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Short Chain Acyclic Crown Ethers[1]

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A series of short chain acyclic crown ethers such as (1,2), (1,3), (1,4)-phenylenediethers and some symmetric or assymmetric *o*-substituted phenyl ethers were prepared. The complexation studies of these compounds were carried out by a) direct UV titration method, b) picrate extraction method and c) isolation of crystalline complex.

(Keywords: Acyclic crown ethers; Complexation studies; Phenylene diethers; Phenyl ethers)

Kurzkettige acyclische Kronen-Ether

Es wurde eine Reihe von kurzkettigen acyclischen Kronen-Ethern hergestellt und ihre Komplexierung mittels direkter UV-Titration, Pikrat-Extraktion bzw. Isolierung der kristallinen Komplexe untersucht.

Simple oligo (ethyleneglycoldimethylethers) such as pentaglyme (**1**), $n = 3$, are reported not to form crystalline complexes with salts of alkali and alkali earth metals[2, 3]; such complexes are readily obtained with "noncyclic crown ethers" (**2**), $n = 1$, which are rendered rigid by aromatic donor end groups (E)[4, 5]. It has been shown that hetero atoms located in terminally fixed groups can serve as donors in a neutral ligand and just one effective end donor group was sufficient to permit isolation of crystalline alkali metal in the complex[6]. We are particularly interested in studying the end group donor effect in the short chain acyclic polyethers type I, II and III.

Polyethers **3**–**5** were prepared by refluxing butoxyethoxyethyl bromide with the diol in question in sodium metal-methanol mixture under nitrogen or in sodium hydroxide—water—*t*-butanol solution. Compounds **6**–**11** were synthesized by reacting the phenol with bromo-

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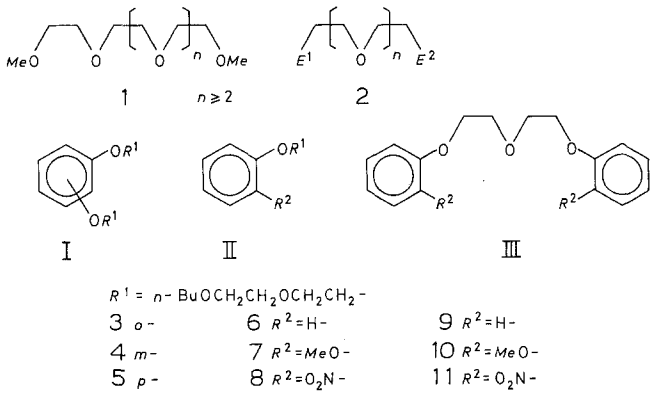
alkylethers. The proof of the structure of the acyclic polyethers is based on elementary composition, molecular weight, IR and NMR spectra. Some of these data are listed in Table 1. All NMR spectra obtained in deuteriochloroform are consistent with the proposed structure. In-



frared and Ultraviolet spectra were also obtained. The former confirms the absence of hydroxy group, and indicates the presence of ether linkages by strong broad bands centering near 1,200 cm^{-1} (aromatic-0-aliphatic) and 1,120 cm^{-1} (aliphatic-0-aliphatic). The ultraviolet spectra of compounds derived from catechol have absorption bands (in methanol) at 273-275 nm. These bands are characteristics for the diols and ethers.

The complexation of various cations with compounds **3**-**11** was studied first by the direct UV titration method[7] in anhydrous methanol, a solvent for which there is much data on the complexation of

Table 1. *Acyclic polyethers of type I, II and III*

Compd. No.	Yield (%)	MS m/e (M^+)	Formula	Calcd. C	Calcd. H	Found C	Found H
3	20	398	$C_{22}H_{38}O_6$	66.30	9.61	66.47	9.40
4	11	398	$C_{22}H_{38}O_6$	66.30	9.61	66.31	9.51
5	21	398	$C_{22}H_{38}O_6$	66.30	9.61	60.12	9.25
6	90	238	$C_{14}H_{22}O_3$	70.56	9.30	70.54	9.23
7	50	268	$C_{15}H_{24}O_4$	67.14	9.01	66.99	9.11
10	80	319	$C_{18}H_{22}O_5$	67.91	6.97	68.18	6.97
11	72	348	$C_{16}H_{16}N_2O_7$	55.17	4.63	54.91	4.74

crown ethers and other molecules. A direct titration by varifying the cation-ligand ratio from 0.1-100 showed that there is no change in the absorbance or peak shape of the pure ligands while adding the solution of K^+, Na^+, NH_4^+, Ca^{++}, Ba^{++}, Mg^{++} or Mn^{++}.

The ability of these acyclic polyethers to bind metal cations was also examined by equilibrating a chloroform solution of each polyether with aqueous picrate solutions. Metal picrates are extracted with complex formation, and the decrease in absorbance of the picrate in aqueous phase was taken to be a measure of efficiency of acyclic polyether as complexing agent for the cation[8]. This method is only applicable to the water insoluble ligands, but not the water soluble ligands, like **6**-**8** and **11**, their UV absorptions interfer that of the picrate salt in aqueous phase. The picrate salts of sodium, potassium, ammonium, calcium, barium and magnesium showed very low ($\sim 2\%$) complexation at the picrate-lingd ratio of 100 for the ligands **3**-**5** and **9**-**10**.

The solid complexes of these acyclic polyethers are prepared by two methods: a) one mole of polyether and one mole (or an excess) of salt are dissolved in a minimum quantity of hot solvent, the mixture was refluxed for two hours, and the complex is precipitated by cooling and recovered by filtration; b) following the same procedure as above, using different solvents for polyethers and the inorganic salts. The only solid complex isolated is **10**-NaSCN, its NMR, IR and analytical data agree with what was reported recently by *Vögtle*[9].

It is known that even glycol with only three donor atoms, like diethylene glycol, forms a 1 : 1 complex with the relatively large barium ion and 2 : 1 complex with the Calcium ion[10]. With three oxygen atoms in the polyether chain, phenyl as a terminal group (**6** and **9**) is incapable of donating while *o*-methoxy-phenyl end group (**10**) forms a stable complex with sodium ion. The inferiority of the 2-nitrophenylethers (**11**) and (**8**) suggested that apart from any group donor effects a geometric factor is also very important.

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Experimental

Infrared spectra were taken on a Perkin-Elmer model 180 spectrophotometer and ultraviolet spectra were recorded on a Perkin-Elmer model 356 spectrophotometer in methanol. The nuclear magnetic resonance spectra were measured in $CDCl_3$ solution with Hitachi Perkin-Elmer R-20 B spectrometer

and *TMS* was used as internal reference. Mass spectra were taken on a Varian Mat. 111 mass spectrometer.

All the solventes used were dried by distillation and if necessary they were purified by following the procedure mentioned in Ref.[11]. All inorganic salts were reagent grade.

1-Bromo-3,6-dioxadecane (**14**) was obtained in 95% yield by reaction of 1-hydroxy-3,6-dioxadecane with tribromophosphorous (1:0.4) without solvent at 80 °C for 2 h and then at room temperature overnight[12].

Polyethers of series I were synthesized in two ways: a) A solution of sodium hydroxide (0.1*M* in 10 ml of water) was added to a solution of diol in question (0.05*M* in 20 ml of *t*-butanol) under nitrogen at 50 °C and the resulted mixture was stirred at this temperature for another 30 min. The mixture was treated with 1-bromo-3,6-dioxadecene (**14**) (0.1 mol in 10 ml of *t*-butanol) and it was then refluxed for 30 h. It was cooled and neutralized with concentrated hydrochloric acid, the solvent was removed and the mixture was extracted three times with 70 ml of chloroform. The combined organic solution was washed twice with 50 ml water, dried with anhydrous magnesium sulfate, filtered and evaporated to dryness to give the crude product.

b) Sodium metal (0.104 mol) was dissolved in 20 ml of dry methanol under nitrogen and it was treated with diol in question (0.05 mol in 15 ml of dry methanol). The mixture was stirred at room temperature for 10 min and (**14**) (0.1 mol) was added dropwise, it was then refluxed for 20 h. A white precipitare formed during the reaction. The mixture was cooled and neutralized with concentrated hydrochloric acid. By following the same work up procedure as mentioned above, the crude product was isolated. The pure products were obtained by column chromatography on alumina neutral, the eluente is shown below:

Polyether	Solvent
3	Toluene-ethyl acetate 9:1
4	toluene-methanol 9.9:0.1
5	toluene-ethyl acetate 8.5, 1.5

Polyether **3**. IR (ν_{max}/cm^{-1}): 2960, 2940, 1590, 1495, 1450, 1350, 1210, 1120, 1050, 935, 750, 670. NMR (δ): 0.76-1.75 (14 H, m, 2 × *n pr*), 3.32-4.24 (20 H, m, 10 × —O—CH_2), 6.85 (4 H, s, *Ph*). UV [λ_{max}/nm (ε)]: 274 (1884).

Polyether **4**. IR (ν_{max}/cm^{-1}): 2960, 2910, 1590, 1490, 1450, 1285, 1260, 1180, 1115, 915, 730, 625. NMR (δ): 0.70-1.70 (14 H, m, 2 × *n-pr*), 3.15-4.07 (2 OH, m, 10 × —OCH_2—), 6.33-7.17 (4 H, m, *Ph*-). UV [λ_{max}/nm (ε)]: 278 (1778), 272 (1937).

Polyether **5**. (ν_{max}/cm^{-1}): 2960, 2940, 2875, 1505, 1350, 1270, 1230, 1115, 830, 760. NMR (δ): 0.75-1.65 (14 H, m, 2 × *n-pr*), 3.32-4.12 (2 OH, m, 10 × —OCH_2—), 6.79 (4 H, s, *Ph*-). UV [λ_{max}/nm (ε)]: 286 (2442).

o-Substituted phenoxy-3,6-dioxadecanes **6, 7, 8** Phenol in question (0.05 mol) in 20 ml of *t*-butanol was treated with a solution of sodium hydroxide (0.55 mol in 10 ml of water), this mixture was heated at 70 °C for 15 min. 1-Bromo-3,6-diosadecane (**14**) (0.053 mol) was added dropwise. The mixture was then refluxed with good agitation, the resulted solution was acidified with hydrochloric acid, it was filtered and the solution was extracted twice 50 ml chloroform. The combined organic solution was washed, dried and the solvent

was removed to give pure enough product. The reaction time of different polyethers is shown below:

Polyether	Reaction Time
6 *o*-H	16 h
7 *o-OMe*	24 h
8 *o*-NO_2	48 h

Polyether **6**. IR (ν_{max}/cm^{-1}): 3070, 2960, 1600, 1580, 1490, 1350, 1295, 1240, 1170, 1130, 1080, 960, 890, 795, 690, 615. NMR (δ): 0.70-1.80 (7 H, m, *n-pr*), 3.32-4.18 (10 H, m, 5 × —OCH_2—), 6.70-7.34 (5 H, m, *Ph*-). UV [λ_{max}/nm (ε)]: 276 (1413), 270 (1712).

Polyether **7**. IR (ν_{max}/cm^{-1}): 3070, 2960, 2880, 1590, 1450, 1350, 1250, 1175, 1120, 740, 620. NMR (δ): 0.77-1.68 (7 H, m, *n-pr*), 3.82 (13 H, a singlet superimposed on a multiplet between 3.34-4.27, —OCH_3 + 5 × —OCH_2—), 6.89 (4 H, s, *Ph*-). UV [λ_{max}/nm (ε)]: 272 (2070).

Polyether **8**. IR (ν_{max}/cm^{-1}): 3080, 2960, 1600, 1525, 1450, 1350, 1275, 1250, 1160, 1115, 1040, 920, 850, 770, 700, 600.

NMR (δ): 0.78-1.65 (7 H, m, *n-pr*), 3.30-4.40 (10 H, m, 5 × —OCH_2—), 6.82-7.82 (4 H, m, *Ph*-). UV [λ_{max}/nm (ε)]: 320 (1951), 255 (2587).

1,5-Bis(o-methoxyphenoxy)-3-oxapentane (**10**). A mixture of *o*-methoxyphenol (0.08 mol), sodium hydroxide (0.08 mol in 10 ml of water) and 30 ml of *t*-butanol was heated at 70 °C for 10 min and then a solution of dibromide **15** (0.04 mol in 10 ml of *t*-butanol) was added dropwise with stirring. The mixture was refluxed for 20 h. At the end of the reaction the mixture was cooled and a white precipitate fromed immediately. The mixture was neutralized and filtered, the isolated solid was washed with *t*-butanol and water. Recrystallization from methanol gave 10.1 g of white crystals (80%), m.p. 70-72 °C. IR (ν_{max}/cm^{-1}): 3070, 2970, 2890, 1595, 1450, 1360, 1290, 1230, 1125, 1060, 1010, 945, 860, 770. NMR (δ): 3.97 (14 H, singlet superimposed on a multiplet between 3.79-4.25, 2 × —OCH_3 + 4 × —OCH_2—), 6.83 (8 H, s, *Ph*). UV [λ_{max}/nm (ε)]: 274 (4777).

1,5-Dibromo-3-oxapentane (**15**). Using the same procedure as for **14**, the dibromide **15** was prepared in 59% yield[12].

1,5-Bis(o-nitrophenoxy)-3-oxapentane (**11**). A mixture of 30 ml *t*-butanol, 0.07 mol of *o*-nitrophenol and 0.07 mol of sodium hydroxide in 10 ml of water was heated at 70 °C for 10 min and them dibromide **15** (0.035 mol) was added dropwise at this temperature. The mixture was further refluxed for 48 h. The reaction mixture was cooled, neutralized and the solvent was removed. The residue was extracted three times with 70 ml of chloroform, this organic solution was then dried and the solvent was removed to give yellow crystals. Recrystallization from methanol gave 11 g (81.3%) of yellow crystals. m.p. 58-60 °C. IR (ν_{max}/cm^{-1}): 3130, 3060, 2960, 1600, 1490, 1380, 1205, 1080, 970, 870, 750, 670. NMR (δ): 3.88-4.30 (8 H, m, —OCH_2—), 6.82-7.83 (8 H, m, *Ph*-). UV [λ_{max}/nm (ε)]: 322 (4140).

Picrate extraction procedure. Aqueous picrate solutions were made up from standardized stock solution of sodium hydroxide, potassium hydroxide and other inorganic reagentes and picric acid. Calcium picrate, for example, was prepared by neutralization picric acid with calcium chloride at $7 \cdot 10^{-5}$ *M* added to a final Ca^{++} of 10^{-2} *M*, or by adding excess calcium chloride solution to picric acid. The polyethers were dissolved in chloroform. Equal volumes of the two solutions in stoppered centrifuge tubes were mixed well by hand for 5 min to ensure complete equilibration. Centrifugation was needed for complete phase

separation. The extraction were conducted at 25 ± 1 °C. Equilibrium picrate concentrations in both phases were measured by UV spectrophotometer.

Direct UV titration method. Anhydrous NaCl, NaI, KI, KSCN, NH_4Cl, $CaCl_2$, $CuCl_2$ ... and other salts were used as received. Ligand solutions in anhydrous methanol were prepared by diluting a 0.1 *M* stock solution to the expected suitable concentration. Cation solution (0.01 *M*, 0.1 *M* or 1.0 *M*) was added via a 10 µl syringe so that volume changes could be neglected. After each addition the cuvet was thoroughtly shaken before the UV spectrum was recorded.

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