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Dipole moments of 12-crown-4, 15-crown-5 and 18-crown-6 have been measured for solutions in benzene and in cyclohexane at 15, 20, 25, and 30°, using the Guggenheim-Smith method. The dipole moments of the more common conformers of these crown ethers have also been calculated. The results indicate that these crown ethers exist in solution as mixtures of conformers. The conformational equilibria shift toward the more polar conformers as temperature increases. There is evidence that the more polar conformers of 12-crown-4 and 15-crown-5 are somewhat more favored in benzene solution than in cyclohexane, possibly as the result of a weak complexation with the former solvent.

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Introduction.

The extraordinary ionophoric ability of macrocyclic polyethers, or "crown ethers", and the application of this property in catalysis of a wide variety of reactions, has led to considerable interest in the conformations which these molecules can assume. Crystallographic studies have yielded information on the conformations of the crown ethers which can be crystallized, and on the conformations of these molecules in an enormous number and variety of crystallizable complexes. Examination of models of these molecules shows that additional conformations are possible, and that some of these conformations cannot accept a guest ion or molecule. Recently molecular mechanics and other computational techniques have been applied to evaluate relative energies of various conformations, both known and postulated, of some of the simpler crown ethers. Of these, the most extensive studies have been made of 18-crown-6 [1-7]; 12-crown-4 has also received attention [1,5,8]. There do not appear to have been any comparable studies of 15-crown-5.

Since the actual complexing process occurs in solution, it is of interest to measure properties which can be related to the conformations of the crown ethers in solution. One such property is the experimental dipole moment. Measurements of the dipole moments of crown ethers have been reported for solutions of these compounds in benzene at a single temperature by Dale and co-workers [9-11]. Perrin and co-workers [4] recently found that the dipole moment of pure liquid 18-crown-6 increases with temperature in the range 50-100°, leading to the conclusions that equilibria among conformers of different polarity exist in the liquid state, and that the proportions in which these conformers exist are temperature-dependent.

In order to learn more about this matter, we have measured the dipole moments of 12-crown-4 (1,4,7,10-tetraoxacyclododecane, **1**), 15-crown-5 (1,4,7,10,13-pentaoxacyclopentadecane, **2**) and 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane, **3**) in both cyclohexane and

benzene solutions at 15, 20, 25, and 30°. We used the Guggenheim-Smith method [12-14] in the form recommended by Exner [15], which relates the orientation polarization, P_o , the dipole moment, μ , in esu cm, and the dielectric constants and refractive indices of the test solutions by the equation:

$$P_o = \left(\frac{4\pi N}{9kT} \right) \mu^2 = \frac{3M_2}{d_1} \left(\frac{\alpha}{(\epsilon_1 + 2)^2} - \frac{\gamma}{(n_1^2 + 2)^2} \right)$$

In this equation, N is Avogadro's number, k is the Boltzmann constant, T is the Kelvin temperature, M_2 is the molecular weight of the solute, d_1 , ϵ_1 and n_1 are respectively the density, dielectric constant and refractive index of the pure solvent, and α and γ are respectively the slopes of plots of $\epsilon_{12} - \epsilon_1$ and of $n_{12}^2 - n_1^2$ vs. w_2 , where ϵ_{12} , n_{12} and w_2 are the dielectric constants, refractive indices and solute weight fractions of the solutions. The values of α , γ , μ and P_o from these measurements are presented in Tables 1-3. The earlier measurements of dipole moments of crown ethers [4,9-11] were made by essentially the same method, using comparable apparatus [16].

For comparison with the experimental values, we have also calculated the dipole moments of some of the more probable conformations of 12-crown-4 and 18-crown-6 whose relative steric energies have been computed by Sutherland [1].

Results and Discussion.

The tabulated least-squares values of α and γ are given with plus or minus one standard deviation. Since the values of γ are generally two orders of magnitude smaller than the values of α , the error in γ is insignificant compared with the error in α . The error in α was thus used to establish the error limits for μ and P_o . The comparatively small magnitude of γ also permitted resolution of an experimental difficulty: at 30°, the cyclohexane solutions evaporated so rapidly in the refractometer that satisfac-

Table 1
Experimental Dipole Moments of 18-Crown-6

Solvent	Temperature °C	α	γ	μ Debyes	P_o ml
Cyclohexane	15.0	2.42 ± 0.06	0.064 ± 0.006	2.63 ± 0.04	147 ± 4
Cyclohexane	20.0	2.34 ± 0.01	0.06 ± 0.02	2.63 ± 0.02 [a]	144 ± 2
Cyclohexane	25.0	2.50 ± 0.09	0.05 ± 0.006	2.76 ± 0.06	156 ± 6
Cyclohexane	30.0	2.47 ± 0.05	0.03 ± 0.04 [b]	2.79 ± 0.05	157 ± 5
Benzene	15.0	2.9 ± 0.1	-0.09 ± 0.01	2.64 ± 0.06	147 ± 7
Benzene	20.0	2.9 ± 0.1	-0.090 ± 0.003	2.66 ± 0.06 [c]	147 ± 7
Benzene	20.0	2.9 ± 0.1	-0.087 ± 0.009	2.68 ± 0.07 [c]	149 ± 7
Benzene	25.0	3.00 ± 0.02	-0.06 ± 0.01	2.73 ± 0.02	152 ± 2
Benzene	30.0	3.03 ± 0.06	-0.047 ± 0.005	2.78 ± 0.03	155 ± 3

[a] Reported [4], 2.66 Debyes. [b] Estimated by extrapolation. [c] Reported [9], 2.65 Debyes.

Table 2
Experimental Dipole Moments of 15-Crown-5

Solvent	Temperature °C	α	γ	μ Debyes	P_o ml
Cyclohexane	15.0	3.8 ± 0.2	0.05 ± 0.01	3.03 ± 0.07	194 ± 9
Cyclohexane	20.0	3.70 ± 0.02	0.06 ± 0.01	3.03 ± 0.01	191 ± 2
Cyclohexane	25.0	3.69 ± 0.03	0.067 ± 0.007	3.06 ± 0.02	192 ± 2
Cyclohexane	30.0	3.66 ± 0.03	0.07 ± 0.01 [a]	3.09 ± 0.02	192 ± 2
Benzene	15.0	5.26 ± 0.05	-0.10 ± 0.02	3.21 ± 0.02	217 ± 3
Benzene	20.0	5.04 ± 0.09	-0.090 ± 0.005	3.18 ± 0.03 [b]	210 ± 4
Benzene	25.0	4.86 ± 0.06	-0.087 ± 0.002	3.17 ± 0.02	205 ± 3
Benzene	30.0	5.0 ± 0.1	-0.064 ± 0.007	3.24 ± 0.04	211 ± 5

[a] Estimated by extrapolation. [b] Reported [9], 3.01 Debyes.

Table 3
Experimental Dipole Moments of 12-Crown-4

Solvent	Temperature °C	α	γ	μ Debyes	P_o ml
Cyclohexane	15.0	2.67 ± 0.06	0.03 ± 0.005	2.28 ± 0.03	110 ± 3
Cyclohexane	20.0	2.63 ± 0.02	0.044 ± 0.002	2.29 ± 0.01	109 ± 1
Cyclohexane	25.0	2.67 ± 0.06	0.054 ± 0.007	2.33 ± 0.03	111 ± 3
Cyclohexane	30.0	2.95 ± 0.06	0.064 ± 0.008 [a]	2.48 ± 0.03	124 ± 3
Benzene	15.0	4.04 ± 0.03	-0.12 ± 0.07	2.53 ± 0.03	135 ± 3
Benzene	20.0	3.85 ± 0.06	-0.095 ± 0.002	2.49 ± 0.02	130 ± 1
Benzene	25.0	3.65 ± 0.03	-0.071 ± 0.008	2.46 ± 0.01 [b]	123 ± 1
Benzene	30.0	4.0 ± 0.2	-0.073 ± 0.007	2.61 ± 0.06	137 ± 6

[a] Estimated by extrapolation. [b] Reported [10], 2.40 Debyes.

tory measurements of their refractive indices could not be obtained. The values of γ for the cyclohexane solutions at 30° were therefore estimated by extrapolation from the values at the other temperatures. It is felt that the error introduced by this estimation is less than that incurred in attempts at direct measurement.

The orientation polarization, P_o , of a rigid molecule

with a single polar group will decrease as temperature increases, as the result of the increasing thermal agitation counteracting the tendency of the dipole to become aligned with the electric field [17]. The P_o values derived from our measurements display no consistent variation with temperature. Such a result is to be expected if we view each crown ether molecule as a non-rigid assembly of

several dipoles, for which several different conformations are possible. As the temperature is increased, the tendency for disalignment with the field may be counterbalanced or even overcome by a tendency to shift the conformational equilibrium in the direction of more highly polar conformations, as suggested by Perrin [4]. This especially appears to be the case for 18-crown-6 in benzene solutions (Table 1).

A clearer picture emerges when the values of the dipole moments, μ , are plotted against temperature. In the case of 18-crown-6 (Figure 1), the measured dipole moments for the two solvents are in agreement within experimental error at each temperature. The dipole moment shows a fairly regular increase with temperature. The dipole moments of 15-crown-5 (Figure 2) and 12-crown-4 (Figure 3) in cyclohexane also increase with increasing temperature. It may be concluded that the conformational equilibria of these compounds in saturated hydrocarbon solvents shift toward the more polar conformations as temperature increases.

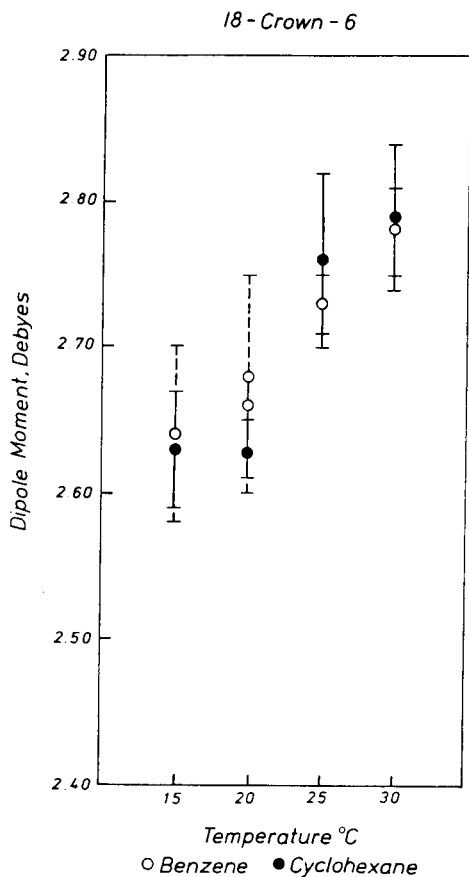


Figure 1. Dipole Moment of 18-Crown-6 in Benzene and Cyclohexane, 15-30°.

The behavior of 15-crown-5 and 12-crown-4 in benzene solution must be considered anomalous. Not only are the dipole moments of these compounds in benzene signifi-

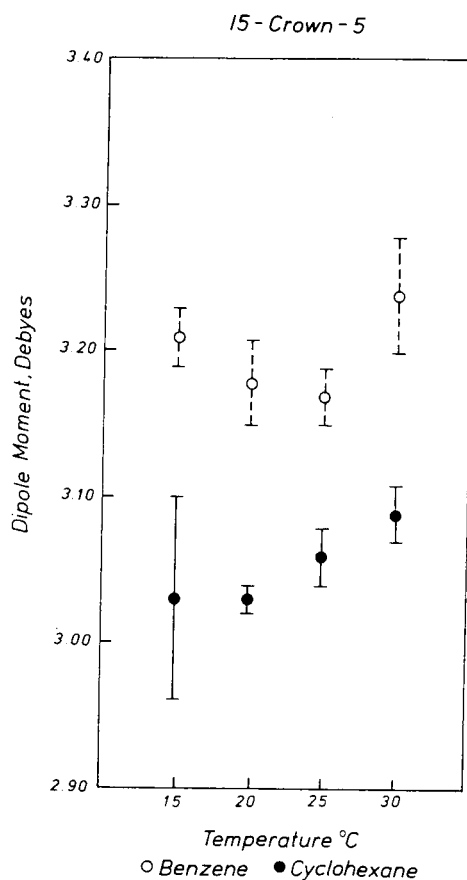


Figure 2. Dipole Moment of 15-Crown-5 in Benzene and Cyclohexane, 15-30°.

cantly higher than in cyclohexane, but they also decrease with increasing temperature from 15 to 25°, then show a sharp rise at 30°. The orientation polarizations of these two compounds in benzene solution also decrease in the 15 to 25° range. A possible explanation is that the conformational equilibria of 12-crown-4 and 15-crown-5 shift in favor of less polar conformations as the temperature increases from 15 to 25°. Such an explanation fails, however, to account for the difference in behavior between solutions in benzene and solutions in cyclohexane.

An alternate explanation is that some form of complexation occurs between benzene and the two smaller crown ethers. This could at least account for the higher values of the dipole moments and orientation polarizations in benzene. That such behavior does not occur between benzene and 18-crown-6 is amply demonstrated by our dipole moment measurements as well as by recent ^{13}C nmr [18] and electronic spectral [19] studies. There do not seem to have been any comparable studies of 12-crown-4 or 15-crown-5.

If the interaction is due to a charge-transfer effect, this should be identifiable by a new absorption band appear-

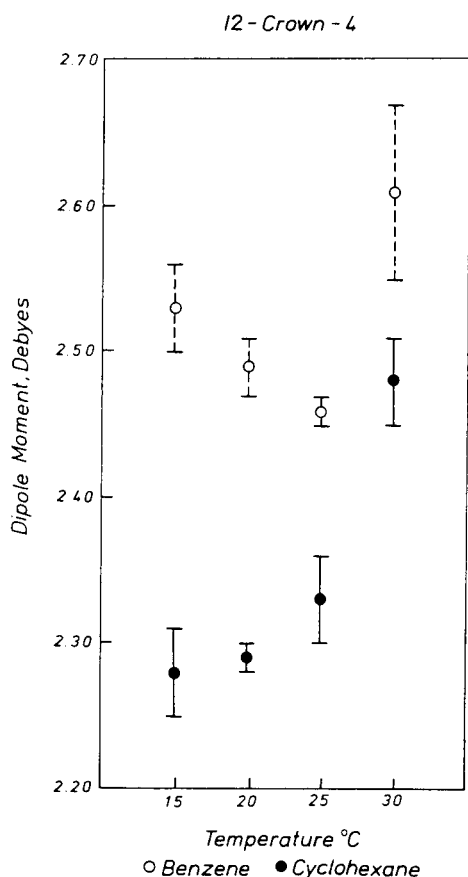
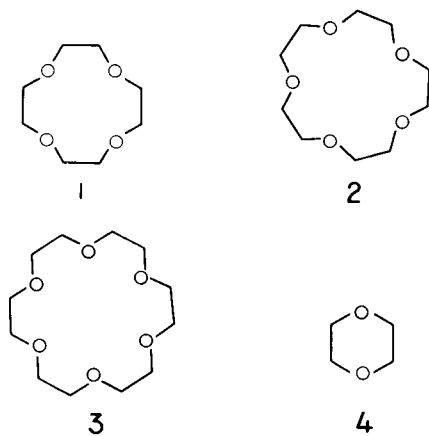


Figure 3. Dipole Moment of 12-Crown-4 in Benzene and Cyclohexane, 15-30°.

ing for a solution containing both the donor and acceptor molecules, at lower energy (longer wavelength) than any of the bands in the spectra of either component [20]. Accordingly, we compared the absorption spectra of cyclohexane solutions of equimolar quantities of each crown ether and benzene, with the spectra of cyclohexane solutions of each of the individual compounds at the same concentrations. No evidence for a charge-transfer effect was observed for either 12-crown-4 or 15-crown-5.



A much better-known compound which can serve as a model for interpretation of these results is the simplest crown ether, 1,4-dioxane, or "6-crown-2" (4). On the negative side, measurements of dielectric constants and refractive indices of the ternary system benzene-cyclohexane-dioxane at 25° have led to the conclusion that the system is "essentially ideal" [21]; and we also found no spectral evidence for a charge-transfer effect in this system. On the other hand, an "anomaly" at 26° has been reported [22] in the relationship between dielectric constant and temperature for a 2% solution of 1,4-dioxane in benzene. Hurwic [23] found that the Guggenheim-Smith dipole moment of 1,4-dioxane in benzene increased from 0.45 to 0.49 Debyes in the temperature range 25 to 35°, while the values for solutions in cyclohexane, *n*-hexane and *n*-heptane remained constant at 0.32-0.33 Debyes. Hurwic suggested that these results can be explained by stabilization of the polar boat conformers of 1,4-dioxane by complexation with benzene, but his efforts to find supporting evidence for this idea in the infrared and Raman spectra of benzene-dioxane solutions gave inconclusive results [24]. A later study of this system, by Raman depolarized light scattering gave clear evidence for a "loose" 1:1 complex of benzene and 1,4-dioxane [25]. No indication of the conformation of this complex was given. By analogy, we can conclude that a similarly loose complexation exists between one or more benzene molecules and both 12-crown-4 and 15-crown-5, that there is an increasing degree of dissociation of these complexes without much change in conformation in the range 15-25°, and that a significant conformational change (or changes), favoring more polar conformers, occurs between 25 and 30°. Since the increase in dipole moment occurs to about the same extent with both benzene and cyclohexane solutions, this conformational change must occur with both the complexed and uncomplexed crown ethers.

The free-energy barrier for conversion of the nonpolar chair conformer of 1,4-dioxane to the twist-boat conformer has been found from nmr measurements to be 9.7 kcal mol⁻¹ [26,27], or slightly less than 1 kcal below the barrier for the corresponding conversion in cyclohexane. The energy difference between the twist-boat and boat has not been measured, but probably is very close to the 1.6 kcal mol⁻¹ that has been measured for the corresponding conversion in cyclohexane [28]. The large energy barrier between the chair conformer and the boat conformers is sufficient to keep the majority of the 1,4-dioxane molecules in nonpolar conformation; but interconversion among the various polar conformations is easy. As ring size increases, we may expect the energy barriers for the most difficult interconversions to decrease. In 18-crown-6 these barriers are probably very close to those for an acyclic polyether of the same size, and interconversion is rapid enough to counteract any tendency for the formation of a weak

association of any particular conformer with benzene.

Sutherland and co-workers [1] have used a modified molecular mechanics program, WBFF2, to calculate the steric energies relative to the minimum energy conformation for several conformers of 12-crown-4 and 18-crown-6 whose bond angles and lengths had been established by crystallographic measurements. We have calculated the dipole moments of some of these conformers with the assistance of the program ATCOOR2 [29], by which dipole moments can be obtained from bond angles, bond lengths, dihedral angles and Pauling electronegativities. The results are summarized in Table 4.

Table 4

Calculated Dipole Moments of Conformers of Crown Ethers

Compound	Conformation [a]	Relative Steric Energy [a], kcal mol ⁻¹	Dipole Moment, Debyes
12-Crown-4	A	0.00	5.63
	B	1.80	2.08
	C	2.90	0.394
	D	2.62	1.39
	E	2.63	5.68
	F	2.88	0.133
18-Crown-6	C	0.00	1.17
	D	4.39	3.38
	E	5.01	1.07
	B	7.84	1.28

[a] Reference [1].

Conformations of 12-crown-4 are shown in Figure 4. The high-polarity conformations **A** and **E** both have the ether group dipoles aligned nearly parallel. The "square" conformer **A**, which is also the minimum energy conformer, has the group dipoles tilted outward slightly, creating the optimum space for a guest ion atop the oxygen "jewels" of the "crown". Conformer **A** has been observed in 12-crown-4 complexes with, for example, lithium and sodium thiocyanates [10]. In conformer **E**, the ether dipoles are tilted inward slightly. The large polarity of either conformer should readily interact with a cation or with the π cloud of a benzene molecule. The interaction of **E** with a cation would necessarily be followed by relaxation to the more open minimum-energy conformation **A** to allow host-guest complexation.

Conformations **C** and **F** of 12-crown-4 have low polarity as the result of almost perfect balancing of ether group dipoles. Group dipoles on opposite sides of the ring are additive in **C** and point in nearly opposite directions in **F**. Although **F** is the conformer with the highest steric energy, it is nevertheless the conformer of 12-crown-4 in the pure crystalline state [30]. Sutherland has attributed this high energy to torsional strain. There is probably compensation for this strain by orientation of the ether

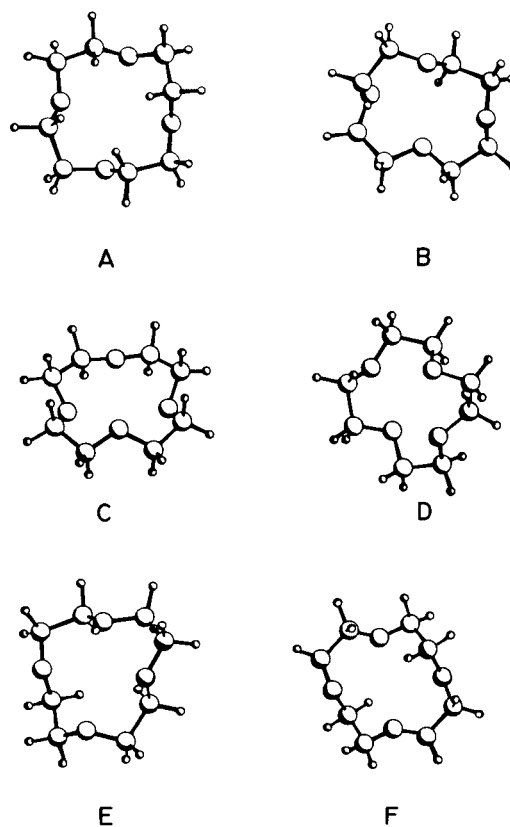


Figure 4. Conformations of 12-Crown-4.

groups so that electrical repulsion among the ether groups is minimized. There may well be comparatively high energy barriers between **F** and the other conformers.

Of the various conformations of 18-crown-6 (Figure 5), the maximum-energy conformation **B** is the commonest one in host-guest complexes [1]. It is an "open" conformation, with space to accommodate larger cations and with the ether group dipoles pointing into this space. With its high steric energy, this conformation should be a minor component of a solution of 18-crown-6 in the absence of a complexing cation to give it stability. The maximum-polarity conformation **D** has all six group dipoles pointing toward the same side of the molecule at a larger angle than in **B**. Conformation **D** is found in 18-crown-6 sodium complexes [31]. Conformation **E**, the low-polarity conformer with three adjacent ether dipoles partially balanced by the orientation of the other three, has been observed in a complex with benzenesulfonamide [32]. The minimum energy conformer **C** is also the shape of 18-crown-6 in the pure crystalline state [33]. It has a collapsed structure with no cavity. We did not calculate the dipole moment of Sutherland's conformation **A** with a relative steric energy of 3.86 kcal mol⁻¹ because no examples with this conformation are known.

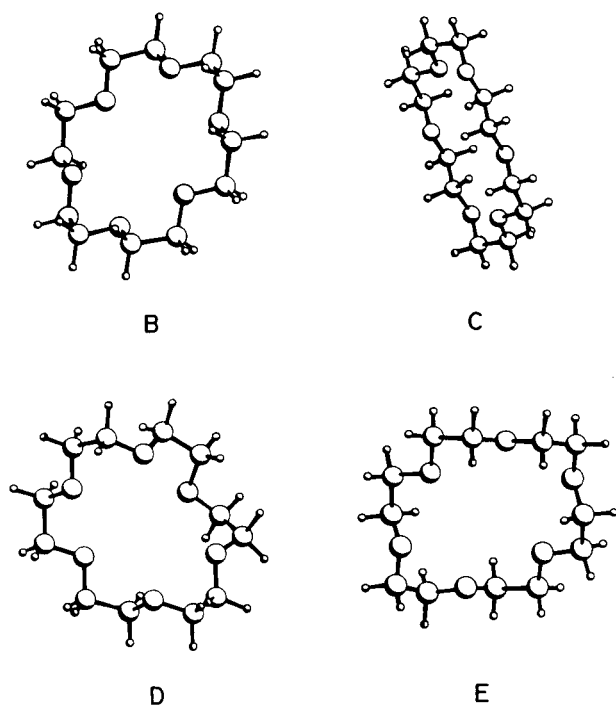


Figure 5. Conformations of 18-Crown-6.

The problem of 15-crown-5 is more difficult in part because it is a liquid, so that crystallographic data for the pure compound have not been obtained, and especially

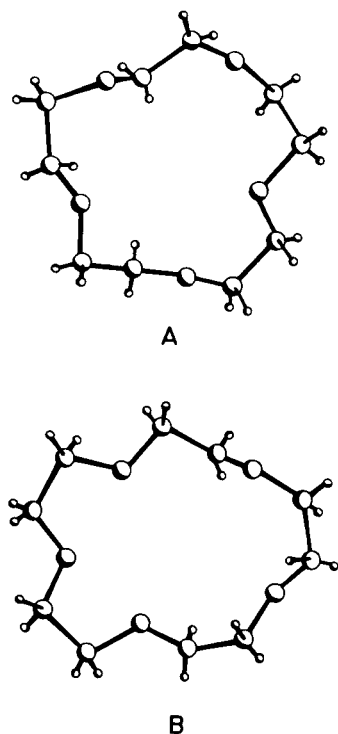


Figure 6. Conformations of 15-Crown-5.

because it is less symmetrical than the even-numbered crown ethers in most of its possible conformations. We were able to calculate dipole moments for two conformations of 15-crown-5 which have been identified by crystallographic studies of complexes. These conformations are shown in Figure 6. The most polar conformation (A) is the one which has all five ether group dipoles aligned as closely parallel as possible. This conformation, which has been found in a 2:1 complex with barium bromide [34], yielded a calculated moment of 5.67 Debyes. A second conformation (B), found in a 1:1 complex with copper(II) bromide dihydrate [35], has three adjacent group dipoles oriented inward and the remaining two oriented toward opposite sides of the molecule. The calculated moment of this conformer is 1.42 Debyes.

None of these calculated dipole moments correspond very closely to the experimental values for the dipole moments for either the cyclohexane or benzene solutions of the crown ethers. This lack of agreement supports Perrin's conclusion [4] that the solutions contain mixtures of conformers in temperature-dependent dynamic equilibria. To this we can add a further conclusion that the more polar conformers of 12-crown-4 and 15-crown-5 are more favored in benzene solution than in cyclohexane, perhaps as the result of a weak dipole-induced dipole interaction.

EXPERIMENTAL

The highest purity 12-crown-4, 15-crown-5 and 18-crown-6 available from Parish Chemical Company were stored in a vacuum desiccator over potassium hydroxide pellets and used as received. Cyclohexane and benzene were Burdick and Jackson "Distilled in Glass" grade, and were maintained anhydrous with type 4A molecular sieve [36]. Calibration liquids were Aldrich "Gold Label" carbon tetrachloride, di-*n*-butyl ether, mesitylene, toluene and *p*-xylene.

Dielectric constants were measured with a WTW Type DMOI Dipolmeter, using a Type DFLI sample holding cell [37]. Refractive indices were measured with a Bellingham and Stanley high-precision Abbe refractometer. Both instruments were maintained at constant temperature from a common circulating thermostat. Absorption spectra were measured with a Cary 15 spectrophotometer.

For the measurement of each dipole moment, six samples of approximately 50 ml each were prepared, with weight fractions of solute, w_2 , ranging from 10^{-3} to 10^{-2} . When a sample had come to temperature in the thermostat, approximately 2 ml of it was transferred to the refractometer and the refractive index was measured immediately. The remainder of the sample was transferred to the dipolmeter cell, the first 15-20 ml being used to rinse the cell. Repeated dipolmeter readings were taken until the same value was obtained for five consecutive readings. Both the refractometer and the dipolmeter cell were thoroughly rinsed with absolute methanol between samples and dried with a stream of dry nitrogen.

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