

over magnesium sulfate, distilled from sodium, and stored under nitrogen. Nujol was obtained from Plough, Inc., and *tert*-dodecanethiol from Phillips Petroleum Co.; both were used as received. *tert*-Butyl alcohol was distilled from calcium hydride. *tert*-Butyl triphenylperacetate (I) was prepared from recrystallized triphenylacetyl chloride and fresh sodium *tert*-butyl peroxide as described previously.¹² The slightly greenish yellow crystals were assayed by CO₂ yield on thermal decomposition in cumene solution at 25°; it has previously been reported that other methods of assay, such as combustion analysis, melting point, or even iodometry, are misleading or useless for the more reactive peresters. A modified Warburg manometer,¹³ which had been calibrated with standard sodium carbonate solution acidified with excess hydrochloric acid, was used to measure the volume increase. This apparatus required only microliter amounts of dilute solutions. Samples of I were used if they evolved 95% or more of the theoretical amount of CO₂.

Stable Radical Concentrations. The triphenylmethyl radical was readily detected by its esr spectrum which was identical with published spectra.²⁶ Its concentration was measured over 2 days by the absorbance at its sharp λ_{max} 515 nm (ϵ 656). The apparatus consisted of a quartz esr tube linearly sealed to a 1-cm² Pyrex cell, and had a T-joint with a stopcock. Into the Pyrex cell was placed 4 ml of a cold toluene solution of I, the solution flushed with nitro-

gen for several minutes through a syringe needle, and the stopcock closed. The solution in the quartz cell was warmed for 10 min at 25°, dried, and placed into the Cary 14 spectrophotometer. The 1,1-diphenylneopentyl radical was generated by decomposition of II in the same apparatus; its concentration was determined by cutting and weighing first derivative spectra and comparing with results for solutions of triphenylmethyl which had been standardized at 515 nm.

Decomposition Products. The same stock solutions were used as for measuring radical concentrations. *tert*-Butyl alcohol was determined by glpc (F&M Model 700 instrument with thermal conductivity detector and disc integrator) using standard solutions of the alcohol for calibration.

To determine nonvolatile products, solutions of decomposition products were stripped of solvent on a rotary evaporator with a vacuum pump and the residues made up to 1 ml with CCl₄. The nmr spectra of these solutions and a standard solution of anisole were integrated using the same instrument settings, on a Jeolco C-60HL spectrometer. This somewhat hazardous procedure was validated by obtaining the same integral for two aliquots of the same solution in different tubes.

Acknowledgments. The authors are grateful to the U. S. Army Research Office—Durham for financial support of this work, and to Professor A. A. Zavitsas for valuable correspondence.

(26) D. B. Chesnut and G. J. Sloan, *J. Chem. Phys.*, **33**, 637 (1960).

Molecular Structure of Ion Pairs from Electric Dipole Moments. II. Complexing of Potassium *p*-Toluenesulfonate and Lithium Chloride with Macrocyclic Polyethers in Octanoic Acid¹

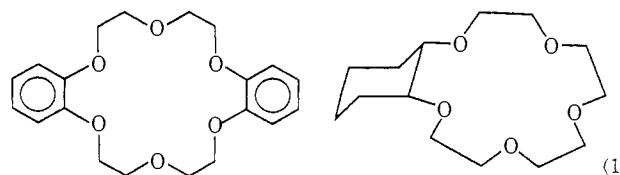
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Abstract: Measurements of the permittivity of dilute solutions of potassium *p*-toluenesulfonate (KTs), LiCl, dibenzo-18-crown-6 ether (crown-6), cyclohexyl-15-crown-5 ether (crown-5), and of their mixtures in octanoic acid at 25° led to the following electric dipole moments (μ , D) and association constants (K , M⁻¹): crown-6, μ = 1.37, crown-5, μ = 4.00; KT_s-crown-6, μ = 8.27, K = 50,000; KT_s-crown-5, μ = 8.92, K = 13,000; LiCl-crown-5, μ = 9.97, K = 6,000; LiCl + crown-6, no detectable association. For KT_s-crown-6, the association constant was confirmed by spectrophotometry. Application of Böttcher's model to the dipole moments identified the most stable ion-pair isomers and led to the following electrostatic interaction energies (W , kcal/mol): KT_s-crown-6, axial contact ion pair, W = -89.9; KT_s-crown-5, axial contact ion pair, W = -87.4; LiCl-crown-5, ligand-separated ion pair, W = -101.4. From the distances between the ionic electrical centers it is inferred that the K⁺...Ts⁻ distance is stretched (relative to that in uncomplexed KT_s ion pairs) by 0.5 Å in KT_s-crown-6 and by 0.15 Å in KT_s-crown-5.

In a recent paper² we showed that electric dipole moments of ion pairs involving noncentric ions can be analyzed to define the sites of attachment of the ions and to estimate the distance between the electrical centers. Because of the current interest in the complexing of alkali and alkaline earth metal ions with macrocyclic polyethers^{3,4} and its effect on ion-pair structure,⁵ we now extend this work to the complexes

of lithium chloride and potassium *p*-toluenesulfonate (KTs) with cyclohexyl-15-crown-5 ether⁶ (crown-5) and of KT_s with dibenzo-18-crown-6 ether⁶ (crown-6) in octanoic acid. Solutions of lithium chloride and crown-6 in this solvent showed no interaction. The structural formulas of the crown ethers are shown below.



(6) C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 7017 (1967).

(1) We gratefully acknowledge support of this work by the National Science Foundation.

(2) Ting-Po I and E. Grunwald, *J. Amer. Chem. Soc.*, **96**, 2387 (1974).

(3) C. J. Pedersen and H. K. Frensdorff, *Angew. Chem., Int. Ed. Engl.*, **11**, 16 (1972).

(4) J. J. Christensen, D. J. Eatough, and R. M. Izatt, *Chem. Rev.*, in press.

(5) J. Smid, *Angew. Chem., Int. Ed. Engl.*, **11**, 112 (1972).

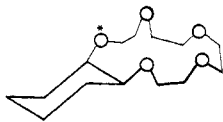


Figure 1. Structure of the cis isomer of crown-5. (*) This oxygen atom lies in the mean plane of the crown carbon atoms.

Because of their strong and specific complexing ability, the crown ethers have proved to be extraordinarily useful as chemical reagents. For instance, by increasing the solubility of electrolytes in nonpolar media,⁶ the crown ethers can act as phase-transfer catalysts⁷ and provide anions in poorly solvated conditions in which their reactivity is high.⁸ The crown ethers have also proved popular as model compounds in the study of selective ion transport through membranes, biological and otherwise.⁹⁻¹¹

The crown ethers derive their strong complexing ability from the presence of a number of oxygen atoms and their specificity from the size of the ring cavity, which must match the size of the cation. In their classic study of ion-pair complexes with alkali metal fluorenides, Smid and coworkers⁵ compared the spectroscopic properties of uncomplexed with those of complexed ion pairs and interpreted the data for the complexed ion pairs in terms of two discrete species: ligand-separated and contact ion pairs. In the former, the ligand sits between the cation and the anion. In the latter, the cation binds the ligand while remaining in contact with the anion; however, the cation-anion interaction may be weaker than in the uncomplexed ion pair. Truter and coworkers¹²⁻¹⁴ have examined several crystalline crown complexes of alkali metal salts by X-ray diffraction. They find crystal structures in which the molecular units correspond either to Smid's contact ion pairs or to complexed cations that are clearly separated in the crystal from the anions.

While these studies give valuable insights, it is fair to say that they indicate rather than demonstrate the geometrical structure of the ion pairs in solution. The spectroscopic data elucidate the effect of complexing on the mutual polarization of cation and anion, while the X-ray diffraction elucidates the molecular geometry under the influence of lattice forces whose constraints are absent in liquid solution.¹⁵ The electric dipole moments obtained in the present study provide complementary information about geometrical structure in solution. The geometrical relationships of cation, anion, and ligand can be reduced to a limited number of possibilities, and the structure with the lowest electrostatic energy can be found. Thus, the most stable isomer of LiCl-crown-5 is the ligand-separated ion pair,

(7) C. M. Starks and R. M. Owens, *J. Amer. Chem. Soc.*, **95**, 3613 (1973). C. M. Starks, First Fall Organic Conference, Cape Cod, Mass., Oct 1, 1973, Abstract No. 12.

(8) C. L. Liotta, H. P. Harris, and T. McDermott, First Fall Organic Conference, Cape Cod, Mass., Oct 1, 1973, Abstract No. 5.

(9) G. Szabo, G. Eisenman, R. Laprade, S. M. Ciani, and S. Krasne, "Membranes, A Series of Advances," Vol. 2, G. Eisenman, Ed., Marcel Dekker, New York, N. Y., 1973, p 179.

(10) G. Eisenman, *Nat. Bur. Stand. (U.S.), Spec. Publ.*, **314** (1969).

(11) D. C. Tosteson, *Fed. Proc.*, **27**, 1269 (1968); H. Lardy, *ibid.*, **27**, 1278 (1968); B. C. Pressman, *ibid.*, **27**, 1283 (1968).

(12) D. Bright and M. R. Truter, *J. Chem. Soc. B*, 1544 (1970).

(13) M. A. Bush and M. R. Truter, *J. Chem. Soc. B*, 1440 (1971).

(14) M. A. Bush and M. R. Truter, *J. Chem. Soc., Perkin Trans. 2*, 341 (1972).

(15) H. C. Freeman, *Advan. Protein Chem.*, **22**, 258 (1967).

while the most stable isomer of KTs-crown-5 and KTs-crown-6 is an axial contact ion pair. In the case of KTs-crown-6, the cation-anion distance is stretched by about 0.5 Å, while in KTs-crown-5, this distance is stretched by about 0.15 Å.

In interpreting these distances of stretch, we note that the crown-6 cavity is of the right size to enclose the potassium ion, while in the crown-5-K⁺ ion, the K⁺ ion is too large to fit into the crown-5 cavity. Thus, when the Ts⁻ ion approaches a crown-6-K⁺ ion, the crown ether around the cation will sterically repel the anion. In the resulting contact ion pair, the K⁺ ion is therefore pulled somewhat out of the cavity, and the K⁺...Ts⁻ distance is somewhat greater than in the uncomplexed ion pair. On the other hand, in crown-5-K⁺, most of the K⁺ ion sits outside the cavity and the Ts⁻ ion can approach without appreciable steric hindrance.

Experimental Section

Materials. Dibenzo-18-crown-6 ether (crown-6, from Aldrich Chemical Co.) was purified as follows. The compound was converted to the solid KSCN complex by dissolving in methanolic KSCN, followed by addition of water to the filtered solution. The resulting precipitate was washed with water to a negative test for thiocyanate, dried, and recrystallized twice from benzene. The pure, feather-like crystals were dried under vacuum, mp 163-167° (lit. mp 164°); the uv spectrum in octanoic acid was in good agreement with Pedersen's spectrum in methanol.⁶

Cyclohexyl-15-crown-5 ether (crown-5) was kindly supplied to us by Dr. H. K. Frensdorff of E. I. du Pont and used without further purification. It is not known at this writing whether the compound is the 1,2-*cis*- or 1,2-*trans*-cyclohexane isomer. The experimental dipole moment (4.00 D, next section) could be consistent with either isomer. For definiteness, we assumed a *cis* structure, as shown in Figure 1.

Octanoic acid, KTs and LiCl were purified as described previously.²

Measurements. The dielectric permittivity of dilute solutions was measured at 25° on a high-precision General Radio Type 1615 A transformer ratio-arm bridge, as described previously.^{2,16} Solutions were prepared with quantitative accuracy in a dry nitrogen atmosphere; details have been given in the previous paper.²

Uv spectra and optical densities at 25° were measured with a Hitachi Perkin-Elmer Model 323 spectrophotometer equipped with a thermostated cell holder.

Results

Crown Ethers. The electric dipole moments of crown-5 and crown-6 in solution do not appear to have been measured previously. Plots of permittivity (ϵ) vs. molar concentration (c) in octanoic acid were accurately linear for both compounds, with intercepts whose positive deviation from the known ϵ_0 of pure octanoic acid was barely outside the experimental error (less than two standard deviations). The following dipole moments (μ) were calculated from the slopes: crown-6, $\mu = 1.37$ D; crown-5, 4.00 D. All calculations of μ in this paper are based on Onsager's equation, method B of ref 16. Auxiliary data used in the calculation are listed in Table I.

Molecular models suggest that the *cis* isomer of crown-5 has a fairly rigid 15-membered ring structure, with four C-O-C dipoles pointing "down" with respect to the plane of the ring and the fifth dipole lying roughly in the plane of the ring (Figure 1). Adopting 1.3 D for each C-O-C dipole (this is the experimental value for diethyl ether), this model is consistent with the experimental dipole moment of 4.00 D.

(16) E. Grunwald and A. Effio, *J. Solution Chem.*, **2**, 373 (1973).

Table I. Dipole Moments and Association Constants in Octanoic Acid at 25°

Reactants	μ_C, D^a	K, M^{-1}
LiCl + crown-5	9.97	6,000
LiCl + crown-6	No interaction	
KTs + crown-5	8.92	13,000
KTs + crown-6	8.27	50,000

^a Calculated by Onsager's equation, method B of ref 16. Auxiliary data used in the calculation: (compd, molar volume (ml), molar refraction (cm³)); crown-5, 274.0 ml, 72.08; crown-6, 375.5, 97.52; LiCl, 10.4, 9.37; KTs, 121.0, 46.34; LiCl-crown-5, 297.0, 81.45; KTs-crown-5, 395.0, 118.42; KTs-crown-6, 496.5, 143.86. Properties of octanoic acid at 25°: density = 0.9066, n_D 1.4261, ϵ_0 2.4812. Dipole moment of LiCl = 6.78 D; dipole moment of KTs = 4.81 D.

In discussions of the complexing of cations with crown-6, the crown ring is usually depicted as in Figure 2b, with all six oxygen atoms nearly coplanar. According to our calculations, this highly polar conformation would have a dipole moment of 4.3 ± 0.3 D, which is completely inconsistent with the experimental value. However, X-ray crystallographic data indicate that the uncomplexed crown-6 ring has the nonpolar conformation of Figure 2a,¹² and infrared data for the unsubstituted 18-crown-6 ether indicate a symmetry other than D_{3d} .¹⁷ Our dipole moment shows that nonpolar or slightly polar conformations of the ring-oxygen atoms also predominate in solution.

Association of Crown Ethers with Ion Pairs. Our work provides three examples in which complex formation takes place and one (LiCl + crown-6) in which it does not. Complex formation was detected by an enhanced permittivity (over that predicted from data for the separate solutes) and, in the case of crown-6 ether, by Pedersen's criterion of a change in the uv spectrum.⁶ In the case of LiCl + crown-6, complex formation was absent at *ca.* 10^{-3} M concentrations according to both criteria.

When complex formation takes place, analysis of the interaction permittivity and of the interaction absorbance at 277 nm shows that the complexes have one-to-one stoichiometry, as shown in the symbolic eq 2.¹⁸ Let c_A and c_B denote formal concentrations of ion



pair and ligand, respectively, and let $[A]$, $[B]$, and $[C]$ denote molar concentrations. The interaction permittivity $\delta\Delta\epsilon$ is defined by eq 3, where $\Delta\epsilon$ denotes $\epsilon -$

$$\delta\Delta\epsilon = \Delta\epsilon_{\text{mixture}} - \Delta\epsilon_A - \Delta\epsilon_B \quad (3)$$

ϵ_0 , and $\Delta\epsilon_A$ and $\Delta\epsilon_B$ are for the solutes measured separately. On introducing molar dielectric increments S_A , S_B , and S_C and mass balance, we arrive at eq 4. S_A

$$\delta\Delta\epsilon = (S_C - S_B - S_A)[C] \quad (4)$$

and S_B are available from experiments on the separate solutes. Analysis of $\delta\Delta\epsilon$ as a function of c_A and c_B by familiar statistical methods¹⁹ then yields K and S_C .

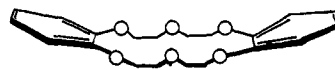
(17) J. Dale and P. O. Kristiansen, *Acta Chem. Scand.*, **26**, 1471 (1972).

(18) Owing to the low solubility of the crown ethers in octanoic acid, the molar ratio of crown ether to ion pair had to be kept well below unity. This fact may account for our failure to detect two-to-one crown-iron pair complexes.

(19) (a) P. R. Bevington, "Data Reduction and Error Analysis for the Physical Sciences," McGraw-Hill, New York, N. Y., 1969; (b) W. C. Hamilton "Statistics in Physical Science, Estimation, Hypothesis Testing and Least Squares," Ronald Press, New York, N. Y. 1964.



(a) CROWN-6, nonpolar conformation



(b) CROWN-6, polar conformation

Figure 2. Some conformations of crown-6. Conformation b is favorable for complex formation.

Finally, the dipole moments of the complexes are calculated from S_C .

Results are listed in Table I. Each value is based on an analysis of at least eight experiments. c_A and c_B typically ranged from 0.002 to 0.01 M, except for crown-6, for which the concentrations ranged from 0.0001 to 0.0006 M. Above about 0.001 M, solutions of crown-6 in octanoic acid form a voluminous white gel-like precipitate at room temperature, which dissolves on heating.

Because of the use we planned to make of the dipole moments for structure elucidation, we thought it worthwhile to confirm their accuracy by an independent method. The two parameters involved in the treatment of the permittivity data, $(S_C - S_A - S_B)$ and K , are interdependent. Thus, if the accuracy of K can be confirmed, the accuracy of S_C and hence of μ_C is substantiated. We were able to do this by quantitative uv absorption measurements in two systems: KTs + crown-6, and LiCl + crown-6. Figure 3 compares the absorption spectrum of crown-6 alone *vs.* octanoic acid with the difference spectrum of crown-6 + KTs (sixfold excess) *vs.* KTs (at precisely the same concentration) in octanoic acid. The latter spectrum is very similar to the spectrum of crown-6, with free ions.⁶ On the other hand, for LiCl + crown-6, the difference spectrum is identical with the spectrum of crown-6 alone, confirming the conclusion based on $\delta\Delta\epsilon = 0$ that complex formation is absent.

Although Figure 3 shows the spectral change on complex formation to be small, we decided that it was sufficiently large to permit evaluation of K with useful accuracy. The results, based on an analysis of 15 experiments at 25°, are as follows: molar extinction coefficients ($M^{-1} \text{ cm}^{-1}$) at 277 nm, 5600 ± 50 for free crown-6 and 4620 ± 50 for crown-6 in the complex (based on the difference spectrum); association constant $K = 53,000 M^{-1}$, in good agreement with the value derived from $\delta\Delta\epsilon$ (Table I).

Interpretation of Dipole Moments

Ligand-Separated *vs.* Contact Ion Pairs. This discussion will follow the same theoretical approach as that of the preceding paper.² In particular, we shall rely heavily on Böttcher's model in which the ions are represented as polarizable point charges superposed on an appropriate dipole.²⁰

The representation of Cl^- and Ts^- in an ion pair

(20) C. F. J. Böttcher, "Theory of Electric Polarization," Elsevier, Amsterdam, 1952.

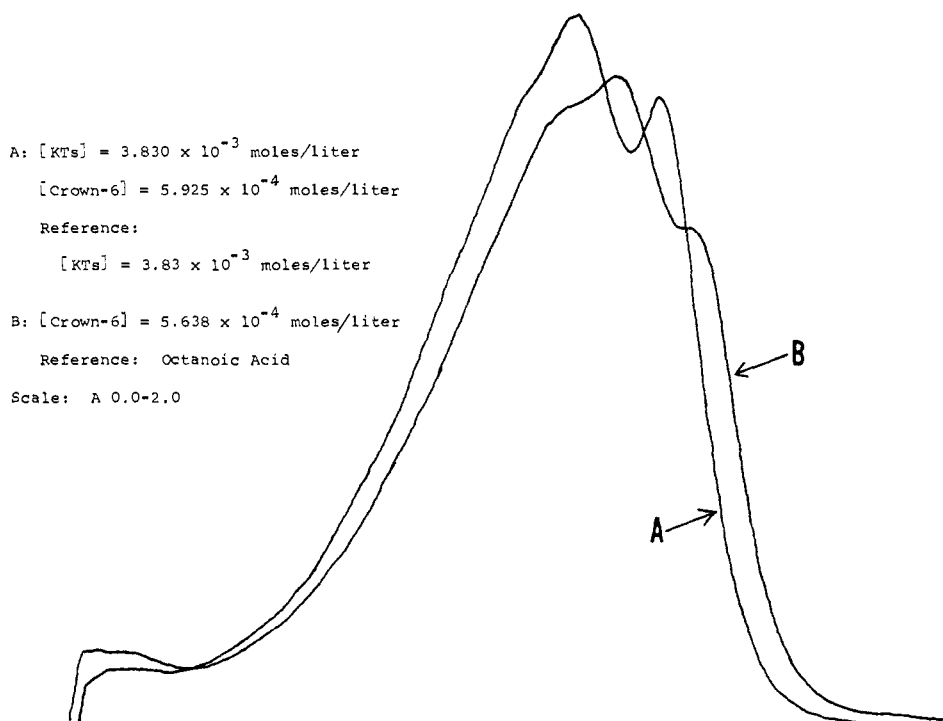


Figure 3. Uv spectrum of complexed (A) and uncomplexed (B) crown-6 in octanoic acid.

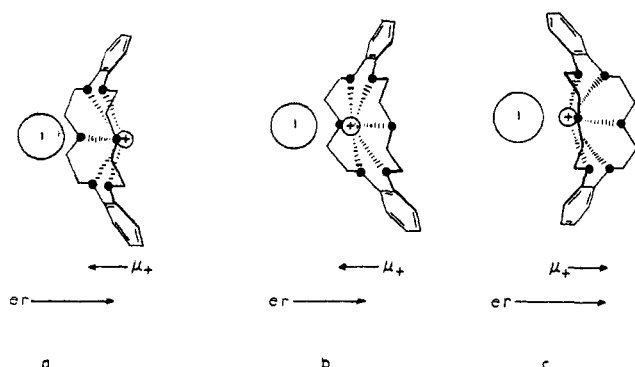


Figure 4. Different types of ion-pair complexes: a and b represent ligand-separated ion pairs; c represents a contact ion pair.

in terms of this model has been described previously. The cation of the ion pair will be identified with the cation-crown complex. Since the dipole moment of free Li^+ and K^+ is zero, the dipole vector μ_+ of the cation-crown complex will be equal to the dipole vector of the crown ligand as it exists in the complex. Some theoretically interesting possibilities for μ_+ in ion-pair complexes with crown-6 are shown in Figure 4. If μ_+ points toward the anion, *i.e.*, if the oxygen atoms point away from the anion, the ion pair is a ligand-separated ion pair (Figure 4a,b). If μ_+ points away from the anion, *i.e.*, if the oxygen atoms face the anion, the ion pair is a contact ion pair (Figure 4c). Of course, within these broad classifications, a variety of structures is possible. For instance, in Figure 4a the cation and anion are far apart, being separated by the macrocyclic ether ring. In Figure 4b, the cation has slipped into the ring cavity so as to be closer to the anion, The dipole moment of the ion pair shown in Figure 4b would of course be much smaller than that of the ion pair in Figure 4a. Similarly, for equal cation-anion

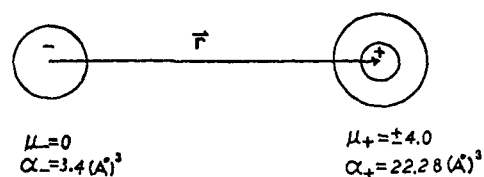


Figure 5. Electrical model for $LiCl$ -crown-5, $\mu_{obsd} = 9.97$ D. For ligand-separated ion pair, $\mu_+ = -4.0$ D, $r = 4.50$ Å, $W = -101.4$ kcal/mol. For contact ion pair, $\mu_+ = 4.0$ D, $r = 3.68$ Å, $W = -97.4$ kcal/mol.

distances the dipole moment of the contact ion pair (Figure 4c) would be greater than that of the ion pair in Figure 4b.

$LiCl$ -crown-5. To interpret the dipole moment of $LiCl$ -crown-5, we apply Böttcher's treatment to the model shown in Figure 5. The point charges represent respectively the chloride ion and the Li^+ -crown-5 complex. Because the ionic polarizabilities are represented as *point* polarizabilities, we decided to let α_+ be simply the polarizability of Li^+ plus the polarizability of unsubstituted 15-crown-5 ether. Polarizabilities were estimated from molar refractions (R_D) with the convention that the polarizability of $Li^+ = 0.00$.

The magnitude of μ_+ is taken to be 4.0 D, which is the actual dipole moment of the uncomplexed crown-5 ligand. Direct experimental evidence concerning the conformation of this ligand in cation complexes is lacking. However, molecular models suggest that the conformation shown in Figure 1 is relatively rigid and likely to be retained in the complex. The models also suggest that the direction of μ_+ will be nearly parallel to that of the vector r between the electrical centers. Thus, for the conformation in Figure 1, the angle between the dipole vector and the normal to the mean plane defined by the four exocyclic oxygen atoms is only 6.5° . Assuming that μ_+ is precisely collinear with

$e\mathbf{r}$, we shall use $\mu_+ = +4.0$ D for the contact ion pair and -4.0 D for the ligand-separated ion pair.

According to Figure 5, the dipole moment, μ_c , of LiCl-crown-5 is given by eq 5. Note that all vectors

$$\mathbf{u}_c = e\mathbf{r} + \mathbf{u}_+ + \mathbf{m}_+ + \mathbf{m}_- \quad (5)$$

are parallel. In the following, explicit vector notation will therefore be dropped; positive values will denote that the given dipole is pointing in the positive r direction. Following Böttcher, the induced moments are given by eq 6 and 7, and the interaction energy, W , is

$$m_+ = \alpha_+ \left[-\frac{e}{r^2} + \frac{2m_-}{r^3} \right] \quad (6)$$

$$m_- = \alpha_- \left[-\frac{e}{r^2} + \frac{2m_+}{r^3} + \frac{2\mu_+}{r^3} \right] \quad (7)$$

given by eq 8. In applying the treatment, we used the

$$W = -\frac{e^2}{r} + \frac{e}{r^2}(\mu_+ + m_+ + m_-) - \frac{2}{r^3}(\mu_+ + m_+)(m_-) + \frac{m_+^2}{2\alpha_+} + \frac{m_-^2}{2\alpha_-} \quad (8)$$

experimental dipole moment to compute r via eq 5-7 and then substituted the result in eq 8 to obtain W . The results are as follows. For the contact ion pair, $r = 3.68$ Å and $W = -97.4$ kcal/mol. For the ligand-separated ion pair, $r = 4.50$ Å and $W = -101.4$ kcal/mol.

Both values of r are physically plausible. The value obtained assuming a contact ion pair, 3.68 Å, is substantially greater than the interionic distance of 2.15 Å calculated from the dipole moment of uncomplexed Li⁺Cl⁻ by a consistent method. However, the electrical center of the Li⁺-crown-5 complexed cation is pulled into the cavity of the crown ring by virtue of the permanent as well as the induced dipole moment. (The location of the electrical centers of polyatomic ions has been discussed in paper I.²) Approximate calculations suggest that if we had a contact ion pair with $r = 3.68$ Å, the Li⁺-Cl⁻ distance would be about 2.83 Å, about 0.7 Å greater than in the uncomplexed ion pair. This calculation assumes that the Li⁺ ion is pulled out of the mean plane of the four exocyclic oxygen atoms by an equal distance of 0.7 Å.

The distance obtained assuming a ligand-separated ion pair, $r = 4.50$ Å, is consistent with an ion pair of the type shown in Figure 4a.

On the basis of the results obtained for W , the ligand-separated ion pair is more stable than the contact ion pair by -4.0 kcal/mol. Although the approximations inherent in the model are such that the errors in W are probably greater than 4 kcal, we may expect that such errors will largely cancel out in the comparison. We conclude, therefore, that the ligand-separated ion pair is the more stable species. It should be noted that the calculation of W is made for the ion pairs in the gas phase. However, because the dipole moments of the two species are identical, the dipole solvation energies on transferring the two species into a liquid solution will be equal. Thus, if we may neglect differences in solvation energy due to higher poles and specific interactions, the relative stability in the gas phase should remain valid in liquid solution.

From a broader point of view, the calculation of W

is instructive because it contradicts a commonly held belief that the ions in an ion pair exist at the distance of closest possible approach. In this case it turns out that the greater distance between electrical centers is actually the more stable configuration because of the marked effect of the dipole moment μ_+ .

KTs-crown-6. Following the previous discussion of the structure of uncomplexed KT_s,² we shall consider edgewise models (Figure 6a) and axial models (Figure 6b). For each geometry we shall consider a contact and a ligand-separated ion pair. The dipole moment of the complexed cation will be taken to be 4.3 D, which is the dipole moment of crown-6 in the polar conformation of Figure 2b, either in the same direction as r (contact ion pair) or in the opposite direction (ligand-separated ion pair). Because of the nonlinear geometry of the edgewise models, it is necessary to apply Böttcher's model in the form of vector equations (eq 9-13).

$$\mathbf{u}_c = e\mathbf{r} + \mathbf{u}_+ + \mathbf{u}_- + \mathbf{m}_+ + \mathbf{m}_- + \mathbf{m}' \quad (9)$$

$$\mathbf{m}_+ = \alpha_+ \left[-\frac{e}{r^3} \mathbf{r} + \frac{3\mathbf{u}_- \cdot \mathbf{r}}{r^5} \mathbf{r} - \frac{\mathbf{u}_-}{r^3} + \frac{3\mathbf{m}_- \cdot \mathbf{r}}{r^5} \mathbf{r} - \frac{\mathbf{m}_-}{r^3} + \frac{3\mathbf{m}' \cdot \mathbf{R}}{R^5} \mathbf{R} - \frac{\mathbf{m}'}{R^3} \right] \quad (10)$$

$$\mathbf{m}_- = \alpha_- \left[\frac{e}{r^3} \mathbf{r} + \frac{3\mathbf{u}_+ \cdot \mathbf{r}}{r^5} \mathbf{r} - \frac{\mathbf{u}_+}{r^3} + \frac{3\mathbf{m}_+ \cdot \mathbf{r}}{r^5} \mathbf{r} - \frac{\mathbf{m}_+}{r^3} + \frac{3\mathbf{m}' \cdot \mathbf{S}}{S^5} \mathbf{S} - \frac{\mathbf{m}'}{S^3} \right] \quad (11)$$

$$\mathbf{m}' = \alpha' \left[-\frac{e}{S^3} \mathbf{S} + \frac{e}{R^3} \mathbf{R} + \frac{3\mathbf{u}_- \cdot \mathbf{S}}{S^5} \mathbf{S} - \frac{\mathbf{u}_-}{S^3} + \frac{3\mathbf{m}_- \cdot \mathbf{S}}{S^5} \mathbf{S} - \frac{\mathbf{m}_-}{S^3} + \frac{3\mathbf{u}_+ \cdot \mathbf{R}}{R^5} \mathbf{R} - \frac{\mathbf{u}_+}{R^3} + \frac{3\mathbf{m}_+ \cdot \mathbf{R}}{R^5} \mathbf{R} - \frac{\mathbf{m}_+}{R^3} \right] \quad (12)$$

$$W = -\frac{e^2}{r} + \frac{e}{r^3} \mathbf{r} \cdot (\mathbf{u}_+ + \mathbf{m}_+) + \frac{e}{S^3} \mathbf{S} \cdot \mathbf{m}' - \frac{e}{r^3} \mathbf{r} \cdot (\mathbf{u}_- + \mathbf{m}_-) - \frac{e}{R^3} \mathbf{R} \cdot \mathbf{m}' - \frac{3}{r^5} [(\mathbf{u}_+ + \mathbf{m}_+) \cdot \mathbf{r}] \times [(\mathbf{u}_- + \mathbf{m}_-) \cdot \mathbf{r}] + \frac{(\mathbf{u}_+ + \mathbf{m}_+) \cdot (\mathbf{u}_- + \mathbf{m}_-)}{r^3} - \frac{3}{S^5} [(\mathbf{u}_- + \mathbf{m}_-) \cdot \mathbf{S}] (\mathbf{m}' \cdot \mathbf{S}) + \frac{(\mathbf{u}_- + \mathbf{m}_-) \cdot \mathbf{m}'}{S^3} - \frac{3}{R^5} [(\mathbf{u}_+ + \mathbf{m}_+) \cdot \mathbf{R}] (\mathbf{m}' \cdot \mathbf{R}) + \frac{(\mathbf{u}_+ + \mathbf{m}_+) \cdot \mathbf{m}'}{R^3} \quad (13)$$

(Because the model adopted for the ion pair is planar, it is convenient, in solving these equations, to resolve each vector into x and y components.) The procedure was to use trial values of r and solve eq 9-12 until the calculated dipole moment \mathbf{u}_c is equal to the observed value. After a solution for \mathbf{r} had been obtained, the electrostatic energy, W , was calculated from eq 13.

Results are listed in Table II. For the edgewise contact ion pair it is not possible to find a value for r that is consistent with the observed dipole moment. This model must therefore be ruled out. For the other models, solutions involving plausible values of \mathbf{r} exist. Of these, the axial contact ion pair has the lowest value of W and is therefore likely to represent the true structure of the actual ion pairs.

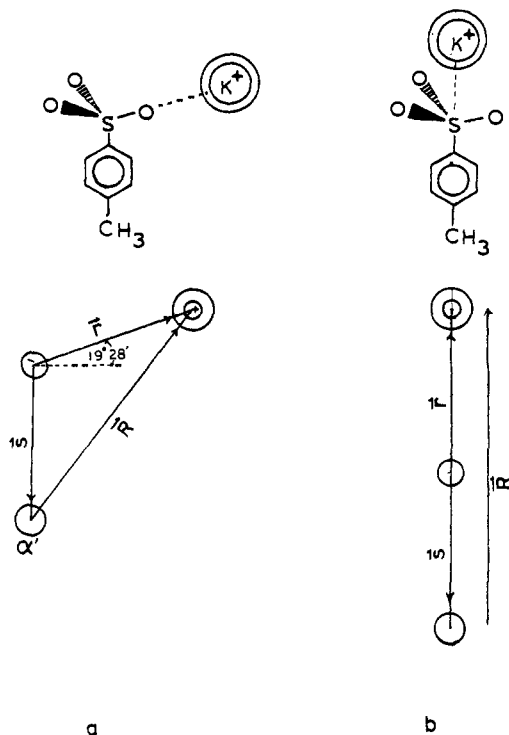


Figure 6. Plausible electric models for KTs-crown ether: (a) edgewise model, (b) axial model. The vector displacement S is from α_- to α' ; the displacement R is from α' to α_- .

Table II. Calculated Structure Parameters for Ion-Pair Complexes of Potassium *p*-Toluenesulfonate with Crown Ethers

Model	—KTs-crown-6 ^a —		—KTs-crown-5 ^b —	
	r , Å	W , kcal/mol	r , Å	W , kcal/mol
Edgewise, contact	No solution		No solution	
Edgewise, ligand-separated	3.77	-86.4	3.83	-85.1
Axial, contact	4.45	-89.9	4.52	-87.4
Axial, ligand-separated	5.56	-87.0	5.58	-85.0

^a Data used in the calculation: $\alpha_+ = 24.07 \text{ Å}^3$, $\alpha_- = 5.8 \text{ Å}^3$, $\alpha' = 11.04 \text{ Å}^3$, $S = 4.58 \text{ Å}$, $\mu_+ = 4.3 \text{ D}$, $\mu_- = 5.2 \text{ D}$. ^b Data used in the calculation: $\alpha_+ = 23.33 \text{ Å}^3$, $\alpha_- = 5.8 \text{ Å}^3$, $\alpha' = 11.04 \text{ Å}^3$, $S = 4.58 \text{ Å}$, $\mu_+ = 4.0 \text{ D}$, $\mu_- = 5.2 \text{ D}$.

The structure of the most stable, contact axial ion pair was analyzed further, as shown in Figure 7. This analysis involves further assumptions, and the result must be considered to be tentative. With this reservation, the dipole moment indicates that the K^+ ion is pulled out of the mean plane of the crown-oxygen atoms toward the anion by 0.50 Å . This conclusion is fully consistent with X-ray crystallographic structures determined for crown-6-NaBr and crown-6-NaNCS, in which the corresponding distances of stretch are 0.27 and 0.54 Å , respectively.^{13,14} On the other hand, for crystalline KTs-15-crown-6 ether, the X-ray evidence favors an edgewise structure. The difference between this structure and the axial structure that appears to predominate in solution, if real, must be ascribed to crystal forces.

KTs-crown-5. The dipole moment observed for KTs-crown-5 was analyzed analogously on the basis of eq 9-13. Results of the analysis are listed in Table II. The values of r and W for the various models show

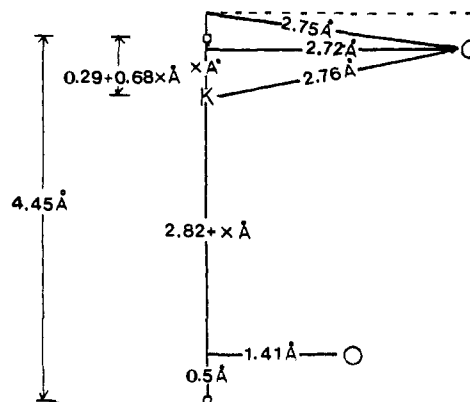


Figure 7. Structure of the axial contact ion pair of KTs-crown-6, based on a distance (r) between electrical centers of 4.45 Å . For the complexed cation, before ion-pair formation, the K^+ ion is assumed to sit in the mean plane of the crown-oxygen atoms. In the complexed ion pair, the K^+ ion is pulled out of the crown ring owing to interactions with Ts^- . It is assumed that the $K^+ \cdots Ts^-$ distance (which is 2.82 Å in the uncomplexed KTs) is stretched by the same amount, x , by which the K^+ ion is pulled out of the mean plane of the crown-oxygen atoms. Owing to the electrical charges associated with the crown dipole moment and the displacement of the K^+ ion, the positive electrical center is pulled ($0.29 + 0.68 \text{ Å}$) from the center of the K^+ ion toward the center of the crown ring. For the anion, the electrical center is pulled 0.50 Å from the plane of the $-SO_3$ oxygen atoms owing to the induced moment (m') of the phenyl ring. (See ref 2.) It is found in this way that $x = 0.50 \text{ Å}$.

a very similar pattern to those obtained for KTs-crown-6. The axial contact ion pair again appears to be the most stable isomer. However, the distance of stretch (analogous to x in Figure 7) is only 0.15 Å . The reason for this is that the potassium ion is too big to fit into the cavity of the crown-5 ring.^{3,4} Thus, in the K^+ -crown-5 complex, before ion pair formation, the center of the K^+ ion is already 0.90 Å outside the mean plane of the four exocyclic crown-oxygen atoms.

Conclusion

The Böttcher model represents a marked improvement over the familiar charged-sphere-in-a-continuum model which has been so influential in the interpretation of ionic association constants. By introducing point polarizabilities and point dipoles in addition to point charges, the Böttcher model can explain that ligand-separated ion pairs are of comparable stability to contact ion pairs; interactions involving the ligand dipole on the whole are attractive in the ligand-separated ion pairs and repulsive in the contact ion pairs and thus tend to compensate for the less favorable charge-charge interaction in the former.

Because the ionic dipoles have characteristic directions, the Böttcher model naturally includes relative orientations and thus stresses the geometrical structures of the ion pairs. Indeed, given the dipole moment of the ion pair, the model leads to an unambiguous prediction of the electrostatically most stable structural isomer. It is too early to decide whether such predictions are generally reliable. However, the marked success of the model on the qualitative level justifies considerable optimism.

(21) P. Groth, *Acta Chem. Scand.*, **25**, 3189 (1971).

(22) M. Szwarc in "Ions and Ion Pairs in Organic Reactions," Vol. 1, M. Szwarc, Ed., Wiley-Interscience, New York, N. Y., 1972, Chapter 1.