Interactions of Macrobicyclic Polyethers with Ions and Ion Pairs of Picrate Salts

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Abstract: The complexation of picrate salts to several macrobicyclic polyethers, synthesized by condensing 4′-carboxybenzo-15-crown-5 with glycol, 1,5-pentanediol, 1,8-octanediol, diethylene glycol, and triethylene glycol, respectively, was investigated in tetrahydrofuran as a function of the length and structure of the chain connecting the two crown moieties. The interaction with the bis(crown ethers) results in the conversion of the tight picrate ion pairs into crown separated ion pairs. The change is accompanied by a shift in the optical spectrum of the picrate anion, making it feasible to determine the complex formation constants spectrophotometrically. Compared with the methyl ester of 4′-carboxybenzo-15-crown-5, the macrobicyclic polyethers are considerably more effective in binding K^+ and NH_4^+ cations, both of which are known to form 2:1 crown cation complexes with monobenzo-15-crown-5. The complex formation constants for the free cations are about 400 times higher than for the respective tight picrate ion pairs. They vary with chain length, the value for both ion pairs and free ions being the largest for a chain with five methylene groups. Replacing a CH_2 group by oxygen results in a fivefold increase in the complex formation constant, probably because of increased chain flexibility. The free ion dissociation constants of the crown separated ion pair complexes in THF were also determined and found to be only slightly affected by the structure of the crown compound. The dissociation constants are in the order of 3×10^{-5} *M*, about 200 to 400 times higher than for the noncomplexed potassium and ammonium picrate tight ion pairs.

The complexation of macrocyclic polyethers or crown ethers to alkali metal and other cations has been well documented,[1] and several new types of ligands have recently been synthesized to enhance the stability of the cation–ligand complex and to achieve better selectivity.[2] The observation that many crown ethers form complexes with two crown moieties per cation induced us to examine the properties of macrobicyclic polyethers containing benzo-15-crown-5 moieties at the end of a short aliphatic chain. We were particularly interested in studying the effect of chain length and chain structure on the ion and ion pair complex formation constants. The experimental approach was based on our recent observation[3] that salts of picric acid in low polarity media frequently exhibit pronounced shifts in their optical spectra in the presence of crown ethers. The shifts occur when a tight ion pair is converted into a loose pair by a cation chelating crown compound, or, to put it more generally, when complexation leads to a significant increase in the interionic distance of the tight ion pair. Combined with conductance measurements, complex formation constants of a series of macrobicyclic polyethers or bis(crown ethers) with potassium and ammonium cations and their ion pairs with the picrate anion were measured in tetrahydrofuran at 25° and compared with data obtained for the methyl ester of 4′-carbomethoxybenzo-15-crown-5.

Experimental Section

Picrate Salts. Potassium and ammonium picrates were prepared in ethanol by neutralizing picric acid with the corresponding metal hydroxides as outlined by Coplan and Fuoss.[4] The salts were recrystallized from water, dried under vacuum, and stored in the dark.

Derivatives of Monobenzo-15-crown-5. 2,3-(4′-Carboxybenzo)-1,4,7,10,13-pentaoxacyclopentadeca-2-ene or 4′-Carboxybenzo-15-crown-5. To a stirred solution of 22 g (0.55 mol) of sodium hydroxide in 150 ml of water at 0–10° was added dropwise 7 ml (0.138 mol) of bromine. To this mixture, 10.5 g (0.033 mol) of 4′-acetobenzo-15-crown-5 (for the synthesis of this compound, see ref 5) was added portionwise in 15 min with vigorous stirring. The temperature, which initially increased to 40°, was maintained at 20° with an ice bath. After 5 hr, 4.16 g (0.04 mol) of sodium bisulfite was added to destroy excess sodium hypobromide. The reaction mixture was filtered, then extracted with chloroform to remove any unreacted ketone. The aqueous layer was acidified with concentrated HCl to precipitate the acid. After cooling to 0–5°, the solution was filtered and the white precipitate washed with water. Recrystallization from ethanol afforded 9.5 g (92%) of pure 4′-carboxybenzo-15-crown-5: mp 180°; NMR (DMSO-*d*) τ 6.0 (m, 16, $-CH_2-$), 3.0 and 2.52 (d, m, 3, aromatic $-CH-$).

Anal. Calcd for $C_{15}H_{20}O_7$: C, 57.69; H, 6.45. Found: C, 57.85; H, 6.37.

2,3-(4′-Carbomethoxybenzo)-1,4,7,10,13-pentaoxacyclopentadeca-2-ene or 4′-Carbomethoxybenzo-15-crown-5 (I). To a solution of 200 ml of methanol saturated with HCl gas was added 3 g (0.0096 mol) of 4′-carboxybenzo-15-crown-5. After refluxing the mixture overnight, the solvent was removed under vacuum and the white residue dissolved in water. The solution was extracted with $CHCl_3$, washed with water, dried with $MgSO_4$, the chloroform evaporated, and the crude product recrystallized from *n*-heptane, affording 2.5 g (81%) of 4′-carbomethoxybenzo-15-crown-5: mp 82°; NMR ($CDCl_3$) τ 6.12 (s, 3, $-OCH_3$), 6.0 (m, 16, $-CH_2-$), 2.40 and 3.10 (m, d, 3, aromatic $-CH-$).

Macrobicyclic Polyethers. The general procedure used in the synthesis of the five macrobicyclic polyethers is illustrated below for one of the compounds.

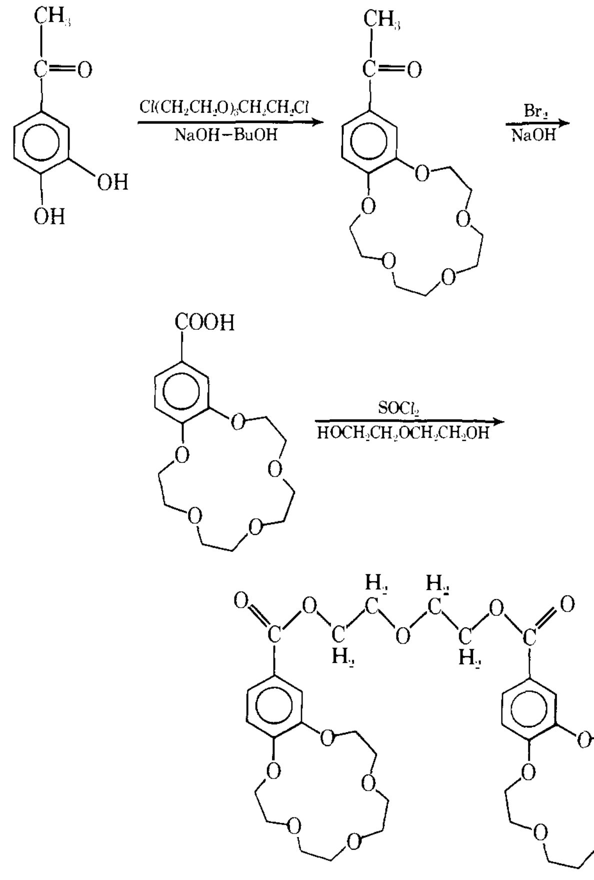
The following diols were used in the reaction with 4′-carboxybenzo-15-crown-5: ethylene glycol, 1,5-pentanediol, 1,8-octanediol, diethylene glycol, and triethylene glycol. All diols were commercially available and carefully distilled before use.

To a mixture of 10 g (0.032 mol) of 4′-carboxybenzo-15-crown-5 in 50 ml of chloroform was added dropwise 7.6 g (0.064 mol) of thionyl chloride. The mixture was refluxed for 3 hr, followed by removal of solvent and excess thionyl chloride under vacuum. Next, 2.6 g (0.033 mol) of pyridine was added, followed by 0.015 mol of the appropriate diol in chloroform. After reluxing overnight, the reaction mixture was extracted with 5% $NaHCO_3$, the chloroform layer washed, then dried over $MgSO_4$. After filtration and solvent evaporation, an oil was left which crystallized upon standing. The crude product was recrystallized from *n*-heptane (in case of compound II, column chromatography with THF was used). The results for the various compounds were as follows.

1,2-Bis[3′,4′-(1″,4″,7″,10″,13″-pentaoxacyclopentadeca-2″-ene)phenylcarboxy]ethane (II): yield 87%; mp 124–125°; NMR ($CDCl_3$) τ 6.0 (m, 32, $-CH_2-$), 5.4 (s, 4, $-COOCH_2-$), 3.1 and 2.4 (d, m, 6, aromatic $-CH-$).

Anal. Calcd for $C_{32}H_{42}O_{14}$: C, 58.89; H, 6.49. Found: C, 59.07; H, 6.50.

1,5-Bis[3′,4′-(1″,4″,7″,10″,13″-pentaoxacyclopentadeca-2″-ene)phenylcarboxy]pentane (III): yield 60%; mp 88–89°; NMR ($CDCl_3$) τ 8.3 (m, 6, $-CH_2-$), 6.0 (m, 32, $-CH_2-$), 5.7 (t, 4, $-COOCH_2-$), 3.10 and 2.40 (d, m, 6, aromatic $-CH-$).



Anal. Calcd for $C_{35}H_{48}O_{14}$: C, 60.68; H, 6.98. Found: C, 60.46; H, 6.96.

1,8-Bis[3′,4′-(1″,4″,7″,10″,13″-pentaoxacyclopentadeca-2″-ene)phenylcarboxy]octane (IV): yield 56%; mp 82°; NMR ($CDCl_3$) τ 8.6 and 8.2 (m, 8, 4, $-CH_2$), 6.0 (m, 32, $-CH_2$), 5.7 (t, 4, $-COOCH_2-$), 3.10 and 2.40 (d, m, 6, aromatic -CH-).

Anal. Calcd for $C_{38}H_{54}O_{14}$: C, 62.11; H, 7.41. Found: C, 62.02; H, 7.49.

Bis[3,4-(1′,4′,7′,10′,13′-pentaoxacyclopentadeca-2′-ene)phenylcarboethoxy] ether (V): yield 64%; mp 89–91°; NMR ($CDCl_3$) τ 6.0 (m, 36, $-CH_2-$), 5.5 (t, 4, $-COOCH_2-$), 3.1 and 2.4 (d, m, 6, aromatic -CH-).

Anal. Calcd for $C_{34}H_{46}O_{15}$: C, 58.78; H, 6.67. Found: C, 58.98; H, 6.69.

1,2-Bis[3′,4′-(1″,4″,7″,10″,13″-pentaoxacyclopentadeca-2″-ene)phenylcarboxyethoxy]ethane (VI): yield 48%; mp 83–84°; NMR ($CDCl_3$) τ 6.0 (m, 40, $-CH_2-$), 5.5 (t, 4, $-COOCH_2-$), 3.1 and 2.4 (d, m, 6, aromatic -CH-).

Anal. Calcd for $C_{36}H_{50}O_{16}$: C, 58.53; H, 6.82. Found: C, 58.74; H, 6.96.

Conductance Measurements. Experiments were carried out in a cell provided with platinum electrodes (cell constant 0.0271) at 25° using a 1673 General Radio Corp. automatic capacitance bridge coupled with a 1672 digital control unit. Acetone and THF were used as solvents and distilled prior to use. The stoichiometry of the potassium ion–bis(crown ether) complex was determined by adding increasing quantities of the crown compound to a 10^{-3} *M* $KBPh_4$[6] solution in acetone, each time measuring the equivalent conductance Λ. A plot of Λ vs. the ratio [crown]/[K^+] yields a sharp break for the completely ionized salt if conditions are such that $K_f[K^+] \gg 1$, where K_f denotes the complexation constant of crown to the free cation. The ratio [crown]/[K^+] at the breaking point in the plot corresponds to the stoichiometric ratio of crown to cation in the complex.[1a,5]

The respective dissociation constants, K_0 and K_d, of the contact and crown separated ion pairs of potassium picrate in THF were derived from conductance data at concentrations between 5×10^{-4} and 5×10^{-6} *M*. At least a ten times excess of the crown compound must be added to the KPi to prevent dissociation of the crown complex according to $K^+,E,Pi^- \rightleftarrows K^+Pi^- + E$, E being the crown ether. The absence of this reaction can be ascertained from spectral measurements since the absorption maxima of the two ion pair species are different. Also, if this dissociation becomes significant, the conductance would increase on addition of more crown, but this was not observed.

Optical Spectra. Complex formation constants of bis(crown ethers) with free potassium ions and their tight ion pairs with picrate anions in THF were measured spectrophotometrically by means of a Cary 14 spectrophotometer. The fractions of tight ion pairs (λ_m 357 nm) and of crown separated ion pairs (λ_m 380 nm) were calculated from the overlapping spectra of the two species present in mixtures of picrate salt and crown compounds in THF.

Calculations. The Fuoss relationship $F/\Lambda = 1/\Lambda_0 + (f^2/F)C\Lambda/K_d\Lambda_0^2$ was applied to calculate the dissociation constants of the picrate salts and their crown complexes. The value $K_d\Lambda_0^2$, derived from the slope of the plot F/Λ, was obtained with an accuracy of 10%, while Λ_0 for the crown separated ion pair salt can be obtained from the intercepts of the slopes with an accuracy of 3%. However, the Fuoss plots for uncomplexed potassium and ammonium picrate in THF are too steep, and we have used the value $\Lambda_0 = 103\ \Omega^{-1}$ cm^2 equiv^{-1} estimated by Gilkerson[7] for potassium picrate and dinitrophenolate in THF. For NH_4Pi, we took $\Lambda_0 = 105$, the cation having a size in between that of K^+ and Rb^+ ($\Lambda_0(RbPi) = 106$, see ref 7). This value is somewhat speculative since the size of the THF solvated cation is not known, but the similarity in the dissociation constants of KPi and NH_4Pi in THF may indicate that the solvation of the two cations is not much different.

Complex formation constants were arrived at by considering the following equilibria:

$$K^+Pi^- \rightleftarrows K^+ + Pi^- \quad K_0 \tag{1}$$

$$E + K^+Pi^- \rightleftarrows K^+, E, Pi^- \quad K_c \tag{2}$$

$$K^+, E, Pi^- \rightleftarrows K^+, E + Pi^- \quad K_d \tag{3}$$

$$E + K^+ \rightleftarrows K^+, E \quad K_f \tag{4}$$

The crown complexed ion pair K^+,E,Pi^- is always of the separated kind in the case of a bis(crown ether), its spectrum (λ_m 380 nm) being identical with that of the free picrate anion. The optical spectrum, therefore, provides us with an apparent concentration of the separated ion pair complex:

$$[K^+, E, Pi^-]_{app} = [K^+, E, Pi^-] + [K^+, E] \tag{5}$$

It is assumed here that $[Pi^-] \simeq [K^+,E]$ or $K_0 \ll K_d$ (see results for the justification of this assumption). Similarly, $K_d = [K^+,E]^2/[K^+,E,Pi^-]$, which, combined with (5), gives

$$[K^+, E, Pi^-] = a + \tfrac{1}{2}K_d - [\tfrac{1}{2}K_d(K_d + 4a)]^{1/2} \tag{6}$$

where $a = [K^+,E,Pi^-]_{app}$, and K_d can be obtained conductometrically.

Having calculated the separated and tight ion pair concentration, K_c is obtained from a plot of *R* vs. [E], *R* being the ratio of the two ion pair concentrations, and [E] being equal to $[E]_0 - a$. As an internal check on the reliability of the data, the conductometrically obtained value of K_d was compared with that calculated from the slope of a plot of $[K^+,E]/[K^+,E,Pi^-]$ vs. $1/[K^+,E]$ (see eq 3).

Once K_0, K_d, and K_c are known, the complex formation constant K_f of the crown compounds to the free cation can be calculated from the relationship $K_f = K_cK_d/K_0$.

The complexation constants of the bis(crown ethers) with NH_4Pi are much lower than with KPi. At the low complex concentrations required for accurate conductance measurements, the NH_4Pi complex dissociates back into the crown ether and the tight NH_4Pi ion pair, making the determination of K_d more difficult. However, the concentration of the free picrate anion can be determined with reasonable accuracy from a conductance measurement at salt concentrations at which the optical spectra are recorded, using the approximation

$$\alpha = \frac{\Lambda}{\Lambda_0} = \frac{[NH_4^+] + [NH_4^+, E]}{[NH_4^+, Pi^-]_0} \simeq \frac{NH_4^+, E}{[NH_4^+, Pi^-]_0} \tag{7}$$

Knowing $[NH_4^+,E]$, one can obtain $[NH_4^+,E,Pi^-]$ from the spectrum. The plot *R* vs. [E] again yields the value for K_c, while K_d, not measured conductometrically, can be obtained from a plot of $[NH_4^+,E]/[NH_4^+,E,Pi^-]$ vs. $1/[NH_4^+,E]$.

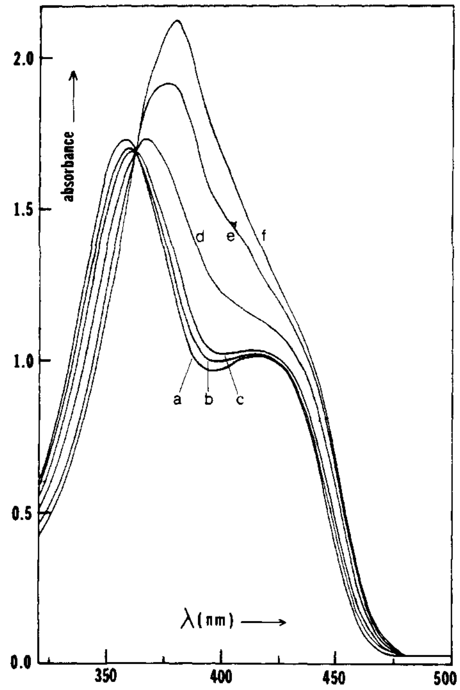


Figure 1. Optical spectra of a 10^{-3} M THF solution of potassium picrate in the presence of varying amounts of 4′-carbomethoxybenzo-15-crown-5 (compound I) at 25°. Molar ratio of crown ether to picrate salt: (a) 0; (b) 1.00; (c) 1.85; (d) 6.83; (e) 24.9; (f) 180.

Results and Discussion

Spectra of Picrate Salts and Their Crown Complexes. We reported recently that the maximum of the main optical absorption band of alkali picrates in THF, chloroform, or other low polarity media shifts to higher wavelengths with increasing radius of the cation.[3,8] In THF, the maxima are found at λ_m 351 nm (ϵ_m 16,500) for NaPi, λ_m 357 nm (ϵ_m 16,800) for KPi, λ_m 362 (ϵ_m 17,700) for CsPi, λ_m 351 nm (ϵ_m 16,200) for NH_4Pi, and λ_m 342 nm (ϵ_m 15,900) for $Ba(Pi)_2$. Conductance data reveal that, above 10^{-5} M, the salt is present in the form of ion pairs, the cation effect on the spectrum indicating that tight ion pairs are involved. The bathochromic shift with increasing cation radius r_c is similar to that reported earlier for ketyls,[9] fluorenyl salts,[10] and phenols.[11] A plot of $1/r_c$ vs. the frequency γ_m of the optical transition is linear, with $\lambda_m \rightarrow 380$ nm for $r_c \rightarrow \infty$. This is also the absorption maximum found for the separated ion pair and the free picrate anion. The identical λ_m values for NH_4Pi and NaPi in spite of the larger size of the NH_4^+ cation (even larger than K^+) may indicate that the negative end of the planar anion slightly penetrates in between the H atoms of the NH_4^+ cation.

Addition of the crown compound I to a 10^{-3} M THF solution of KPi leads to the formation of a 1:1 crown coordinated tight ion pair Pi^-,K^+,I. The spectrum shifts from 357 to 360 nm, and the conversion is complete on addition of about twice the excess of I. Addition of a large excess of I results in the formation of a 2:1 crown separated ion pair complex, with λ_m shifting to 380 nm (see Figure 1). Although two isosbestic points are to be expected (and found for 4′-methylbenzo-15-crown-5, see ref 3), only one was found at 362 nm, the first shift being very small. For NH_4Pi, the 1:1 complex is formed at 353 nm and the 2:1 complex at 378 nm with a large excess of I.

The formation of externally crown coordinated 1:1 tight ion pair complexes was also observed with fluorenyl salts and monobenzo-15-crown-5.[12] The same crown compound, added in excess, combines with fluorenyl potassium[12] and with other potassium salts[13,14] to yield 2:1 crown–salt complexes.

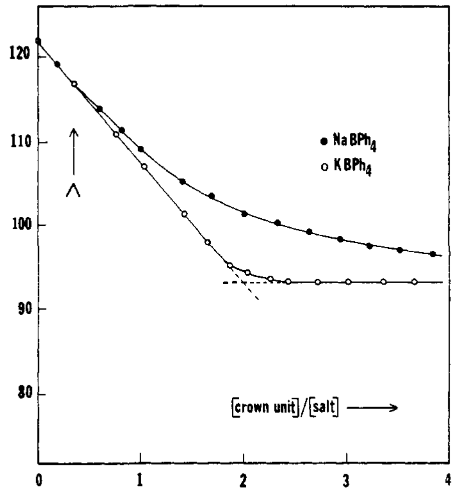


Figure 2. Equivalent conductance of sodium and potassium tetraphenylboron in acetone at 25° in the presence of the macrobicyclic polyether V. Salt concentration 10^{-3} M.

The bis(crown ethers) II through VI produce only one complex with KPi, a crown separated ion pair with an absorption maximum at 380 nm, the cation being sandwiched in between the two crown moieties of the polyether. This is also evident from a plot of Λ vs. [crown units]/[K^+] for $KBPh_4$ in acetone shown in Figure 2. The breaking point clearly occurs at a 2:1 crown to cation ratio, i.e., a bis(crown ether) to salt ratio of 1:1. A similar plot for $NaBPh_4$ is a smooth curve (Figure 2), probably because the complex formation constant of the 1:1 crown-Na^+ complex is not very high, or because the binding of a second Na^+ to the adjacent crown unit is affected by the presence of the neighboring crown cation complex.

The crown separated ion pair of NH_4Pi could only be obtained quantitatively with V and VI; the other bis(crown ethers) precipitated before conversion to the complex was complete.

The molar absorptivities, ϵ_m, of the separated ion pair complexes of KPi with compounds I through VI were found to be 20,900 (I), 19,400 (II), 19,700 (III, V), 19,000 (IV), and 20,000 (VI). The values found with NH_4Pi were 16,700 for compound V and 15,800 for VI. The absorptivities for the separated KPi ion pairs are considerably higher than those of the tight ion pairs, partly because a transition of lower intensity at 420 nm found in the picrate spectrum in low polarity media (see Figure 1) apparently is not affected by a change in interionic distance. It, therefore, overlaps more with the main transition of the loose ion pair than with that of the tight ion pair.

Conductance Data. Fuoss plots for the bis(crown ether) complexes with KPi are depicted in Figure 3. All of the plots show excellent linearity in the investigated concentration region, and Λ_0 can be determined within 3% accuracy. Similar plots were found for the uncomplexed KPi and NH_4Pi. The Λ_0 and K_d values derived from the various plots can be found in Table I.

The dissociation constant, $K_d = 9.2 \times 10^{-8}$ M, of KPi in THF at 25° is about six times larger than that of potassium dinitrophenolate in the same solvent[7] most likely because of the increased charge delocalization in the trinitrophenolate anion. The magnitude of K_d clearly suggests that tight ion pairs are the main species in this solvent. The value for NH_4Pi, $K_d = 8.5 \times 10^{-8}$ M, is not much different from that of the potassium salt. One would have expected a much

Table I. Limiting Conductances, Dissociation Constants, and Complex Formation Constants of Macrobicyclic Polyethers with Potassium and Ammonium Picrate in THF at 25°

Chain connecting crown ester moieties	Λ_0, Ω^{-1} cm^2 equiv^{-1}	$K_d \times 10^5, M$	$K_c \times 10^{-3}, M^{-1}$	$K_f \times 10^{-5}, M^{-1}$	K_f/K_c
	Potassium Picrate, $K_0 = 9.2 \times 10^{-8} M$				
$(CH_2)_2$ (II)	98	2.4	11	29	265
$(CH_2)_5$ (III)	96	3.2	37	130	350
$(CH_2)_8$ (IV)	89	3.7	15	60	400
$CH_2CH_2OCH_2CH_2$ (V)	96	3.5	170	650	380
$(CH_2CH_2O)_2CH_2CH_2$ (VI)	91	4.1	72	320	445
	Ammonium Picrate, $K_0 = 8.5 \times 10^{-8} M$				
V	98	3.3	0.19	0.74	390
VI	93	3.0	0.17	0.60	350

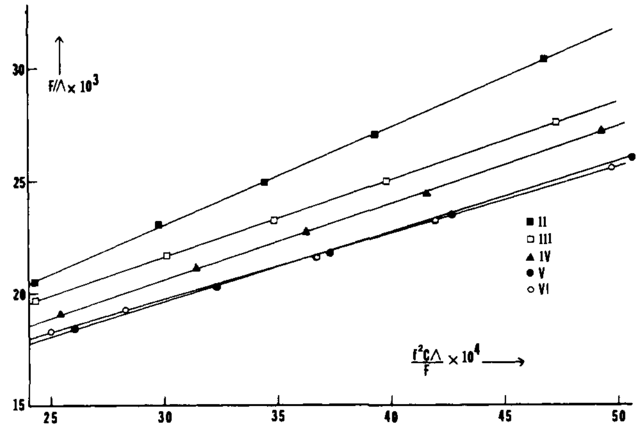


Figure 3. Plots of F/Λ vs. $f^2c\Lambda/F$ in THF at 25° for complexes of potassium picrate with the macrobicyclic polyethers II (■), III (□), IV (▲), V (●), and VI (○).

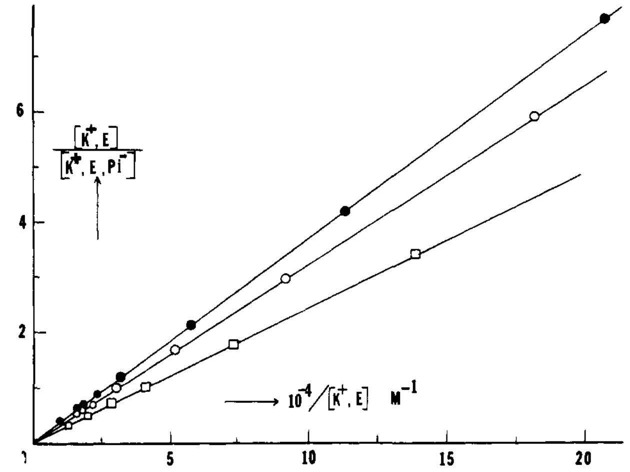


Figure 4. Plots of $[K^+,E]/[K^+,E,Pi^-]$ vs. $1/[K^+,E]$ for potassium picrate in THF at 25° in the presence of macrobicyclic polyether II (□), III (○), and IV (●).

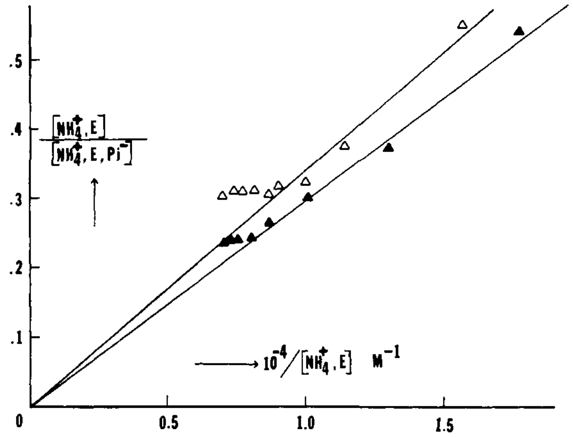


Figure 5. Plots of $[NH_4^+,E]/[NH_4^+,E,Pi^-]$ vs. $1/NH_4^+,E$ for macrobicyclic polyether V (△) and VI (▲).

lower K_d value for the former salt if indeed the interionic distance of its tight ion pair is comparable to that of the sodium salt as the spectral data appear to indicate (the K_d of sodium dinitrophenolate is 16 times smaller than that of its potassium salt, see ref 7). Apparently, effective solvation of the free NH_4^+ cation by THF compensates for the strong coulomb interaction in the ammonium ion pair.

The trend in the Λ_0 values of the five macrobicyclic polyether-picrate complexes reveals the effect of chain length (Table I). Replacing the THF solvation shell of the K^+ ion by compound V changes Λ_0^+ from 50 to 43, the Λ_0^- for the picrate anion being 53.[7] This change is much less than that observed in acetone (see Figure 2), where Λ decreases from 122 to 93 (the actual change in Λ_0 will not be much different). The smaller acetone molecule together with its weaker interaction with alkali ions as compared with THF is the main reason for the large drop in the mobility of the cation in acetone. Such changes in mobility of alkali cations on complexation with crown ethers have been found in other solvents,[1a,16,17] the magnitude of the change being a function of the solvent, the crown ether, and the extent to which the solvation shell is replaced by the crown ligand.

The extension of the chain connecting the two crown ester moieties from two to eight methylene groups lowers Λ_0 by approximately 14%, which is definitely outside the experimental error. The progressively larger volume of the crown complex with increasing chain length must be the reason for this decrease in mobility. Replacement of a CH_2 group by an oxygen atom has little or no effect (see Table I, compare III with V and IV with VI). Also the change from K^+ to NH_4^+ does not appear to affect the overall size of the complex.

The variation in the dissociation constant of the complex with chain length is not more than 50%. The data seem to indicate an increase in K_d with longer chain length. A slightly larger size of the complexed cation could account for this increase. It should also be noted that calculation of the dissociation constants from eq 3, combining both optical and conductance data, yields K_d values identical with those listed in Table I. Some of the pertinent plots are depicted in Figures 4 and 5. The plots are linear except those for NH_4Pi with IV and VI where, at high concentrations of the NH_4^+ complex, the ratio $[NH_4,E]/[NH_4E,Pi]$ appears to be too high. The application of the Arrhenius relationship in this system (see Experimental Section) yields values of $[NH_4E]$ which, at high salt concentrations, are too high, resulting in the observed deviation from linearity.

Complex Formation Constants. As pointed out, addition of the monobenzo-15-crown-5 ester I to potassium picrate results in the formation of the crown complexed tight ion

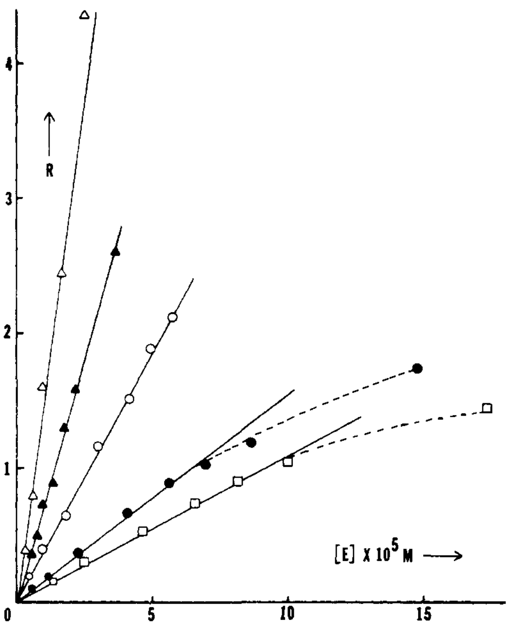


Figure 6. Plots of R (ratio of crown separated ion pairs to tight ion pairs) vs. the free macrobicyclic polyether concentration in a THF solution of potassium picrate at 25° for macrobicyclic polyether II (□), III (○), IV (●), V (△), and VI (▲).

pair Pi^-,K^+,E. The close proximity of the absorption maxima of the complexed and noncomplexed salt does not permit an accurate determination of the formation constant of Pi^-,K^+,E. It was estimated to be about $6 \times 10^3\ M^{-1}$. Excess I converts Pi^-,K^+,E into the 2:1 crown separated ion pair complex Pi^-,E,K^+,E. The plot of R vs. [E] (see experimental procedure) is a perfect straight line, and the equilibrium constant of the reaction $Pi^-,K^+,E + E \rightleftarrows Pi^-,E,K^+,E$, calculated from the slope of this plot, was found to be $7.9 \times 10^2\ M^{-1}$. This compares with a value $2.0 \times 10^2\ M^{-1}$ found for potassium picrate with 4′-methylbenzo-15-crown-5, which in turn is about ten times lower than the value of the equilibrium constant found with this crown ether and fluorenylpotassium.[12] Better charge delocalization in the carbanion salt facilitates its conversion to a loose ion pair.

The complex formation constants K_c (eq 2) of macrobicyclic polyether complexes with potassium and ammonium picrate ion pairs were derived from plots of R vs. [E] shown in Figure 6. The plots are linear except for potassium picrate with compounds II and IV. The relevant data are collected in Table I and include the calculated complex formation constants, K_f (from $K_f = K_cK_d/K_0$), of the bis(crown ether) complexes with the free K^+ and NH_4^+ cations.

The tendency of K^+ and NH_4^+ cations to form 2:1 crown cation complexes with the benzo-15-crown-5 moiety causes the macrobicyclic polyethers to be much more effective chelating agents than the monocyclic polyether I, at least in the formation of separated ion pairs. Compound I has a complexation constant K_1 (i.e., formation of Pi^-,K^+,E) comparable to that of II but, in the latter case, complexation leads to ion pair separation. With I, the formation of a loose ion pair requires a second crown molecule and occurs only in the presence of a considerable excess of this crown compound. Although rotational entropy is lost on forming the bis(crown ether) complex, the larger loss in translational entropy on forming the crown separated ion pair with compound I is the deciding factor. Loose ion pair formation is important in systems where crown ethers are utilized for the purpose of enhancing the reactivity of anionic species and, in this sense, bis(crown ethers) would be more effective. The same result is found with polymers containing benzo-15-crown-5 moieties as dependent groups.[5,8,17] Their proximity on the polymer chain enhances formation of loose ion pairs.

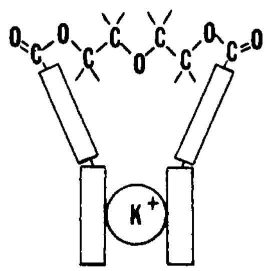
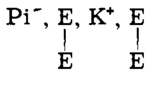


Figure 7. Schematic representation of the complex of K^+ and the macrobicyclic polyether V. The parallel blocks denote the two polyether rings; the tilted ones are the two benzo groups.

Inspection of Table I reveals that K_c depends on both the length and structure of the chain connecting the crown ester moieties. In extending the chain from two to eight methylene groups, K_c passes through a maximum. Probably the most effective interaction between cation and crown moieties is achieved when the five oxygen atoms of each polyether ring are nearly coplanar, the two planes being parallel with respect to each other.[14] An electron rich environment for the cation is created when the lone electron pairs of the oxygen atoms are closest to the cation.[18] CPK models indicate that, to obtain this conformation and the parallel arrangement of the two polyether rings, the benzo groups are not parallel but tilted in the direction shown in Figure 7, minimizing at the same time repulsion between the Π clouds (for 2:1 complexes of monobenzo-15-crown-5 with potassium iodide in the solid state, the benzo groups are found at opposite ends, see ref 14). The distance between the C=O carbon atoms at opposite ends of the chain is therefore considerably larger than the distance between the crown moieties in the complex and amounts to about 8 Å if the angle between the planes of the benzo group and polyether ring reaches 30°. Such a distance can be bridged by a chain in which the ester moieties are linked by five methylene groups, but not by two. In the latter case, the benzo groups are forced closer together, and the position of the polyether rings are also affected. A short linkage will therefore adversely affect the stability of the bis(crown ether) complex. It is interesting in this respect to find that homopolymers of vinylbenzo-15-crown-5 have considerably lower extraction equilibrium constants for potassium picrate in H_2O-$CHCl_3$ than a copolymer with styrene containing 20 mol % of vinylbenzo-15-crown-5.[8]

Extending the chain of the bis(crown ether) too much will result in a further loss of conformational entropy, resulting in a decrease of K_c. Other chain length dependent variables are known to affect the conformational energy in the cyclization of short chains,[19] and it is possible that higher K_c values can be found for bis(crown ether) compounds with three, four, six, or seven CH_2 groups, but these were not investigated.

It is interesting to note that plots of R vs. [E] for compounds II and IV deviate from linearity at higher crown concentration (see Figure 6). These are the compounds with K_c values that are only slightly higher than the K_1 value found for I. One may expect, therefore, species of the type Pi^-,K^+ E-E, where E-E represents the bis(crown ether). This would result in an R value which is too low since the crown coordinated species is still a tight ion pair. At high bis(crown ether) concentrations, formation of species of the type


$$Pi^-,\ \underset{\displaystyle E}{\underset{|}{E}},\ K^+,\ \underset{\displaystyle E}{\underset{|}{E}}$$

may occur, similarly as with I. While this species is a loose ion pair, the R vs. [E] plot would again deviate in the direction shown in Figure 6, since the calculated free bis(crown ether) concentration will be too high. With increasing chain length or chain stiffness, formation of polymeric species of the type $[\text{E-E,K}^+]_n$ can be visualized. Such a competition between intra- and intermolecular complexation of cations by bis(crown ethers) is analogous to that observed in systems containing mixtures of potassium tetraphenylboron and copolymers of styrene and 4′-vinylbenzo-15-crown-5 in methyl ethyl ketone.[20] At a molar crown content in the polymer of more than 10%, the complexation of K^+ involves closely adjacent crown moieties of the same polymer chain. At a crown content of 5%, the chelating groups are getting so far apart that intermolecular 2:1 crown cation complexes are formed as evidenced by a steep rise in the reduced viscosity on concentrating the polymer salt solution.

In addition to chain length, the structure of the chain also affects K_c. Replacing the center CH_2 group of III by oxygen results in a fivefold increase in K_c, while a similar enhancement is found when two of the CH_2 groups of IV are changed to oxygen. It is doubtful that the additional chain oxygen atom of compound V contributes significantly to the binding of a cation sandwiched in between the two crown moieties. Models show that the distance of closest approach between K^+ and this oxygen atom is about 5 Å, assuming that the cation remains centered between the two polyether rings. It is more likely that the oxygen provides more flexibility to the chain and lowers the conformational energy of the bis(crown ether) in the cyclized form. Recent studies on intramolecular electron transfer involving phtalimide moieties at the end of a short polymethylene chain show a higher probability of cyclization when some of the CH_2 groups are replaced by oxygen, as evidenced by the increased rate of intramolecular electron transfer in these compounds.[21] It may be interesting to synthesize a bis(crown ether) in which the center CH_2 group in III is replaced by an sulfoxide group and to check whether this group will act as an additional binding site for cations.

Ion pair separation of NH_4Pi by V or VI is considerably more difficult than for KPi. Although ammonium salts do form stable 2:1 complexes with benzo-15-crown-5,[1a] the interaction of NH_4^+ with the two crown moieties may be weaker than with K^+ in spite of the nearly identical ionic diameters. Also, the shorter interionic distance suggested by the optical data for NH_4Pi and a more effective solvation of NH_4^+ by THF (see above) may be a contributing factor. Monobenzo-15-crown-5 as well as poly(vinylbenzo-15-crown-5) are also much more effective in transferring K^+ than NH_4^+ from water into an organic phase, but again desolvation may be an important factor.[5]

Finally, note the difference between the complexation constants for ion pairs and free ions, the K_f values being 300 to 400 times larger than the corresponding K_c values. The cation in both cases must be completely desolvated to accommodate the bis(crown ether). In the case of ion pairs, this involves less solvent molecules, but the ions must be separated and, consequently, the interionic ion pair distance will be the dominant factor affecting the difference between K_f and K_c. For example, the two constants for tetraglyme with $NaBPh_4$ in THP were found to be $K_f = 1.6 \times 10^5\ M^{-1}$ and $K_c = 5.7 \times 10^4\ M^{-1}$, respectively, while, for the much tighter ion pair polystyrylsodium in THP, K_c is only $4 \times 10^3\ M^{-1}$.[22]

In conclusion, macrobicyclic polyethers endowed with a benzo-15-crown-5 moiety on each end of a short aliphatic chain are effective chelating agents for cations such as K^+ and NH_4^+ which can chelate with two 15-crown-5 molecules. The interaction of the bis(crown ethers) with tight ion pairs of potassium and ammonium picrate in THF results in the formation of 1:1 loose ion pair complexes as indicated from conductance data and shifts in optical spectra. The complex formation constants to both the tight ion pairs and free cations vary by almost a factor of 20 depending on the length and structure of the connecting chain. The dissociation constants of the complexes into the free ions are nearly independent of the nature of the bis(crown ether).

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