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Synthesis and Complexation Properties of Some Novel Lariat-Crown Ethers

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Summary. Several new lariat-crown ethers bearing either bridged bisdioxine or tetraoxaadamantane units as chiral substituents are prepared by reacting the corresponding amino-crown ether derivatives with the dimeric α-oxoketene, the latter obtained by flash vacuum pyrolysis of a furan-2,3-dione precursor. Complexation properties towards differently charged metal ions are investigated by ^{1}H NMR titration to obtain complexation constants (K_c-values for potassium/sodium rhodanides: 480–1100 mol dm^{-3}), as well as extraction experiments to explore the metal ion transportation abilities of the new lariat crown derivatives. In particular, a significantly increased ability to transport metal ions from water into chloroform was found with spherical tetraoxaadamantyl derivatives when compared with the free amino-benzocrown ethers.

Keywords. Lariat-crown compounds; Complexes; NMR titration; Extraction experiments.

Introduction

Flash vacuum pyrolysis of *t*-butyl-pivaloylfuran-2,3-dione generates dipivaloylketene (**1**), a remarkably stable α-oxoketene, which smoothly dimerizes to afford the extraordinarily stable dimeric dipivaloylketene **2** in nearly quantitative yield [1]. Oxoketene **2**, when reacted with primary arylamines, rearranges into functionalized 2,6,9-trioxabicyclo[3.3.1]nona-3,7-dienes (''bridged bisdioxines'') **3**, rather rare concave heterocyclic systems exhibiting axial chirality [2]. Furthermore, compounds **3** may easily be converted into 2,4,6,8-tetraoxaadamantanes **4** in high yields by simple acidic hydrolysis [3]. Both heterocyclic systems (**3** and **4**) have been applied as novel spacer units by incorporation into macrocyclic systems of the

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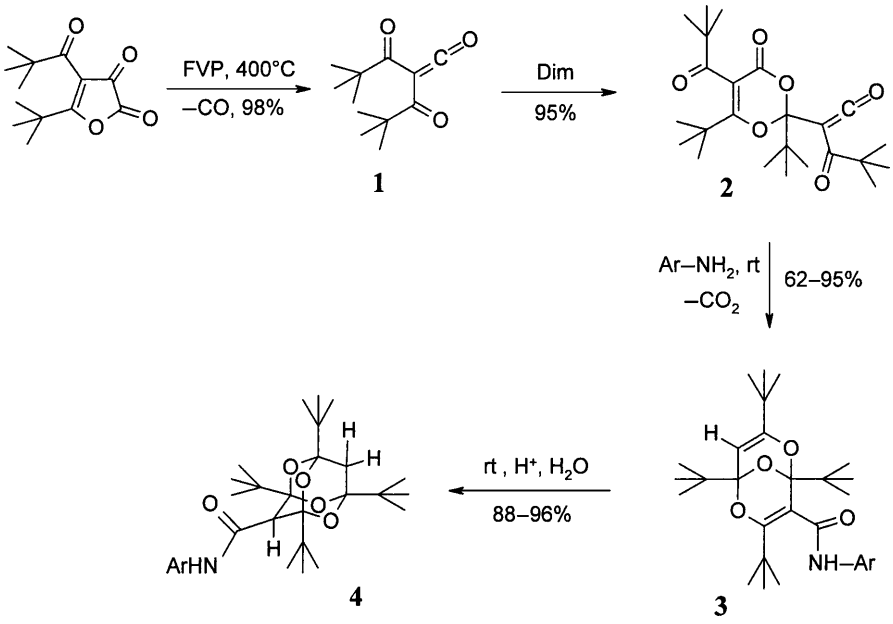


Scheme 1

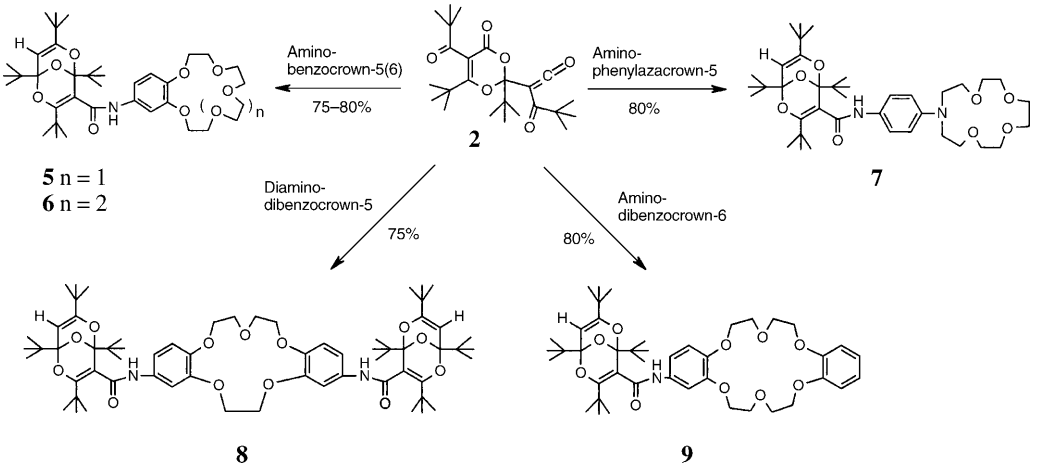
crown ether type in order to gain access to novel host-molecules possibly offering new complexation properties [4].

As an additional aspect, by using this methodology suitable NH_2- substituted benzo- and/or dibenzo- crown ethers may be convertible into new lariat-crown ethers bearing bridged bisdioxines or tetraoxaadamantanes as additional functionalities, thereby possibly changing and/or improving their abilities to encapsulate various guest molecules or metal ions. This should be achieved by reacting the corresponding amino-benzocrown ethers with the oxoketene **2** and subsequent H^+-catalyzed hydrolysis of the bridged bisdioxine derivatives initially formed.

Results and Discussion

Preparation of Lariat-Crown Ethers

When commercially available aminobenzo-, aminodibenzo-, diaminodibenzo-crown ethers, as well as 4-aminophenyl-aza-15-crown-5, prepared from commercially available phenyl-aza-15-crown-5 according to Ref. [5], were reacted with equimolar amounts of oxoketene **2** in anhydrous dichloromethane at room temperature for two days, the corresponding bridged bisdioxine lariat crown ether derivatives **5**–**9** were obtained in 75–80% yields (Scheme 2). The term ''lariat ether'' refers to a crown ether with one or more appendages designed to enhance complexation abilities by giving some three-dimensionality to the binding [6]. The crude products of **5**, **6**, **7**, and **9** could be purified by recrystallization from acetonitrile, while purification of the bis-product **8** required use of dry flash chromatography. Strong evidence for the presence of the trioxabicyclo[3.3.1]nona-3,7-diene skeleton came from the ^1H and ^{13}C NMR spectra, particularly when compared with



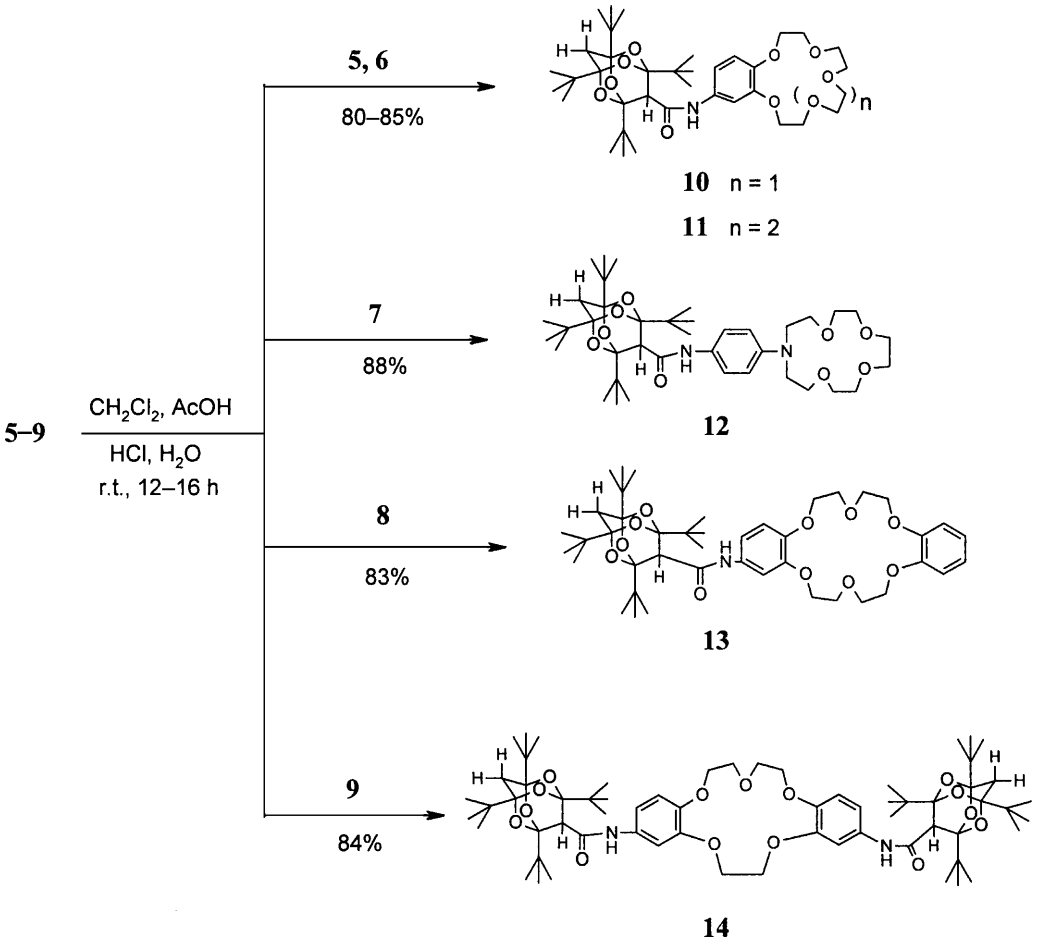
Scheme 2

corresponding data of several further derivatives [2]: the olefinic proton of the bisdioxine ring appears at 4.85 ppm, in the ^{13}C NMR spectra the ring carbons C-1/C-5 (acetalic sp^3-carbons) are found at 97.3–99.8 ppm, C-4/C-8 (sp^2-carbons) at about 92 and 105 ppm, while the signals of the enolic carbons (C-3/C-7) appear at 161–163 ppm (for further details of NMR spectroscopic data see the Experimental part).

The bridged bisdioxine unit of the lariat-crown ethers **5**–**9**, when treated under aequeous acidic conditions [3], were easily converted into the corresponding tetraoxaadamantane scaffold, thus affording the functionalized crown ether derivatives **10**–**14** in high yields (80–88%, Scheme 3). The presence of the spherical tetraoxaadamantane skeleton was established by highly significant spectroscopic data, *e.g.* in the ^1H NMR spectra the adamantyl- CH_2 appears at 1.75–1.78 ppm, and the CH at 3.01–3.06 ppm. The corresponding signals in the ^{13}C NMR spectra are found at 26.3 (t, $J = 128.6$ Hz) and 50.5–50.7 (d, $J = 136.7$ Hz) ppm for **10**, **12**, and **13** as examples. These data also agree exactly with those found of various analogous tetraoxaadamantanes [3]. Compound **10** crystallizes as a di-hydrate, a behaviour which is occasionally observed in lariat-crown ether chemistry [7].

Determination of Complexation Constants

In order to get some information on the complexation abilities of the new lariat-crown ethers **5**–**14** in general, ^1H NMR titration experiments by means of some selected compounds (**5**, **8**, and **14**) were performed to determine the values of the complexation constants (K_c – values). The experimental procedure applied followed the methodology described by *Sterk et al.* [8]. The ligand was dissolved in d_6-acetone and increasing amounts of sodium or potassium rhodanide were added with control of the corresponding chemical shift values, which were found within the range of $\Delta\delta = 0.11$ for the unchanged 4-aminobenzo-15-crown-5 and $\Delta\delta = 0.32$ for **5** with potassium rhodanide as guests in both cases. The K_c – values were calculated according to the equation: $K_c = C_C/[(C_{I\,tot} - C_C)\ (C_{L\,tot}\ C_C)]$ and are listed in Table 1 (C_C = concentration of the complex, $C_{I\,tot}$ = total concentration



Scheme 3

Table 1. Complexation constants of ligands **5**, **8**, and **14**

Crown ether	Salt	$\Delta\delta$-max ppm	K_c mol dm^{-3}
5	KSCN	0.32	570
	NaSCN	0.16	1100
8	KSCN	0.02	550
14	KSCN	0.10	480
4-aminobenzo-15-crown-5	KSCN	0.08	590

of the metal ion, $C_{L\,tot}$ = total concentration of the ligand). As expected, the flexibility of the macrocycle decreases with increasing addition of salt which became evident from a distinct broadening and splitting of the ethylene glycol protons.

From the K_c-values obtained it can be concluded that the lariat-unit obviously does not significantly enhance the complexation abilities of the crown ethers themselves. However, due to a small but significant difference of the chemical shift

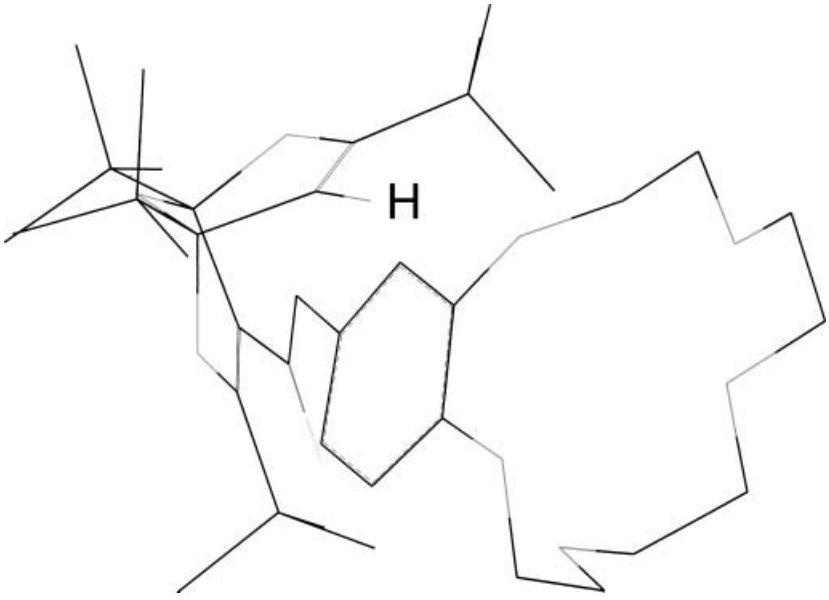


Fig. 1. Force field calculated wire frame model of **5** without hydrogens

values of the olefinic protons at C-7 ($\delta = 4.85$ ppm, $\Delta\delta = 0.005$ ppm) of the bridged bisdioxine moiety in the free ligands **5** and **8** compared to the metal-occupied species, a conformation of the host-guest system with the olefinic hydrogen occupying a position nearly perpendicular to the crown ether loop as indicated in Fig. 1 becomes more likely. This is also supported by some preliminary TRIPOS-force field calculations [9].

Solvent Extraction Experiments

The crown ether derivatives **5**, **8**, and **9** as well as the tetraoxaadamantyl analogues **10**–**14** were also tried as ligands in some preliminary solvent extraction experiments (water/chloroform) applying variably charged metal ions, namely Na^+, K^+, Ca^{++}, and Ce^{+++} as picrates. First attempts to use metal perchlorates or rhodanides were unsuccessful, thus the nature of the anion plays an important role which is a general experience in the area of host-guest interactions [10]. The metal picrates were prepared according to Ref. [11], dissolved in water and mixed with equimolar amounts of the ligands **5**–**14**, dissolved in chloroform. Then the mixture was vigorously shaken for 10 min, the two layers were separated, and the decrease of the concentration of the picrate anion in the water layer was measured by means of UV-spectroscopy (details see Experimental). Control experiments made evident that the metal picrates themselves without any ligand applying the identical procedure were not detectable in the organic layer. Furthermore, for comparison the free aminobenzocrown ethers (4-aminobenzo-15-crown-5, 4-aminodibenzo-18-crown-6, 4,4′-diaminodibenzo-15-crown-5) were subjected to the same extraction procedure (Table 2).

Table 2. Extraction of metal ions (%, system $H_2O/CHCl_3$) with aid of lariat crown ether **5**, **8**–**10**, **12**–**14**, and the corresponding non-functionalized aminobenzo crown ethers

Ligand	Na^+%	K^+%	Ca^{++}%	Ce^{+++}%
5	5	6	13	14
8	8	7	15	12
9	5	9	13	16
10	21	24	17	9
12	21	21	13	–
13	17	28	13	15
14	22	21	10	10
4-Aminobenzo-15-crown-5	4	4	6	8
4-Amino-dibenzo-18-crown-6	3	7	7	9
4,4′-Diamino-dibenzo-15-crown-5	7	5	10	9

The results presented in Table 2 indicate that there is nearly no improvement of extraction properties for the alkali metal ions when comparing ligands **5**, **8**, and **9** to the free aminobenzocrown ethers. But there is a significantly increased ability to transport ions from water into chloroform when using the ball-shaped tetraoxaadamantyl compounds compounds **10**–**14**. This is also to some extent the case for Ca^{++} and Ce^{+++}, as seen by comparing the lariat-crown ethers **5**–**14** with the free amino crown ether derivatives.

Conclusion

The lariat crown ethers **5**–**9** were obtained in yields of 75–80%, which is remarkable, since the formation of the chiral bridged bisdioxine system takes place *via* several intermediates as well as various rearrangements (detailed discussion of the reaction mechanism see Ref. [2b]), obviously not hindered or influenced by the rather bulky crown ether moieties. This is also true for the conversion of **5**–**9** into the tetraoxaadamantane derivatives **10**–**14**. The results of the extraction experiments encourage us to extend those investigations to liquid membrane studies, in particular since the increase of lipophilicity should be mainly responsible for the partially significant increase of transport abilities of metal ions into organic solvents.

Experimental

IR spectra were run on a Perkin-Elmer Model 298 spectrometer, UV/Vis -spectra on a Perkin-Elmer Lambda 5 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on Varian XL 200 or Bruker B 360 MHz spectrometers using *TMS* as internal standard. The MS of **10** was recorded on a HP-MS 902 (CI mode). Elemental analyses were performed on a Carlo Erba Elemental Analyzer Mod 1106. The results found agreed favourably with the calculated values. Melting points were detected on a Buechi-Tottoli apparatus or a Gallenkamp MFB-595 apparatus and are uncorrected.

The crown ethers 4-aminobenzo-15-crown-5, 4-aminodibenzo-18-crown-6 and 4,4′-diaminodibenzo-15-crown-5 were purchased from Sigma-Aldrich and Fluka. 4-Aminophenylaza-15-crown-5

was prepared according to Ref. [5]. The dimeric dipivaloylketene **2** was made following our own improved procedure [1b].

Reaction of **2** *and Aminobenzo Crown Ethers – General Procedure*

To a solution of 215 mg **2** (0.05 mmol) in 5 cm^3 dry CH_2Cl_2 0.05 mmol of the corresponding aminobenzo-crown ether are added and the reaction mixture is kept at 20°C for 2 d with stirring. Then the solvent is evaporated and the oily residue triturated with 2 cm^3 dry acetonitrile. After cooling to − 20°C the crude product precipitates and is recrystallized from *n*-hexane. In the case of **8**, after a reaction time of 3 d, the crude product is purified by dry-flash chromatography (silicagel 60H, eluant ethyl acetate/*n*-hexane 1:5).

4′-(1,3,5,7-Tetra-t-butyl-3,6,9-trioxabicyclo[3.3.1]nona-3,7-diene-4-yl-carbonylamino)-benzo-15-crown-5 (**5**, $C_{37}H_{57}NO_9$)

From 4-aminobenzo-15-crown-5; yield 245 mg (75%); mp 110°C; IR(KBr): $\bar{\nu} = 3440$ (NH), 3000–2860 (CH), 1680 (C=O), 1660, 1600 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 1.06$, 1.14, 1.20, 1.25 (s, 9H each, *t*-Bu), 3.7–4.2 (m, 16H, O–CH_2), 4.85 (s, C–H8), 6.98 (b, 2 ArH), 7.1 (s, 1ArH), 7.35 (b, NH) ppm.

4′-(1,3,5,7-Tetra-t-butyl-2,6,9-trioxabicyclo[3.3.1]nona-3,7-diene-4-yl-carbonylamino)-benzo-18-crown-6 (**6**, $C_{39}H_{61}NO_{10}$)

From 4-aminobenzo-18-crown-6; yield 280 mg (80%); mp 150°C; IR(KBr): $\bar{\nu} = 3440$ (NH), 3000–2860 (CH), 1680 (C=O), 1660, 1605 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 1.04$, 1.14, 1.20, 1.25 (s, 9H each, *t*-Bu), 3.7–4.4 (m, 20H, O–CH_2), 4.85 (s, C–H8), 6.75 (b, 2ArH), 7.1(s, 1ArH), 7.35 (s, NH) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 23.9$, 24.8, 28.2, 28.8 (C(CH_3)$_3$), 34.8, 37.6, 37.8, 39.8 (C(CH_3)$_3$), 69.0, 69.5, 69.7, 69.8, 70.7 (OCH_2), 91.9 (C-8), 97.3, 99.7 (C-1, C-5) 105.4 (C-4), 107.0, 111.8, 115.2, 132.4, 145.0, 149.3 (Ar–C), 161.5, 161.9 (C-3, C-7), 166.5 (C=O) ppm.

4′-(1,3,5,7-Tetra-t-butyl-2,6,9-trioxabicyclo[3.3.1]nona-3,7-diene-4-yl-carbonylamino)-phenylaza-15-crown-5 (**7**, $C_{39}H_{62}N_2O_8$)

From 4-aminophenyl-aza-15-crown-5 [5]; yield 275 mg (80%); mp 144°C; IR(KBr): $\bar{\nu} = 3435$ (NH), 3000–2850 (CH), 1660 (C=O), 1615 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 1.05$ (s, 9H, *t*-Bu), 1.14 (s, 9H, *t*-Bu), 1.22 (s, 18H, 2 × *t*-Bu), 3.5–3.8 (m, 20H, OCH_2, NCH_2), 4.85 (s, C–H8), 6.60 (m, 2 ArH), 7.3 (m, 2Ar-H), 7.05 (s, NH) ppm.

4,4′-Bis-(1,3,5,7-tetra-t-butyl-2,6,9-trioxabicyclo[3.3.1]nona-3,7-diene-4-yl-aminocarbonyl)-dibenzo-15-crown-5 (**8**, $C_{64}H_{94}N_2O_{13}$)

From 4′,4″-diamino-dibenzo-15-crown-5; yield 160 mg (75%); mp 218°C; IR(KBr): $\bar{\nu} = 3440$ (NH), 3000–2860 (CH), 1660 (C=O), 1600 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 1.02$, 1.12, 1.22, 1.23 (4s, 9H each, *t*-Bu), 3.92 (b, 2 OCH_2), 4.19 (b, 2 OCH_2), 4.34 (b, 2 OCH_2), 4.85 (s, 2 C–H8), 6.73–7.48 (m, 8 ArH + NH) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 24.1$, 25.0, 28.4, 29.0 (C(CH_3)$_3$), 35.0, 37.8, 38.1, 40.0 (C(CH_3)$_3$), 67.9, 68.6, 69.7, 69.8, 70.0, 71.1 (OCH_2), 92.0 (C-8), 97.1, 99.6 (C-1, C-5), 105.5 (C-4), 107.1, 107.6, 111.9, 112.0, 115.8, 117.4, 133.0, 133.2, 145.6, 149.8, 150.1 (Ar–C), 161.7, 162.1 (C-3, C-7), 166.8 (C=O) ppm.

4′-(1,3,5,7-Tetra-t-butyl-2,6,9-trioxabicyclo[3.3.1]nona-3,7-diene-4-yl-carbonylamino)-dibenzo-18-crown-6 (**9**, $C_{43}H_{61}NO_{10}$)

From 4-amino-dibenzo-18-crown-6; yield 300 mg (80%); mp 170°C; IR(KBr): $\bar{\nu} = 3440$ (NH), 3010–2800 (CH), 1665 (C=O), 1600 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz): 1.03, 1.116, 1.20, 1.226 (4s, 9H each, *t*-Bu), 4.02 (b, 4 OCH_2), 4.17 (b, 4 OCH_2), 4.85 (s, C–H8), 6.78–7.27 (m, 7 ArH), 7.35 (s, NH) ppm; ^{13}C NMR ($CDCl_3$, 90.5 MHz): $\delta = 24.07$, 24.88, 28.01, 28.89 ($C(CH_3)_3$), 35.01, 37.72, 38.04, 39.9 ($C(CH_3)_3$), 68.77, 69.38, 69.96 (OCH_2), 92.01 (C-8), 97.02, 101.6 (C-1, C-5), 106.2 (C-4), 111.50, 112.39, 113.73, 114.18, 121.32, 132.41, 145.30, 148.79 (ArC), 161.66, 162.06 (C-3, C-7), 166.72 (C=O) ppm.

Conversion of Lariat-Crown Ethers **5–9** *into Tetraoxaadamantyl Derivatives* **10–14** *– General Procedure*

Hydrochloric acid conc. (100 mg) is added to a solution of 100 mg lariat-crown ethers **5–9** in 1 cm^3 CH_2Cl_2/1 cm^3 acetic acid. The reaction mixture is stirred at 20°C for 12 h. After removal of CH_2Cl_2, colourless precipitates are formed which can be recrystallized from acetonitrile.

4′-(1,3,5,7-Tetra-t-butyl-2,4,6,8-tetraoxaadamantan-9-yl-carbonylamino)-benzo-15-crown-5 (**10**, $C_{37}H_{59}NO_{10} \cdot H_2O$)

From **5**; yield 78 mg (80%); mp 165°C; IR(KBr): $\bar{\nu} = 3410$–3880 (NH, OH), 3000–2860 (CH), 1670 (C=O), 1600, 1510 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz): $\delta = 0.96$ (s, 9H, *t*-Bu), 1.03 (s, 18H, *t*-Bu), 1.16 (s, 9H, *t*-Bu), 1.78 (s, CH_2), 3.04 (s, CH), 3.75 (m, 4 OCH_2), 3.91 (m, 2 OCH_2), 4.13 (m, 2 OCH_2), 6.82 (m, 2ArH), 7.25 (b, 1ArH), 8.16 (s, 1H, NH) ppm; ^{13}C NMR ($CDCl_3$, 90.5 MHz): $\delta = 23.36$ (qu, $J = 122.3$ Hz, $C(CH_3)_3$), 24.10 (qu, $J = 122.3$ Hz, $C(CH_3)_3$), 24.66 (qu, $J = 122.3$ Hz, $C(CH_3)_3$), 26.34 (t, $J = 130.5$ Hz, CH_2), 38.07, 38.76, 40.87 ($C(CH_3)_3$, 50.73 (d, $J = 136.7$ Hz, *C*H), 68.9, 69.53, 69.74, 70.55, 70.69, 71.05 (6 × t, $J = 78.5$ Hz, OCH_2), 99.38, 101.66 (C-1, C-3, C-5, C-7), 107.24, 112.40, 114.91 (3 × d, $J = 157.3$, Ar–*C*H), 131.83, 145.67, 149.37 (quart.Ar–C), 167.95, 168.02 (C=O, rotamers) ppm; MS (APCI): $m/z = 678.4$ ($M^+ + 1$; 100%).

4′-(1,3,5,7-Tetra-t-butyl-2,4,6,8-tetraoxaadamantan-9-yl-carbonylamino)-benzo-18-crown-6 (**11**, $C_{39}H_{63}NO_{11}$)

From **6**; yield 85 mg (85%); mp 180°C; IR(KBr): $\bar{\nu} = 3400$ (NH), 3000–2820 (CH), 1675 (C=O), 1600, 1520 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): $\delta = 0.98$ (s, 9H, *t*-Bu), 1.05 (s, 18H, *t*-Bu), 1.17 (s, 9H, *t*-Bu), 1.78 (s, CH_2), 3.02 (s, CH), 3.72 (m, 6 OCH_2), 3.90 (m, 2 OCH_2), 4.12 (m, 2 OCH_2), 6.82 (m, 2 ArH), 7.21 (b, ArH), 8.18 (s, NH) ppm.

4′-(1,3,5,7-Tetra-t-butyl-2,4,6,8-tetraoxaadamantan-9-yl-carbonylamino)-phenylaza-15-crown-5 (**12**, $C_{39}H_{64}N_2O_9$)

From **7**; yield 90 mg (88%); mp 250–52°C; IR(KBr): $\bar{\nu} = 3430$ (NH), 3010–2800 (CH), 1680 (C=O), 1620, 1580, 1520 cm^{-1}; 1H NMR ($CDCl_3$, 200 MHz): $\delta = 0.97$ (s, 9H, *t*-Bu), 1.06 (s, 18H, *t*-Bu), 1.08 (s, 9H, *t*-Bu), 1.77 (s, CH_2), 3.02 (s, CH), 3.50–3.85 (m, 20H, OCH_2, NCH_2), 6.60, 7.30, (A,A′,B,B′-system, $J = 8$ Hz, 4H, ArH), 8.10 (s, NH) ppm; ^{13}C NMR ($CDCl_3$, 90.5 MHz): $\delta = 23.37$, 24.07, 24.75 ($C(CH_3)_3$), 26.38 (CH_2), 38.08, 38.72, 40.84 ($C(CH_3)_3$), 50.52 (*C*H), 52.54 (NCH_2), 68.61, 70.17, 71.32 (OCH_2), 99.33, 101.62, 101.68 (C-1, C-3, C-5, C-7), 111.43, 121.98, 126.52 (ArC), 144.58, 144.62 (quart.ArC), 167.52 (C=O) ppm.

4′-(1,3,5,7-Tetra-t-butyl-2,4,6,8-tetraoxaadamantan-9-yl-carbonylamino)-dibenzo-18-crown-6 (**13**, $C_{43}H_{63}NO_{11}$)

From **8**; yield 85 mg (83%); mp 245°C; IR(KBr): $\bar{\nu} = 3420$ (NH), 3010–2820 (CH), 1675 (C=O), 1610, 1530, 1510 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): $\delta = 0.95$ (s, 9H, *t*-Bu), 1.03 (s, 18H, *t*-Bu), 1.16 (s, 9H, *t*-Bu), 1.76 (s, CH_2), 3.02 (s, CH), 4.02 (m, 4 OCH_2), 4.16 (m, 4 OCH_2), 6.88 (m, 5 ArH), 7.22 (m, 2 ArH), 8.18 (s, NH) ppm; ^{13}C NMR ($CDCl_3$, 90.5 MHz): $\delta = 23.36$, 24.10, 24.66 ($C(CH_3)_3$) 26.34 (CH_2), 38.07, 38.74, 40.84 ($C(CH_3)_3$), 50.71 (*C*H), 68.79, 69.96 (OCH_2), 99.37, 101.65, 101.70 (C-1, C-3, C-5, C-7), 106.88, 112.37, 113.69, 121.31 (ArC), 131.68, 145.10, 148.81 (quart.ArC), 167.97 (C=O) ppm.

4′,4″-Bis(1,3,5,7-tetra-t-butyl-2,4,6,8-tetraoxaadamantan-9-yl-carbonylamino)-dibenzo-15-crown-5 (**14**, $C_{64}H_{98}N_2O_{15}$)

From **9**; yield 85 mg (84%); mp 240°C; IR(KBr): $\bar{\nu} = 3420$ (NH), 3020–2820 (CH), 1685 (C=O), 1600, 1510 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): $\delta = 0.98$ (s, 18H, *t*-Bu), 1.02 (s, 36H, *t*-Bu), 1.18 (s, 18H, *t*-Bu), 1.76 (s, 2 CH_2), 3.02 (s, 2 CH), 3.92 (m, 2 OCH_2), 4.19 (m, 2 OCH_2), 4.32 (m, 2 OCH_2), 6.88 (m, 4 ArH), 7.22 (m, 2 ArH) ppm.

Determination of Complexation Constants

(a) Increasing amounts of sodium rhodanide, dissolved in d_6-acetone, ($2.24 \cdot 10^{-1}$ mol dm^{-3}, $9 \cdot 4\,mm^3$) are added step by step to a solution of crown ether derivative **5** (d_6-acetone, 750 mm^3, $10.6 \cdot 10^{-3}$ mol dm^{-3}) in an NMR tube, and after each addition, the change of the chemical shift of the signal of OCH_2 – protons at $\delta = 3.93$ ppm is monitored by ^1H NMR spectroscopy. The signal ultimately moved to 4.12 ppm ($\Delta\delta = 0.19$ ppm).
(b) In a similar way, potassium rhodanide ($9.95 \cdot 10^{-1}$ mol dm^{-3}, $13 \cdot 2\,mm^3$) is added to the solution of **5** (d_6-acetone, 750 mm^3, $10.6 \cdot 10^{-3}$ mol dm^{-3}, NMR-tube). The signal at $\delta = 3.72$ ppm is continuously monitored to give a maximum $\Delta\delta = 0.32$ ppm.
(c) Complexation behaviour of **8** towards potassium ions is monitored analogously employing a solution of **8** (750 mm^3, $2.02 \cdot 10^{-3}$ mol dm^{-3}, d_6-acetone) and adding potassium rhodanide ($19.5 \cdot 10^{-2}$ mol dm^{-3}) in $11 \cdot 2\,mm^3$ portions ($\Delta\delta_{max} = 0.02$ ppm at $\delta = 4.14$ ppm).
(d) Complexation of potassium rhodanide ($9.95 \cdot 10^{-1}$ mol dm^{-3}, $11 \cdot 2\,mm^3$, d_6-acetone) by crown ether derivative **14** ($1.58 \cdot 10^{-3}$ mol dm^{-3}) resulted in a $\Delta\delta_{max}$ of 0.10 ppm by monitoring the signal at $\delta = 3.18$ ppm.
(e) Unfunctionalized 4-aminobenzo-15-crown-5 as host-molecule (750 mm^3, $10.59 \cdot 10^{-3}$ mol dm^{-3}, d_6-acetone) binds potassium rhodanide ($9.95 \cdot 10^{-1}$ mol dm^{-3}, $10 \times 2\,mm^3$, d_6-acetone) to a $\Delta\delta_{max} = 0.11$ ppm by monitoring the OCH_2 – signal at $\delta = 3.65$ ppm.

Extraction Experiments

The experimental procedure basically follows similar experiments described in Refs. [10, 12].

(a) Preparation of Metal Picrates [11]: equivalent amounts of NaOH, KOH, $Ca(OH)_2$, and $Ce_2(CO_3)_2$ and picric acid are dissolved in H_2O with stirring until a clear solution is formed. The solution is evaporated, methanol is added, and the solution is evaporated to dryness (this procedure is repeated 2×). The crude residue is thoroughly treated with toluene to remove a possible slight excess of picric acid. The corresponding picrates are isolated by suction as yellow crystals.
(b) Calibration Diagram: suitable amounts of the picrates (2.5–3.3 mg) are dissolved in 100 cm^3 H_2O, gradually diluted (5×) and the corresponding extinctions ($\lambda = 354$ nm) measured and correlated.

A straight line is obtained for every picrate thus enabling the determination of molar concentrations of the picrates for any extinction value found.

(c) Determination of Extraction Rates: equimolar amounts of the corresponding metal picrates and ligands (see Table 2) are dissolved in H_2O and H_2O saturated $CHCl_3$ (10 cm^3 each) and frequently shaken in a separatory funnel for 10 min. After standing for 10 min in order to achieve a clear separation of the layers, 7 cm^3 of every aequous layer are diluted to 100 cm^3 and the concentrations of picrate determined photometrically at $\lambda = 354$ nm by means of the calibration curves. The calculated percentages of extraction are given in Table 2.

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