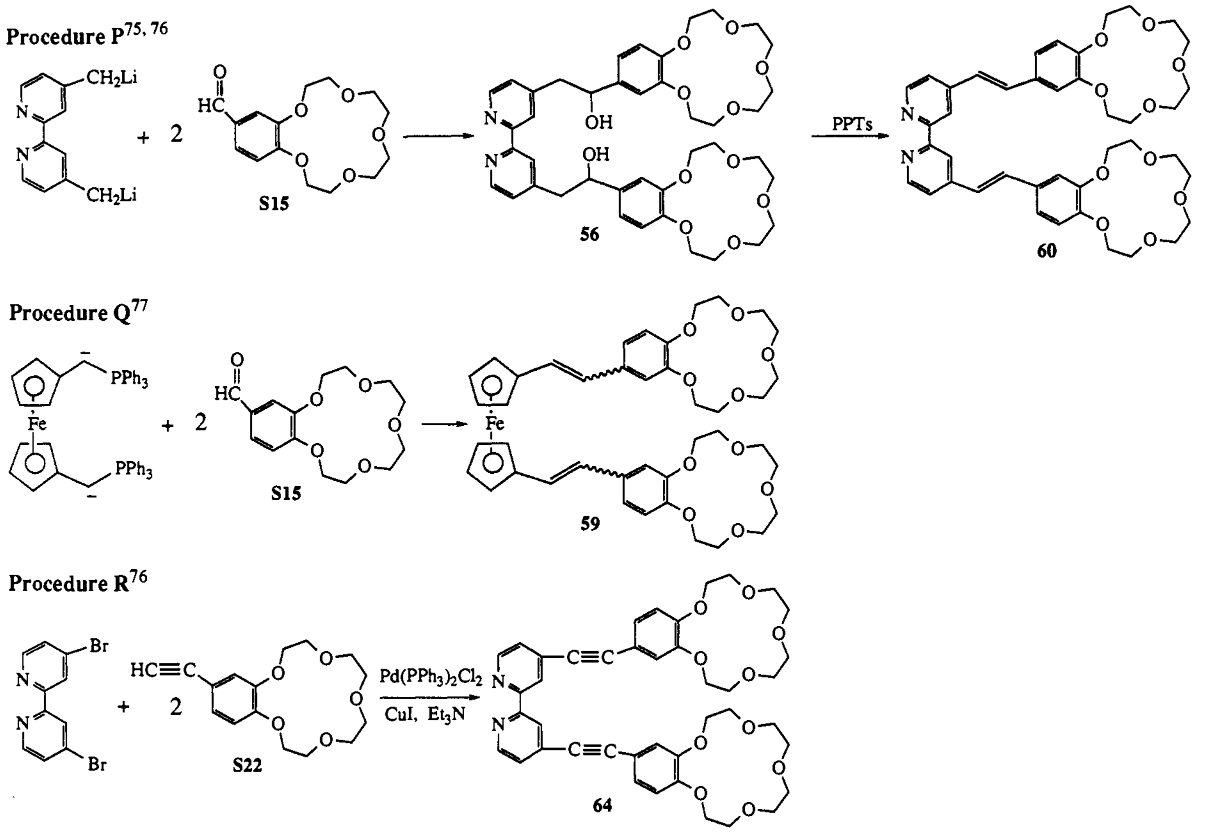
no.	remarks (X =)	mp, °C	yield, %	procedure	ref(s)
39	C(O)	143.5–144.5	92–93	L	55,56
		143–144	36	L	57
		142–143	86.5	L	58
40	$C(O)(CH_2)_3C(O)$	133–134	51.4	A	59
		124–126	25	A	60
		124–126	63	M	60
41	$C(O)(CH_2)_4C(O)$	142–144	37	A	61
42	$C(O)(CH_2)_6C(O)$	137–138	73.1	A	59
43	$C(O)(CH_2)_7C(O)$	116.5–117	58.4	A	59
44	$C(O)(CH_2)_8C(O)$	122–123	64.1	A	59
		120–121	40	A	61
45	$C(O)(CH_2)_{11}C(O)$	93–95	31	A	60
46	$C(O)CH_2SCH_2C(O)$	178–180	75	N	62,63
47		142–143	45	O	62,63
48		162–163	45	O	62,63
49		144–145	49	O	62,63
50		177–178	54	O	62–63
51	CH(OH)	101–103	44.1		58
52	$CH(OH)(CH_2)_3CH(OH)$	136–138	79.5	A	59
53	$CH(OH)(CH_2)_6CH(OH)$	105–106	89.5	A	59
54	$CH(OH)(CH_2)_7CH(OH)$	109–111	84.6	A	59
55	$CH(OH)(CH_2)_8CH(OH)$	102–103	89.4	A	59
56				P	75
57	CH═CH (*E*)	190–192	26	S	79
58	CH═CH (*Z*)	oil	86		79
59		153–154	55	Q	77
60		219–220	70–95	P	75,76
61	C≡C	125.4–127	98	J	53
		129.1–130.8	98	T	53
		125.4–127	98	T	80
62	$C{\equiv}C(CH_2)_2C{\equiv}C$	172.7–174.5	71	U	53
63	$C{\equiv}C(CH_2)_4C{\equiv}C$	108.5–110.7	88	U	80
64		224–225	85	R	76
65	CH_2	105.5–106.5	4–9.1	V	82
66	CH_2CH_2	114–115	69	S	79
		106.5–108.7	75	T	80
		106.7–108.7	75	J	53
67	$(CH_2)_3$	83–84	43	YY	60

Table 2 (Continued)

no.	remarks (X =)	mp, °C	yield, %	procedure	ref(s)
68	$(CH_2)_6$	86–88	55.8	A	59
		86–87	70.8	A	59
		68–72	18	A	60
69	$(CH_2)_8$	97.1–99.9	76	U	80
		98–99	66	A	59
		98–99	80.5	A	59
70	$(CH_2)_9$	90–91	66.1	A	59
		91–92	79.4	A	59
71	$(CH_2)_{10}$	95–96	61.9	A	59
		96–97	74.4	A	59
72	$(CH_2)_{13}$	93–96	42	A	60

Scheme 12. Procedures P,[75,76] Q,[77] and R[76]

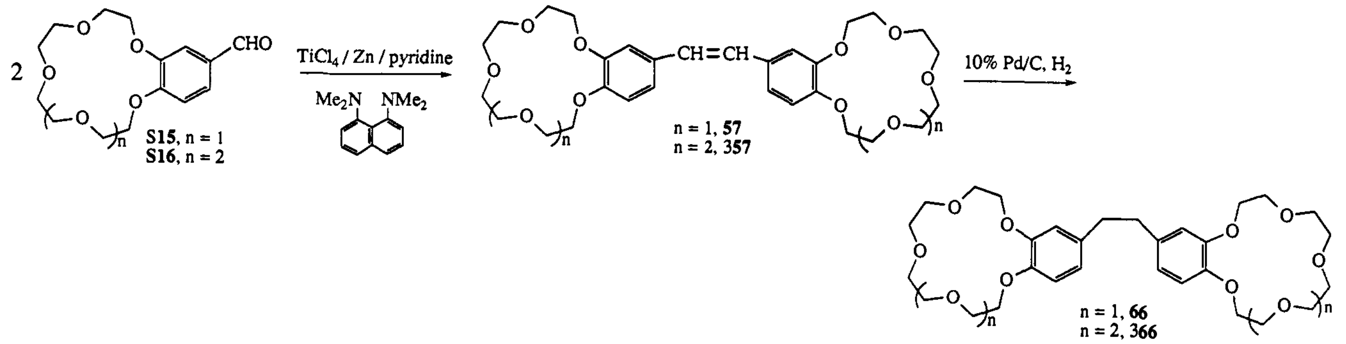


tive electrodes with biscrowns as neutral carriers were determined.[73] Biscrowns 47–50 were also used for the preparation of K^+ ion-selective electrodes.[63,74] Studies indicated that selectivity coefficients for many of these new electrodes were better than those of electrodes based on natural valinomycin. Luboch and co-workers[60] concluded from their electrode studies that the biscrown with a trimethylene bridge, e.g. 67 (its preparation will be discussed later), exhibited the best selectivity and that electrodes based on ketone-containing biscrowns deteriorated in a short time.

Beer and co-workers[75–78] reported bis(benzo-15-crown-5) derivatives with bipyridine and ferrocene bridges. The dilithium derivative of 4,4′-dimethyl-2,2′-bipyridine was treated with 2 mol of formyl-substituted crown **S15** to give alcohol-containing biscrown **56** (Scheme 12, procedure P).[75] *trans*-Biscrown **60** was obtained by dehydration of **56**.[75,76] Ferrocene bis-ylide was treated with 2 mol of **S15** to give ferrocene-bridged biscrown **59** as a *cis–trans* mixture (procedure Q).[77] The reaction of 4,4′-dibromo-2,2′-bipyridine with 2 mol of ethynyl-substituted crown **S22** in the presence of $Pd(PPh_3)_2Cl_2$ and CuI gave bipyridylbisalkynyl-bridged biscrown **64** (procedure R).[76] Fluorescence emission spectrometry and electopolymerization of biscrowns **60** and **64** were studied.[75,76] The results indicated that polymer films made from these biscrowns represent a new class of spectrochemical sensing devices for group IA and IIA metal cations. Cyclic voltammetry of biscrown **60** and its Ru(II) complex was also determined.[78] Ferrocene-bridged biscrown **59** selectively complexed, electrochemically recognized, and responded to K^+ in the presence of equimolar amounts of Na^+ and Mg^{2+} ions.[77]

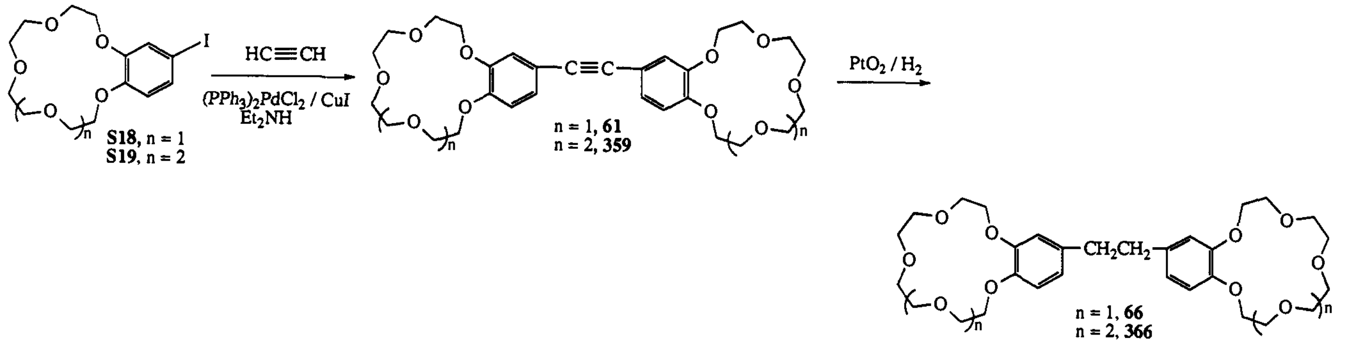
trans-Stilbene-containing bis(crown ether) **57** was synthesized by reductive coupling of formyl-substituted crown **S15** using $TiCl_4$ and Zn as the catalysts in the presence of a proton sponge, *N,N,N′,N′*-tetramethyl-1,8-diaminonaphthalene (Scheme 13, procedure S).[79] Irradiation of *trans*-biscrown **57** by UV light (300 nm, Rayonet reactor) produced a mixture of *trans*- and *cis*-isomers (**57** and **58**) which consisted of 85% *cis*-isomer and 13% *trans*-isomer. *Cis*-isomer **58** was obtained by recrystallization of the isomeric mixture. Pure *cis*-

Scheme 13. Procedure S[79]

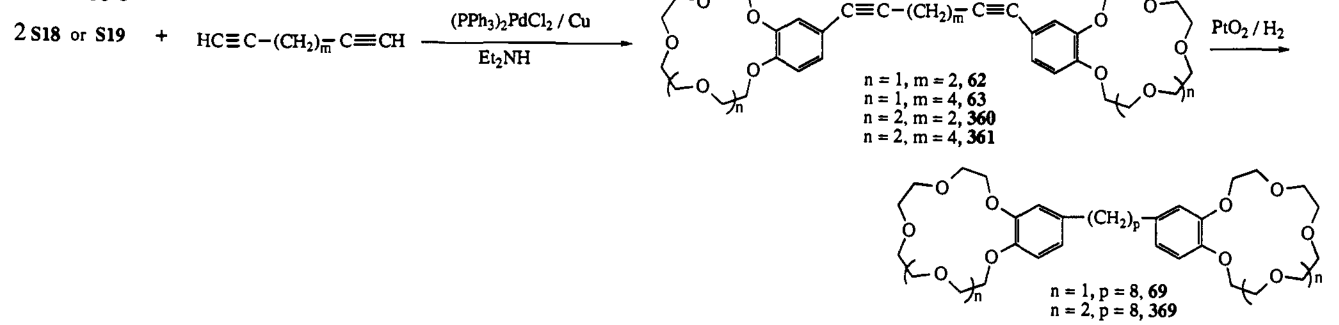


Scheme 14. Procedures T[53,80] and U[53,80]

Procedure T[53, 80]



Procedure U[53, 80]



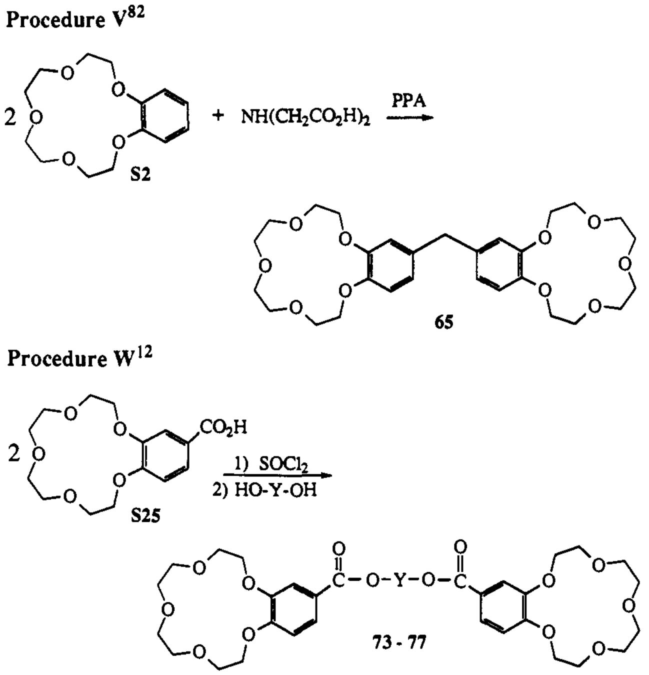
isomer **58** was irradiated to give the same photostationary state as obtained in the initial reaction. Catalytic hydrogenation with Pd on charcoal in glacial acetic acid gave dimethylene-bridged biscrown **66**. Complexation properties of these biscrowns with the alkali metal cations were also studies.[79]

Kikukawa and co-workers[53,80] reported the preparation of alkyne-bridged biscrowns **61–63**. Bis(benzo-15-crown-5-yl)acetylene **61** was synthesized by two methods. Iodocrown **S18** was treated with acetylene-substituted crown **S22** using $(Ph_3P)_2PdCl_2/CuI$ as the catalyst to give biscrown **61** (Scheme 7, procedure J).[53] Two molecules of iodocrown **S18** were reacted with acetylene under the same conditions to also give biscrown **61** (Scheme 14, procedure T).[53,80] Alkadiyne-bridged biscrowns **62** and **63** were synthesized similarly by the reaction of iodocrown **S18** with 1,5-hexadiyne and 1,7-octadiyne, respectively (procedure U).[53,80] Hydrogenation of **61** and **63** using PtO_2 as the catalyst produced the corresponding alkane-bridged biscrowns **66** and **69**, respectively (Scheme 7, procedure J, and Scheme 14, procedure U).[53,80] Biscrowns **66** and **69** selectively extracted K^+ from aqueous solutions.[81]

Huang and co-worker[82] reported the synthesis of methylene-bridged bis(benzo-15-crown-5) (**65**) by an unusual reaction (Scheme 15, procedure V). Benzo-15-crown-5 (**S2**) was heated with *N,N*-aminodiacetic acid in PPA to form biscrown **65**. Using iminodiacetic acid, nitrilotriacetic acid, ethylenediaminetetraacetic acid, or diaminocyclohexanetetraacetic acid instead of aminodiacetic acid also gave the same biscrown. Other amino acids without the $N(CH_2COOH)_2$ group did not give **65**. The mechanism of this reaction was discussed.

Smid and co-workers[12] reported the series of ester-bridged bis(benzo-15-crown-5) derivatives **73–77** (Table 3). 4′-Carboxybenzocrown **S25** was first converted to its acyl chloride derivative using thionyl chloride. The acid chloride was treated with the appropriate diols or glycols to form bisester-bridged crowns **73–77** (Scheme 15, procedure W). Complexation of picrate salts by these biscrowns was investigated in THF as a function of the length and structure of the chain connecting the two crown moieties.[11,12] They formed sandwich-type complexes with K^+ and NH_4^+ cations. Complexes of biscrown **74** with five methylene groups in the bridge has the highest stabilities among biscrowns **73–75**. Replacing a CH_2 group by an oxygen atom (forming biscrown **76**) resulted in a 5-fold increase in the association constant.

Scheme 15. Procedures V[82] and W[12]



Kimura and co-workers[83-86] reported the synthesis of another series of ester-bridged biscrowns **78–89** (Table 3). Biscrowns **78** and **80–82** were synthesized by the reaction of 4′-(hydroxymethyl)benzo-15-crown-5 (**S29**) with the appropriate dicarboxy dichlorides (Scheme 16, procedure X).[83] Biscrowns **79** and **83–89** were synthesized by esterification of the appropriate dipotassium dicarboxylates with chloromethyl- or bromomethyl-substituted benzo-15-crown-5 (**S5**) (procedure Y). Starting crown **S5** also acted as a phase-transfer catalyst.[84-86] Potassium-selective PVC membrane electrodes using biscrowns **78**, **80–82**, and **86–89** as neutral carriers were prepared and the selectivity coefficients for various monovalent ions were measured.[83,85,87] Selectivity coefficients for K^+ over Na^+ and other interfering ions for biscrowns **81** and **86** were superior to those for the corresponding monocrowns and valinomycin.[83,85,87,88] Tl^+ ion-selective PVC membrane electrodes using biscrowns **80–82** were prepared.[89] Selectivity coefficients for various alkali and alkaline earth metal ions were good. These electrodes exhibited excellent electrode properties. Because biscrown **81**, containing five methylene groups between two crown moieties, showed excellent PVC membrane-selective electrode properties, it was also used for the studies of a coated wire potassium-selective electrode[90] and a PVC matrix membrane uranyl ion-selective electrode.[91] The potassium-selective electrode based on biscrown **81** was used for determination of K^+ in human urine or serum.[92,93] FTIR-ATR and extraction studies of liquid membranes containing biscrown **81** were also investigated.[94] Complexation and extraction properties of biscrowns **79**, **81**, **84**, and **85** were studied.[86,95,96] *cis*-Biscrown **84** formed sandwich complexes with certain metal cations, while the *trans*-biscrown isomer **85** formed 1:1 crown ether unit/cation complex.[86] Photoresponsive biscrown **90** was synthesized by the reaction of 4,4′-bis(chlorocarbonyl)azobenzene with 4′-(hydroxymethyl)benzo-15-crown-5 (**S29**) (procedure X).[97] Photocontrolled ion permeation through a PVC membrane containing **90** and the photoinduced potential changes in that membrane were studied.[97,98]

Bis(keto ester)-bridged bis(benzo-15-crown-5) derivatives **91–95** were synthesized by the reaction of 2 mol of α-(bromoacetyl)benzocrown **S27** with the appropriate potassium dicarboxylate (Scheme 17, procedure Z).[99] Extraction experiments of potassium picrate with biscrowns **91–95** indicated that all of these biscrowns form sandwich (2:1 crown unit/K^+) complexes.[100]

Bis(crown ether)s **96–107** containing various bisamide bridges were synthesized by the reaction of 2 mol of 4′-aminobenzo-15-crown-5 (**S11**) with the appropriate dicarboxylyl dichloride in the presence of triethyl amine (Scheme 4, procedure E, and Table 3).[46,101-106] Most of these biscrowns were obtained as solids with high melting points and in high yields. Water-soluble biscrowns **108** and **109** were prepared by the acylation of 4′-aminobenzo-15-crown-5 (**S11**) with the EDTA or EGTA dianhydrides (Scheme 4, procedure F).[47,107] 4′-Carboxylbenzo-15-crown-5 (**S25**) was first converted into its acid chloride and then treated with 1,4-bis(3-aminopropyl)piperazine and 5,15-bis(2-aminophenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin to give biscrowns **110**[108] and **111**[109] (Scheme 17, procedure AA). *o*-Phenylenediamine was acylated by an excess of 4′-(chlorosulfonyl)benzo-15-crown-5 (**S31**) to give biscrown **112** (procedure BB).[110]

A potassium-selective PVC membrane electrode using biscrown **96** was studied.[83] Solvent extraction of alkali, alkaline earth, silver, and thallium picrates by biscrown **96** was studied in a water–chloroform system.[101,111-113]

Scheme 16. Procedures X[83,88,90,97,219] and Y[84-86,220]

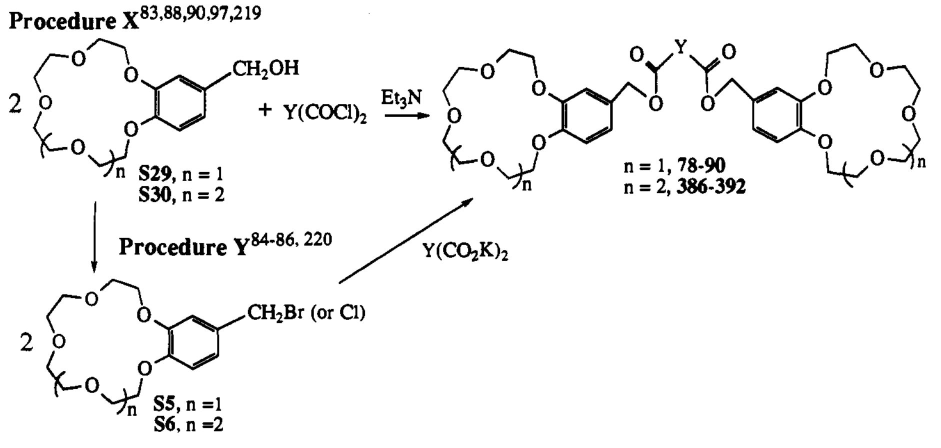
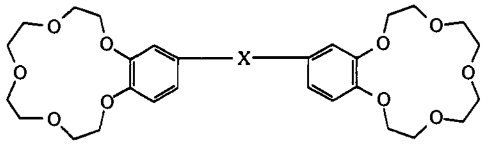


Table 3. Bis(benzo-15-crown-5) Derivatives Containing Ester, Keto Ester, and Amide Bridges



73–112

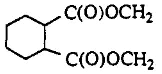
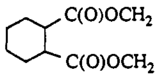
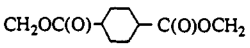
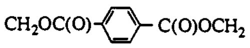
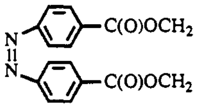
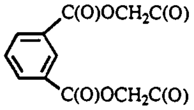
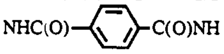
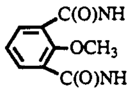
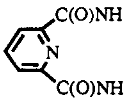
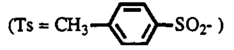
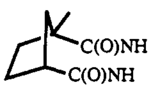
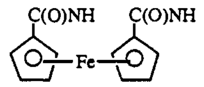
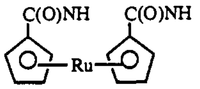
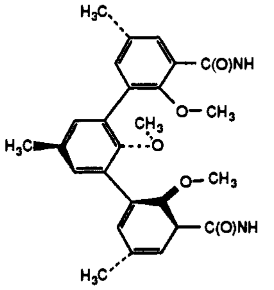
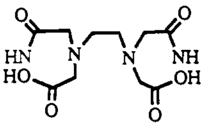
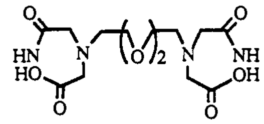
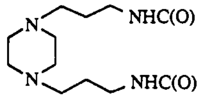
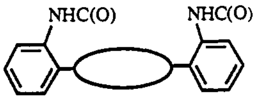
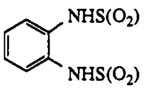
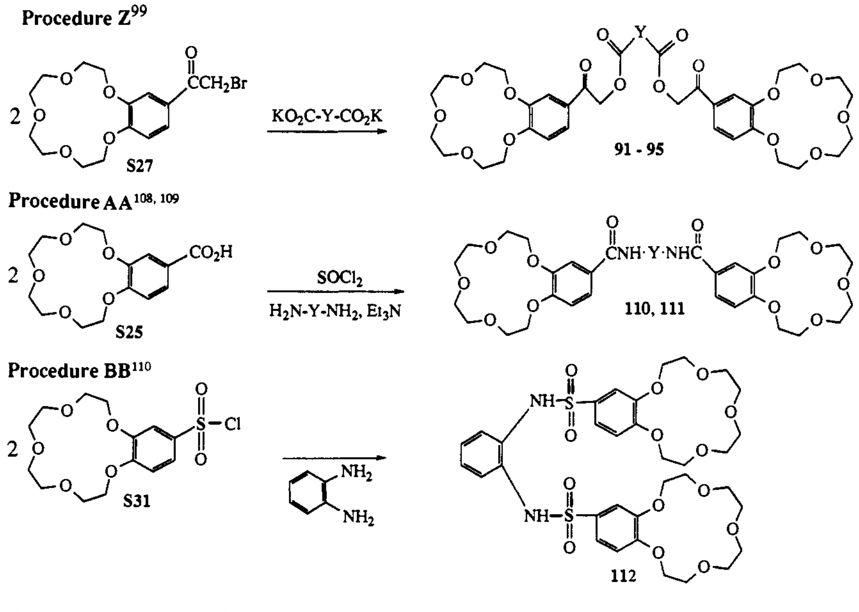
no.	remarks (X =)	mp, °C	yield, %	procedure	ref(s)
73	$C(O)O(CH_2)_2OC(O)$	124–125	87	W	12
74	$C(O)O(CH_2)_5OC(O)$	88–89	60	W	12
75	$C(O)O(CH_2)_8OC(O)$	82	56	W	12
76	$C(O)O(CH_2CH_2O)_2C(O)$	88–91	64	W	12
77	$C(O)O(CH_2CH_2O)_3C(O)$	83–84	48	W	12
78	$CH_2OC(O)CH_2C(O)OCH_2$	82–83		X	83
79	$CH_2OC(O)(CH_2)_2C(O)OCH_2$			Y	86
80	$CH_2OC(O)(CH_2)_3C(O)OCH_2$	94–95		X	83
81	$CH_2OC(O)(CH_2)_5C(O)OCH_2$	76–77		X	83
		61.5–62.5		X	88
82	$CH_2OC(O)(CH_2)_7C(O)OCH_2$	85–86		X	83
83	$CH_2OC(O)CH(CH_3)CH_2CH(CH_3)C(O)OCH_2$				
	(*meso*)	oil	67	Y	84
	(*dl*)	oil	76	Y	84
84	$CH_2OC(O)CH{=}CHC(O)OCH_2$ (*cis*)	72–73	71	Y	84
85	$CH_2OC(O)CH{=}CHC(O)OCH_2$ (*trans*)	149–150	65	Y	84
86	 (*cis*)	oil		Y	85
87	 (*trans*)	oil		Y	85
88	 (*cis*)	oil		Y	85
89		100–102		Y	85
90		169–170	73	X	97
91	$C(O)CH_2OC(O)(CH_2)_2C(O)OCH_2C(O)$	122.5–123.5	37.4	Z	99
92	$C(O)CH_2OC(O)(CH_2)_3C(O)OCH_2C(O)$	129–130	66.2	Z	99
93	$C(O)CH_2OC(O)(CH_2)_4C(O)OCH_2C(O)$	113–113.5	12	Z	99
94	$C(O)CH_2OC(O)(CH_2)_{10}C(O)OCH_2C(O)$	166.5–167.5	32.7	Z	99
95		166.5–167.5	51.1	Z	99
96	$NHC(O)(CH_2)_3C(O)NH$	175–176.5		E	101
97	$NHC(O)(CH_2)_4C(O)NH$	205–206	85	E	102
98	$NHC(O)(CH_2)_7C(O)NH$	218–219	95	E	102
99	$NHC(O)(CH_2OCH_2)_2C(O)NH$	189–190	89	E	102
100		286–288	85	E	102
101		140–142	85	E	102
102		262–263	88	E	102
103	NHC(O)CH2N(Ts)CH2C(O)NH 	199.5–200	32.1	E	103
104				E	46
105		198–199	80	E	104,105

Table 3 (Continued)

no.	remarks (X =)	mp, °C	yield, %	procedure	ref(s)
106		206–207	75	E	104,105
107		cream powder	60	E	106
108		187–188	34.1	F	47
109		55–57	45.7	F	107
110				AA	108
111[a]				AA	109
112		124–126	75	BB	110

[a] ⬭ = 2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin *α,α′*-substituted.

Scheme 17. Procedures Z,[99] AA,[108,109] and BB[110]



Biscrown **96** exhibited higher extractability for the metal picrates studied than the corresponding monocrown ether. In particular, **96** was found to be an effective extracting agent for Rb^+, Ba^{2+}, and Tl^+ ions. Biscrown **103** was used for extractive-spectrophotometric determinations of trace amounts of K^+ ions.[103]

Metallocene biscrowns **105** and **106** formed K^+ intramolecular sandwich-type complexes.[104,105] This latter result was observed by fast-atom bombardment (FAB) mass spectrometry, and the sandwich complex of biscrown **105** with K^+ ions was also confirmed by an X-ray crystal structure analysis.[105] Biscrown **107** with a rigid trisanisyl bridge formed a 1:1 (crown unit/cation) complex with Na^+ and 1:2 sandwich (crown unit/cation) complexes with K^+, Rb^+, and NH_4^+ ions at the crown ether binding sites.[106] Biscrown **107** exhibited a high degree of selectivity toward K^+. Porphyrin-bridged biscrown **111** bound the bipyridinium guests paraquat, diquat, and Pt(bypyridinium)$(NH_3)_2$ dications in several solvents.[109]

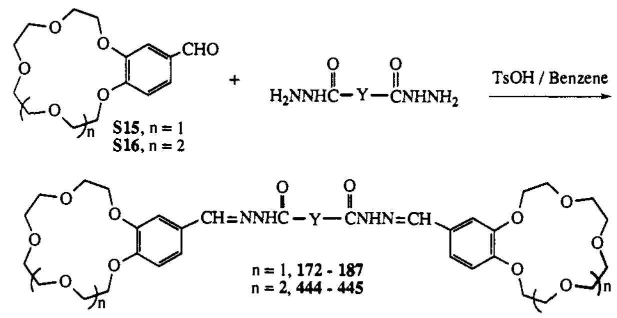
Three series of Schiff base-bridged bis(benzo-15-crown-5) derivatives are listed in Table 4. Biscrown **113** with the shortest bridge was prepared by the reaction of 2 mol of 4′-formylbenzo-15-crown-5 (**S15**) with hydrazine (Scheme 6, procedure H).[114-117] The condensation of **S15** with various α,ω-diaminoalkanes produced the alkane-containing Schiff base-bridged biscrowns **114–126** (procedure H, Table 4).[50,56,115-118] The Schiff base-bridged biscrowns **127–132** containing an extra ligating site in the bridge were synthesized by condensation of **S15** with the appropiate aza-, thia-, or oxadiamines.[119-122] Schiff base-bridged biscrowns **133–170** containing various aromatic rings in the bridges were prepared by the reaction of **S15** with the appropriate aromatic diamines by procedure H.[51,118,122-124] Phthalazine-bridged biscrown **171** was obtained by the condensation of **S15** with 1,4-dihydrazinophthalazine.[125] Most of the Schiff base-bridged biscrowns **113–141** and **171** were obtained in high yields, while aromatic ring-containing biscrowns **142–170** were obtained in relatively low yields.

Biscrown **113** was used as a K^+ absorbent.[114] The interaction of biscrowns **115–124** and **126** with alkali cations was investigated by spectroscopic techniques and solvent extraction.[50] These biscrowns formed pocket complexes with cations larger than Na^+. PVC membrane potassium-selective electrodes based on biscrowns **113** and **115–126** were studied[116,118] and were used in the analysis of K^+ in blood serum.[116]

A calorimetric titration study of the formation of intramolecular sandwich complexes of K^+ and Tl^+ ions with biscrowns **115**, **120**, **124**, and **141** and biscrowns **40**, **43**, **44**, **52–55**, **65**, **68–71**, **79**, and **84** provided stability constants and thermodynamic parameters for these complexes.[123,126,127] All biscrowns studied formed sandwich-type complexes with K^+ and/or Tl^+. Complexes formed from polymethylene-bridged biscrowns **65** and **68–71** and their dihydroxy analogues **52–55** had similar stability constants with the maximum stabilities for the complexes of the biscrowns with five carbon atoms in the bridge. The diketone-bridged biscrowns **40** and **42–44** and Schiff base-bridged biscrowns **115**, **120**, and **124** provided maximum stability constants where the bridges were 8–10 atoms long. NMR spectroscopic studies for the complexation of biscrowns **113**, **134**, and **135** with the alkali metal salts showed a noticeable "biscrown effect" for KI.[128]

Biscrowns **127–131** formed 1:1 (crown unit/cation) complexes with Na^+ and 2:1 sandwich complexes with K^+.[119-121] Homometallic copper(I) complexes and heteropolymetallic Cu^I–Na^+ and $-K^+$ complexes were isolated and the Cu^I–K^+ complex of **129** was verified by an X-ray crystal structure determination. Heteropolymetallic Ag^+–Na^+ and $-K^+$ complexes were also prepared.

Scheme 18. Procedure CC[129,130]



Holdt and co-workers[129,130] reported a series of acylhydrazone-bridged biscrown ethers **172–187**. Since these biscrowns are similar to Schiff base-containing biscrowns in their bond characteristics and preparation, they are listed in Table 4 and discussed following the Schiff base-containing biscrowns. Formyl-substituted benzocrown **S15** and the appropriate dicarboxylic acid dihydrazides (diacyldihydrazine) containing aliphatic or aromatic chains were refluxed in benzene containing *p*-toluenesulfonic acid to give biscrowns **172–187** in high yields (Scheme 18, procedure CC).[129,130] These biscrowns are useful as drug intermediates and for the preparation of ion-selective electrodes. The complexing properties of biscrowns **172–181** with alkali metal cations were studied by spectrophotometric titrations.[131-133] Sandwich complexes with K^+, Rb^+, and Cs^+ were observed in all cases. High complex selectivity and stability are caused by an increase in rigidity of the sandwich structure due to the formation of hydrogen bonds between the acylhydrazone groups. Biscrown **175** with a glutaric acid residue [$X = (CH_2)_3$] in the bridge exhibited a striking K^+ selectivity. K^+ ion-selective PVC membrane electrodes based on some of these biscrowns were prepared and their properties studied.[132,133]

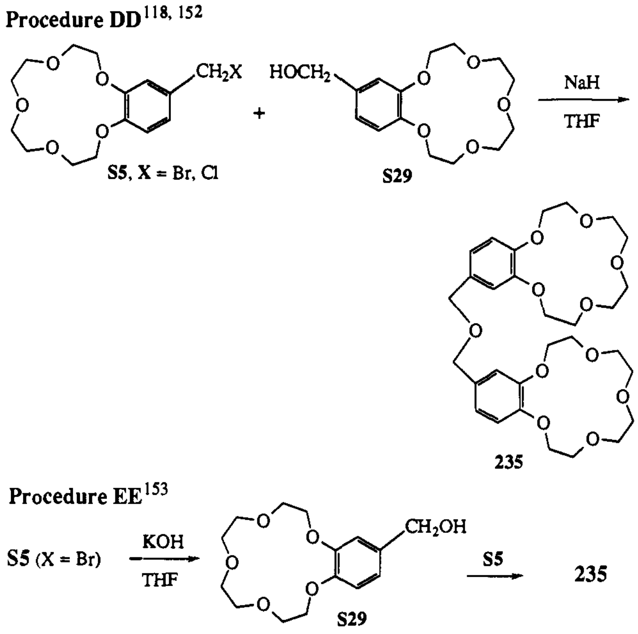
Another series of aromatic hydrocarbon-containing Schiff base-bridged biscrown ethers (**188–199**) are listed in Table 4. Aminobenzo-15-crown-5 (**S11**) was condensed with various dialdehydes to give the corresponding Schiff base-containing biscrowns **188–199** (Scheme 6, procedure I).[134-136] Conductivity measurements showed that biscrowns **188–198** formed 2:1 (crown unit/cation) sandwich-type complexes with K^+, Rb^+, and Cs^+ tetraphenyl borates, while they formed 1:1 complexes with Na^+. PVC membrane K^+ ion-selective electrodes prepared from biscrowns **193–198** were found to have low selectivity coefficients for Na^+ ions.[134,135] Alkali metal ion selectivities for bilayer membranes modified by these biscrowns were investigated.[137] The crystal structures of the complexes of K^+ and Rb^+ picrates with biscrown **188**, having a rigid *m*-phenylene bridge, was reported.[138,139] Experimental results indicated that the intermolecular 4:2 (crown unit/cation) sandwich complexes with both K^+ and Rb^+ were formed.

Bis(benzo-15-crown-5) derivatives **200–234** containing diamine bridges are listed in Table 5. Reduction of Schiff base-bridged bis(benzo-15-crown-5)s **113–115** and **117–126** by $NaBH_4$ gave the corresponding diamine-bridged biscrowns **200–212** in high yields (Scheme 6, procedure H).[117,118] Lockhart and co-workers[108,140] designed and synthesized biscrown **213** with a polyamine bridge to provide simultaneous multiple binding sites for anions by the bridge and cations by the crown moieties. Biscrown **213** was synthesized by two different methods. **213** was obtained by the reduction of its diamide-bridged analogue **110** with LiAlH$_4$. Condensation of 1,4-bis(3-aminopropyl)piperazine with two molecules of 4′-formylbenzo-15-crown-5 gave the Schiff base-containing biscrown which was then reduced in situ by NaBH(OAc)$_3$. Complexation of Cl$^-$ ions by the protonated form of ligand **213** was studied by an NMR technique. The physical properties and the synthetic yield of biscrown **213** and the diamide analogue **110** were not reported.

Diamine-bridged biscrowns **214–224** (Table 5) were obtained by the reduction of their Schiff base-bridged biscrown analogues **188–198** (Table 4) with NaBH$_4$ (Scheme 6, procedure I).[141,135] Hu and co-workers[48,49,142–147] reported a series of bis(crown ether)s (**225–234**) (Table 5) containing active functional groups in the bridges. Cyanuric chloride (2,4,6-trichloro-1,3,5-triazine) was treated with two molecules of 4′-aminobenzo-15-crown-5 (**S11**) at 40–45 °C to produce 1,3,5-triazine-bridged biscrown **225** (Scheme 5, procedure G).[142] Monosubstituted dichloro-1,3,5-triazines derived from cyanuric chloride were similarly treated with two molecules of aminocrown **S11** to give the substituted 1,3,5-triazine-bridged bis(benzo-15-crown-5) derivatives **226–231** (procedure G, Table 5).[143,144] Similar to biscrown **17**, quinoxaline-bridged biscrown ether **232** was synthesized by the reaction of amino crown **S11** with 2,3-dichloroquinoxaline.[48] The two chloro groups in 1,5-dichloro-2,4-dinitrobenzene are reactive to nucleophiles because of the electron-withdrawing effect of the two nitro groups. Therefore, 1,5-dichloro-2,4-dinitrobenzene was treated with aminocrown **S11** to give biscrown **233** (procedure G, Table 5).[147] Biscrown **234** was obtained by the same procedure.[49]

PVC membrane potassium-ion selective electrodes based on Schiff base-bridged biscrowns **188**, **190**, and **191** and diamine-bridged biscrowns **202**, **206**, **210**, **214**, **216**, **217**, **225**, and **228–231** were prepared, and their properties were investigated.[89,118,144,148] A Tl$^+$ ion-selective electrode was prepared from a PVC membrane containing biscrown **225**.[149] Extraction of alkali metal picrates with Schiff base-bridged biscrowns **188–192** and diamine-bridged biscrowns **214–218** was studied.[150] The results indicated that secondary amine-bridged biscrowns have higher distribution ratios and extraction equilibrium constants than the corresponding Schiff base-bridged biscrowns. Biscrown **214** exhibited the highest extraction capacity and selectivity for K$^+$ ions. Alkali metal picrate extraction studies with triazine-bridged biscrowns **225–231** showed that the bis(crown ether)s having lipophilic substituents in the triazine ring exhibited higher extractability.[143] Conductance studies showed that quinoxaline-bridged biscrown **232** formed sandwich-type complexes with K$^+$.[48] The FAB mass spectra of biscrowns **228–232** (Table 5) and **468** (Table 10) were studied.[145] The crystalline complex of biscrown **233** with KSCN was prepared, and its structure was determined by X-ray diffraction.[147] A sandwich-type complex was confirmed. Selectivity of a film made by attaching **225** onto diacetyl cellulose for K$^+$ was higher than the film containing the corresponding monocrown. The order of the ion selective permeability of the membrane was K$^+$ > Na$^+$ > Li$^+$ ~ NH$_4^+$.[151]

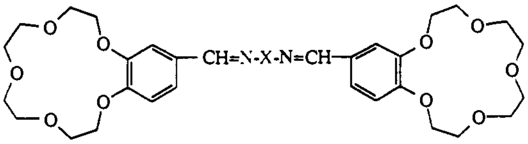
Scheme 19. Procedures DD[118,152] and EE[153]



Bis(benzo-15-crown-5) derivatives **235–250** containing ethereal bridges are listed in Table 6. Biscrown **235** with the shortest ethereal chain was synthesized by several different methods. 4′-(Bromomethyl)- or 4′-(chloromethyl)benzo-15-crown-5 (**S5**) was treated with its 4′-hydroxymethyl analogue (**S29**) to give biscrown **235** (Scheme 19, procedure DD).[118,152] 4′-(Bromomethyl)benzocrown **S5** was hydrolyzed by KOH to 4′-(hydroxymethyl)benzocrown **S29** which was then treated with the unreacted bromo analogue (**S5**) producing biscrown **235** (procedure EE).[153] Hyde and co-workers[154] unexpectedly obtained biscrown **235** during the reduction of 4′-formylbenzo-15-crown-5 (**S15**) (Scheme 20, procedure FF). They obtained reduced hydroxymethyl product **S29** and side-product biscrown **235** in 64% and 25% yields, respectively. Unexpectedly, 5′-methyl-4′-formylbenzo-15-crown-5 (**S32**) under the similar conditions gave only methylene-bridged biscrown **311** (Table 9) in a 53% yield and none of the normal reduced product (procedure GG).[154] The mechanisms for the formation of biscrowns **235** and **311** were not reported.

Bis(benzocrown ether)s **236–239** were synthesized by the reaction of 4′-(bromomethyl)benzocrown ether **S5** with the corresponding ethylene, diethylene, and triethylene glycols, and 5,5′-dimethyl-2,2′-biphenol using sodium hydride as the base (Scheme 2, procedure B).[153,118] Allosteric biscrown **240** was prepared similarly by treating 4′-chlorobenzo-15-crown-5 with 3,3′-bis(hydroxymethyl)-2,2′-bipyridine.[155,156] Biscrowns **241–243** with a benzene ring in each bridge were obtained in high yields by the reaction of (bromomethyl)benzocrown **S5** with catechol, hydroquinone, and resorcinol, respectively, using K$_2$CO$_3$ as the base in acetone (procedure B).[118] Biscrown **237** was also prepared by the reaction of 4′-(hydroxymethyl)benzo-15-crown-5 (**S29**) with diethylene glycol ditosylate using

Table 4. **Schiff Base-Bridged Bis(benzo-15-crown-5) Derivatives**



113-171

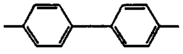
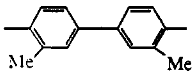
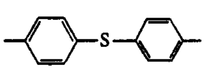
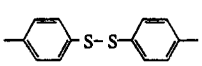
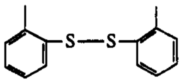
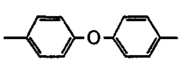
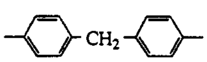
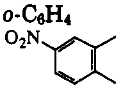
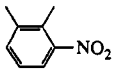
no.	remarks (X =)	mp, °C	yield, %	procedure	ref(s)
113	none	189–191	60	H	114
		189–191	72	H	115–117
114	CH_2	99–101	75	H	115–117
115	$(CH_2)_2$	104–105	82	H	117
		127–128	82	H	118
		128		H	50
		131–132	64	H	56
116	$CH(CH_3)CH_2$	120.5		H	50
117	$(CH_2)_3$	105–107	83	H	115–117
		108.6		H	50
118	$(CH_2)_4$	122–123	88	H	115–117
		129.5		H	50
119	$(CH_2)_5$	105–107	86	H	115–117
		105		H	50
120	$(CH_2)_6$	119–121	82	H	115–117
		124–125	59	H	118
		124		H	50
121	$(CH_2)_7$	103–104	85	H	115–117
		97		H	50
122	$(CH_2)_8$	110–112	81	H	115–117
		109		H	50
123	$(CH_2)_9$	103–105	79	H	115–117
		110		H	50
124	$(CH_2)_{10}$	108–110	77	H	115–117
		109–110	93	H	118
		109		H	50
125	$(CH_2)_{11}$	105–107	80	H	115–117
126	$(CH_2)_{12}$	106–108	72	H	115–117
		110		H	50
127	$CH_2CH_2NHCH_2CH_2$	92–94	79	H	119
128	$CH_2CH_2SCH_2CH_2$	83.5–85.5	90	H	119
129	$CH_2(CH_2SCH_2)_2CH_2$	98–99	90	H	120,121
130	$CH_2CH_2S(CH_2)_3SCH_2CH_2$	86–88	55	H	119
131	$(CH_2)_3SCH_2CH_2S(CH_2)_3$	72–74	16	H	119
132	$CH_2(CH_2OCH_2)_2CH_2$	74.5–76	91	H	122
133	*m*-C_6H_4	112–113	80	H	122
134	*p*-C_6H_4	224–226	90	H	122
135		192	72	H	51
		281–282	87	H	122
		240–241	53	H	51
136	 Me Me	218–219	63	H	122
137	 S	140.5–141.5	78	H	122
138	 S- S	109–110	74	H	122
139	 S—S	85–87	81	H	122
140	 O	143–145	79	H	118
		95–97	58	H	51
141	 CH_2			H	123
142	*o*-C_6H_4	yellowish-brown solid	38	H	124
143	 O_2N	yellowish solid	28	H	124
144	 NO_2	yellow solid	13	H	124

Table 4 (Continued)

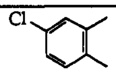
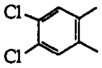
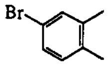
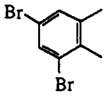
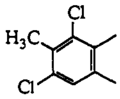
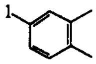
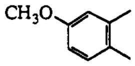
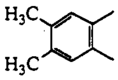
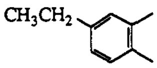
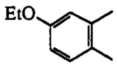
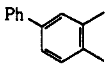
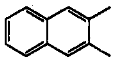
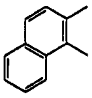
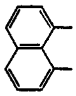
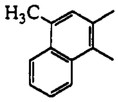
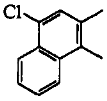
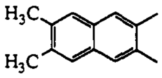
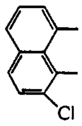
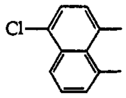
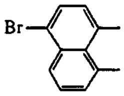
no.	remarks (X =)	mp, °C	yield, %	procedure	ref(s)
145		yellowish-white solid	34	H	124
146		yellowish-white solid	29	H	124
147		yellowish-white solid	31	H	124
148		brown solid	16	H	124
149		yellow-white solid	26	H	124
150		brown solid	30	H	124
151		yellowish-white solid	29	H	124
152		yellowish-white solid	27	H	124
153		yellowish-white solid	23	H	124
154		yellowish-white solid	31	H	124
155		yellowish-white solid	39	H	124
156		yellowish-white solid	30	H	124
157		yellowish-white solid	19	H	124
158		yellowish-brown solid	4	H	124
159		yellowish-white solid	27	H	124
160		yellowish-white solid	28	H	124
161		yellowish-white solid	33	H	124
162		yellowish-brown solid	8	H	124
163		yellowish-brown solid	11	H	124
164		brown solid	11	H	124

Table 4 (Continued)

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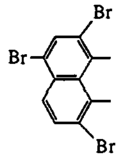
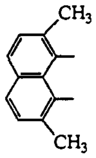
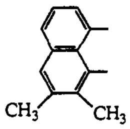
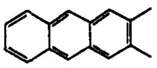
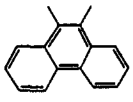
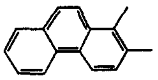
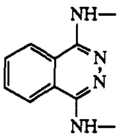
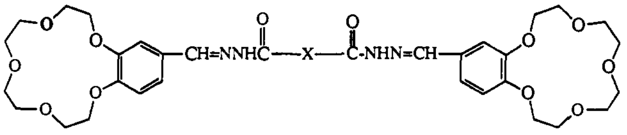
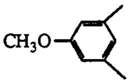
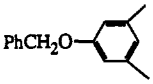
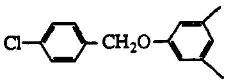
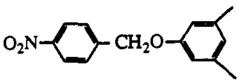
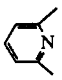
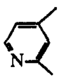
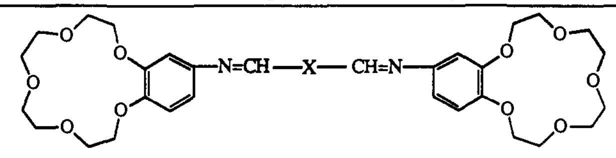
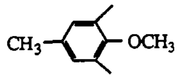
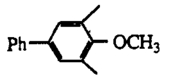
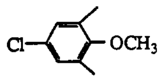
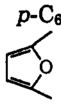
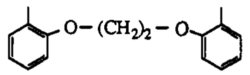
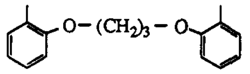
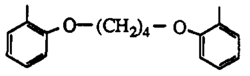
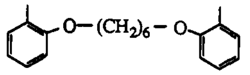
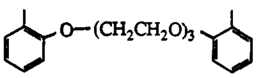
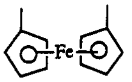
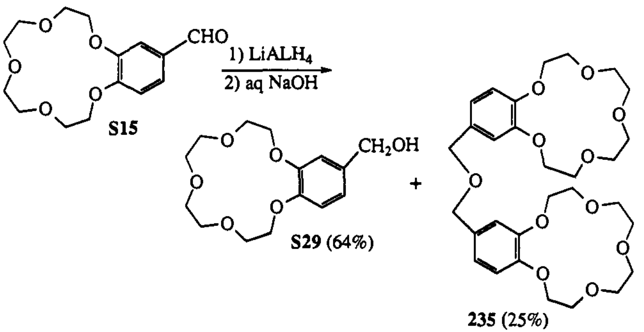
165		brown solid	10	H	124
166		yellowish-brown solid	14	H	124
167		yellowish-brown solid	12	H	124
168		brown solid	25	H	124
169		brown solid	20	H	124
170		brown solid	22	H	124
171		119–121	73	H	125
	 172-187				
172	none	280–283	84	CC	129
173	CH_2	212–214	75	CC	129
174	$(CH_2)_2$	206–209	76	CC	129
175	$(CH_2)_3$	157–160	80	CC	129
176	$(CH_2)_4$	230–232	97	CC	129
177	$(CH_2)_5$	192–194	94	CC	129
178	$(CH_2)_6$	224–226	91	CC	129
179	$(CH_2)_7$	191–194	92	CC	129
180	$(CH_2)_8$	202–204	91	CC	129
181	m-C_6H_4	247–249	82	CC	130
182		250–252	88	CC	130
183		266–268	90	CC	130
184		242–244	83	CC	130
185		225–227	91	CC	130
186		264–266	95	CC	130
187		170–172	97	CC	130

Table 4 (Continued)

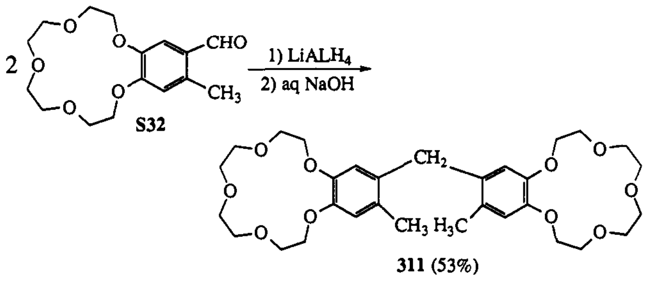
no.	remarks (X =)	mp, °C	yield, %	procedure	ref(s)
	 **188-199**				
188	*m*-C_6H_4	128–130	79	I	134
189		149–150	59	I	134
190		166–168	82	I	134
191		152–154	91	I	134
192	*p*-C_6H_4	224–226	88	I	134
193		64–67	76	I	134
194		139–140	97	I	135
195		116–118	97	I	135
196		140–142	90	I	135
197		155–156	95	I	135
198		102–104	90	I	135
199				I	136

Scheme 20. Procedures FF[154] and GG[154]

Procedure FF[154]



Procedure GG[154]

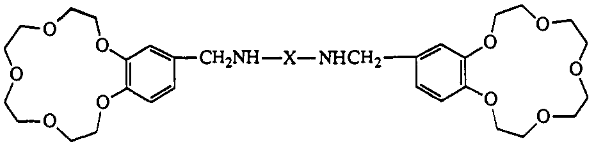


NaH as a base (Scheme 21, procedure HH).[152] Biscrowns **236** and **240** can also be obtained by this method from **S29**.

Baeyer–Villiger oxidation of 4′-acetylbenzo-15-crown-5 (**S33A**) followed by hydrolysis gave 4′-hydroxybenzocrown ether **S34** (Scheme 21, procedure II). Wada and co-workers[157,158] synthesized biscrowns **244–248** containing ethereal bridges by treating **S34** with diethylene glycol ditosylate, triethylene glycol ditosylate, tetraethylene glycol dichloride, pentaethylene glycol ditosylate, and 1,6-dibromohexane, respectively. High yields were obtained when ditosylates or dibromides were used, while the dichloride gave a low yield in the preparation of **246**. Biscrown **249** was prepared by treating **S34** with α,α'-dihalo-*m*-xylene using KOH as a base.[159,160] Similarly, biscrown **250** was obtained by the condensation of 4,5,α,α'-tetrabromo-*o*-xylene with two molecules of crown **S34**.[34]

Potassium-selective PVC membrane electrodes based on biscrowns **235–237**, **239**, and **241–243** were prepared, and their characteristics were investigated.[118,161] A UV–visible spectroscopic study of the complexes of biscrown **235–238** with alkali metal picrates indicated that they formed sandwich-type complexes with K^+, Rb^+, and

Table 5. Bis(benzo-15-crown-5) Derivatives Containing Diamine Bridges



200-213

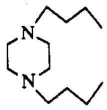
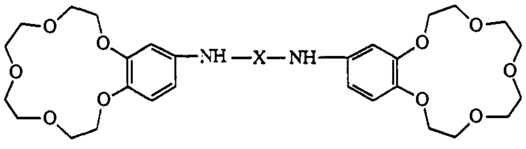
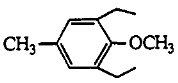
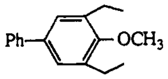
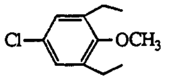
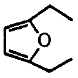
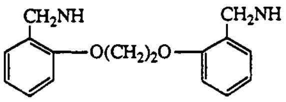
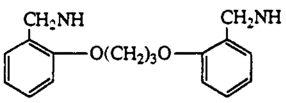
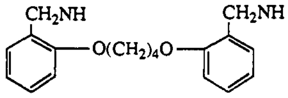
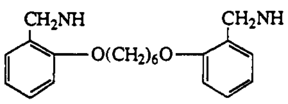
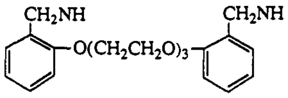
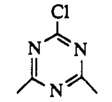
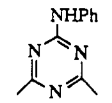
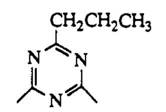
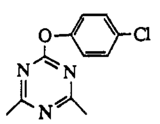
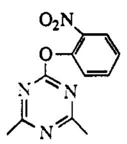
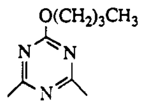
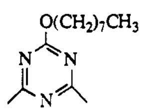
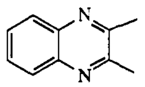
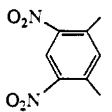
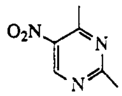
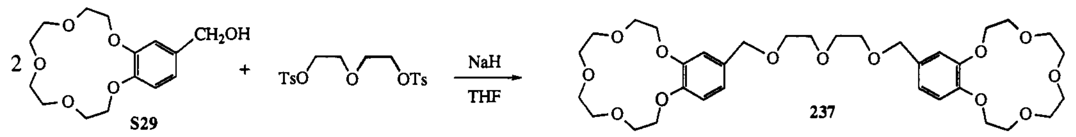
no.	remarks (X =)	mp, °C	yield, %	procedure	ref(s)
200	none	>150	73	H	117
201	CH_2	60–62	86	H	117
202	$(CH_2)_2$	63–65	78	H	117
		57–58	25	H	118
203	$(CH_2)_3$	66–67	81	H	117
204	$(CH_2)_4$	70–72	84	H	117
205	$(CH_2)_5$	68–69	80	H	117
206	$(CH_2)_6$	69–71	82	H	117
		72–73	33	H	118
207	$(CH_2)_7$	70–72	84	H	117
208	$(CH_2)_8$	68–70	92	H	117
209	$(CH_2)_9$	67–69	88	H	117
210	$(CH_2)_{10}$	68–70	91	H	117
		75–76.5	51	H	118
211	$(CH_2)_{11}$	67–69	90	H	117
212	$(CH_2)_{12}$	67–69	91	H	117
213				H,AA	108,140
	 $NH—X—NH$ 214-234				
214	*m*-xylylene	oil	83	I	141
215	 CH_3 OCH_3	132–134	82	I	141
216	 Ph OCH_3	118–120	88	I	141
217	 Cl OCH_3	148–150	93	I	141
218	*p*-xylylene	150–152	90	I	141
219		oil	90	I	141
220	 CH_2NH CH_2NH $O(CH_2)_2O$	140–142	90	I	135
221	 CH_2NH CH_2NH $O(CH_2)_3O$	142–144	92	I	135
222	 CH_2NH CH_2NH $O(CH_2)_4O$	124–126	88	I	135
223	 CH_2NH CH_2NH $O(CH_2)_6O$	148–150	70	I	135
224	 CH_2NH CH_2NH $O(CH_2CH_2O)_3$	oil	80	I	135

Table 5 (Continued)

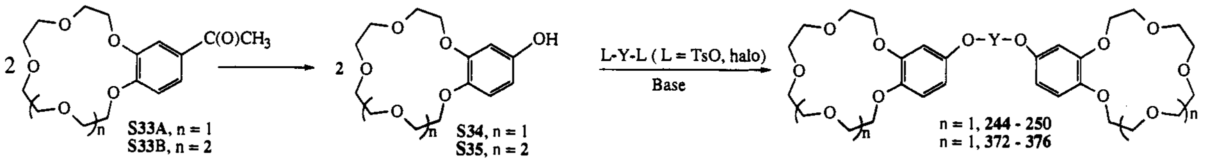
no.	remarks (X =)	mp, °C	yield, %	procedure	ref(s)
225		180–181	50	G	142
226		112–114	35.1	G	143
227		105–107	41.2	G	143
228		165–167	32	G	144,145
229		193–194	66	G	144,145
230		115–116	61	G	144,145
231		159–160	63	G	144,146
232		95–96	66	G	48
233		216–217	75.3	G	147
234		195–196	65	G	49

Scheme 21. Procedures HH[152] and II[34,157-160]

Procedure HH[152]



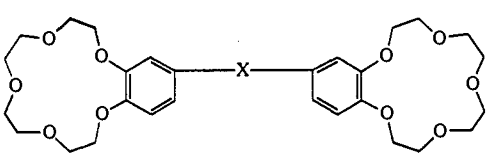
Procedure II[34,157-160]



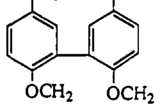
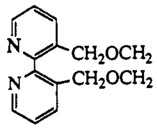
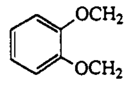
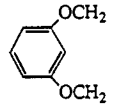
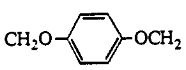
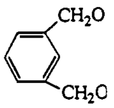
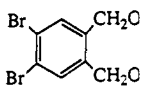
Cs^+ ions.[43] The selectivity order of extracting alkali metal picrates from aqueous solutions into chloroform were $K^+ > Rb^+ > Na^+ > Cs^+$.[43] Solvent extraction of alkali metal picrates by biscrowns **244–248** gave high extractability and selectivity for K^+ ions with an intramolecular 2:1 (sandwich) crown ether–K^+ complex.[81,158] Li^+ isotope separation ability of biscrown **239** in a $CHCl_3$ solution using LiSCN was determined.[162]

Biscrown **240** exhibited interesting complexation properties.[155,156] Free ligand **240** formed crystalline complexes with two Na^+ ions, one K^+, and one molecule of diquat dication substrate. When the chelation of Ru(II) at the bipyridyl function occurred, only one Na^+ (or K^+) was wrapped in an intramolecular sandwich complex with the two benzocrown ether units. Chelation of the transition metal ion by the bipyridyl

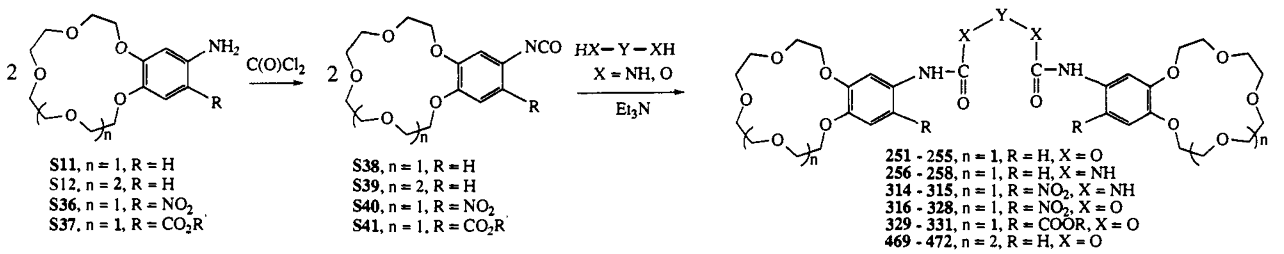
Table 6. Bis(benzo-15-crown-5) Derivatives Containing Ethereal Bridges



235-250

no.	remarks (X =)	mp, °C	yield, %	procedure	ref(s)
235	CH_2OCH_2	105–107	57	DD	118
		110–111	57	DD	152
		111–112	30[a]	EE	153
		107–109	25	FF	154
236	$CH_2OCH_2CH_2OCH_2$	48–50	30	B	153
237	$CH_2(OCH_2CH_2)_2OCH_2$	oil	35	B	153
		oil	61	HH	152
238	$CH_2(OCH_2CH_2)_3OCH_2$	oil	35	B	153
239		oil	70	B	118
240		oil oil	67 77	B B	155 156
241		130–131	82	B	118
242		109–110	86	B	118
243		171–172	75	B	118
244	$OCH_2CH_2OCH_2CH_2O$	73–74.5	67	II	157
245	$OCH_2(CH_2OCH_2)_2CH_2O$	88.9–92.2	83	II	157
246	$OCH_2(CH_2OCH_2)_3CH_2O$	73–74	21	II	157
247	$OCH_2(CH_2OCH_2)_4CH_2O$	oil	63	II	157
248	$O(CH_2)_6O$	102–104.1	75	II	158
249		glassy	73	II	159,160
250		128	44	II	34

Scheme 22. Procedure JJ[163–166,201,202]

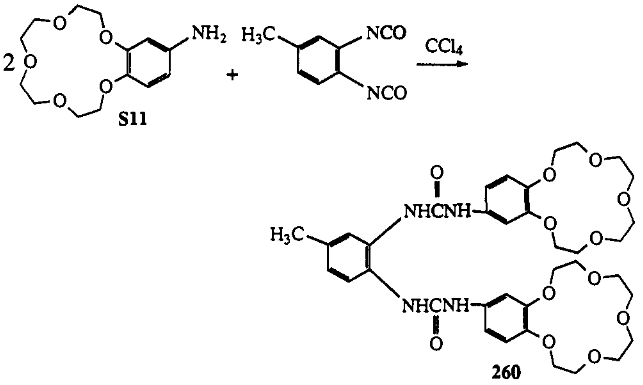


nitrogens forces the bipyridyl function toward coplanarity, restricting the crown units in such a way as to favor the formation of an intramolecular sandwich complex with Na^+. However, this effect disfavors the binding of diquat dication between the crown units.

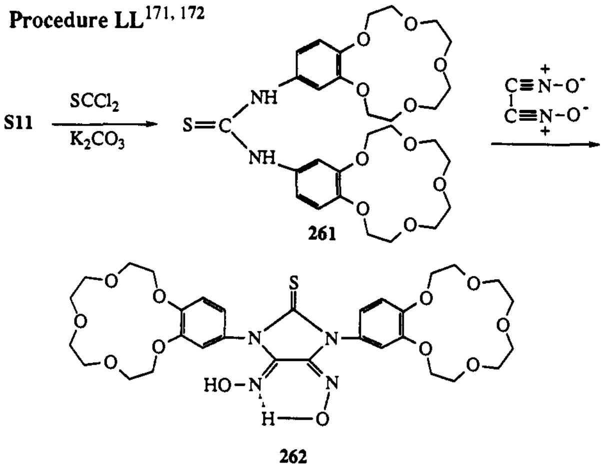
A number of bis(benzo-15-crown-5) derivatives (251–285) containing other bridges are listed in Table 7. Töke and co-workers[163–166] reported a series of bisurethane- and bisurea-bridged bis(crown ether)s **251–258**. 4′-Aminobenzo-15-crown-5 (**S11**) was transformed into its isocyanate analogue **S38** by treatment with an excess of phosgene in refluxing chlorobenzene (Scheme 22, procedure JJ).[163–166] Two molecules of **S38** were condensed with 1,5-pentanediol, 3-oxa-1,5-pentanediol,

Scheme 23. Procedures KK[99] and LL[171,172]

Procedure KK[99]



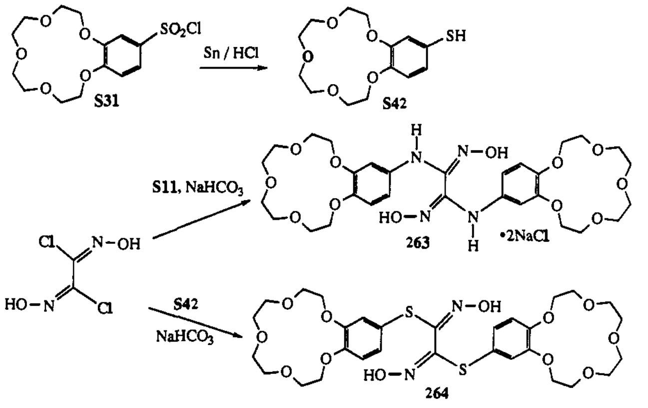
Procedure LL[171, 172]



3-thia-1,5-pentanediol, 1,2-bis(1-hydroxyethoxy)benzene, and 2,6-bis(hydroxymethyl)pyridine in the presence of triethylamine producing the corresponding bisurethane-bridged biscrowns 251–255. Condensation of S38 with 1,3-propanediamine, 1,6-hexanediamine, and 3,6-dioxa-1,8-octanediamine gave bisurea-bridged biscrowns 256–258. Urea-bridged biscrown 259 was obtained unexpectedly together with triscrown 554 (Figure 5) from the reaction of isocyanate-containing benzocrown S38 with 4′,4″-diaminodibenzo-18-crown-6.[165] Biscrown 259 could be also prepared by the reaction of aminobenzocrown S11 with phosgene or by the reaction of S11 with S38. Potassium-selective PVC membrane electrodes based on biscrowns 251–254 were prepared, and their properties were studied.[164,167–169] The influence of biscrowns 251–254 on various plant-related bacteria and the correlation of their membrane-damaging effect on biological activity were also investigated.[170]

Bisurea-bridged biscrown 260 was prepared in high yield by the condensation of toluene 3,4-diisocyanate with two molecules of 4′-aminobenzo-crown S11 in refluxing carbon tetrachloride (Scheme 23, procedure KK).[99] Gök and co-workers[171,172] reported thiourea- and vicinal dioxime-bridged bis(benzo crown)s 261 and 262. The crystalline sandwich complex of thiourea-containing biscrown 261 with KCl was first obtained in a 90% yield by the condensation of thiocarbonyl dichloride with two molecules of aminobenzocrown S11 in the presence of K_2CO_3 (procedure LL).[171,172] Decomplexation of the crystalline complex in water-chloroform gave free ligand 261. Cyclization of 261 with cyanogen *N,N′*-dioxide, prepared from (*E,E*)-dichloroglyoxime, gave vicinal dioxime-bridged biscrown 262. Biscrown 262 formed crystalline complexes with Ni^{2+}, Pd^{2+}, Cu^{2+}, Co^{2+}, and Co^{3+} with a metal/ligand ratio of 1:2 by coordination of dioxime nitrogen atoms to the metal cations.[171,172] The extraction properties of 261 and 262 toward Li^+, Na^+, and K^+ picrates from aqueous solution into dichlorobenzene were studied.[172]

Scheme 24. Procedure MM[173,174]

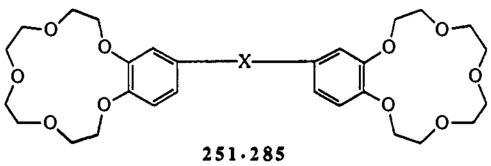


Bekaroglu and co-workers[173,174] reported the diaminoglyoxime- and dithioglyoxime-bridged biscrowns 263 and 264 (Table 7). Treatment of *anti*-dichloroglyoxime with two molecules of aminobenzocrown S11 in the presence of $NaHCO_3$ gave biscrown 263 (Scheme 24, procedure MM).[173] The 263·2NaCl crystalline complex was isolated in a 66.8% yield. Decomposition of this complex was not attempted. Complexes of 263·2NaCl with Cu^{2+}, Ni^{2+}, and Co^{2+} were prepared and showed a metal/ligand ration of 1:2 by the coordination of glyoxime nitrogen atoms to the metal cations.

4′-Mercaptobenzo-15-crown-5 (S42) was prepared by the reaction of tin on chlorosulfonyl-substituted benzocrown S31, which was obtained by the reaction of S2 with sulfuric acid and then thionyl chloride (Scheme 24, procedure MM). The reaction of *anti*-dichloroglyoxime with two molecules of mercaptobenzocrown S42 in the presence of $NaHCO_3$ gave dithioglyoxime-bridged biscrown 264 in a high yield (procedure MM).[174] Biscrown 264 formed crystalline complexes with two molecules of LiCl and one of NaSCN and sandwich-type complexes with one molecule each of KSCN and NH_4SCN. Free ligand 264 with its crown unit complexed with Na^+ formed complexes with Ni^{2+}, Pd^{2+}, Pt^{2+}, Cu^{2+}, Co^{2+}, and Co^{3+} in a metal/ligand ratio of 1:2 by the interaction of the glyoxime nitrogen atoms and the metal cations.[174]

Shinkai and co-workers[175,176] reported the redox-switchable bis(crown ether)s 265 and 266 containing disulfide bridges (Table 7). 4′-(Bromomethyl)benzo-15-crown-5 (S5) was treated with thiourea to give the thiouronium salt which was then treated with an aqueous solution containing NaOH and $Na_2S_2O_4$ to give 4′-(mercaptomethyl)benzo crown S43.[176] 4′-Mercapto- and 4′-(mercaptomethyl)benzocrowns S42 and S43 were oxidized to the corresponding disulfide-bridged bis(benzocrown)s 265 and 266 (Scheme 25, procedure NN).[175,176] Solvent-extraction and membrane-transport

Table 7. Bis(benzo-15-crown-5) Derivatives Containing Other Bridges



251-285

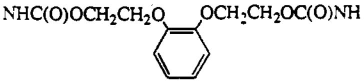
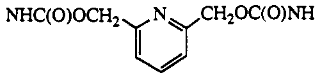
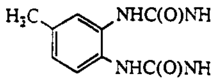
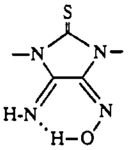
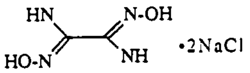
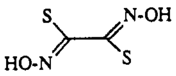
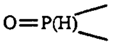
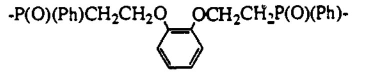
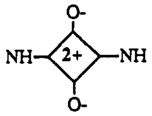
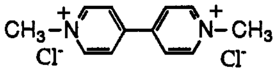
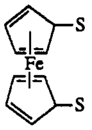
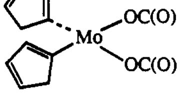
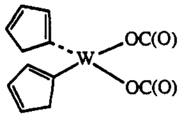
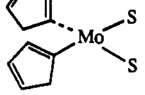
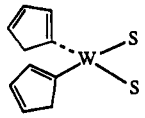
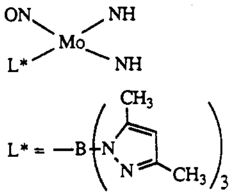
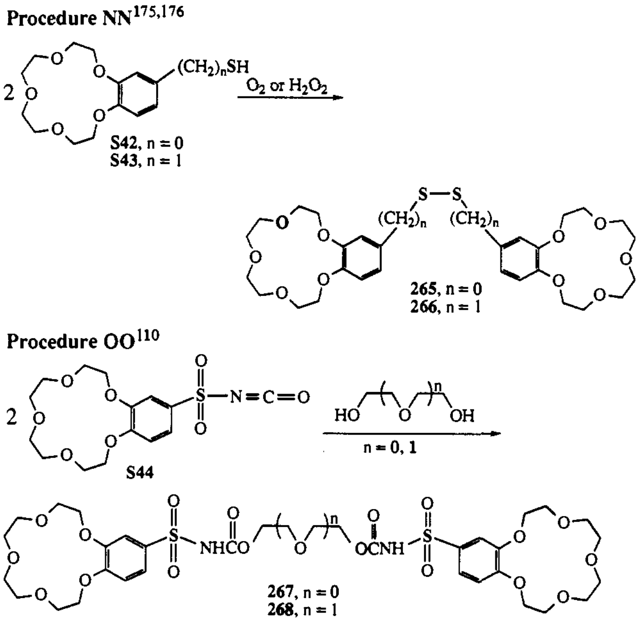
no.	remarks (X =)	mp, °C	yield, %	procedure	ref(s)
251	$NHC(O)O(CH_2)_5OC(O)NH$	88	70–80	JJ	164–166
252	$NHC(O)OCH_2CH_2OCH_2CH_2OC(O)NH$	84	70–80	JJ	163–166
253	$NHC(O)OCH_2CH_2SCH_2CH_2OC(O)NH$	135	70–80	JJ	163–166
254		150	70–80	JJ	163–166
255		134	70–80	JJ	163–166
256	$NHC(O)NH(CH_2)_3NHC(O)NH$	183	70–80	JJ	163–166
257	$NHC(O)NH(CH_2)_6NHC(O)NH$	180	70–80	JJ	164,165
258	$NHC(O)NHCH_2(CH_2OCH_2)_2CH_2NHC(O)NH$	134	70–80	JJ	163–166
259	$NHC(O)NH$	190–191	53		165
260		213.2–213.7	82	KK	99
261	$NHC(S)NH$	106	72	LL	171,172
262		141	55	LL	171,172
263		102	66.8	MM	173
264		126	83	MM	174
265	S–S	83–85	48.4	NN	175,176
266	CH_2SSCH_2	120–122	59.1	NN	176
267	$S(O_2)NHC(O)OCH_2CH_2OC(O)NHS(O_2)$	85	119–120	OO	110
268	$S(O_2)NHC(O)O(CH_2CH_2O)_2C(O)NHS(O_2)$	80	70–71	OO	110
269		124–126	35	PP	177
270	$-P(O)(Ph)CH_2(CH_2OCH_2)_2CH_2P(O)(Ph)-$	amorphous	20	QQ	178
271	$-P(O)(Ph)CH_2(CH_2OCH_2)_3CH_2P(O)(Ph)-$	amorphous	40	QQ	178
272	$-P(O)(Ph)CH_2(CH_2OCH_2)_4CH_2P(O)(Ph)-$	92–94	40	QQ	178
273	$-P(O)(Ph)CH_2(CH_2OCH_2)_5CH_2P(O)(Ph)-$	glassy	50	QQ	178
274	$-P(O)(Ph)CH_2(CH_2OCH_2)_6CH_2P(O)(Ph)-$	78–82	40	QQ	178
275		77–81	50	QQ	179
276	N=N	187–188 190–191	9.1 53	C RR	180–182 21
277		308–310	83.7	SS	186
278				TT	187
279		112	51		188
280					136,189

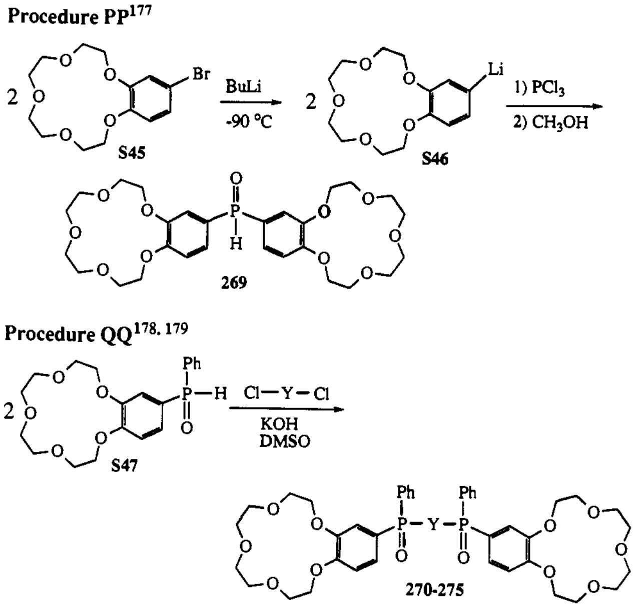
Table 7 (Continued)

no.	remarks (X =)	mp, °C	yield, %	procedure	ref(s)
281			16	UU	190
282			8	UU	190
283			14	UU	190,191
284			14	UU	190,191
285				UU	192

Scheme 25. Procedures NN[175,176] and OO[110]



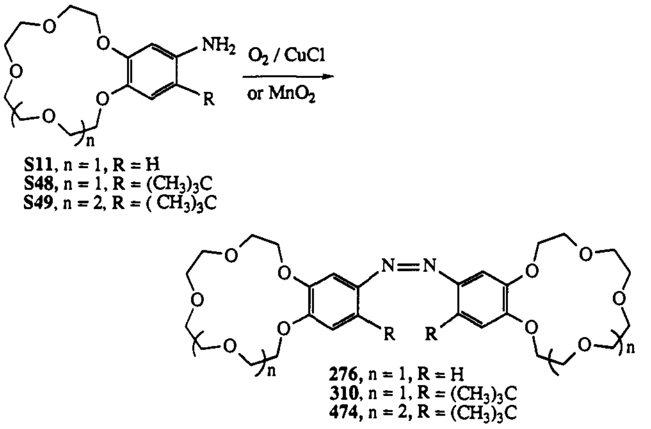
Scheme 26. Procedures PP[177] and QQ[178,179]



studies using these ligands were carried out. Sulfonamide-bridged biscrowns **267** and **268** were synthesized by treating ethylene glycol and diethylene glycol with two molecules of 4′-(isocyanatosulfonyl)benzo-15-crown-5 (**S44**), respectively (procedure OO).[110]

Kal'chenko and co-workers[177–179] reported a series of bis(benzo-15-crown-5) derivatives (**269–275**) with phosphorus-containing bridges (Table 7). 4′-Bromobenzo-15-crown-5 (**S45**), obtained by the bromination of benzo-15-crown-5 (**S2**) with NBS, was treated with butyllithium to give lithium derivative **S46**. Condensation of the latter with phosphorus trichloride led to the intermediate bis(crown-substituted) chlorophosphine. This intermediate, without being isolated, was treated with methanol giving the phosphine oxide-bridged biscrown **269** (Scheme 26, procedure PP).[177] 4′-(Phenylphosphinyl)benzo-15-crown-5 (**S47**) was prepared by the reduction of 4′-[(alkoxyphenyl)phosphinyl]benzo-15-crown-5.[178] Condensation of **S47** with tri-, tetra-, penta-, hexa-, and heptaethylene glycol dichlorides, or *o*-bis(β-chloroethoxy)benzene using KOH as a base in DMSO produced the corresponding bis(phenylphosphinyl)-bridged biscrowns **270–275**, respectively (procedure QQ).[178,179] The rate of transport of alkali and alkaline earth metal picrates by biscrowns **269–275** in a water–chloroform–water solvent system was investigated.[177,179] These ligands formed a 1:1 (crown unit/metal cation) complex with Na^+ and 2:1 sandwich-type complexes with K^+ and Cs^+ cations. Transport rate

Scheme 27. Procedure RR[21,22]



increased as the connecting chain length increased. Substitution of the central ethylene fragment of biscrown **270** by the rigid *o*-phenylene unit in biscrown **275** caused an overall increase in ion-transport characteristics.[179]

Photoresponsive azobis(benzo-15-crown-5) (**276**) was reported by Shinkai and co-workers.[21,22,180-182] Similar to the preparation of azobis(benzo-12-crown-4) (**12**), azobiscrown **276** was synthesized in a 9% yield by the zinc reductive coupling of 4′-nitrobenzo-15-crown-5 (**S8**) using Zn in the presence of KOH (Scheme 3, procedure C).[180-182] The oxidative coupling of 4′-aminobenzo-15-crown-5 (**S11**) with molecular oxygen using CuCl as the catalyst in pyridine gave biscrown **276** in a 53% yield (Scheme 27, procedure RR).[21] The *trans*-isomer was isomerized by UV light to the *cis*-isomer, and the latter was isomerized thermally to the *trans*-isomer.[180,181] The *trans*-isomer had high selectivity and extractability for Na^+, while the *cis*-isomer efficiently extracted K^+, Rb^+, and Cs^+ ions since the *cis*-isomer can form stable sandwich-type complexes with these larger cations.[21,22,181-183] Various properties of the photoresponsive azobiscrown **276** were studied by the research groups of Shinkai and others.[21,22,180-185]

A novel bis(benzo-15-crown-5) (**277**) containing a squarylium bridge was synthesized in a high yield by treating squaric acid, 3,4-dihydroxy-3-cyclobutene-1,2-dione, with two molecules of aminobenzocrown **S11** (Scheme 28, procedure SS).[186] Treatment of 4,4′-bipyridine with two molecules of 4′-(chloromethyl)benzocrown (**S5**) in acetonitrile gave a novel viologen-bridged biscrown **278** (procedure TT).[187] Bis(benzocrown) **279** was prepared by the reaction of 1-(2,4-dinitrophenyl)pyridinium chloride with 4′-aminobenzocrown **S11**.[188] Ferrocene-bridged biscrown **280** was made from **265** and lithium ferrocene as a redox-active receptor.[136,189] Treatment of $[M(C_5H_5)_2Cl_2]$ (M = Mo or W) with 4′-carboxybenzo-15-crown-5 (**S25**) and 4′-mercaptobenzo-15-crown-5 (**S42**) in the presence of base gave metal-bridged biscrowns **281**–**284** (Scheme 29, procedure UU).[190,191] These latter biscrowns can undergo reversible oxidation. Biscrown **285** was similarly prepared stepwise from $[Mo(NO)L^*Cl_2]$ and 4′-aminobenzocrown **S11**.[192]

So far, only symmetric bis(benzo-15-crown-5) derivatives containing the same crown units and symmetric bridges have been reported in this section. Bis(benzo-15-crown-5) derivatives with asymmetric bridges have also been prepared. In section 6, bis(benzocrown ether)s containing different crown units will be reported. Bis(benzo-15-crown-5) derivatives **286**–**309** containing asymmetric bridges are listed in Table 8. Biscrown **286** was obtained by the condensation of phthalic dialdehyde with aminobenzocrown **S11** (procedure I).[134] The condensation of formyl- and aminobenzocrowns **S15** and **S11** gave Schiff base-bridged biscrown **287** in a high overall yield. **287** was then reduced to its amine analogue **288** by $NaBH_4$ (Scheme 8, procedure K).[56] Reduction of 4′-nitrobenzo-15-crown-5 (**S8**) by poly(pyridinomethylstyrene chloride) (PPyCl) with zinc as the catalyst gave azoxybis(benzocrown) **289** (Scheme 3, procedure D).[44,193,194] **289** was also obtained in our lab by the reduction of **S8** with a KOH–Zn catalyst (procedure D).[56] Azoxybis(benzocrown) **289** has properties similar to those of azobisbenzocrown **276**. The *trans*-isomer can be isomerized to the *cis*-isomer by UV irradiation from a high-pressure Hg lamp, and the reverse process takes place on storage in the dark.

Scheme 28. Procedures SS[186] and TT[187]

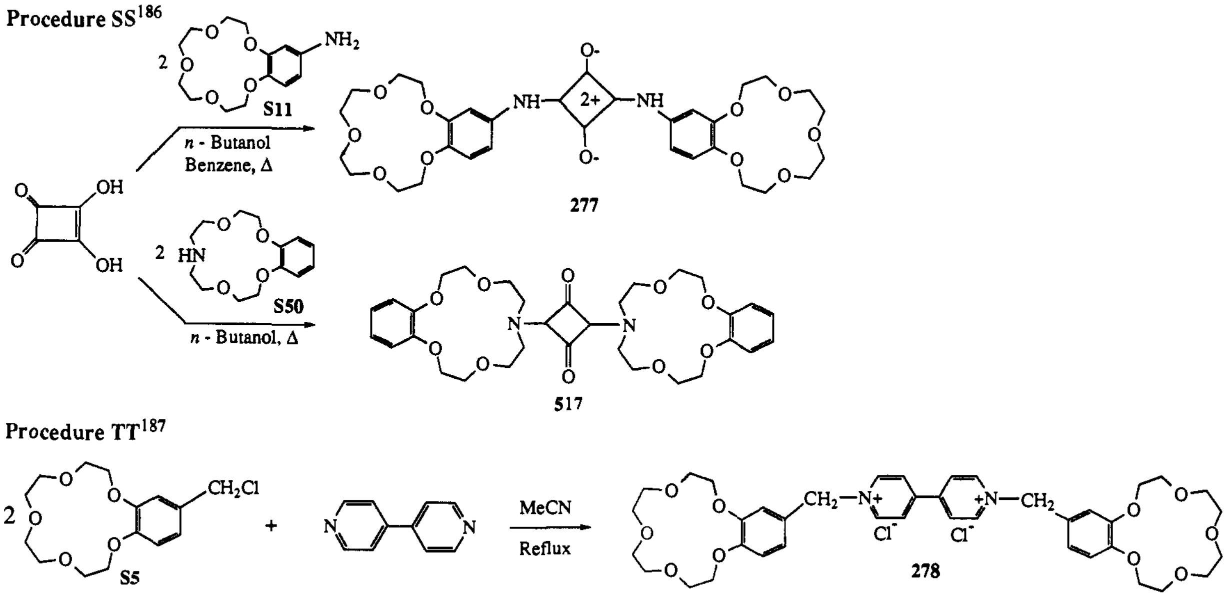
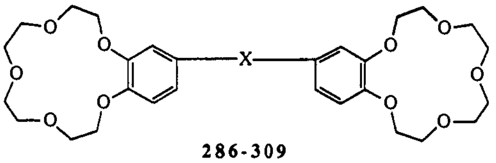
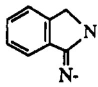
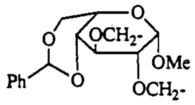
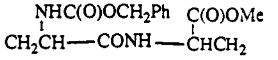
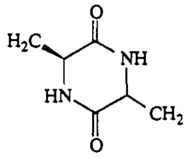


Table 8. Bis(benzo-15-crown-5) Derivatives Containing Asymmetric Bridges

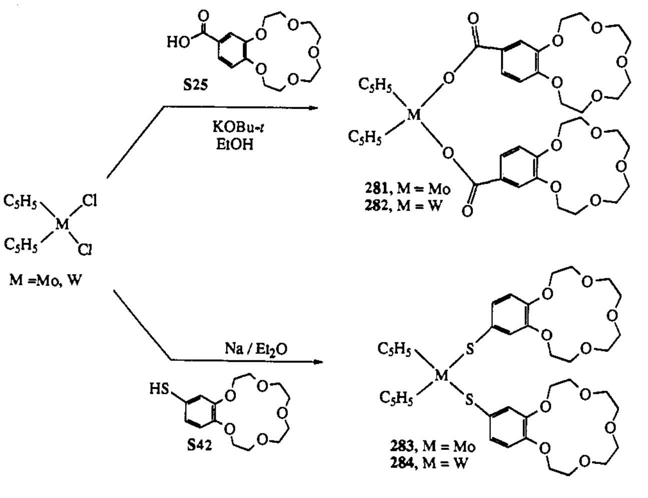


286-309

no.	remarks (X =)	mp, °C	yield, %	procedure	ref(s)
286		129–130	74	I	134
287	CH=N	152.5–153.5	96[a]	K	56
288	CH_2NH	124–125	91	K	56
289	N=N(O)	159–160	24.2	D	193,194
			65.3	D	44
		171.5–172.5	45	D	56
290	CH_2O	115–116	74	VV	152
291	$CH_2CH_2CH_2O$	102.8–103.9	53	VV	53,195
292		141–143	59	VV	196
293	$S(O_2)NH$	116–118	70	WW	110
294	$C(O)OCH_2C(O)$	156.5–157.5	26	XX	99
295	C(O)CH=CH	111–114	58	YY	60
296	$CH(OH)CH_2CH_2$	106–109	90	YY	60
297	$CH(OC_8H_{17}\text{-}n)CH_2CH_2$	57–58	20	YY	60
298	$CH(OC_{12}H_{25}\text{-}n)CH_2CH_2$	45–46	27	YY	60
299	$CH(OC_{16}H_{33}\text{-}n)CH_2CH_2$	43–44	41	YY	60
300	 $CH_2\underset{}{\overset{NHC(O)OCH_2Ph}{CH}}\text{—}CONH\text{—}\overset{C(O)OMe}{CH}CH_2$	179		ZZ	197
301		118		ZZ	197
302	NH-Ala-C(O)			AAA	198
303	NH-Pro-C(O)			AAA	198
304	NH-Ala-Ala-C(O)			AAA	198
305	NH-Ala-Pro-C(O)			AAA	198
306	NH-Ala-Ala-Ala-C(O)	266		AAA	198
307	NH-Ala-Pro-Ala-C(O)			AAA	198
308	$NH\text{-}C(O)(CH_2)_7NHC(O)$				198
309	NHC(O)				198

[a] Overall yield.

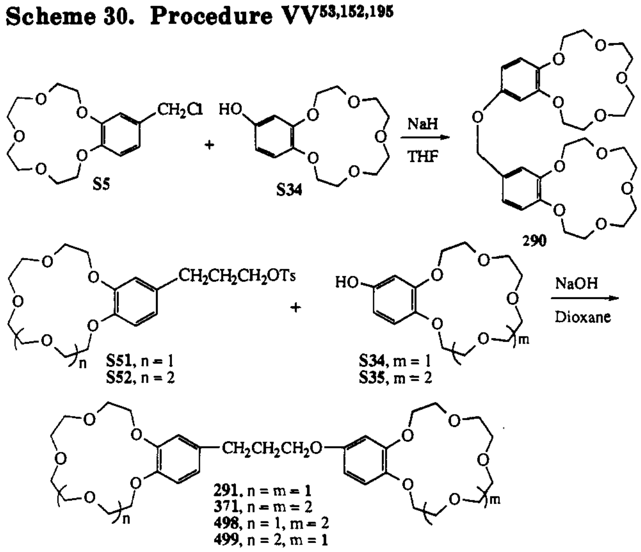
Scheme 29. Procedure UU[190,191]



Photoisomerization and thermal isomerization and spectral and extraction properties of **289** were studied.[23,44,193,194] K$^+$ ion-selective PVC membrane electrodes based on biscrown **286–289** were prepared.[56,134] The electrode based on **289** has higher selectivity than the commercially available K$^+$-selective electrode based on valinomycin.[56]

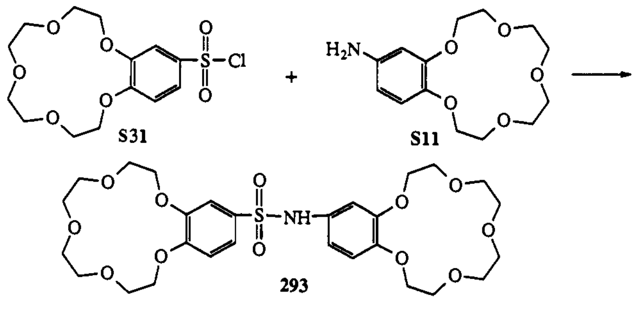
The reaction of chloromethyl-substituted benzocrown **S5** with hydroxy-substituted benzocrown **S34** under strong basic conditions gave biscrown **290** (Scheme 30, procedure VV).[152] This method can also be used to prepare biscrowns containing two different crown units. Tosylation of 4′-(3-hydroxypropyl)benzo-15-crown-5 and its benzo-18-crown-6 analogue gave the corresponding 4′-[3-(tosyloxy)propyl]benzo-15-crown-5 (**S51**) and 4′-[3-(tosyloxy)propyl]benzo-18-crown-6 (**S52**). **S51** was treated with 4′-hydroxybenzo-15-crown-5 (**S34**) under basic conditions to give bis(benzo-15-crown-5) **291** (procedure VV).[53,195] Other bis(benzocrown)s with asymmetric bridges and with two different or the same crown units were also prepared by this method (see the following sections). Glucopyranoside-bridged bis-

Scheme 30. Procedure VV[53,152,195]

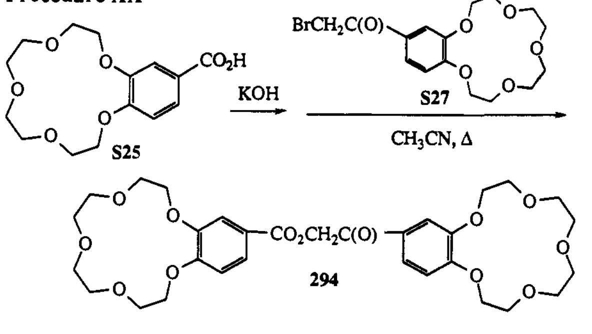


Scheme 31. Procedures WW[110] and XX[99]

Procedure WW[110]



Procedure XX[99]



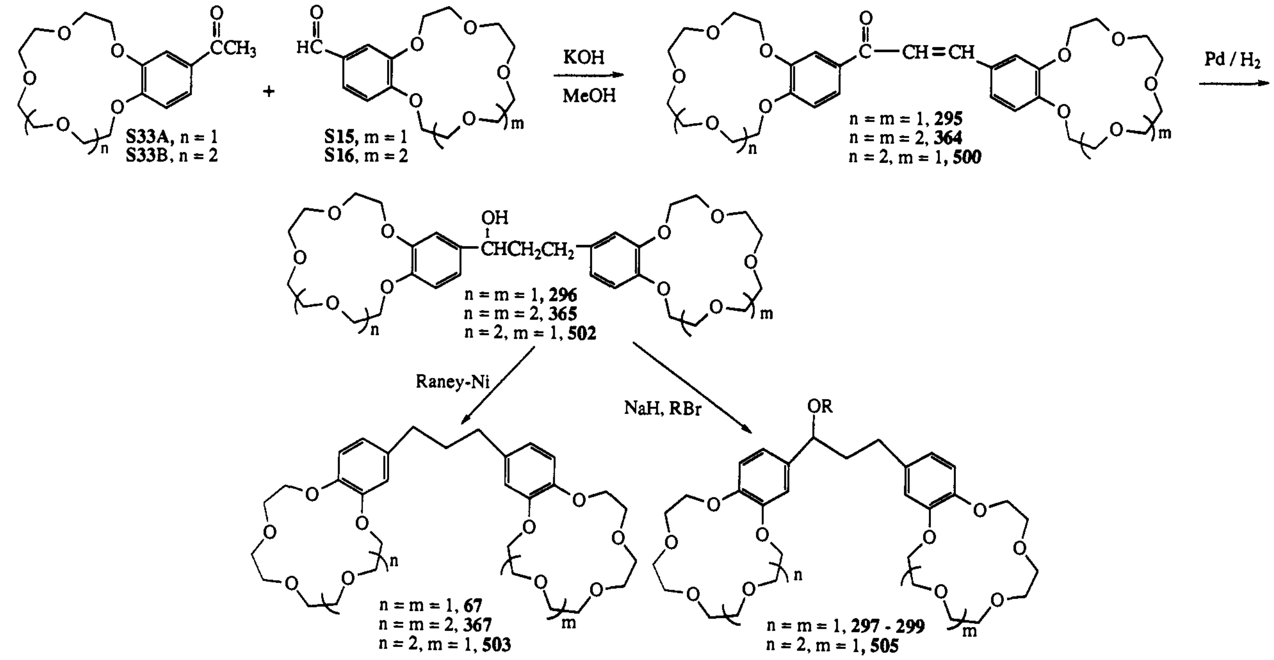
(benzocrown) 292 was similarly prepared by treating methyl 4,6-*O*-benzylidene-α-D-glucopyranoside with 2 equiv of chloromethyl-substituted benzocrown **S5** using NaH and in the presence of tetra-*n*-butylammonium iodide.[196] Biscrown **290** with a short-chain bridge formed an intramolecular sandwich complex with K^+ but not with Rb^+, Cs^+, or Tl^+.[152] However, the connecting chain of biscrown **291** is long enough to let it form sandwich complexes with K^+ and Rb^+.[53,195] The extraction of alkali picrates by **291** gave the following selectivity order: $K^+ > Rb^+ > Cs^+ > Na^+$.

4′-(Chlorosulfonyl)benzo-15-crown-5 (**S31**) was treated with 4′-aminobenzo-15-crown-5 (**S11**) to give sulfonamide-bridged biscrown **293** (Scheme 31, procedure WW).[110] Keto ester-bridged biscrown **294** was prepared by first converting 4′-carboxybenzo-15-crown-5 (**S25**) to its sodium salt which was then treated with bromoacetyl-substituted benzocrown **S27** (procedure XX).[99] Biernat and co-workers[80] reported a series of bis(benzocrown ether)s containing asymmetric bridges and the same or different crown units (Scheme 32, procedure YY). The Claisen–Schmidt reaction of 4′-formylbenzocrown **S15** with 4′-acetylbenzo-15-crown-5 (**S33A**) gave chalcone-containing biscrown **295** which was then hydrogenated to the corresponding alcohol **296** using palladium as a catalyst. Further hydrogenation of **296** using Raney Ni yielded the trimethylene-bridged biscrown **67** (Table 2). Lipophilic biscrowns **297–299** were obtained by treating hydroxy derivative **296** with the appropriate long-chain alkyl bromides in the presence of a strong base. PVC membrane studies showed that lipophilic biscrowns **297–299** exhibited high selectivity for K^+ over Na^+ and very promising electroactive properties to satisfy conditions for clinical analysis applications.[60]

Sonveaux and co-workers[197,198] reported the series of peptide-bridged bis(benzo-15-crown-5) derivatives **300–309** (Table 8). Amino acid-substituted benzocrowns **S53** and **S54** were coupled using *N*-(ethoxycarbonyl)-2-ethoxy-1,2-dihydroquinoline (EEDQ) as a condensing agent to give peptide-bridged biscrown **300** (Scheme 33, procedure ZZ).[197] Deprotection of **300** by hydrogenolysis followed by cyclization gave diketopiperazine-bridged biscrown **301**. The synthesis of alanine-bridged biscrown **302** is an example of the preparation of biscrowns **303–307** (procedure AAA).[198] Condensation of 4′-aminobenzo-15-crown-5 (**S11**) with Boc-protected alanine followed by N-deprotection in anhydrous HCl–dioxane–$CHCl_3$ gave alanine-substituted benzocrown **S55**. **S55** was treated with 4′-(chlorocarbonyl)benzo-15-crown-5 (**S56**) producing alanine-bridged biscrown **302**.[198] Biscrowns **303–307** containing various amino acid bridges were synthesized in the same manner from the appropiate Boc-protected amino acids. Biscrown **308** was obtained by the acylation of ω-aminocaprylic acid with (chlorocarbonyl)benzocrown **S56** under Schotten–Baumann conditions followed by EEDQ condensation with aminobenzocrown **S11**. Amide-bridged biscrown **309** was reported but without the synthetic procedure or physical properties. It was probably synthesized from aminobenzocrown **S11** and (chlorocarbonyl)benzocrown **S56**. Biscrowns **300** and **301** formed complexes with K^+ and NH_4^+ as well as with protonated leucine and glycine in THF and MeOH.[197] The association constants for the complexes of **302–308** with KSCN were determined.[198] The complexation of amide-containing biscrown **309** and azobiscrown **276** with KSCN was also studied for comparison. Biscrowns **302–309** exhibited much larger association constants than the similarly substituted monocrown ethers.

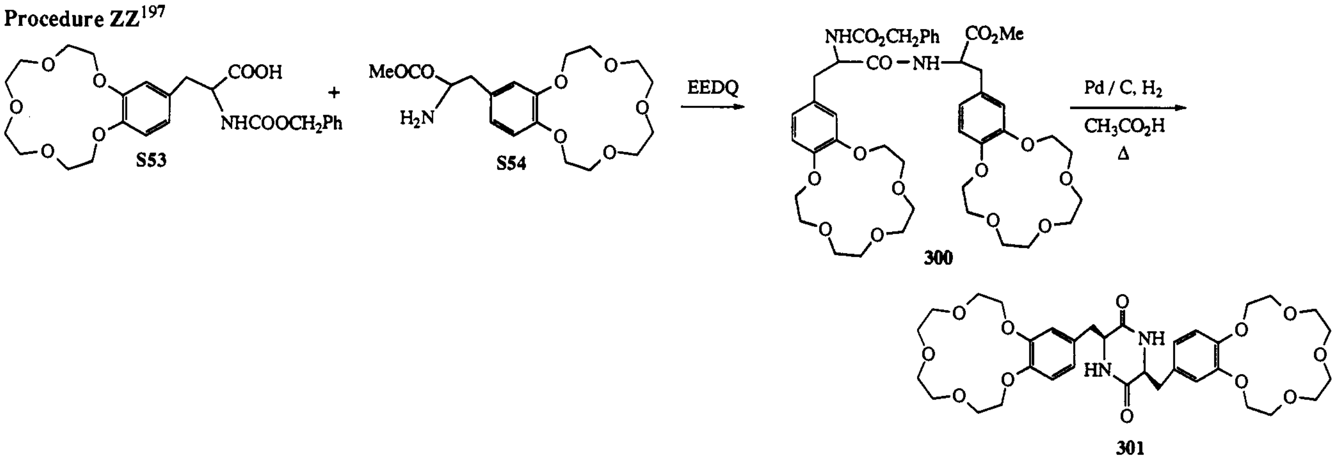
Bis(benzo-15-crown-5) derivatives **310–356** containing other substituents on the benzene rings are listed in Table 9. Di-*tert*-butyl-substituted azobiscrown **310** was prepared by the oxidation of 4′-amino-5′-*tert*-butylbenzo-15-crown-5 (**S48**) using MnO_2 as the oxidizing agent (Scheme 27, procedure RR).[22] The synthesis of biscrown **311** has been discussed before (Scheme 20).[154] Bis(*N*,*N*-dimethylamino)-substituted methylene-bridged biscrown **312** was synthesized by the simultaneous condensation and methylation of **S11** using HCHO and HCO_2H as methylating agents (Scheme 34, procedure BBB).[199] A general condensation procedure (procedure H) was used for the prepa-

Scheme 32. Procedure YY[60]

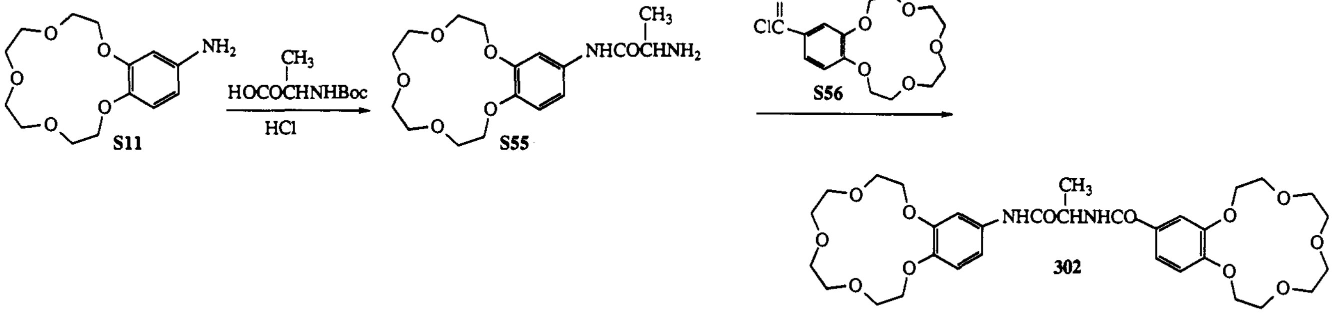


Scheme 33. Procedures ZZ[197] and AAA[198]

Procedure ZZ[197]



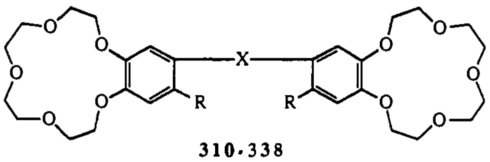
Procedure AAA[198]



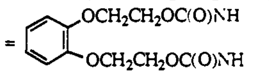
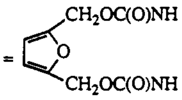
ration of hydroxy-substituted, Schiff base-containing biscrown 313 formed from ethylenediamine and 4′-hydroxy-5′-formylbenzo-15-crown-5.[200] 313 formed trinuclear complexes with two Na$^+$ ions in the polyether macrorings and another transition metal ion, Co(II), Cu(II), Ni(II), or uranyl(VI) ions, in the connecting chain coordination center.

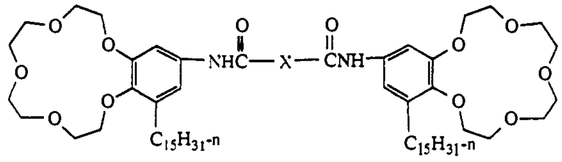
Tőke, Toth, and co-workers[163-170,201-212] reported a number of bis(benzocrown ether)s (**314–336**) with nitro or alkoxycarbonyl groups on the benzene rings (Table 9). Similar to the preparation of biscrowns **251–258**, substituted bisurea- and bisurethane-bridged biscrowns **314–331** were obtained by the condensation of substituted isocyanate-containing benzocrowns with the appropriate diols or diamines (Scheme 22).[163-166,201] The authors gave a detailed account of the preparation and physical properties for most of these derivatives. Biscrown **332** was synthesized by acylation of 5′-(*N*-methylamino)-4′-nitrobenzo-15-crown-5 (**S57**) with the appropriate bis(chloroformate) (Scheme 34, procedure CCC).[202] Direct nitration of ether-bridged biscrown **237** (Table 6), and ester-bridged biscrown **80** and **81** (Table 2) by nitric acid gave nitro-substituted biscrowns **333–336**, respectively.[202] Biscrown **336** was also ob-

Table 9. Bis(benzo-15-crown-5) Derivatives with Other Substituents on the Benzene Rings



310-338

no.	remarks	mp, °C	yield, %	procedure	ref(s)
310	X = N═N, R = CMe_3	143.7-145.5	40	RR	22
311	X = CH_2, R = CH_3	111-112	53	GG	154
312	X = CH_2, R = NMe_2	>160	33	BBB	199
313	X = CH═N$(CH_2)_2$N═CH, R = OH	165-166	85	H	200
314	X = NHC(O)NH$(CH_2)_3$NHC(O)NH, R = NO_2	235	70-80	JJ	163,165
315	X = NHC(O)NH$(CH_2)_6$NHC(O)NH, R = NO_2	230	70-80	JJ	163,165
316	X = NHC(O)O$(CH_2)_2$OC(O)NH, R = NO_2	172	70-80	JJ	163,165
		170-172	60-85	JJ	164
317	X = NHC(O)O$(CH_2)_5$OC(O)NH, R = NO_2	131	70-80	JJ	165
318	X = NHC(O)O$(CH_2)_8$C(O)NH, R = NO_2			JJ	169,201
319	X = NHC(O)O$(CH_2)_{18}$C(O)NH, R = NO_2			JJ	169,201
320	X = NHC(O)O$(CH_2CH_2O)_2$C(O)NH, R = NO_2	120	70-80	JJ	163,165
		98	60-85	JJ	164
321	X = NHC(O)$OCH_2CH_2SCH_2CH_2OC$(O)NH, R = NO_2	116	70-80	JJ	163,165
322	X = 	100	60-85	JJ	164
		119	70-80	JJ	163,165
		118-119	60-85	JJ	164
	R = NO2				
323	X =  R = NO_2	192	70-80	JJ	163,168
324	X = $(CH_3CH_2)_2C[CH_2OC(O)NH]_2$, R = NO_2			JJ	169,170,201
325	X = $(n\text{-}C_4H_9)_2C[CH_2OC(O)NH]_2$, R = NO_2			JJ	169,170,201
326	X = $n\text{-}C_{12}H_{25}C(CH_3)[CH_2OC(O)NH]_2$, R = NO_2			JJ	169,170,201
327	X = $n\text{-}C_{16}H_{33}C(n\text{-}C_4H_9)[CH_2OC(O)NH]_2$, R = NO_2			JJ	169,201
328	X = $n\text{-}C_{12}H_{25}CH[CH_2OC(O)NH]_2$, R = NO_2			JJ	164,201
329	X = NHC(O)O$(CH_2)_5$OC(O)NH, R = $COOC_{12}H_{25}\text{-}n$			JJ	169,201
330	X = NHC(O)O$(CH_2CH_2O)_2$C(O)NH, R = C(O)OCH_3			JJ	169,201
331	X = NHC(O)O$(CH_2CH_2O)_2$C(O)NH, R = C(O)$OC_{12}H_{25}\text{-}n$			JJ	169,201
332	X = $S[CH_2CH_2OC(O)NMe]_2$, R = NO_2	oil	40	CCC	202
333	X = $CH_2O(CH_2CH_2O)_2CH_2$, R = NO_2	108-110	68		202
334	X = $CH_2OC(O)(CH_2)_3C(O)OCH_2$, R = NO_2	133-137	60-65		202
335	X = $CH_2OC(O)(CH_2)_5C(O)OCH_2$, R = NO_2	124-125	60-65		202
336	X = $C(O)(OCH_2CH_2)_2OC(O)$, R = NO_2	103	70	W	202
337	X = S-S, R = NO_2	212-213	81	HHH	25
338	X = Se-Se, R = NO_2	194-196	52	HHH	25



339-348

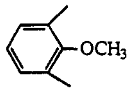
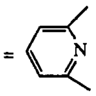
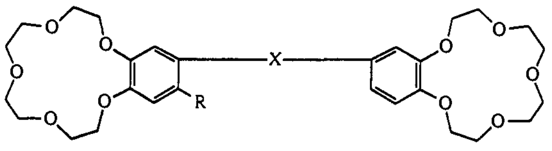
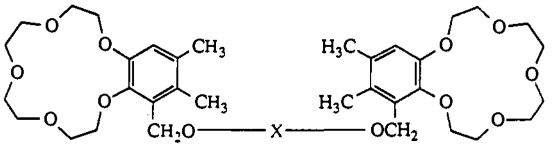
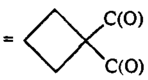
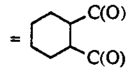
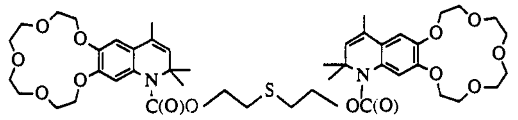
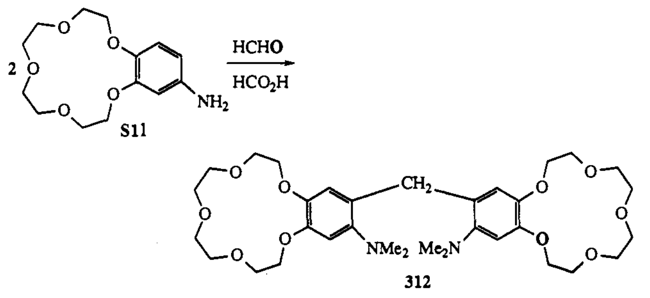
339	X = $(CH_2)_2$	139-140	79	E	213
340	X = $(CH_2)_4$	135-136	79	E	213
341	X = $(CH_2)_6$	125-126	75	E	213
342	X = $(CH_2)_8$	121-122	71	E	213
		121-122	68	E	214
343	X = CH_2OCH_2	oil	85	E	213
344	X = $o\text{-}C_6H_4$	82-83	74	E	213
		82-83	70	E	214
345	X = $m\text{-}C_6H_4$	147-148	83	E	213
346	X = $p\text{-}C_6H_4$	152-153	92	E	213
347	X = 	101-102	80	E	213

Table 9 (Continued)

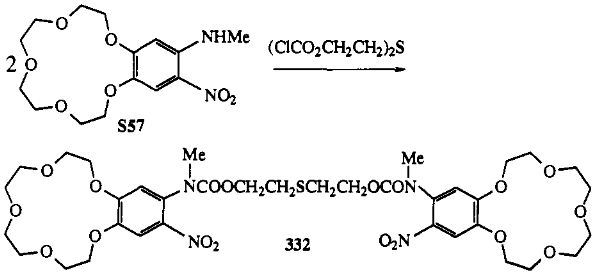
no.	remarks	mp, °C	yield, %	procedure	ref(s)
348	X = 	85–86	61	E	213
	 349-352				
349	X = C(O)CH=CH, R = C_2H_5	81–85	50	YY	60
350	X = C(O)CH=CH, R = n-C_8H_{17}	oil	48	YY	60
351	X = $(CH_2)_3$, R = C_2H_5	54–58	40	YY	60
352	X = $(CH_2)_3$, R = n-C_6H_{17}	49–50	35	YY	60
	 353-355				
353	X = $(n\text{-}C_4H_9)_2C[C(O)]_2$	oil	40	DDD	217
354	X = 	oil	44	DDD	217
355	X =  (*cis*)	oil	42	DD	217
356					169,201,204

Scheme 34. Procedures BBB[199] and CCC[202]

Procedure BBB[199]



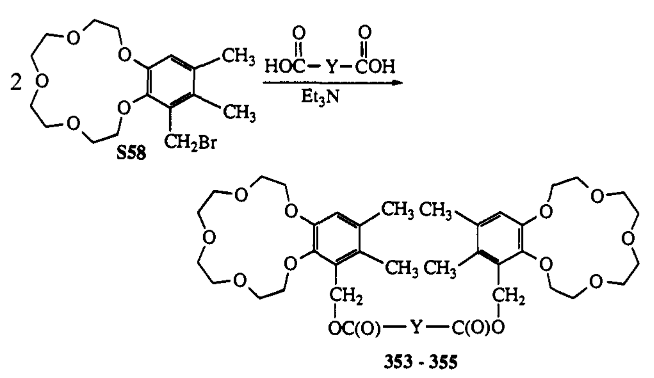
Procedure CCC[202]



tained by the reaction of diethylene glycol with 4′-nitro-5′-(chlorocarbonyl)benzo-15-crown-5 (procedure W).[202] Most of these substituted bisurea- and bisurethane-containing biscrowns were used as neutral carriers in PVC membrane K^+ ion-selective electrodes.[164,166–169,201,204,205] Electrode characteristics for these systems were investigated. Substitution of nitro groups on both benzene rings is of utmost importance with respect to potentiometric performance. Biscrowns with nitro groups exhibit performance characteristics sufficient for biological applications which are comparable with those of the valinomycin-based electrodes. A K^+ ion-selective microelectrode based on biscrown **326** gave good K^+ selectivity.[206,207] The electrode was proved by monitoring the changes in K^+ activity in different areas of the brain of anaesthetized rats after administration of veratrine. Biscrown **326** was also used for detecting the concentration of K^+.[208] These ion-selective PVC membranes were investigated by FTIR-ATR spectroscopic analysis.[209–212] The influence of some of these biscrowns on various plant-related bacteria also was determined.[170]

Huang and co-workers[213,214] reported bisamide-bridged bis(benzocrown ether)s **339–348** containing n-pentadecyl groups on the 3′-position of each benzocrown (Table 9). 3′-n-Pentadecylbenzo-15-crown-5 was nitrated followed by the reduction with hydrazine producing 3′-n-pentadecyl-4′-aminobenzo-15-crown-5. In a manner similar to that of procedure E, the latter macrocycle was condensed with various diacyl dichlorides in dry benzene to give the corresponding saturated diamide-bridged biscrowns **339–348** in high yields. K^+ ion-selective PVC membrane electrodes based on these biscrowns were prepared, and their electrode behaviors were evaluated.[215] Most of these

Scheme 35. Procedure DDD[217]



electrodes exhibited high K$^+$ selectivity with respect to all other alkali and alkaline earth metal ions. Tl$^+$ ion-selective PVC membrane electrodes based on biscrowns **342** and **344** were prepared and studied.[214] Fragmentation of these biscrowns was studied by the EIMS (electron-impact MS) method.[216] Biscrowns **339–348** with long lipophilic groups should be useful in the membrane transport of cations.

Asymmetric chalcone-containing biscrowns **349** and **350** with an ethyl or octyl group on one benzocrown unit were synthesized by the Claisen–Schmidt reaction of formyl-substituted benzocrown **S15** and the appropriate alkyl-substituted acetyl-containing benzocrown ether (Scheme 32, procedure YY).[60] Hydrogenation of **349** and **350** with palladium catalyst followed by Raney Ni reduction gave the corresponding alkyl-substituted propylene-bridged biscrowns **351** and **352**, respectively. 3′-(Bromomethyl)-4′,5′-dimethylbenzo-15-crown-5 (**S58**) was prepared by the bromomethylation of 4′,5′-dimethylbenzo-15-crown-5 with paraformaldehyde and HBr in acetic acid. Treatment of **S58** with di-*n*-butylmalonic, 1,1-cyclobutanedicarboxylic, and 1,2-*cis*-cyclohexanedicarboxylic acids using triethylamine as a catalyst gave the corresponding diester-bridged biscrowns **353–355** (Scheme 35, procedure DDD).[217] Biscrown **356** was reported without the preparation procedure.[169,201,204]

4. Bis(benzo-18-crown-6) Derivatives

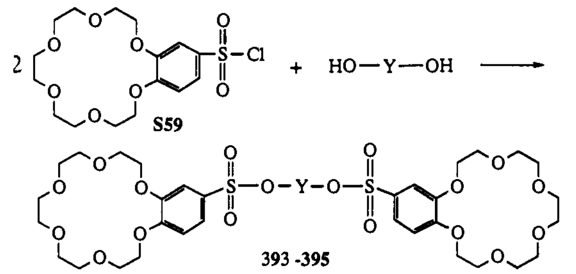
Bis(benzo-18-crown-6) derivatives are bis(crown ether)s containing two identical 4′-benzo-18-crown-6 moieties connected by various organic units. Bis(benzo-18-crown-6) derivatives **357–475** are listed in Table 10. These biscrowns were synthesized by the same procedures used to prepare the bis(benzo-15-crown-5) analogues. The procedures are listed in Table 10. Therefore, the synthesis for only some of them will be discussed.

trans-Vinyl-bridged bis(benzo-18-crown-6) (**357**) was prepared by the reductive coupling of 4′-formylbenzo-18-crown-6 (**S16**) using TiCl$_4$ and Zn as the catalysts in the presence of a proton sponge (procedure S).[79] *Cis*-isomer **358** was obtained from the UV irradiation of **357**. Hydrogenation of **357** produced dimethylene-bridged biscrown **366** in a 74% yield. Bis(benzo-18-crown-6) **359** was prepared in high yields by two different methods. Iodobenzocrown **S19** was treated with acetylene-containing benzocrown (**S23**) using CuI/(Ph$_3$P)$_2$PdCl$_2$ as the catalyst to give **359** (Scheme 7, procedure J).[53] **359** was also obtained by the reaction of acetylene with two molecules of iodobenzocrown **S19** using the same catalyst (Scheme 14, procedure T).[53,80] Dialkyne-bridged bis(benzocrown)s **360** and **361** were synthesized similarly by the reaction of 1,5-hexadiyne and 1,7-octadiyne with iodobenzocrown **S19** (procedure U).[53,80] Catalytic hydrogenation of **359** and **361** gave polymethylene-bridged biscrowns **366** and **369**, respectively. Diketone-bridged biscrowns **362** and **363** were synthesized by one- or two-step condensations of the dicarboxylic acids with benzo-18-crown-6 (**S3**) (Scheme 10, procedure M, and Scheme 1, procedure A).[60] Reduction of **362** and **363** gave polymethylene-bridged biscrowns **368** and **370**, respectively.[60] Condensation of 4′-acetyl- and 4′-formylbenzo-18-crown-6 (**S33B** and **S16**, respectively) yielded the chalcone-bridged biscrown **364**. The latter biscrown was reduced to propylene-bridged biscrown **367** through alcohol derivative **365** with Raney Ni as the catalyst (Scheme 32, procedure YY).[60]

Bis(benzo-18-crown-6) derivatives **371–385** with different ethereal bridges were prepared by three different methods. Bis(benzocrown) **371** containing an asymmetric bridge was synthesized by the reaction of 4′-[3-(tosyloxy)propyl]benzo-18-crown-6 (**S52**) with its 4′-hydroxy analogue **S35** (Scheme 30, procedure VV).[195] Ether-bridged biscrowns **372–376** were obtained by the reaction of 4′-hydroxy-benzocrown (**S35**) with 1,6-dibromohexane, and di-, tri-, tetra-, and pentaethylene glycol ditosylates under strong basic conditions (Scheme 21, procedure II).[157,158] Biscrowns **377–379** were synthesized by treating 4′-(bromomethyl)benzo-18-crown-6 (**S6**) with the appropriate ethylene or polyethylene glycols by using sodium hydride as the base,[153] while **380–382** containing aromatic ethereal bridges were similarly obtained from **S6** and catechol, hydroquinone, and resorcinol in acetone under weak K$_2$CO$_3$ basic conditions (Scheme 2, procedure B).[118] Biscrown **380** was also prepared by the reaction of catechol with 4′-[(tosyloxy)methyl]benzo-18-crown-6 using NaH as a base.[218] Nitration of **380** with fuming nitric acid in acetic acid–chloroform gave the corresponding nitro analogue **383**. Subsequent reduction of the nitro group with hydrogen using Pd/C as a catalyst yielded amino derivative **384**. **384**, without isolation, was coupled with 1-chloro-2,4-dinitro-6-(trifluoromethyl)benzene to give chromogenic biscrown **385** in a 71% overall yield.[218] Bis(benzo-18-crown-6)s **363**, **367**, **368**, and **370** exhibited selectivity toward Cs$^+$ with the best resulting provided by **367**, containing a trimethylene bridge.[60] Sandwich-type complexes of bis(benzo-18-crown-6) derivatives with Cs$^+$ were also confirmed by high Cs$^+$ extractability by **371–376**.[195] Bis(benzocrown)s **366**, **369**, and **371–376** were found to selectively extract Cs$^+$.[43,81] K$^+$ ion-selective electrode studies indicated that the electrodes based on bis(benzo-18-crown-6) derivatives **377–382** have lower K$^+$ selectivity over Na$^+$ than those based on the corresponding bis(benzo-15-crown-5) analogues.[118,161]

Diester-bridged biscrowns **386–391** were prepared by esterification of the appropriate dicarboxy dichlorides with two molecules of 4′-(hydroxymethyl)-benzo-18-crown-6 (**S30**) in the presence of triethylamine (Scheme 16, procedure X).[86,219] *d,l*- and *meso*-bis(crown ether) **392** was prepared from the dipotassium salt of α,α'-dimethylglutaric acid and chloromethyl-substituted benzocrown **S6** (procedure Y).[220] Disulfonate-bridged

Scheme 36. Procedure FFF[221]



biscrowns **393–395** were prepared by the sulfonylation of ethylene, diethylene, and triethylene glycols with chlorosulfonyl-substituted benzocrown ether **S59** (Scheme 36, procedure FFF).[221] Complexation and extraction studies of alkali metal picrates by diester-bridged biscrowns **386–388** showed that biscrown **388** and *cis*-biscrown **387** formed intramolecular 2:1 crown unit/cation complexes with Cs^+, while the *trans*-isomer **386** formed only a 1:1 complex because of the unfavorable *trans* configuration.[86,89] Cs^+ ion-selective PVC membrane electrodes based on bis(benzo-18-crown-6) ligands **389–391** were prepared and selectivity coefficients for various interfering monovalent ions were determined.[219,222] These electrodes have excellent electrochemical selectivity compared to those based on the corresponding monocyclic analogues and valinomycin. **390** and **391** were found to exceed **389** in selectivity coefficients, which reflect the formation of stable 2:1 complexes of **390** and **391** with Cs^+.

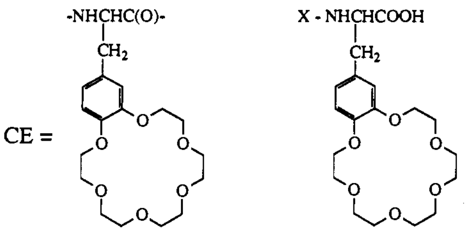
Diamide-bridged bis(benzo-18-crown-6) **396** was synthesized by treating amino(benzocrown ether) **S12** with glutaryl dichloride in benzene in the presence of triethylamine (Scheme 4, procedure E).[101] **396** is a remarkably effective extracting agent for Cs^+ [101,111] and Sr^{2+},[112] but not as good as its benzo-15-crown-5 analogue **96** for the extraction of Tl^+.[113] Azobiscrown **397** was prepared by the reductive coupling of nitrobenzocrown **S9** using Zn/NaOH as catalysts (Scheme 3, procedure C),[22] but **397** was not obtained by the oxidative coupling of aminobenzocrown **S12** (Scheme 27, procedure RR). Cs^+ was extracted efficiently from an aqueous solution to an organic phase by *cis*-**397**.[22] Azoxy analogue **398** was obtained in high yield by the reductive coupling of nitrobenzocrown **S9** using Zn/PPyCl as the catalyst (Scheme 3, procedure D).[44] Schiff base-containing biscrown **399** was prepared by condensing aminobenzocrown **S12** with formyl-substituted benzocrown **S16** (Scheme 8, procedure K).[223] Reduction of **399** with $NaBH_4$ gave the corresponding amine derivative **400**.

Bis(Schiff base)-bridged bis(benzo-18-crown-6 ether)s **401–442** containing aliphatic or aromatic chains in the bridge were synthesized by condensation of 4′-formylbenzo-18-crown-6 (**S16**) with the appropriate aliphatic and aromatic diamines (Table 10, Scheme 6).[50,114,117,124] Condensation of 1,4-dihydrazinophthalazine with **S16** by procedure H[125] gave biscrown **443** containing Schiff base-like functions. 1,5-Pentanedicarbohydrazide and 1,3-benzenedicarbohydrazide were condensed with **S16** to form biscrowns **444** and **445**, respectively (Scheme 18).[129,130] Another series of aromatic bis(Schiff base)-bridged biscrowns (**446–449**) were synthesized in high yields by treating aminobenzocrown **S12** with the appropriate benzenedialdehydes (Scheme 6, procedure I).[223,224] Reduction of bis(Schiff base)-containing biscrowns **401–413** and **446–449** gave the corresponding diamine derivatives **450–466**.[117,223] Quinoxaline- and pyrimidine-bridged bisbenzocrowns **467**[48] and **468**[49] were prepared by treating aminobenzocrown **S12** with 2,3-dichloroquinoxaline and 2,4-dichloro-5-nitropyrimidine, respectively (Scheme 5, procedure G). Solvent extraction and spectroscopic studies indicated that bis(Schiff base)-containing biscrowns **405**, **407–411**, and **413** formed pocket complexes with cations larger than K^+.[50] Extraction of alkali metal picrates with Schiff base-containing biscrowns **399** and **446–448** and secondary amine-containing biscrowns **400** and **463–465** indicated that these bis(benzo-18-crown-6) derivatives formed 1:1 crown unit/cation complexes with Na^+, K^+, and Rb^+ and a 2:1 complex with Cs^+.[49] The extractive ability of secondary amine-containing biscrowns were much higher than that of the corresponding Schiff base-containing biscrowns. **463** exhibited the highest extractive ability and selectivity for Cs^+ ion. Conductance studies showed that quinoxaline-bridged biscrown **467** formed 2:1 complexes with Rb^+ and Cs^+ cations.[48] Bis(crown ether)s **401** and **450–462** were used as K^+ adsorbents.[114,117] Cs^+ ion-selective PVC membrane electrodes based on Schiff base-bridged bis(crown ether)s **400** and **446–449** were prepared, and electrode properties were studied.[224]

Diurethane-bridged bis(benzo-18-crown-6 ether)s **469–472** were prepared by condensing 4′-isocyanate-substituted benzocrown **S39** with the appropiate diols (Scheme 22, procedure JJ).[163–165] Urea-bridged biscrown **473** was reported without physical properties.[163] Di-*tert*-butyl-substituted azobis(benzo-18-crown-6) (**474**) was prepared from 4′-amino-5′-*tert*-butylbenzo-18-crown-6 (**S49**) by oxidative coupling with MnO_2 (Scheme 27, procedure RR).[22] The presence of *tert*-butyl groups in **474** reduces the cavity size as compared to azobis(crown ether) **397** which has no *tert*-butyl groups.[22]

Voyer and co-workers[226,227] reported bis(benzo-18-crown-6 ether) peptides **476–481** (Figure 1), in which each peptide contains two benzo-18-crown-6 units. The benzo-18-crown-6 residue is located on the β-carbon of alanine (see **S60**). **S60** was prepared from dihydroxyphenylalanine (DOPA). The crown units in these peptides are separated systematically by one, two, or three alanines. Biscrown-containing peptides **476–481** were synthesized by the solid-phase method on a *p*-nitrophenyl oxime resin from *N*-Boc- or *N*-*t*-Boc-benzo-18-crown-6 containing L-alanine (**S60**). After the coupling steps, the peptides were cleaved from the oxime

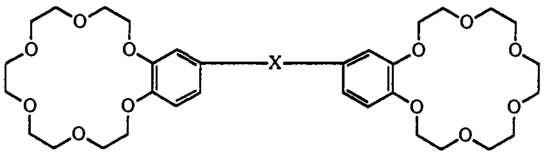
476, Boc - NH - Ala - Ala - Ala - CE - Ala - CE - Ala - Ala - CONH - *n*-Pr (86%)
477, Boc - NH - Ala - Ala - CE - Ala - Ala - CE - Ala - Ala - CONH - *n*-Pr (65%)
478, Boc - NH - Ala - CE - Ala - Ala - Ala - CE - Ala - Ala - CONH - *n*-Pr (75%)
479, N-tert - Boc - Ala - Ala - Ala - CE - Ala - CE - Ala - CONH - *n*-Pr (41%)
480, N-tert - Boc - Ala - Ala - CE - Ala - Ala - CE - Ala - CONH - *n*-Pr (54%)
481, N-tert - Boc - Ala - CE - Ala - Ala - Ala - CE - Ala - CoNH - *n*-Pr (38%)



S60 (X = Boc or tert-Boc)

Figure 1. Bis(benzo-18-crown-6 ether) peptides 476–481[226,227] and starting 18-crown-6-containing alanine (S60).

Table 10. Bis(benzo-18-crown-6) Derivatives



357-400

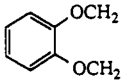
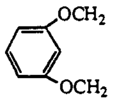
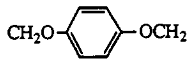
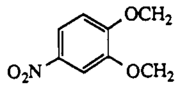
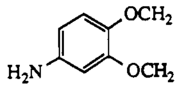
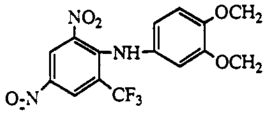
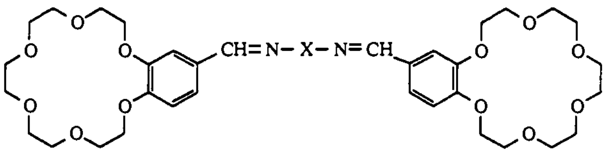
no.	remarks (X =)	mp, °C	yield, %	procedure	ref(s)
357	$CH{=}CH$ (*E*)	154–156	31	S	79
358	$CH{=}CH$ (*Z*)	oil	87		79
359	$C{\equiv}C$	139.8–141.4	83	J	53
		144.1–145.8	88	T	53,80
360	$C{\equiv}C(CH_2)_2C{\equiv}C$	160.1–162.8	84	U	53
361	$C{\equiv}C(CH_2)_4C{\equiv}C$			U	80
362	$C(O)(CH_2)_3C(O)$	75–80	7	M	60
363	$C(O)(CH_2)_{11}C(O)$	78–80	22	A	60
364	$C(O)CH{=}CH$	99–101	15	YY	60
365	$CH(OH)CH_2CH_2$	oil	82	YY	60
366	CH_2CH_2	81–82.5	74	S	79
		87.6–89.4	69	J	53
		87.6–89.4	69	T	53,80
367	$(CH_2)_3$	83–85	76	YY	60
368	$(CH_2)_5$	56–58	25	A	60
369	$(CH_2)_8$	88.4–89.4	69	U	80
370	$(CH_2)_{13}$	71–74	22	A	60
371	$CH_2CH_2CH_2O$	36.2–37.8	41	VV	195
372	$O(CH_2)_6O$	74.9–77.1	72	II	158
373	$OCH_2CH_2OCH_2CH_2O$	74.6–77.5	52	II	157
374	$OCH_2(CH_2OCH_2)_2CH_2O$	69.5–72.0	78	II	157
375	$OCH_2(CH_2OCH_2)_3CH_2O$	52.0–54.5	50	II	157
376	$OCH_2(CH_2OCH_2)_4CH_2O$	oil	58	II	157
377	$CH_2OCH_2CH_2OCH_2$	83–85	38	B	153
378	$CH_2(OCH_2CH_2)_2OCH_2$	oil	34	B	153
379	$CH_2(OCH_2CH_2)_3OCH_2$	oil	32	B	153
380		103–104	87	B	118
		viscous oil	65	B	218
381		87–88	82	B	118
382		130–131	80	B	118
383		viscous oil	86	B	218
384				B	218
385		viscous oil	71	B	218
386	$CH_2OC(O)CH{=}CHC(O)OCH_2$ (*trans*)	105–106		X	86
387	$CH_2OC(O)CH{=}CHC(O)OCH_2$ (*cis*)	oil		X	86
388	$CH_2OC(O)CH_2CH_2C(O)OCH_2$			X	86
389	$CH_2OC(O)(CH_2)_3C(O)OCH_2$	81–82		X	219
390	$CH_2OC(O)(CH_2)_5C(O)OCH_2$	90–91		X	219
391	$CH_2OC(O)(CH_2)_7C(O)OCH_2$	82–83		X	219
392	$CH_2OC(O)CH(CH_3)CH_2CH(CH_3)C(O)OCH_2$				
	d,l			Y	220
	meso			Y	220
393	$S(O_2)OCH_2CH_2OS(O_2)$	120–121	65	FFF	221
394	$S(O_2)O(CH_2CH_2O)_2S(O_2)$		63	FFF	221
395	$S(O_2)O(CH_2CH_2O)_3S(O_2)$		60	FFF	221
396	$NHC(O)(CH_2)_3C(O)NH$	178–178.5		E	101
397	$N{=}N$	173–174	1.6	C	22
398	$N{=}N(O)$	142–144	59.6	D	44
399	$N{=}CH$	133–135	83	K	223
400	CH_2NH	118–120	77	K	223

Table 10 (Continued)



401-445

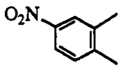
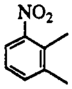
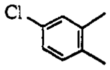
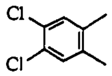
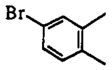
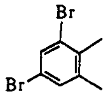
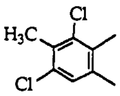
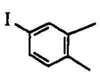
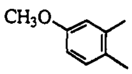
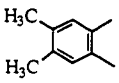
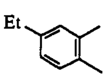
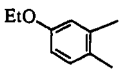
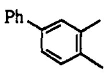
no.	remarks (X =)	mp, °C	yield, %	procedure	ref(s)
401	None		70	H	114
402	CH_2		51	H	117
403	$(CH_2)_2$		65	H	117
404	$(CH_2)_3$		67	H	117
405	$(CH_2)_4$		74	H	117
		105		H	50
406	$(CH_2)_5$		70	H	117
407	$(CH_2)_6$		74	H	117
		95		H	50
408	$(CH_2)_7$		72	H	117
		68		H	50
409	$(CH_2)_8$		75	H	117
		102		H	50
410	$(CH_2)_9$		78	H	117
		75		H	50
411	$(CH_2)_{10}$		83	H	117
		104		H	50
412	$(CH_2)_{11}$		81	H	117
413	$(CH_2)_{12}$		75	H	117
		104		H	50
414	m-C_6H_4	brown solid	32	H	124
415		yellow solid	24	H	124
416		yellow solid	8	H	124
417		yellowish-white solid	39	H	124
418		yellowish-white solid	28	H	124
419		yellowish-white solid	32	H	124
420		brown solid	22	H	124
421		yellowish-white solid	20	H	124
422		brown solid	23	H	124
423		yellowish-white solid	34	H	124
424		yellowish-white solid	25	H	124
425		yellowish-white solid	28	H	124
426		yellowish-white solid	19	H	124
427		yellowish-white solid	30	H	124

Table 10 (Continued)

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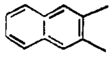
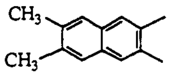
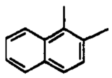
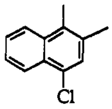
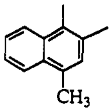
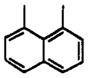
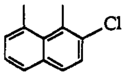
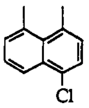
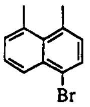
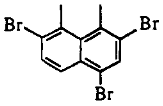
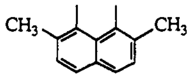
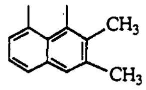
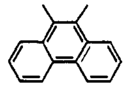
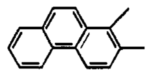
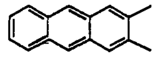
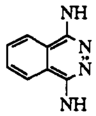
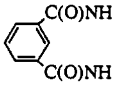
428		yellowish-white solid	28	H	124
429		yellowish-white solid	30	H	124
430		yellowish-white solid	21	H	124
431		yellowish-white solid	23	H	124
432		yellowish-white solid	27	H	124
433		yellowish-brown solid	6	H	124
434		yellowish-brown solid	15	H	124
435		yellowish-brown solid	11	H	124
436		brown solid	21	H	124
437		brown solid	14	H	124
438		yellowish-brown solid	17	H	124
439		yellowish-brown solid	9	H	124
440		brown solid	19	H	124
441		brown solid	26	H	124
442		brown solid	32	H	124
443		170–172	65	H	125
444	HNC(O)(CH$_2$)$_6$C(O)NH	148–151	62	CC	129
445		226–228	73	CC	130

Table 10 (Continued)

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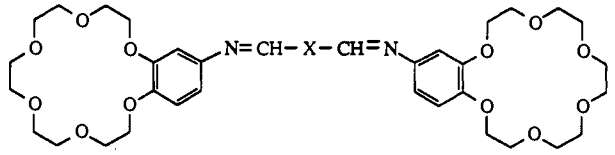
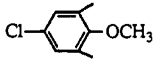
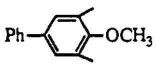
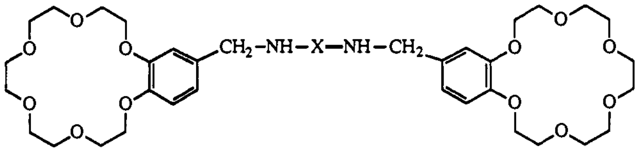
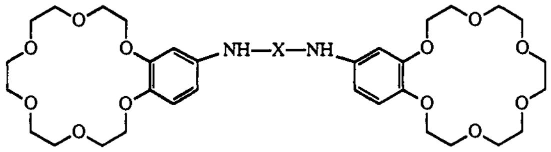
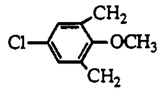
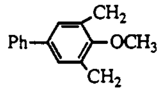
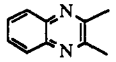
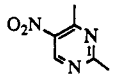
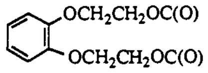
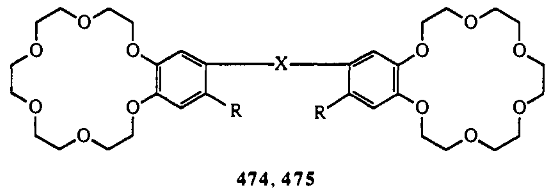
	 446-449				
446	*m*-C_6H_4	118–120	93	I	223
447		88–90 88–90	93	I I	223 224
448		129–132 129–130	73	I I	223 224
449	*p*-C_6H_4	196–198	89	I	223
	 450-462				
450	none		48	H	117
451	CH_2		58	H	117
452	$(CH_2)_2$		60	H	117
453	$(CH_2)_3$		64	H	117
454	$(CH_2)_4$		61	H	117
455	$(CH_2)_5$		77	H	117
456	$(CH_2)_6$		60	H	117
457	$(CH_2)_7$		74	H	117
458	$(CH_2)_8$		66	H	117
459	$(CH_2)_9$		56	H	117
460	$(CH_2)_{10}$		68	H	117
461	$(CH_2)_{11}$		77	H	117
462	$(CH_2)_{12}$		62	H	117
	 463-472				
463	*m*-xylylene	oil	83	I	223
464		82–84	60	I	223
465		102–104	63	I	223
466	*p*-xylylene	80–82	86	I	223
467		74–75	67	G	48
468		206–208	48	G	49
469	$C(O)OCH_2CH_2OC(O)$	132 130–132	70–80 60–85	JJ JJ	163,165 164
470	$C(O)O(CH_2CH_2O)_2C(O)$	64	70–80	JJ	163–165
471	$C(O)OCH_2CH_2SCH_2CH_2OC(O)$	87	70–80	JJ	163–165
472		109	70–80	JJ	163–165
473	C(O)				163

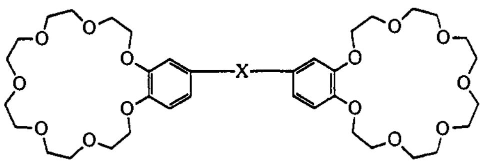
Table 10 (Continued)



474, 475

no.	remarks (X =)	mp, °C	yield, %	procedure	ref(s)
474	X = N=N, R = *t*-Bu	173.1-174	33	RR	22
475	X = S-S, R = NO_2	148-150	75	HHH	24

Table 11. Bis(benzo-21-crown-7) Derivatives



482-484

no.	remarks (X =)	mp, °C	yield, %	procedure	ref
482	C≡C	110.1-111.2	93	J	53
483	CH_2CH_2	86.9-88.1	83	J	53
484	$NHC(O)(CH_2)_3C(O)NH$	153.5-154.5		E	228

resin by treatment with 0.5 M *n*-propylamine. The synthetic yields are shown in parentheses. Extraction results obtained with Cs^+ using biscrown peptides 476-478 demonstrated strong side-chain cooperative binding between two distant crown units.[226] Picrate salt extraction results showed that biscrown peptides 479-481 have high binding affinity toward α,ω-primary alkylidenediammonium substrates [$H_3N^+(CH_2)_nNH_3^+$, n = 2-9], especially where n = 6-9. Among the peptide-bridged crowns, 480, having the crown units separated by two alanine units, exhibited the best binding ability.[227]

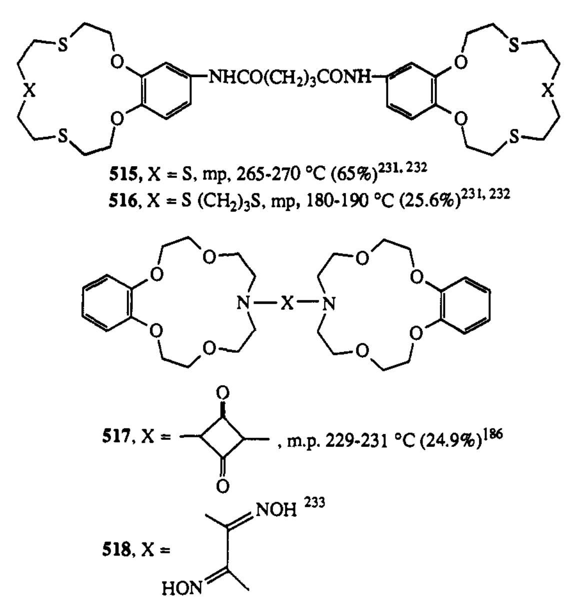
5. Bis(benzo-21-crown-7) Derivatives

Three reported symmetric bis(benzo-21-crown-7 ether)s are listed in Table 11. Acetylene-bridged bis(benzo-21-crown-7) (482) was synthesized by procedure J (Scheme 7) from iodo- and acetylene-substituted (S20 and S24, respectively) (benzo-21-crown-7)s using CuI/$(Ph_3P)_2PdCl_2$ as the catalyst.[53] Hydrogenation of 482 gave the corresponding dimethylene-bridged bis(crown ether) 483. Diamide-bridged bis(benzo-21-crown-7) 484 was prepared by acylation of 4′-aminobenzo-21-crown-7 (S13) with glutaryl dichloride (Scheme 4, procedure E).[228] Few bis(benzo-21-crown-7)s have been synthesized because starting benzo-21-crown-7 derivatives are not available. As described in previous sections, the "biscrown effect" makes bis(benzo-12-crown-4), bis(benzo-15-crown-5), and bis(benzo-18-crown-6) ligands have high affinity for Na^+, K^+, and/or Rb^+ and Cs^+ and/or Rb^+ cations, respectively. Bis(benzo-21-crown-7 ether)s should have affinity for cations with the diameters larger than that of Cs^+ since biscrown 483 did not exhibit the biscrown effect with the alkali metal cations.[81] Biscrown ether 484 extracted alkali metal cations in the order of $Cs^+ > Rb^+ > K^+ > Na^+$ and is a more efficient extraction agent than the corresponding monomeric analogue.[219] However, 484 is not as good an extractor as the bis(benzo-18-crown-6) and bis(benzo-15-crown-5) analogues.

6. Asymmetric Bis(benzocrown ether)s

In this section, bis(benzocrown ether)s containing benzo-15-crown-5/benzo-18-crown-6, benzo-15-crown-5/benzo-21-crown-7, and benzo-18-crown-6/benzo-21-crown-7 units will be discussed. Asymmetric biscrown ethers 485-514, are listed in Table 12. Theoretically, procedures J, K, L, M, DD, VV, WW, XX, YY, ZZ, and AAA can all be used for the preparation of asymmetric bis(benzocrown ether)s; however, only some of these procedures were used. Some asymmetric bis(benzocrown ether)s were synthesized by taking advantage of different reactivities of the starting materials. Asymmetric acetylene-bridged bis(crown ether)s 485-487 were synthesized by the reaction of iodobenzo-15-crown-5 (S18) with acetylene-substituted benzo-18-crown-6 (S23), acetylene-substituted benzo-21-crown-7 (S24), and by the reaction of iodobenzo-18-crown-6 (S19) with S24, respectively (Scheme 7, procedure J).[53] Hydrogenation of 485-487 using PtO_2 as a catalyst gave dimethylene-bridged asymmetric bis(crown ether)s 488-490. Asymmetric bis(crown ether)s 491-493 were reported without details.[118] Beer and co-workers[229] reported the synthesis of asymmetric bipyridine-bridged bis(crown ether)s 494-497 by a stepwise method (procedure P). 4,4′-Dimethyl-2,2′-bipyridyl was first monolithiated and then treated with the appropriate formyl-substituted benzocrown ether. The remaining methyl substituent of these intermediates was then lithiated and treated with another molecule of the appropriate formyl-substituted benzocrown ether to give diol-bridged biscrowns 494 and 495. Dehydration of 494 and 495 with pyridinium *p*-toluenesulfonate (PTPS) gave *trans*-diene-containing biscrowns 496 and 497 in high yields.

Asymmetric bis(benzocrown ether) 498 with an asymmetric bridge was synthesized by the reaction of 4′-[3-(tosyloxy)propyl]benzo-15-crown-5 (S51) with 4′-hydroxybenzo-18-crown-6 (S35) under strong base conditions (Scheme 30, procedure VV).[53] Bis(crown ether) 499, an analogue of 498 with the benzocrowns reversed, was obtained from 4′-[3-(tosyloxy)propyl]benzo-18-crown-6 (S52) and 4′-hydroxybenzo-15-crown-5 (S34).[53,195] Chalcone-containing bis(crown ether)s 500 and 501 were synthesized by condensation of 4′-acetylbenzo-18-crown-6 (S33B) and its 5′-ethyl-substituted analogue with 4′-formylbenzo-15-crown-5 (S15) following procedure YY.[60] Hydrogenation of 500 gave alcohol-containing biscrown 502. 502 was further reduced with Raney Ni to produce the corresponding



515, X = S, mp, 265-270 °C (65%)[231, 232]
516, X = S (CH₂)₃S, mp, 180-190 °C (25.6%)[231, 232]

517, X = , m.p. 229-231 °C (24.9%)[186]

518, X = [233]

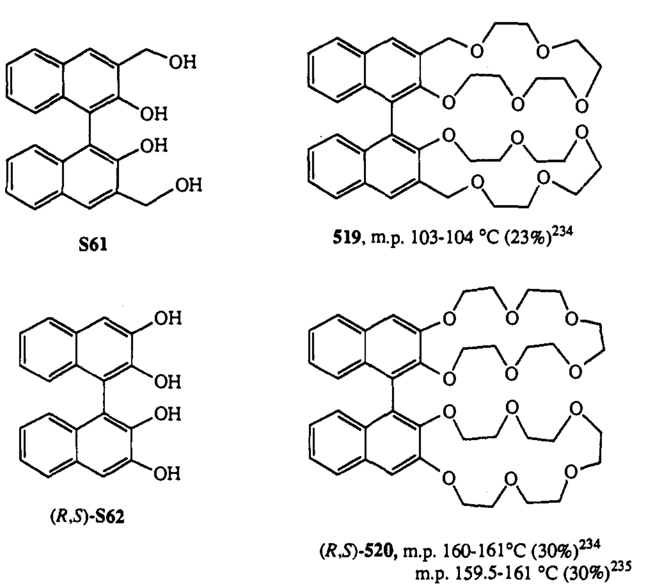
Figure 2. Bis(benzocrown ether)s containing other heteroatoms in the macroring.

trimethylene-bridged bis(benzocrown) **503**. Treatment of **502** with *n*-octyl bromide gave lipophilic bis(benzocrown) **505**. A two-step reduction of **501** gave **504**.[60] Stepwise acylation by glutaric acid on benzo-15-crown-5 (**S2**) and benzo-18-crown-6 (**S3**) gave diketone-bridged biscrown **506** which was subsequently reduced to **507** containing a pentamethylene bridge (Scheme 10, procedure M).[60] Condensation of 4′-aminobenzo-15-crown-5 (**S11**) and 4′-formylbenzo-18-crown-6 (**S16**) gave Schiff base-bridged bis(crown ether) **508**, which was then reduced to its secondary amine derivative **509** with $NaBH_4$ (Scheme 8, procedure K).[223] Bishydrazone-bridged bis(benzocrown ether)s **510–514** were prepared by treatment of the appropriate bishydrazines with 4′-formylbenzo-15-crown-5 (**S15**) and -18-crown-6 (**S16**) (procedure H).[230]

Bis(benzocrown ether)s containing different crown units have intermediate complexation properties between the symmetric bis(crown ether)s with two large and two small crown units. The combination of different crown units can improve certain complexation properties. For example, bis(benzocrown ether) **498** or **499** exhibited the highest selectivity for Rb^+, while bis(benzo-15-crown-5) **291** (Table 8) and bis(benzo-18-crown-6) **371** (Table 10) were selective for K^+ and Cs^+, respectively.[53,195] Asymmetric bis(crown ether)s containing benzo-18-crown-6 and benzo-15-crown-5 units generally exhibited selectivity toward Rb^+ (e.g. **502**, **505–507**) and Cs^+ (e.g. **505** and **506**).[60]

7. Bis(benzocrown ether)s Containing Other Heteroatoms in the Macroring

In the previous sections, bis(benzocrown ether)s containing only oxygen doner atoms in macrorings were reported. In this section, bis(benzocrown ether)s containing oxygen and other heteroatoms will be discussed. Sulfur-containing (**515** and **516**) and nitrogen-containing (**517** and **518**) bis(benzocrown ether)s have been reported (Figure 2). Diamide-bridged bis(benzothiacrown ether)s **515** and **516** were synthesized by treating the appropiate aminobenzothiacrown ether with glutaryl dichloride in the presence of triethylamine (Scheme 4, procedure E).[231,232] These biscrowns bind Ag^+ and Hg^{2+} more effectively than the corresponding monomeric analogues. As expected, they have very poor cation binding ability for alkali and alkaline earth metal cations. Bis(benzoazacrown ether) **517** was obtained by the reaction of benzoazacrown **S50** with squaric acid (Scheme 28, procedure SS, Figure 2).[186] Glyoxime-bridged bis(benzoazacrown ether) **518** was synthesized by the reaction of **S50** and dichloroglyoxime in ethanol using Na_2CO_3 as a base.[233] **518** formed complexes with Cu^{2+}, Ni^{2+}, Pd^{2+}, Co^{2+}, Co^{3+}, and Pt^{4+}.



S61

519, m.p. 103-104 °C (23%)[234]

(*R,S*)-**S62**

(*R,S*)-**520**, m.p. 160-161°C (30%)[234]
m.p. 159.5-161 °C (30%)[235]

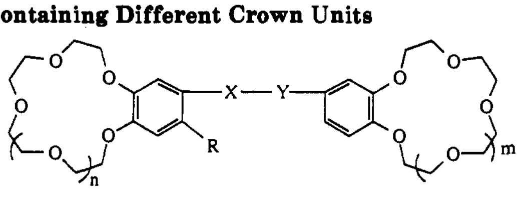
Figure 3. Bis(naphthocrown ether)s.

8. Other Bis(aromatic ring-containing crown ether)s

This section will include bis(naphthocrown ether)s, bis(dibenzocrown ether)s, and bis(benzoheterocrown ether)s. Cram and co-workers[234,235] reported bis(naphthocrown ether)s **519** and **520** (Figure 3). 3,3′-Bis(hydroxymethyl)-2,2′-dihydroxy-1,1′-binaphthyl (**S61**) was treated with tetraethylene glycol ditosylate to give bisnaphthocrown **519** in a 23% yield. (*R,S*)-Bisnaphthocrown **520** was synthesized by treating (*R,S*)-2,2′,3,3′-tetrahydroxy-1,1′-binaphthyl (**S62**) with pentaethylene glycol ditosylate. Other isomers were also isolated.[234] Complexation properties of **519** and **520** with inorganic and organic guests were studied.

Bis(dibenzo-16-crown-5) derivatives **521–536** are listed in Table 13. Diester-bridged biscrowns **521–530** were synthesized in a manner similar to that shown in procedure X (Scheme 16) by treating 6-hydroxy-2,3:9,10-dibenzo-16-crown-5 derivatives with the appropiate dicarboxy dichloride. Most of the biscrowns were obtained in high yields. Biscrown **531** was obtained from maleic anhydride using sulfuric acid as a catalyst in $CHCl_3$.[239] Ethereal bridged biscrowns **532–536** were synthesized by treating 6-hydroxy-2,3:9,10-dibenzo-16-crown-5 with sodium metal followed by the appropriate α,ω-dibromoalkanes or oligo(ethylene glycol) dichlorides in benzene.[238] Biscrowns **521**, **523**, **526**, and **528** have higher binding abilities for Hg^{2+}, Sr^{2+}, K^+, Rb^+, and Na^+ than that of the monomer, and all of them have selectivity sequences of $Hg^{2+} > Sr^{2+} > K^+ > Rb^+ > Na^+$.[236] A Rb^+-selective PVC membrane

Table 12. Bis(benzocrown ether)s Containing Different Crown Units



485-514

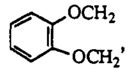
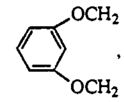
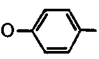
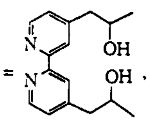
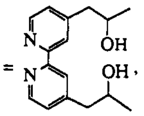
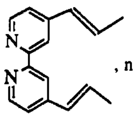
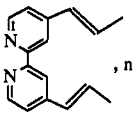
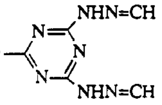
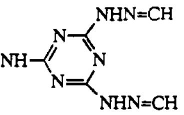
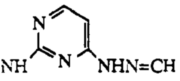
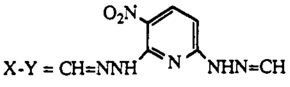
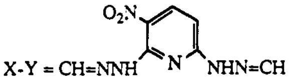
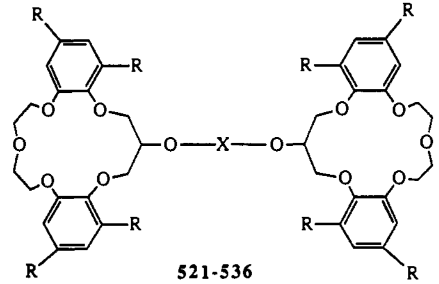
no.	remarks[a]	mp, °C	yield, %	procedure	ref(s)
485	X-Y = C≡C, $n = 1, m = 2$	129.9–181.1	61	J	53
486	X-Y = C≡C, $n = 1, m = 3$	62.3–65.1	47	J	53
487	X-Y = C≡C, $n = 2, m = 3$	86.1–89.3	70	J	53
488	X-Y = CH_2CH_2, $n = 1, m = 2$	102.1–103.6	93	J	53
489	X-Y = CH_2CH_2, $n = 1, m = 3$	70.1–71.8	87	J	53
490	X-Y = CH_2CH_2, $n = 2, m = 3$	75.5–77.1	49	J	53
491	X-Y=  , n = 1, m = 2	125–126	84		118
492	X-Y=  , n = 1, m = 2	94–96	87		118
493	X-Y= CH_2O  OCH_2, n = 1, m = 2	149–151	86		118
494	X - Y =  , n = 1, m = 2		58	P	229
495	X - Y =  , n = 2, m = 3		54	P	229
496	X - Y =  , n = 1, m = 2		90	P	229
497	X - Y =  , n = 2, m = 3		85	P	229
498	X-Y = $CH_2CH_2CH_2O$, $n = 1, m = 2$	89.1–90.8	56	VV	53
499	X-Y = $CH_2CH_2CH_2O$, $n = 2, m = 1$	100.1–100.9	55	VV	53,195
500	X-Y = C(O)CH=CH, $n = 2, m = 1$	77–82	40	YY	60
501	X-Y = C(O)CH=CH, $n = 2, m = 1$, R = Et	90–96	41	YY	60
502	X-Y = $CH(OH)CH_2CH_2$, $n = 2, m = 1$	71–75	70	YY	60
503	X-Y = $CH_2CH_2CH_2$, $n = 2, m = 1$	56–57	23	YY	60
504	X-Y = $CH_2CH_2CH_2$, $n = 2, m = 1$, R = Et	42–46	14	YY	60
505	X-Y = $CH(OC_8H_{17}\text{-n})CH_2CH_2$, $n = 2, m = 1$	46–48	28	YY	60
506	X-Y = $C(O)(CH_2)_3C(O)$, $n = 1, m = 2$	121–122	18	M	60
507	X-Y = $(CH_2)_5$, $n = 1, m = 2$	62–66	22	M	60
508	X-Y = N=CH, $n = 1, m = 2$	124–126	83	K	223
509	X-Y = $NHCH_2$, $n = 1, m = 2$	110–111	97	K	223
510	X-Y = n-Pr  n = 1, m = 2			H	230
511	X-Y = PhNH  n = 1, m = 2			H	230
512	X-Y = CH=NNH  n = 1, m = 2			H	230

Table 12 (Continued)

no.	remarks[a]	mp, °C	yield, %	procedure	ref(s)
513	 n = 1, m = 2			H	230
514	 n = 2, m = 3			H	230

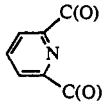
[a] R = H unless otherwise indicated.

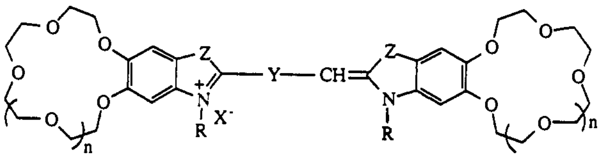
Table 13. Bis(dibenzocrown ether)s and Bis(benzoheterocrown ether)s



521-536

(R = *t*-C_4H_9 for **524**, R = H for all others)

no.	remarks (X =)	mp, °C	yield, %	procedure	ref(s)
521	$C(O)C(O)$	146–149	91	X	236
522	$C(O)CH_2C(O)$	104–106	65.9	X	237
523	$C(O)(CH_2)_2C(O)$	154–156	80	X	236
524	$C(O)(CH_2)_2C(O)$	315–317	91	X	238
525	$C(O)(CH_2)_3C(O)$	124–126	68	X	237
526	$C(O)(CH_2)_4C(O)$	138–142	64	X	236
527	$C(O)(CH_2)_7C(O)$	132–134	83	X	238
528	$C(O)(CH_2)_8C(O)$	160–162	58	X	236
529	*p*-$C(O)C_6H_4C(O)$	134–135	65	X	237
530		68–70	70.7	X	237
531	$C(O)CH{=}CHC(O)$ (*cis*)	123–124	58		239
532	$(CH_2)_3$	84–86	56	HH	238
533	$(CH_2)_4$	80–82	60	HH	238
534	$(CH_2)_5$	76–78	58	HH	238
535	$(CH_2CH_2O)_2CH_2CH_2$	90–92	23	HH	238
536	$(CH_2CH_2O)_3CH_2CH_2$	79–81	18	HH	238

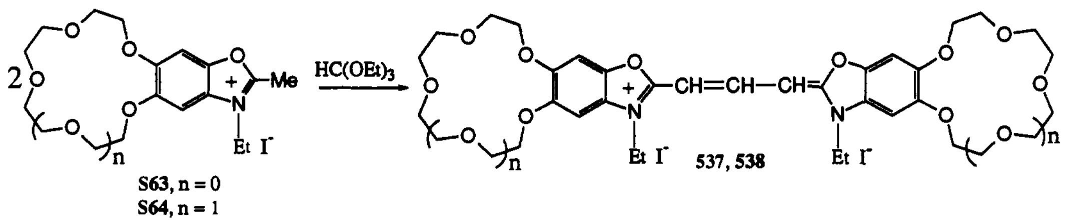


537-547

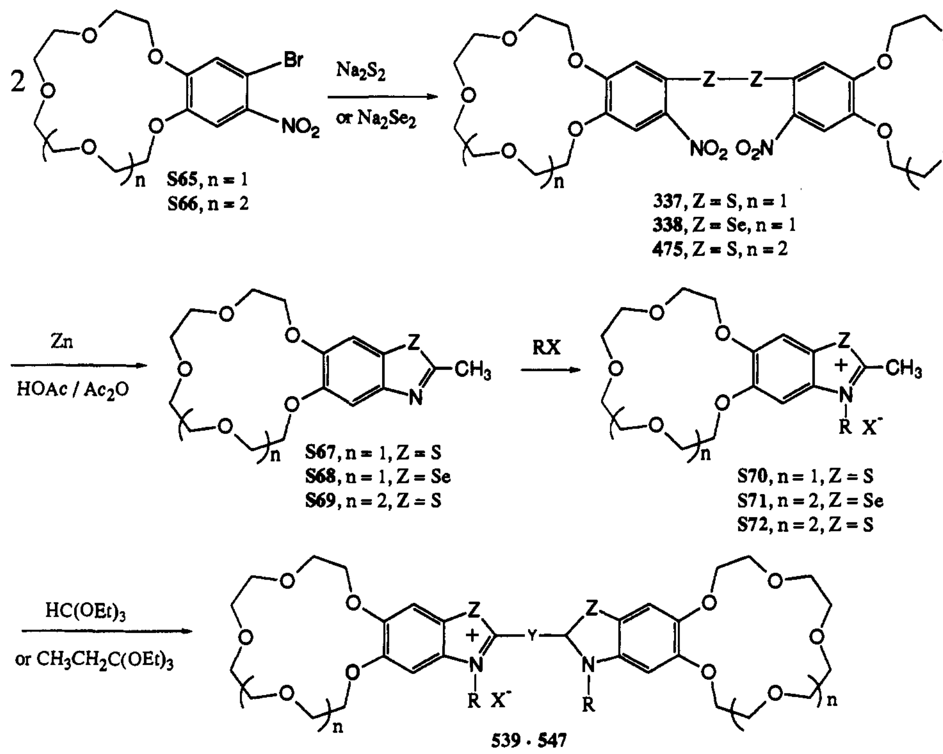
no.	remarks	mp, °C	yield, %	procedure	ref(s)
	Z = O, R = Et, Y = CH=CH, X = I				
537	$n = 0$	235–236	17.4	GGG	26,241
538	$n = 1$	257–258	15.8	GGG	26,241
	Z = S, $n = 1$				
539	R = Et, Y = CH=CH, X = I	296–298	67	HHH	242
		296–298	72	HHH	243
540	R = Et, Y = CH=C(Et), X = I	256–258	25	HHH	244
541	R = CH_2CH_2OH, Y = CH=CH, X = Cl	>292	16	HHH	24
542	R = CH_2CH_2OH, Y = CH=C(Et), X = Cl	248–250	10.8	HHH	24
	Z = S, $n = 2$				
543	R = Et, Y = CH=CH, X = I	268–270	21	HHH	24
544	R = Et, Y = CH=C(Et), X = I	236–238	25	HHH	24
545	R = CH_2CH_2OH, Y = CH=CH, X = Cl	269–271	22	HHH	24
546	R = CH_2CH_2OH, Y = CH=C(Et), X = Cl	228–230	16	HHH	24
	Z = Se, $n = 1$				
547	R = Et, Y = CH=CH, X = I	279	44	HHH	25

Scheme 37. Procedures GGG[26,241] and HHH[24,25,242-244]

Procedure GGG[26,241]



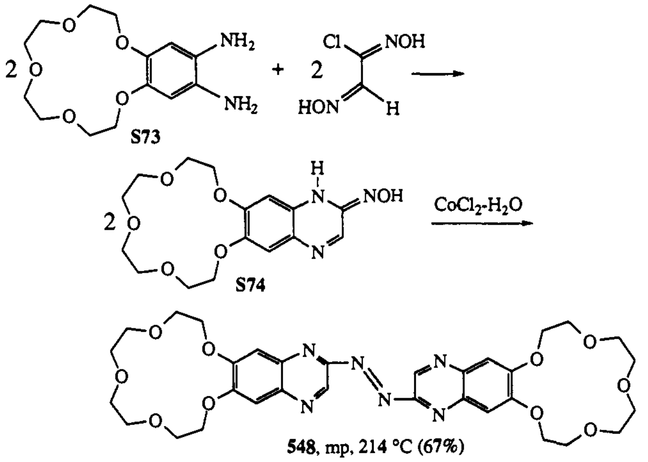
Procedure HHH[24,25,242-244]



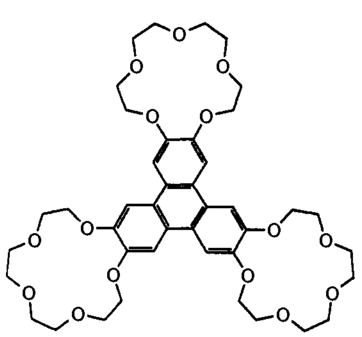
electrode based on biscrown **530** was prepared and studied.[240]

Xu and co-workers[24-26,241-244] reported a series of bis(benzoheterocrown ether)-containing cyanine dyes **537–547** (Table 13, Scheme 37). Quaternary ammonium salts **S63** and **S64** were first prepared by quaternizing the corresponding benzoxazole-containing crown derivatives with ethyl iodide. Treatment of **S63** and **S64** with triethyl orthoformate gave bis(crown ether)-containing cyanine iodides **537** and **538**, respectively (procedure GGG).[26,241] Biscrown-containing cyanine dyes **539–547** were synthesized by a similar procedure. However, key starting materials **S67–S69** were prepared by reduction of the corresponding biscrowns **337**, **338**, and **475** (procedure HHH). Starting substituted benzocrowns **S65** and **S66** were treated with Na_2S_2 or Na_2Se_2 to yield sulfur- or selenium-containing bis(benzocrown ether)s **337**, **338**, and **475** (Tables 9 and 10). Reduction of these biscrowns with zinc yielded monocrowns **S67–S69**. Quaternization of **S67–S69** by alkyl halides produced quaternary salts **S70–S72**, respectively. **S70–S72** were then reacted with triethyl orthoformate or triethyl orthopropionate to give the corresponding biscrowns **539–547** (procedure HHH).[24,25,242-244] This group of biscrown dyes exhibited high photographic and spectral sensitizing ability compared to the conventional cyanine dyes.[244-246] For instance, the photographic materials containing biscrown **539** or **540** as a spectral sensitizer exhibited excellent storage stability.[245]

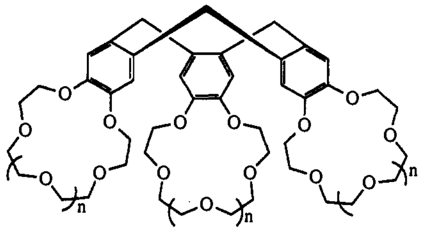
Scheme 38. Procedure III[247]



Azobis(quinoxaline)-containing biscrown **548** was synthesized as shown in procedure III (Scheme 38).[247] 2′,3′-Diaminobenzo-15-crown-5 (**S73**) was treated with *s-trans*-chloroethanedial dioxime to give quinoxalinone



549, m.p. 285 °C (30%)[248,249]
m.p. 268 °C (46%)[31]



550, n = 1, m.p. 203.5-205.5 °C (4%)[250]
551, n = 2, m.p. 169-172 °C (32%)[250]

Figure 4. Threefold tris(benzocrown ether)s.

oxime (S74). Coupling of S74 using cobalt (II) as a template gave biscrown 548.

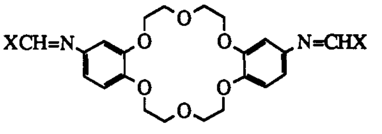
9. Tris(benzocrown ether)s

In the previous sections, various bis(benzocrown ether)s were described. The oligo(benzocrown ether)s, which include the tris- to the octakis(benzocrown ether)s will now be discussed. A series of tris(crown ether)s are shown in Figures 4–8. Figure 4 shows the 3-fold tris(crown ether)s 549–551. Simonet and co-workers[31,248,249] reported the electrochemical synthesis of tris-(15-crown-5)-containing triphenylene 549. This ligand consists of a triphenylene core surrounded by the three polyether rings. 549 was obtained in 30–46% yields by a cyclic anodic trimerization of benzo-15-crown-5 using zinc powder as the chemical reductor in a nonnucleophilic solvent. Frensch and Vögtle[250] reported the synthesis of 3-fold tris(benzocrown)s 550 and 551 containing the cyclotriveratrylene skeleton. Benzo-15-crown-5 and benzo-18-crown-6 were treated with formaldehyde under acidic conditions to yield triscrowns 550 and 551, respectively. Crystalline 1:3 complexes of 550·NaSCN and 551·KSCN were prepared and characterized.

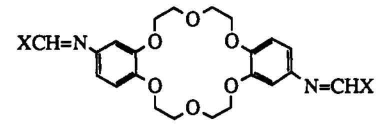
Tris(benzocrown ether)s 552–556, connected by single bonds, are shown in Figure 5. Two equivalent amounts of 4′-formylbenzo-15-crown-5 (S15) were treated with 4′,4″- and 4′,5″-diaminodibenzo-18-crown-6 to give Schiff base-bridged tris(benzocrown ether)s 552 and 553, respectively.[122] 4′,5″-Diaminodibenzo-18-crown-6 was treated with two equivalent amounts of the isocyanate derivatives of benzo-15-crown-5 and benzo-18-crown-6 to yield tris(benzocrown ether)s 554 and 555, respectively.[163,165] Sulfonamide-bridged triscrown 556 was synthesized by treating an isomeric mixture of 4′,4″- and 4′,5″-dibenzo-18-crown-6 disulfonyl chloride with 4′-aminobenzo-15-crown-5 (S12).[110]

Tris(4′-benzo-15-crown-5) derivatives 557–559, in which benzocrown units are bonded onto the 1,3,5 positions of benzene, were reported by Weber (Figure 6).[159,160] 1,3,5-Tris(bromomethyl)benzene and 1,3,5-tris(chloromethyl)-2,4,6-trimethylbenzene were reacted with 4′-hydroxybenzo-15-crown-5 (S34) to produce the corresponding triscrowns 557 and 558. Triamide-bridged triscrown 559 was obtained by the reaction of 1,3,5-benzenetricarboxylic acid trichloride with 4′-aminobenzo-15-crown-5 (S12).

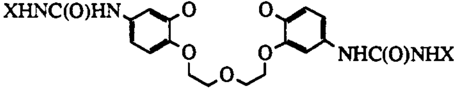
Tris(Schiff base-containing benzo-15-crown-5) 560 was synthesized in a 98% yield by treating tris(2-aminoethyl)amine with 3 equiv of formyl-substituted crown S15 (Figure 7).[121] Refluxing 560 with NaPF$_6$ gave crystalline complex 560•3NaPF$_3$ in which the sodium ions are encapsulated in crown ether units. Four



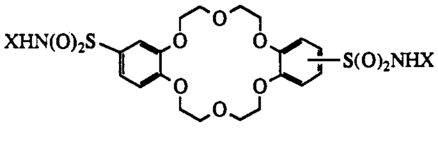
552, X = -B15C5, m.p. 188.5-190 °C (59%)[122]



553, X = -B15C5, m.p. 184-185 °C (54%)[122]



554, X = -B15C5[163,165]
555, X = -B18C6[163,165]



556, X = -B15C5, m.p. 88 - 91 °C (60%)[110]

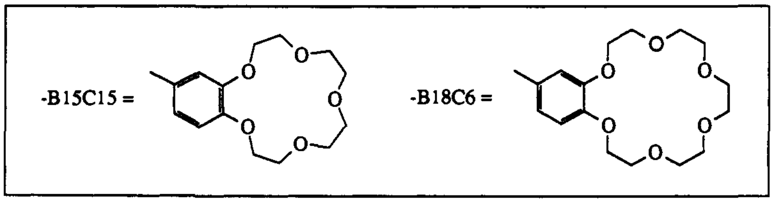
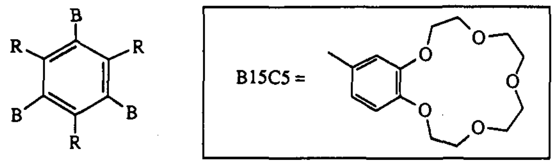
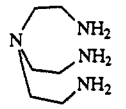


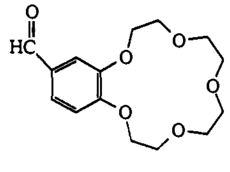
Figure 5. Tris(benzocrown ether)s.



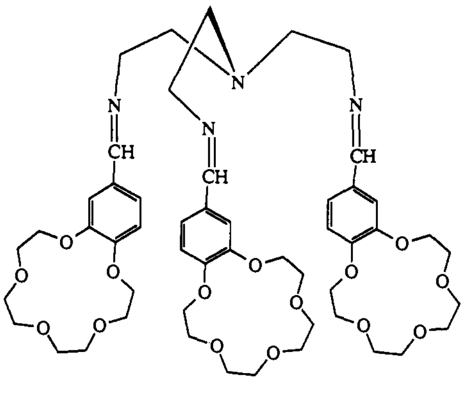
557, R = H, B = $CH_2OB15C5$, Glassy (72%)[159, 160]
558, R = CH_3, B = $CH_2OB15C5$, m.p. 192-195 °C (61%)[159, 160]
559, R = H, B = C(O)NHB15C5, m.p. 117-120 °C (decomp.) (76%)[159, 160]

Figure 6. Tris(benzo-15-crown-5)s **557–559**.



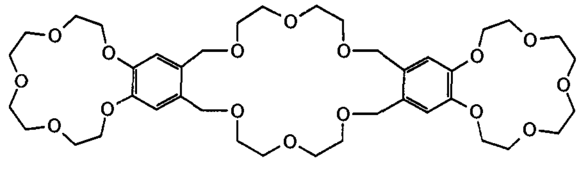


S15

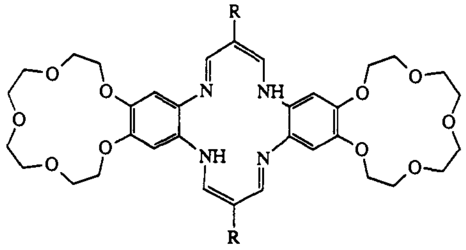


560, m.p. 83.85 °C (98%)

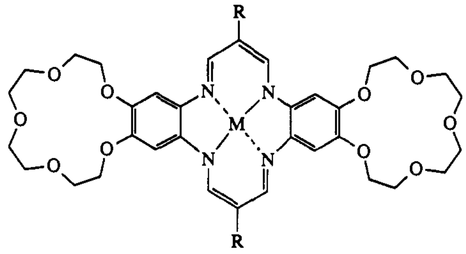
Figure 7. Tris(Schiff base-containing benzo-15-crown-5) **560**[121] and starting materials.



561, m.p. 145-147 °C (54%)[152]



562, R = $(CH_3)_2CH$
m.p. 251-252 °C (30%)[252]
563, R = CH_3CH_2
m.p. 251-252 °C (30%)[252]



564, R = $(CH_3)_2CH$, M = Ni, m.p. 279 °C (15.6%)[251]
565, R = $(CH_3)_2CH$, M = Co, m.p. 280 °C (30%)[251]
566, R = CH_3CH_2, M = Ni, m.p. >300 °C (20%)[252]

Figure 8. Triloop tris(benzocrown ether)s.

nitrogen atoms in the bridge of **560** interact with Cu^+ to give complex **560**•$CuPF_6$. This complex was treated with excess $NaPF_6$ to give the tetranuclear complex [**560**•Cu•3Na]•$(PF_6)_4$.[121]

Triloop triscrowns **561–566** are shown in Figure 8. Triscrown **561** was synthesized in a 54% yield by a 2:2 cyclization of 4′,5′-bis(chloromethyl)benzo-15-crown-5 with diethylene glycol using NaH as a base and KCl as a template.[152] **561** provided a high extractability for K^+, Tl^+, Rb^+, and Ba^{2+} cations. Polynuclear complexes of **561**•3NaSCN and $(\mathbf{561})_2$•$[Ba(SCN)_2]_5$ were prepared. Triscrown **562** was synthesized by condensation of 4′,5′-diaminobenzo-15-crown-5 with 3-ethoxy-2-isopropylacrolein (Figure 8).[251] When $Ni(Ac)_2$ and $Co(Ac)_2$ were used as templates, the corresponding complexes **564** (Ni•**562**) and **565** (Co•**562**) were obtained. Triscrown **563** was also synthesized by treating 4′,5′-diaminobenzo-15-crown-5 with 3-ethoxy-2-ethylacrolein without a template.[252] **566** was obtained when using $Ni(Ac)_3$ as a template. The complexes of **563** with Ni^{2+} and Cu^{2+} were also obtained by treatment of **563** with $Ni(Ac)_2$ and $Cu(Ac)_2$, respectively. Complexation of **563** with Na^+, K^+, and NH_4^+ was studied by electronic and ESR spectroscopy.[252]

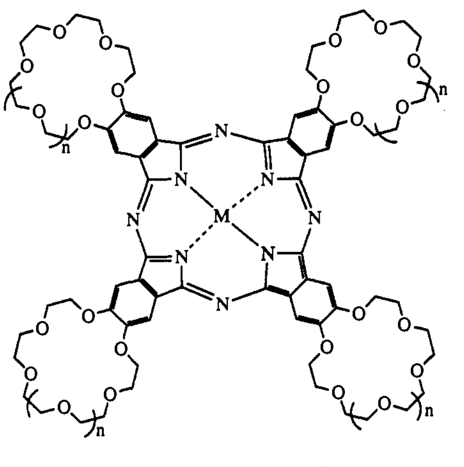
10. Tetrakis(benzocrown ether)s

In this section, phthalocyanine-bridged, porphyrin-bridged, and other tetrakis(benzocrown ether)s are reported.

A. Phthalocyanine-Bridged Tetrakis(benzocrown ether)s

Phthalocyanine-bridged tetrakis(benzocrown ether)s include crown ether-substituted phthalocyanines and tetrakis(benzocrown ether)-containing phthalocyanines. These polytopic ligands consist of a phthalocyanine core to which four benzocrown ether rings are attached. Attachment of crown ether units to the phthalocyanine ring significantly increases the solubility of phthalocyanine in many organic solvents leading to significant advances in research areas such as biological modeling and homogeneous catalysis.

Crown ether-substituted phthalocyanines and their various complexes (**567–572**) are shown in Figure 9. Their syntheses are summerized in Figure 10. In 1986, three groups of researchers, Bekaroglu,[253] Kobayashi,[254] and Nolte[255] and their co-workers, simultaneously reported tetrakiscrown **568**·Cu. 4′,5′-Dibromobenzo-15-crown-5 (**S75**) was treated with CuCN in refluxing quinoline to produce **568**·Cu in a 48% yield.[253] **568**·Cu was similarly synthesized by treating **S75** with a large excess of CuCN[254] or 5 equiv of CuCN in DMF using pyridine as a catalyst.[255] The reaction of 4′,5′-di-



567, n = 0, M = 2H (32.1%[256], 38%[258], 16%[267])
568, n = 0, M = Cu (48%[253], 49%[254], 35%, m.p. > 200 °C[255], 38.1%[256], 34%, m.p. > 250 °C[257]); Co (45.5%)[256]; Ni(49.7%)[256]; Fe (16.2%)[256]; Pb (18%)[267]; Si(Cl)$_2$ (47%[267], 30%[268]); Si(OH)$_2$ (95%[267], 30%[268]); Sn(Cl)$_2$ (35%)[267]; Sn(OH)$_2$ (73%)[267]; Ge(Cl)$_2$ (51.3%, 59%)[269]; Ge(OH)$_2$ (50%)[269]; Ge(SPh)$_2$ (53%)[269]; Ge(Cl)$_2$(4-SB15C5)$_2$ (63%).[269]
569, n = 1, M = 2H (26%, m.p. >200 °C)[257]
570, n = 1, M = Cu (36%, m.p. >250 °C)[257]; Si(Cl)$_2$[268]; Si(OH)$_2$ (25%)[268]
571, n = 2, M = 2H[269]
572, n = 2, M = Cu (41%, m.p. >250 °C)[257]; Si(Cl)$_2$[268]; Si(OH)$_2$ (32%)[268]

Figure 9. Crown ether-substituted phthalocyanines.

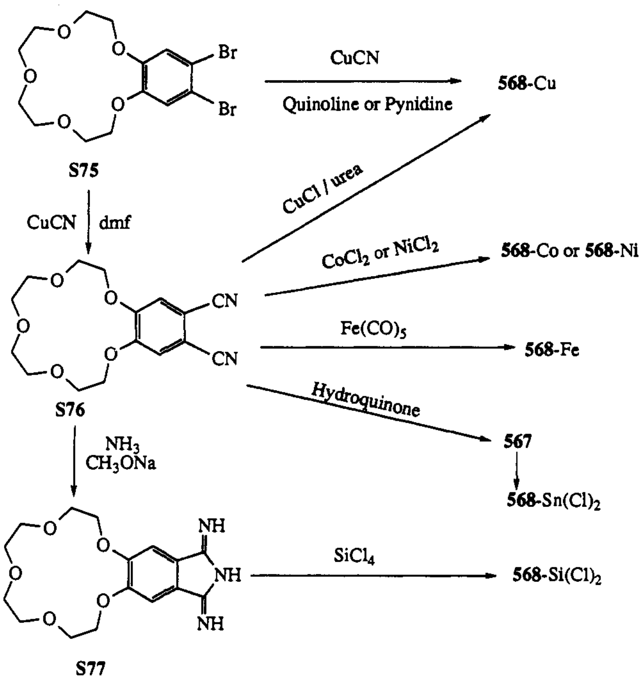
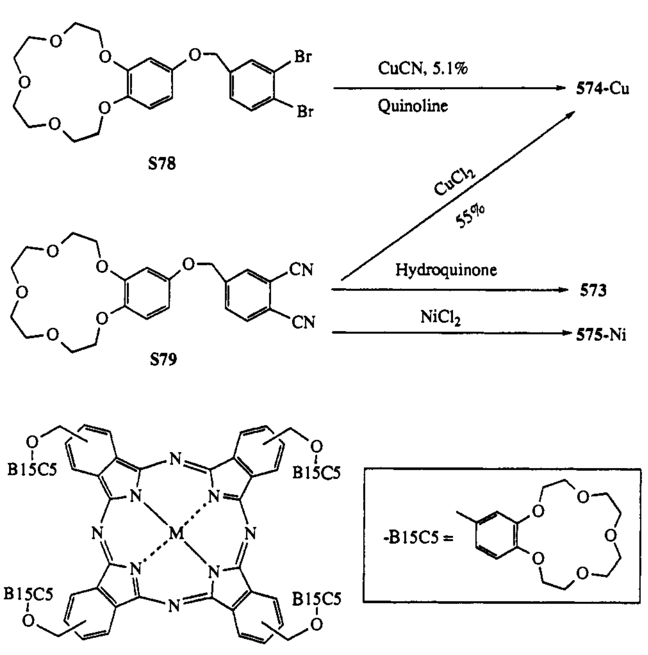


Figure 10. Synthetic methods for crown ether-substituted phthalocyanines.

cyanobenzo-15-crown-5 (**S76**) with urea in the presence of CuCl also gave tetrakiscrown complex **568**·Cu in a 38.1% yield.[256] The **568**·Cu products obtained from **S75** and **S76** were identical.[256,257] Other tetrakiscrown complexes **568**·Co, **568**·Ni, and **568**·Fe were similarly prepared from **S76** and the corresponding metal salts (Figure 10). Free tetrakis(benzo-15-crown-5)-substituted phthalocyanine **567** was obtained in a 32% yield by the reaction of **S76** with hydroquinone.[256] Free tetrakis(benzo-18-crown-6)-substituted phthalocyanine **569** and tetrakis(benzo-21-crown-7)-substituted phthalocyanine **571** were similarly synthesized by refluxing the appropiate 4′,5′-dicyanobenzocrowns in 2-(dimethylamino)ethanol.[257-259] The copper complexes of tetrakis(benzo-18-crown-6)- and tetrakis(benzo-21-crown-7)-substituted phthalocyanines (**570**·Cu and **571**·Cu) were synthesized by the reaction of CuCN with the corresponding 4′,5′-dicyanobenzo-18-crown-6 and 4′,5′-dicyanobenzo-21-crown-7.[257] Most of these tetrakiscrowns were obtained in high yields.

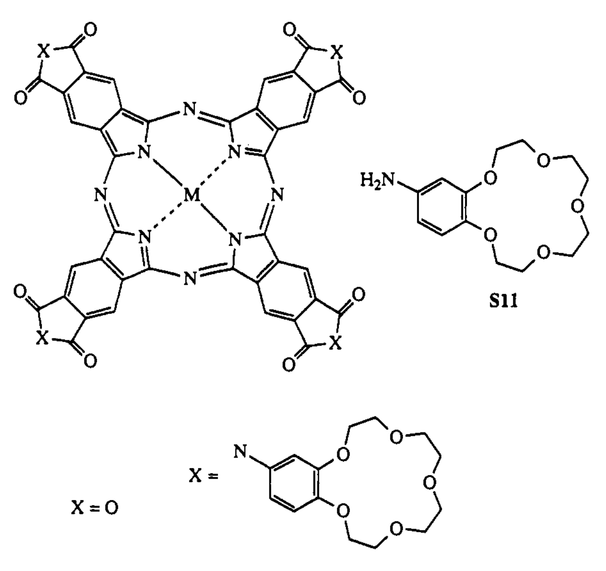
These crown-substituted phthalocyanines exhibited very interesting complexation properties. The alkali metal binding abilities of **568**·Cu, **568**·Co, **568**·Ni, and **568**·Fe were studied by the solvent extraction of alkali metal picrates from water into chloroform.[253,256] The results indicated that all four **568**·M compounds exhibited the highest affinity for K^+ among the alkali metal cations. The selectivity of **568**·Co for K^+ was the highest.[256] **568**·Cu can be used as a colorimetric reagent for the detection of K^+ at concentrations as low as 10^{-8} M.[254] These tetrakiscrowns formed complexes with alkali metal cations with different stoichiometries depending on the diameters of the cations.[257] **568**·Cu, containing benzo-15-crown-5 units, formed 4:4 (crown unit/cation) complexes with Li^+ and Na^+, and 8:4 complexes with K^+, Rb^+, and Cs^+. **570**·Cu, containing benzo-18-crown-6 units, formed 4:4 complexes with Li^+, Na^+, and K^+, and 8:4 complexes with Rb^+ and Cs^+. **572**·Cu, containing benzo-21-crown-7 units, formed 4:4 complexes with all studied cations. The crystalline complexes of **570**·Cu with K^+, Rb^+, and Cs^+ picrates were prepared.[260,261] The aggregation of crowned phthalocyanine **570**·Cu by K^+, Rb^+, and Cs^+ picrates increased the electrical conductivity as compared to that of nonaggregated phthalocyanines.[260] Possible structures for the aggregates were proposed on the basis of computer analysis of X-ray powder diffration patterns.[261] Aggregation of **570**·Cu with these monovalent metal ions resulted in cofacially ordered phthalocyanine stacks, while aggregation with Ba^{2+} lead to the formation of phthalocyanine networks.[262] X-ray determinations at small angles indicated that the phthalocyanine moieties in **567** and **568**·Cu were superimposed in an eclipsed comformation and the crown ether units formed channels.[263] The effects of NO_2 and NH_3 on semiconductivity of solution deposited thin films of free tetrakiscrown-containing phthalocyanines **567**, **569**, and **571**, and their Cu^{2+} complexes, **568**·Cu, **570**·Cu, and **572**·Cu, were investigated.[259] **567**, **568**·Cu, **568**·Ni, **568**·Co, and **568**·Zn were studied using optical absorption and magnetic circular dichroism spectroscopies.[264] The effect of iodine doping on the structure and electrical properties of **569**, **570**·Cu, **571**, and **572**·Cu were also studied.[265]

4′,5′-Dicyanobenzo-15-crown-5 (**S76**) was converted into its 1,3-diimino-1,3-dihydroisoindole derivative (**S77**) by treatment with $NaOCH_3$ and NH_3 in methanol (Figure 10).[266,267] Treating **S77** with $SiCl_4$ in quinoline at an elevated temperature produced the dichlorosilicon-containing phthalocyanine tetrakis(crown ether) **568**·$SiCl_2$. This compound was readily hydrolyzed in the presence of water to give the dihydroxysilicon-containing phthalocyanine tetrakis(crown ether) **568**·Si(OH)$_2$ (see Figure 9). Dichlorosilicon-containing phthalocyanine tetrakis(crown ether)s **570**·$SiCl_2$ and **572**·$SiCl_2$ and dihydroxysilicon-containing derivatives **570**·Si(OH)$_2$ and **572**·Si(OH)$_2$ containing benzo-18-



573, M = 2H, (77.7%, m.p. >300 °C)
574, M = Cu (5.1%, m.p. >300 °C; 55%, mp, >300 °C)
575, M = Ni (45%, m.p. >300 °C)

Figure 11. Phthalocyanine-bridged tetrakis(benzo-15-crown-5)s.[270]



S80, M = 2H
S81a, M = Fe
S81b, M = Co
S81c, M = Cu

576, M = 2H (42%)
577, M = Fe (58%)
M = Co (64%)
M = Cu (71%)

Figure 12. Phthalocyanine-bridged tetrakis(benzo-15-crown-5)s.[271]

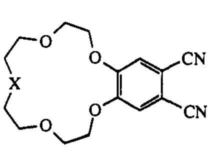
crown-6 and benzo-21-crown-7 units were synthesized in the same manner from the corresponding dicyanobenzocrowns.[268] Metal-free phthalocyanine tetrakis(crown ether) **567** was converted into its dichlorotin-containing phthalocyanine tetrakis(crown ether) **568**·$SnCl_2$ by treating **567** with $SnCl_4$ in quinoline.[267] **568**·$SnCl_2$ was then hydrolyzed into its dihydroxytin derivative **568**·$Sn(OH)_2$. Dichlorogermanium derivative **568**·$GeCl_2$ was synthesized using both methods described above in 51.3% and 59% yields by treating $GeCl_4$ with **567** and **S77**.[269] Hydrolysis of **568**·$GeCl_2$ gave its dihydroxy derivative **568**·$Ge(OH)_2$. Replacement of the hydroxy groups in **568**·$Ge(OH)_2$ with thiophenolates was carried out by treating **568**·$Ge(OH)_2$ with an excess of thiophenol and 4′-mercaptobenzo-15-crown-5 to give derivatives **568**·$Ge(SPh)_2$ and **568**·Ge(4′-SB15C5)$_2$.[269] Polycondensation of dihydroxysilicon-containing phthalocyanine tetrakis(crown ether)s **568**·$Si(OH)_2$, **570**·$Si(OH)_2$, and **572**·$Si(OH)_2$ using Cl_2 as a catalyst in the presence of quinoline gave their cofacially arrayed polymers.[268-268]

The syntheses of tetrakis(benzo-15-crown-5)-substituted phthalocyanines **573**–**575** are shown in Figure 11.[270] Metal-free phthalocyanine tetrakis(crown ether) **573** was synthesized in a 77.7% yield by heating dicyano-substituted crown **S79** in hydroquinone. Copper-containing phthalocyanine derivative **574**·Cu was prepared in a low yield directly from dibromocrown **S78** and CuCN in quinoline. **574**·Cu was also prepared in a good yield by treating dicyano crown **S79** with $CuCl_2$. Nickel-containing phthalocyanine **575**·Ni was similarly obtained from **S79** and $NiCl_2$. These products should be mixtures of isomers in which 4′-benzo-15-crown-5 units are attached to two different positions on the phthalocyanine benzene rings. Solvent extraction of alkali metal picrates indicated that these tetrakiscrowns exhibited high selectivity for K^+ and Rb^+ over other cations. These results indicate that these ligands form sandwich complexes with metal cations whose diameters are larger than the diameter of benzo-15-crown-5 leading to an aggregation of molecules.[270]

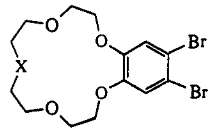
Two other phthalocyanine-bridged tetrakis(benzo-15-crown-5) derivatives (**576** and **577**) are shown in Figure 12.[271] Metal-free tetraanhydride **S80** and excess 4′-aminobenzo-15-crown-5 (**S11**) were reacted in *N*-methyl-2-pyrrolidone at 70 °C to give metal-free tetrakiscrown-substituted phthalocyanine **576** in a 42% yield. Metal phthalocyanines **577**·Fe, **577**·Co, and **577**·Cu were synthesized in high yields from **S11** and the appropiate tetraanhydride **S81b,c** in *N*-methyl-2-pyrrolidone at 200 °C.

Phthalocyanines **578**–**583** containing four azacrown ether units are shown in Figure 13.[272,273] Cyclotetramerization of dicyanocrown **S82** in the presence of hydroquinone gave metal-free phthalocyanine derivative **578**.[272] **S82** was cyclotetramerized in the presence of $NiCl_2$, PbO, and $Lu(OAc)_3$ to produce the corresponding metal-containing phthalocyanine derivatives **579**·Ni, **579**·Pb, and bis(phthalocyaninato)lutetium(III) compound (**579**·HLu·**579**). Hydrolysis of *N*-acetyl-substituted phthalocyanines **578**, **579**·Ni, **579**·Pb, and **579**·HLu·**579** in H_2SO_4 gave unsubstituted phthalocyanine derivatives **580**, **581**·Ni, **581**·Pb, and **581**-HLu·**581**, respectively. The *N*-acetyl-substituted phthalocyanine derivatives were treated with excess dimethyl sulfate in chloroform to give the corresponding quaternary ammonium salts **582**, **583**·Ni, **583**·Pb, and **583**·HLu·**583**. The water-soluble lutetium-containing bis(phthalocyaninate) derivatives were the first to be reported.[272] Dibromo-substituted crown **S83** was treated with excess CuCN in pyridine to give N-unsubstituted phthalocyanine crown **581**·Cu.[273] Similarly, quaternary ammonium salt **583**·Cu was obtained by the reaction of **S84** with CuCN in pyridine.

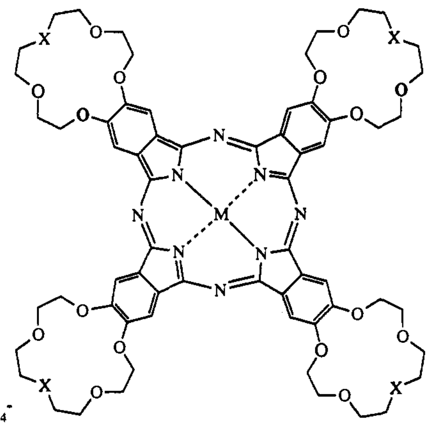
Copper-containing phthalocyanine derivatives **584**–**589**, substituted with four tetraazacrown ether units, were reported by Bekaroglu and co-workers (Figure



S82, X = $NCOCH_3$

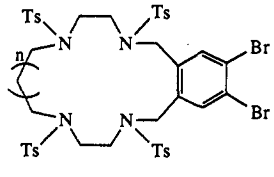


S83, X = NH
S84, X = $^{+}N(CH_3)_2{\cdot}CH_3SO_4^-$

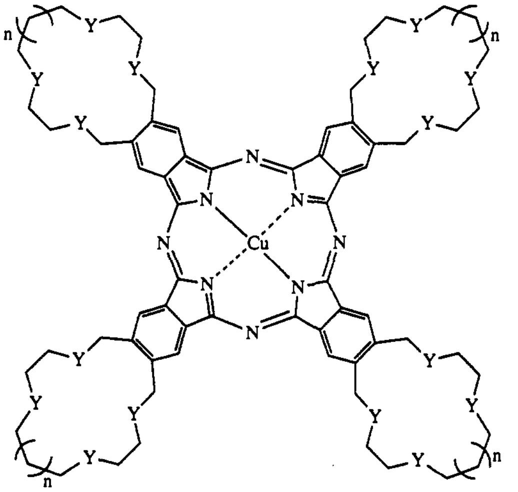


578, X = $NCOCH_3$, M = 2H (27%)
579, X = $NCOCH_3$, M = Ni (43%), M =Pb (17.5%)
M = 1 / 2 HLu (26%)
580, X = NH, M = 2H (47%)
581, X = NH, M = Ni (47%), M = Pb (51%)
M = 1 / 2 HLu (27.5%), M = Cu (28%)
582, X = $^{+}N(CH_3)_2{\cdot}CH_3SO_4^-$, M = 2H (61%)
583, X = $^{+}N(CH_3)_2{\cdot}CH_3SO_4^-$, M = Ni (31.5%), M = Pb (53%)
M = 1 / 2 HLu (61%), M = Cu (22%)

Figure 13. Phthalocyanine-bridged tetrakis(azacrown ether) derivatives **578–583**.[272,273]



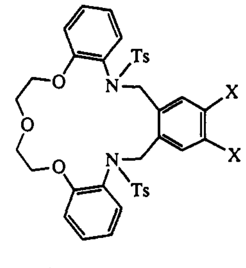
S85, n = 0
S86, n = 1



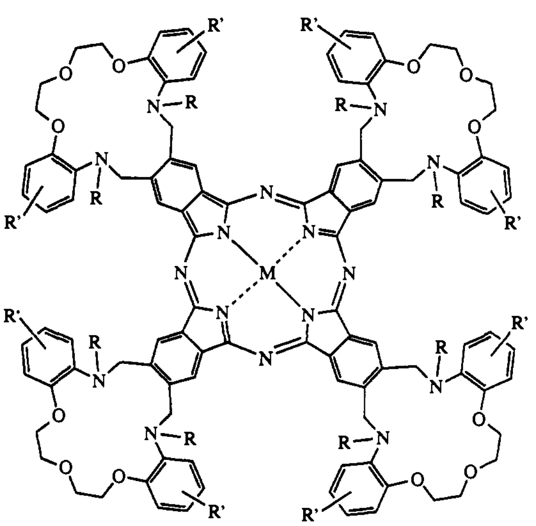
n = 0
584, Y = NTs (31%)[274]
585, Y = NH[274]

n = 1
586, Y = NTs (35%)[275]
587, Y = NH (37%)[275]
588, Y = $^{+}NMe_2{\cdot}MeOSO_3^-$ (25%)[275]
589, Y = $^{+}NMe_2{\cdot}ClO_4^-$ (79%)[275]

Figure 14. Phthalocyanine-bridged tetrakis(tetraazacrown ether) derivatives **584–589**.



S87, X = CN
S88, X = Br



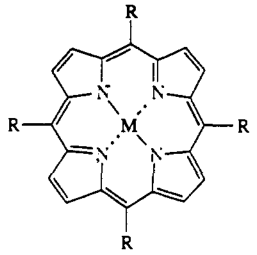
	M	R	R'	yield
590,	2H	Ts	H	10%
591,	Cu	Ts	H	52.6%
	Ni	Ts	H	17%
	Zn	Ts	H	18%
	Co	Ts	H	13%
592,	Cu	H	SO_3H	53%
	Co	H	SO_3H	66%
593,	Cu	H	SO_3Na	27%
	Co	H	SO_3Na	72%

Figure 15. Phthalocyanine-bridged tetrakis(diazacrown ether) derivatives **590–593**.[27]

14).[274,275] The cyclotetramerization of tosyl-protected dibromobenzocrowns **S85** and **S86** in tetramethylurea in the presence of CuCN gave the corresponding copper-containing phthalocyanine derivatives **584**[274] and **586**.[275] Detosylation of the peripheral aza groups of **584** and **586** in H_2SO_4 gave **585** and **587**, respectively. More water-soluble phthalocyanine **588** was obtained by the quaternization of **585** with dimethyl sulfate. **588** was treated with H_2O–$HClO_4$ to give **589**. **585** and **587** were treated with Cl^- or ClO_4^- salts of transition metal ions (Ni^{2+} or Co^{2+}, Cu^{2+}, Ni^{2+}, and Zn^{2+}) in methanol to give the corresponding pentanuclear complexes.

Metal-free phthalocyanine-containing tetrakis(crown ether) **590** was synthesized by the cyclotetramerization of dicyanotribenzocrown **S87** in the presence of PbO and 1-chloronaphthalene (Figure 15).[276] Direct cyclotetramerization of dibromotribenzocrown **S88** with CuCN in tetramethylurea gave copper-containing phthalocyanine **591**·Cu in a 52.6% yield. **591**·Ni, **591**·Zn, and **591**·Co were prepared from **S87** and the corresponding metal salts $NiCl_2$, $Zn(Ac)_2$, and $CoCl_2$ in quinoline or ethylene glycol. Detosylation of **591**·Cu and **591**·Co in H_2SO_4 lead to products **592**·Cu and **592**·Co with one sulfonic acid group on each aromatic ring of the crown ether units. Consequently, the products were mixtures of regioisomers. Conversion of these SO_3H groups to SO_3Na groups (to form **593**·Cu and **593**·Co) was carried out by neutralization with NaOH. Addition of these polar groups makes these phthalocyanine

Table 14. Tetrakis(benzocrown ether) Porphyrins

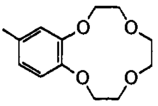


596-608

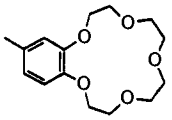
no.	remarks[a]	mp, °C	yield, %	procedure	ref(s)
596	R = -B12C4, M = 2H	353–355	15	JJJ	278
597	R = -B15C5, M = 2H	348–349		JJJ	278
				JJJ	279,280
					281
598	R = -B15C5, M = Fe		6	JJJ	282
	M = Co, Cu, Zn, Mn, Sn, VO				279–281
					283
599	R = *m*-C_6H_4-NHC(O)B15C5				284
	M = 2H, Zn, Fe				
600	R = -B18C6, M = 2H	277–278	4	JJJ	278
			4	JJJ	32
			10	KKK	32
601	R = -B24C8, M = 2H	135–137	1.3	JJJ	278
602	R = -(O_2N)B12C4, M = 2H		16	JJJ	285
603	R = -(O_2N)B15C5, M = 2H		10	JJJ	285
604	R = -(H_2N)B12C4, M = 2H		85		285
605	R = -(H_2N)B15C5, M = 2H		70		285
606	R = -(H-aza)B15C5, M = 2H	290–292	90		286
607	R = -(Ts-aza)B15C5, M = 2H	210–211	16	JJJ	286
		210–211	96		286
608	R = -($PhCH_2$-aza)B15C5, M = 2H	219–220	10	JJJ	286
		219–220	90		286

[a] Note:

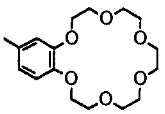
-B12C14 =



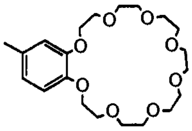
-B15C5 =



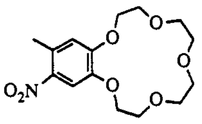
-B18C6 =



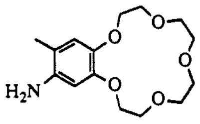
-B24C8 =



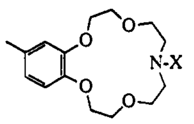
-(O_2N)B15C5 =



-(H_2N)B15C5 =



-(X-aza)B15C5 =

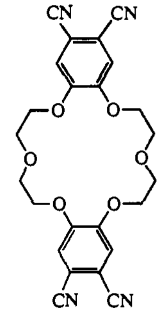


(X = H, Ts, $PhCH_2$)

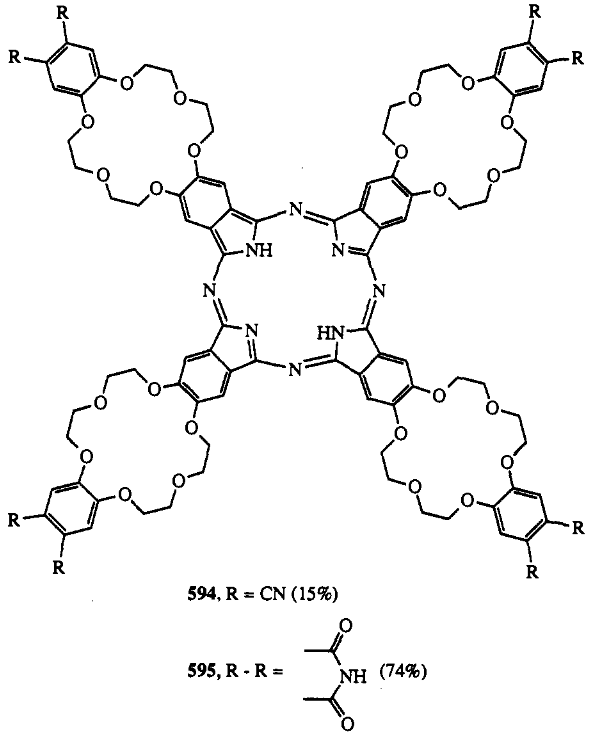
derivatives extremely soluble in water. The electrical conductivities of these phthalocyanines were studied.[276] Tetracyano-substituted dibenzo-18-crown-6 (**S89**) was cyclotetramerized in the presence of lithium 1-pentanolate in 1-pentanol to give metal-free phthalocyanine derivative **594** (Figure 16).[277] Conversion of **594** to **595** was carried out in H_2SO_4.

B. Porphyrin-Bridged Tetrakis(benzocrown ether)s

Another series of tetrakis(benzocrown ether)s, their melting points, and yields are listed in Table 14. These tetrakis(benzocrown ether)s consist of four benzocrown units bridged by a porphyrin molecule. Metal-free tetrakis(benzocrown ether)s **596**, **597**, **600**, and **601** were synthesized by the cyclotetramerization of the appropriate 4′-formylbenzo-12-crown-4 (**S14**), 4′-formylbenzo-15-crown-5 (**S15**), 4′-formylbenzo-18-crown-6 (**S16**), and 4′-formylbenzo-24-crown-8 with pyrrole in propionic acid (Scheme 39, procedure JJJ).[32,278–281] Tris- and bis(benzo-15-crown-5)-substituted porphyrin derivatives were also obtained in the presence of benzaldehyde during the preparation of **597**.[279,283] Cyclotetramerization of **S15** with pyrrole in the presence of an iron salt gave iron–porphyrin derivative **598**·Fe.[282] Other metallo–porphyrin derivatives of **598** with Co, Cu, Zn, Mn, Sn, and VO were prepared by refluxing metal-free porphyrin **597** with the appropiate metal salts.[279–281,283] **600** was also synthesized by the cyclization of **S90** with pentaethylene glycol dichloride as shown in procedure KKK.[32] Tetrakis(nitrobenzocrown ether)-substituted porphyrins **602** and **603** were synthesized by the reaction of pyrrole with 4′-formyl-5′-nitrobenzo-12-crown-4 and -15-crown-5.[285] Reduction of **602** and **603** with $SnCl_2$ gave the corresponding amine derivatives **604** and **605**, respectively. Tetrakis(*N*-tosylmonoazabenzo-15-crown-5)- and (*N*-benzylmonoazabenzo-15-crown-5)-substituted porphyrin derivatives **607** and **608** were synthesized by the reaction of pyrrole and the appropiate 4′-formyl-*N*-substituted-monoazabenzo-15-crown-5 derivatives.[286] Detosylation of **607** in hydrobromic acid gave unsubstituted compound **606**. Tosylation and benzylation of **606** gave **607** and **608** in high yields.[286] Porphyrin-bridged



S89



594, R = CN (15%)

595, R - R = (74%)

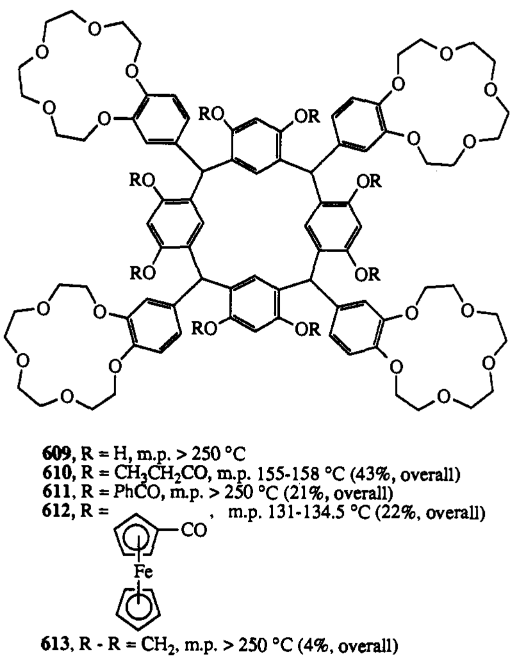
Figure 16. Phthalocyanine-bridged tetrakis(dibenzocrown ether) derivatives **594** and **595**.[277]

tetrakis(benzo-15-crown-5) derivative **599** was synthesized by treating 4′-chlorocarbonyl-substituted benzo-15-crown-5 (**S56**) with α,α,α,α-tetrakis(*m*-aminobenzo)porphyrin.[283]

Attachment of crown ether units onto the porphyrin ring greatly increases its solubility in many solvents, therefore, the properties of the crowns are easier to study. These compounds may act as catalysts in some reactions which require the simultaneous presence of both crown ether and porphyrin moieties. The ability of metallo–porphyrins **598** to complex cations (Na^+, K^+, Mg^{2+}, Co^{2+}, Ba^{2+}, and NH_4^+) was investigated by various spectral techniques.[279-281,283,287] These tetrakiscrowns exhibited a very high selectivity for K^+. Cations (K^+, Cs^+, Ba^{2+}, and NH_4^+), which require two crown ether cavities for complexation, induced dimerization of the porphyrins.[279,283,288] The electrochemical redox and photophysical properties of these porphyrin complexes with metal cations were studied.[281,286]

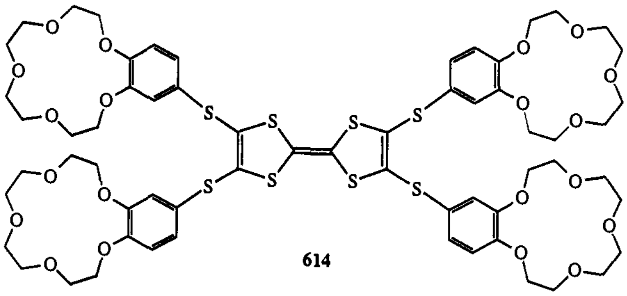
C. Other Tetrakis(benzocrown ether)s

Beer and co-workers[289,290] reported cyclophane and cavitand-bridged tetrakis(benzo-15-crown-5) derivatives (Figure 17). The reaction of 4′-formyl-substituted benzo-15-crown-5 (**S15**) and resorcinol in the presence of hydrochloric acid and ethanol gave dihydroxybenzene-containing tetrakis(benzo-15-crown-5) **609**. **609** was acylated using propionic anhydride, benzoyl chloride, and chlorocarbonyl-substituted ferrocene in



609, R = H, m.p. > 250 °C
610, R = CH_3CH_2CO, m.p. 155-158 °C (43%, overall)
611, R = PhCO, m.p. > 250 °C (21%, overall)
612, R = , m.p. 131-134.5 °C (22%, overall)
613, R - R = CH_2, m.p. > 250 °C (4%, overall)

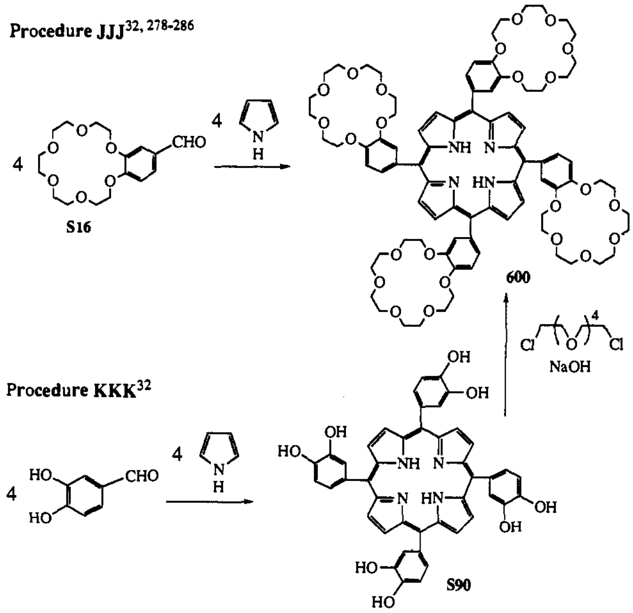
Figure 17. Cyclophane- and cavitand-bridged tetrakis(benzo-15-crown-5)s.[289,290]

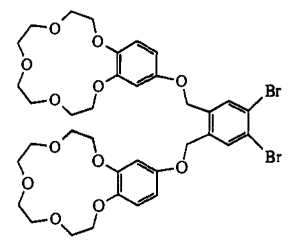


614

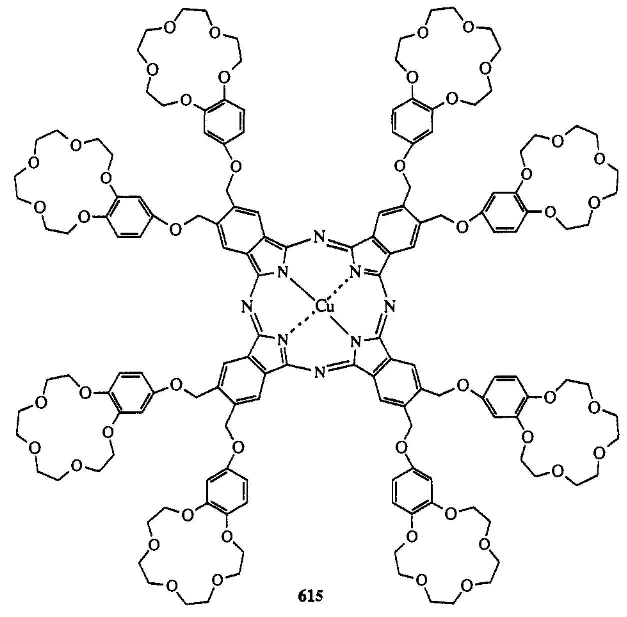
Figure 18. Tetrathiafulvalene-bridged tetrakis(benzo-15-crown-5) **614**.[189]

Scheme 39. Procedures JJJ[32,278-286] and KKK[32]





250 (Table 6)



615

Figure 19. Copper-containing phthalocyanine-bridged octakis(benzo-15-crown-5) **615**.[34]

the presence of base to give octaester derivatives **610**–**612** in overall yields of 43, 21, and 22%, respectively. Treatment of **609** with bromochloromethane in DMF using K_2CO_3 as a base produced cavitand-bridged tetrakis(benzo-15-crown-5) **613**. Complexation studies using NMR spectroscopy revealed that **611**–**613** formed complexes with bipyrininium guest species at the benzocrown ether binding sites. Beer and co-wokers[189] also reported tetrathiafulvalene-bridged tetrakis(benzo-15-crown-5) **614** (Figure 18). Detail synthesis and properties of this compound were not reported.

11. Octakis(benzocrown ether)

This section should include pentakis(and higher)-(benzocrown ether) derivatives, however, only a copper-containing phthalocyanine-bridged octakis(benzo-15-crown-5) **615** has been reported (Figure 19).[34] Cyclotetramerization of bromophenylene-bridged bis(benzo-15-crown-5) (**250**, Table 6) in the presence of CuCN in refluxing quinoline or pyridine gave **615** in a 37% yield. This is the largest oligo(benzocrown ether) yet reported. The crown ether units in **615** were shown to prefer intramolecular complexation with the alkali metal ions.[34]

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