bond orders of the C(1,1′)-N and C(1)-C(1′) bonds. The LUMO of the diquat dication is strongly bonding between C(1) and C(1′) and antibonding between C(1,1′)-N. This indicates that the 1,1′ bond in the cation radical may be shortened whereas the C(1,1′)-N bonds may be lengthened. The total bond orders of the N-C(1)-C(1′)-N fragment are, however, 1.490 in the dication and 1.392 in the cation radical which is consistent with a higher barrier in the dication. Interestingly this predicted lower barrier in the cation radical may be significant to the biological activity of diquat. It has been inferred from studies of many compounds that only those compounds which are reversibly reduced to a cation radical and which are essentially planar and of a certain size are good herbicides.$^{1-3,23}$ Therefore the observation that the diquat cation radical can more easily pass through the planar configuration than can the dication is probably important to the herbicidal action of diquat.

Conclusion

Molecular orbital calculations are consistent with the interpretation of the ESR spectra of the diquat cation radical in terms of an intermediate rate of ring inversion. Experimentally the barrier to inversion can be no more than 7.25 kcal/mol. The INDO calculated inversion barrier (using the atomic coordinates generated from the crystal structure of the dication) is 3.98 kcal/mol for the cation radical and 6.0 kcal/mol for the dication.

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Supplementary Material Available: numbering scheme, atomic fractional coordinates, structure factors and bond lengths and angles for diquat dibromide (12 pages). Ordering information is given on any current masthead page.

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Molecular Structure of Ion Pairs from Electric Dipole Moments. IV. Ion-Pair Solvation in Acetic Acid[1,2]

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Abstract. Electric dipole moments were measured in acetic acid for ion pairs of LiCl, KCl, KBr, LiTs (Ts = *p*-toluenesulfonate), KTs, CsTs, TlTs, *p*-toluidinium *p*-toluenesulfonate, and tetraisoamylammonium nitrate. Except for the latter, the dipole moments show considerable effects of solvation, deviating from intrinsic dipole moments measured in the gas phase or in inert solvents by amounts ranging from +4.8 D for KTs to −1.8 D for KCl. Measurements were made at 0.001–0.01 F concentrations. Corrections were made for solute-induced medium effects and for the effect of the free ions on the dielectric constant, the latter according to the theory of Onsager and Provencher which allows for dynamic equilibrium between free ions and ion pairs. Structure and dipole moment are considered for various models of solvated ion pairs. It is concluded, from the observed dipole moments and other properties, that the solvated ion pairs are best described as follows: LiCl·HAc, monodentate attachment of *cis*-HAc to cation; KCl·HAc and KBr·HAc, cyclic bidentate complex with *cis*-HAc; KTs·HAc, cyclic bidentate complex of *cis*-HAc with corner structure of KTs or monodentate attachment of *trans*-HAc to the axial structure of KTs. For $(i\text{-Am})_4NNO_3$, the dipole moment indicates the absence of discrete solvation complexes with acetic acid.

The behavior of ion pairs in acetic acid is of special interest for practical as well as historical reasons. Considering the fairly low dielectric constant ($\epsilon_0 = 6.265$ at 25 °C), acetic acid is a remarkably good solvent for electrolytes. It is perhaps for this reason that acetic acid has become a classic solvent for demonstrating the properties of ion pairs.$^{3-8}$ In particular, the isomerism between intimate and solvent-separated or "loose" ion pairs was first demonstrated by means of kinetic studies carried out in acetic acid.^{6}

Our aim in this study is to examine ion-pair structure and solvation by measuring the electric dipole moment. In acetic acid, such measurements are extraordinarily difficult for

Table I. Results for Electrolytes in Acetic Acid at 25 °C[a]

Solute[a]	10^7K_d[b]	Λ[c]	S_2[d]	V_2[e]	R_2[e]
LiCl	2.5	(40.4)	13.1 ± 0.3[f] (0.992)	10.4	9.37
KCl	1.3	36.7	12.9 ± 0.8 (0.983)	27.0	13.95
KBr	2.2	(36.7)	15.2 ± 0.6 (0.978)	(34)	(17.6)
LiTs	0.7	36.6	11.8 ± 0.7 (0.987)	108.1	42.46
KTs	1.1	33.7	12.2 ± 0.5 (0.991)	121.0	46.34
CsTs	(1.5)	31.1	12.1 ± 0.5 (0.992)	130.1	50.42
TlTs	(1.0)	29.4	11.8 ± 0.5 (0.980)	129.9	50.37
BHTs	0.74	37.3	14.6 ± 0.3 (0.990)	218.4	77.83
R_4NNO_3	43[h]	(30)	35.9 ± 3.0 (0.970)	366.6[g]	(111.9)

[a] Values in parentheses are estimates. Ts = *p*-toluenesulfonate, BH = *p*-toluidinium, R_4N = tetraisoamylammonium. [b] Concentrations in mol/l. [c] Mean value of $1000L/I$. Ionic strength I based on given K_d. [d] Liters/mole; $k_a/A = 0.5$. Number in parentheses is the correlation coefficient. [e] Milliliters/mole; V_2 measured by L. E. Mayer, R_2 measured by C. D. Brown. [f] Dr. Stephen E. Gould repeated these measurements and obtained $S_2 = 12 \pm 1$. [g] Measured by E. R. Grunwald in chlorobenzene. [h] K_d varies with the ion-pair concentration: $10^6K_d = 3.04 + 87(c_2 - I)$; $c_2 \leq 0.003$.

the following reasons. (1) The relatively high conductivity reduces the precision of capacitance measurements and necessitates substantial corrections for the effect of the free ions on the dielectric constant. (2) Owing to the mobile hydrogen-bonded structure of the solvent, solute-induced medium effects are relatively large.[9] (3) There are technical problems owing to deteriorating performance of metal electrodes exposed to salt solutions in acetic acid. In the present work, errors stemming from these difficulties have been reduced to acceptable levels so that dipole moments of useful accuracy can be reported for a variety of ion pairs. The results show unmistakable effects of solvation for all ion pairs except those of $(i\text{-Am})_4NNO_3$.

Experimental Section

Materials. Anhydrous acetic acid and the salts were reagent grade materials subjected to further purification, or were synthesized from reagent grade materials, as described in previous papers.[2,8]

Apparent Molar Volumes. Densities of 0–0.1 *m* solutions were measured with a precision approaching 0.001% at 25 °C by Lydia E. Mayer using calibrated twin-necked pycnometers with graduated necks. Solvent and solutions were equilibrated side-by-side in a massive brass block. Apparent molar volumes were calculated from the linear relationship of density and molality. Results are listed in Table I.

Apparent Molar Refractions. Refractive-index differences between solvent and 0–0.017 *m* solutions were measured at 25 °C by Charles D. Brown using a Hilger-Rayleigh interferometer and technique described elsewhere.[10] Apparent molar refractions were calculated from these data, making use of the apparent molar volumes. Results for Na-D are listed in Table I.

Capacitance and Conductance. Electrical measurements were made using a General Radio Type 1615A audiofrequency transformer ratio-arm bridge with matching generator and null detector.[11] Measurements were made over a period of several years during which our technique gradually improved. Initial measurements were made using a Balsbaugh stainless steel three-terminal guarded cell[12] with an air capacitance of 58.27 pF. Because of the fairly high conductances (as high as 500 micromho), the conductance range of the Type 1615A measuring bridge was expanded by connecting a General Radio Type 1433N 10 000 ohm decade resistor in parallel with the standard capacitors. The distributed reactance of the decade resistors was determined as a function of switch position by means of 0.25 W carbon resistors. In this laborious procedure one measures a large number of carbon resistors in a fixed circuit geometry and assumes that all resistors have the same, constant capacitance. The calibration was accurate within ±0.2 pF.

In later work we used an Eaton stainless-steel cell,[11] with an air capacitance of 18 pF, and a Pribadi-Kay conductance balancing network,[13] as described by Grunwald and Effio.[11] All data were corrected for double-layer capacitance at the electrodes and for the capacitive effect of conductance-to-ground in the cell.[11] The *cell constants* required for the calculation of the specific conductivity L were calculated from the air capacitances.

Table II. Results for KBr in Acetic Acid at 25 °C

			$\Delta\epsilon_D/c_2$	
10^3c_2, M	10^6L	$\Delta\epsilon$	$k_a/A = 1$	$k_a/A = 0.5$
1.048	0.494	0.0378	19.35	10.78
1.571	0.609	0.0459	16.88	10.54
2.071	0.696	0.0695	23.55	18.40
2.298	0.765	0.0700	21.21	16.44
2.555	0.801	0.0688	18.40	13.99
2.588	0.780	0.0749	20.49	16.13
2.731	0.930	0.0859	23.31	19.12
3.143	0.908	0.0779	17.47	13.70
4.311	1.087	0.1003	17.50	14.52
5.462	1.272	0.1218	17.47	14.98
6.466	1.404	0.1442	18.05	15.85
6.895	1.607	0.1490	17.55	15.45
7.664	1.590	0.1623	17.43	15.49
7.765	1.558	0.1512	15.76	13.84
8.622	1.707	0.1761	16.99	15.22
9.194	1.971	0.2005	18.54	16.85
10.218	1.946	0.1929	15.85	14.30
		Mean	18.58	15.04
		Std dev	2.31	2.22

Deterioration of Cell Electrodes. Measurements on new cells gave precise results which were reproducible in repeated series of measurements. For LiCl, early measurements with the Balsbough cell were repeated by Dr. Stephen E. Gould using an almost new Eaton cell, with adequate agreement. However, cells that had been used extensively for work in other organic solvents, such as chlorobenzene, dichloroethylene, or octanoic acid, failed to give adequately precise results for salt solutions in acetic acid, although the average experimental curves agreed with the more precise data obtained with newly made cells.

Results and Calculations

Conductivity Data. The conductivity L of the solutions was only of marginal interest, being required mainly for correcting for the effect of the free ions on the dielectric constant. Our data were consistent with the model of ion pairs in equilibrium with free ions, subject to ion-atmosphere effects. To the approximation required here, the ion-atmosphere effects could be neglected. Thus our results are summarized in Table I in terms of ion-pair dissociation constants K_d and equivalent conductivities Λ. For KCl, LiTs, KTs, and BHTs, values of K_d were available from previous work.[5,7,8] For CsTs and TlTs, K_d could be estimated with adequate accuracy by analogy to other data.[8b] These dissociation constants were used to calculate free-ion concentrations which, in conjunction with experimental values of L, gave the results for Λ listed in Table I. For LiCl, KBr, and $(i\text{-Am})_4NNO_3$, Λ was then estimated and (using the experimental values of L) K_d was calculated.

Dielectric Data. To illustrate the quality of the results and calculations, data for KBr are listed in Table II. Because of the relatively high conductivity, KBr is one of our more difficult solutes. The standard deviation of $\Delta\epsilon \equiv \epsilon - \epsilon_0$ from a smooth function is about 0.007.

As stated before, $\Delta\epsilon$ is a sum of two terms which will be denoted ϵ_I and $\Delta\epsilon_D$, respectively, as in eq 1.

$$\Delta\epsilon \equiv \epsilon - \epsilon_0 = \epsilon_I + \Delta\epsilon_D \qquad (1)$$

ϵ_I is the contribution due to the 90° out-of-phase component of the conductivity of the free ions, expressed in units of dielectric permittivity. In water, ϵ_I would be given by the clas-

Table III. Dipole Moments of Solvated Ion Pairs in Acetic Acid[a]

	$m = 0$		$m = 1$		
Ion pair	$\mu_{2,\mathrm{app}}$	$\mu_{2,\mathrm{solv}}$	$\mu_{2,\mathrm{app}}$	$\mu_{2,\mathrm{solv}}$	μ_2[b]
R_4NNO_3	16.0	14.5	16.1	14.6	14.0 (CB)
LiCl	9.5	8.4	9.6	8.5	7.12 (G), 6.8 (HOct)
KCl	9.4	8.3	9.5	8.5	10.27 (G)
KBr	10.3	9.1	10.4	9.3	10.41 (G)
LiTs	9.1	8.2	9.2	8.4	
KTs	9.3	8.4	9.4	8.6	4.8 (HOct)
CsTs	9.2	8.4	9.3	8.5	
TlTs	9.1	8.3	9.2	8.5	
BHTs	10.2	9.3	10.3	9.5	6.1 (HOct)

[a] Dipole moments in Debye units. m = assumed solvation number. $R_4N = (i\text{-Am})_4N$, Ts = *p*-toluenesulfonate, BH = *p*-toluidinium. Data for acetic acid at 25 °C: $\epsilon_0 = 6.265$, $n_0 = 1.3699$, $V_1{}^0 = 57.54$ ml/mol, $R_1(\text{Na–D}) = 13.01$ ml/mol. [b] CB = chlorobenzene, G = gas phase, HOct = octanoic acid. μ_2 for BHTs in HOct estimated from measured μ_2 for *p*-fluoroanilinium *p*-toluenesulfonate. References 2, 11, and 19.

sical theory of Debye and Falkenhagen[14] for the interionic effect on the dielectric constant. When ion pairs are present, it is necessary to use the more general theory due to Onsager and Provencher (OP),[15] which has recently been tested experimentally.[16] In the present case, where the free-ion fraction I/c_2 is small (I = ionic strength; c_2 = formal concentration of the electrolyte), the OP theory reduces to eq 2, in which ϵ_ω denotes the value of ϵ_1 in an alternating field of angular frequency $\omega = 2\pi f$.

$$\frac{\epsilon_\omega}{\epsilon_0} = \frac{7.002 \times 10^5 \sqrt{I}(1 + \alpha\sqrt{1 + y^2} - \sqrt{2\alpha R})}{(\epsilon_0 T)^{3/2}\sqrt{2\alpha R}([1 - \alpha]^2 + \alpha^2 y^2)} \qquad (2)$$

The parameters appearing in (2) are defined in (3)-(6).

$$\alpha - \tfrac{1}{2} = k_a/A = k_a\epsilon_0/(1.130 \times 10^{10}\Lambda) \qquad (3)$$

$$y = \omega\tau/2\alpha \qquad (4)$$

$$\tau = \epsilon_0/4\pi L_{\mathrm{esu}} = 8.85 \times 10^{-14}\epsilon_0/L \qquad (5)$$

$$R = 1 + (1 + y^2)^{1/2} \qquad (6)$$

In these equations, k_a is the second-order rate constant for ion-pair association; A is the theoretical rate constant for the diffusion-controlled combination of opposite univalent point charges; τ is the Maxwell relaxation time for the ionic atmosphere (τ neglects relaxation by the association-dissociation mechanism); and L_{esu} or L is the conductivity of the electrolytic solution, in esu cm^{-1} or mhos cm^{-1}, respectively.

Because K_d is known, I can be calculated, and because L is known, τ can be calculated. Thus the only unknown parameter is k_a/A, whose upper limit is unity. In 1-octanol, k_a/A can be measured[16] and is found to be ca. 0.3 for three electrolytes of quite different structure. In acetic acid, rate constants for diffusion-controlled processes tend to be similarly high, as evident from proton-transfer studies.[7a,8a]

Because our data are not accurate enough to treat k_a/A as an adjustable parameter for each electrolyte, we decided to adopt a single value which gives overall best fit, and which gives satisfactory fit to all data. The value chosen is $k_a/A = 0.5$. In Table II, the effect on $\Delta\epsilon_D$ (eq 1) of allowing k_a/A to vary is illustrated for KBr. It may be assumed that for $c_2 < 0.01$, the electrolyte exists predominantly in the form of ion pairs, and that $\Delta\epsilon_D/c_2$ therefore should be essentially constant. The data in Table II show that this criterion is satisfied somewhat better when $k_a/A = 0.5$. The data also show that $\Delta\epsilon_D/c_2$ is fairly sensitive to the value chosen for k_a/A. Inasmuch as $\Delta\epsilon_D/c_2$ is identified with the molar dielectric increment S_2, whose uncertainty in turn determines the error in the dipole moment calculated for the ion pair, it is clear that highly accurate values will not be obtained for the dipole moment.

According to our analysis, the uncertainty in k_a/A is the largest source of error, causing an uncertainty in the final dipole moment which in extreme cases may be as large as 1 D. Normally, the error in the dipole moment owing to the uncertainty in k_a/A will be 0.3-0.5 D.

In Table I are listed the molar dielectric increments S_2, together with their statistical errors and the correlation coefficients for fitting the data, based on the assumption that $k_a/A = 0.5$. We have convinced ourselves in each case that the correlation coefficient is not significantly different from that for optimum k_a/A.

Calculation of Dipole Moments. The evaluation of solute-induced medium effects and of dipole moments for solvated solutes in acetic acid will be fully described in a future publication.[9] Briefly, we use Kirkwood theory to calculate an apparent dipole moment $\mu_{2,\mathrm{app}}$, which is related to real dipole moments (μ_1, μ_2) and Kirkwood correlation factors (g_1, g_2) according to (7).

$$\mu_{2,\mathrm{app}}{}^2 = g_2\mu_2{}^2 + c_1{}^0\mu_1{}^2(dg_1/dc_2)_{c_2=0} \qquad (7)$$

To calculate dipole moments $\mu_{2,\mathrm{solv}}$ for solvated ion pairs, we adopt the model that one ion pair associates with m solvent molecules, and that the resulting discrete solvation complexes are not coupled by hydrogen bonds to the hydrogen-bonded liquid lattice of acetic acid. Under those conditions, in eq 7, $g_2 = 1$, μ_2 becomes $\mu_{2,\mathrm{solv}}$ and dg_1/dc_2 becomes simply the result of a solute-induced medium effect, dg_{11}/dc_2, due to the solvation complex (eq 8).

$$\mu_{2,\mathrm{app}}{}^2 = \mu_{2,\mathrm{solv}}{}^2 + c_1{}^0\mu_1{}^2(dg_{11}/dc_2) \qquad (8)$$

For solutes that are not coupled by hydrogen bonds to the liquid lattice, the solute-induced medium effect in acetic acid was derived in an independent study.[9] Substituting the result in (8) and rearranging, we obtain our working eq 9.

$$\mu_{2,\mathrm{solv}}{}^2 = \mu_{2,\mathrm{app}}{}^2 - 1.526S_2 + 1.265V_{2,\mathrm{solv}}/V_1{}^0 \qquad (9)$$

The solvation number m enters the calculation of both $\mu_{2,\mathrm{app}}{}^2$ and $\mu_{2,\mathrm{solv}}{}^2$ inasmuch as the molar volume $V_{2,\mathrm{solv}} = V_2 + mV_1{}^0$, and the molar refraction $R_{2,\mathrm{solv}} = R_2 + mR_1$. When $m = 0$, the treatment reduces to that for an unsolvated, nonhydrogen bonding solute.[9]

Table III lists dipole moments calculated by this approach for $m = 0$ and 1. It can be seen that the results are only slightly dependent on the unknown value of m. For this reason, and assuming that m must be small, comparison of $\mu_{2,\mathrm{solv}}$ with the intrinsic dipole moment μ_2 will be significant even if the value adopted for m is in error.

Discussion

Comparison of $\mu_{2,\mathrm{solv}}$ with intrinsic dipole moments μ_2 for various ion pairs in Table III shows that there are considerable differences, except for tetraisoamylammonium nitrate for which the inert structure and large size of the cation makes the formation of discrete solute-solvent complexes inherently improbable. The demonstration of the *existence* of distinctive solvation complexes is perhaps the most important qualitative result of our studies. In principle, the dipole moments can elucidate the molecular structure of the solvation complexes, and previous work[17] on complex formation of ion pairs with crown ethers has illustrated the power of this approach. The present problem is more diffi-

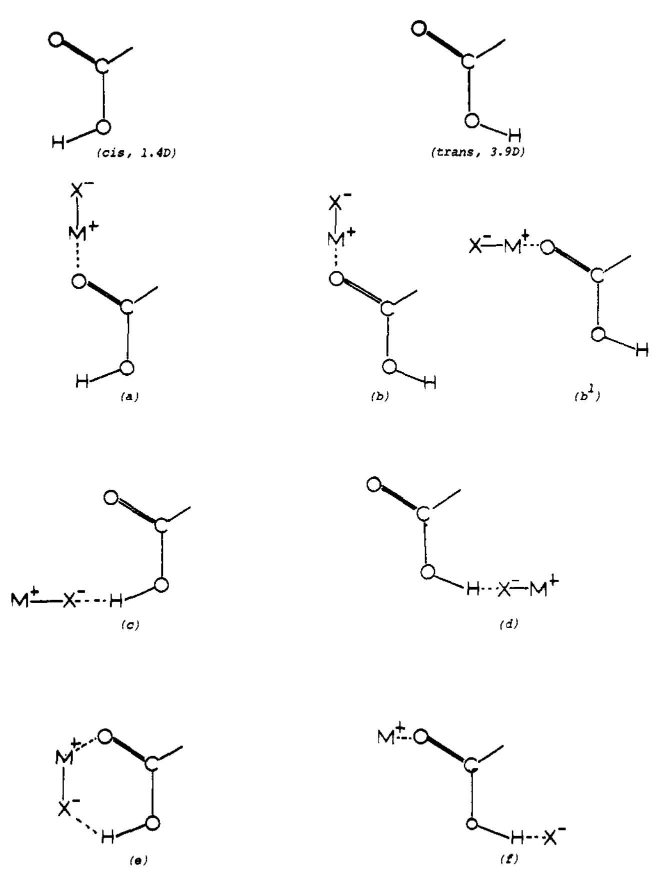

Figure 1. Models for solvation of M^+X^- ion pairs by a molecule of *cis*- or *trans*-AcOH. For further description, see text.

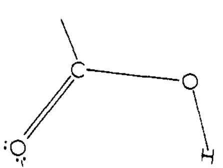

Figure 2. Points of van der Waals contact in *cis*-AcOH for the formation of a cyclic bidentate solvation complex with M^+X^-

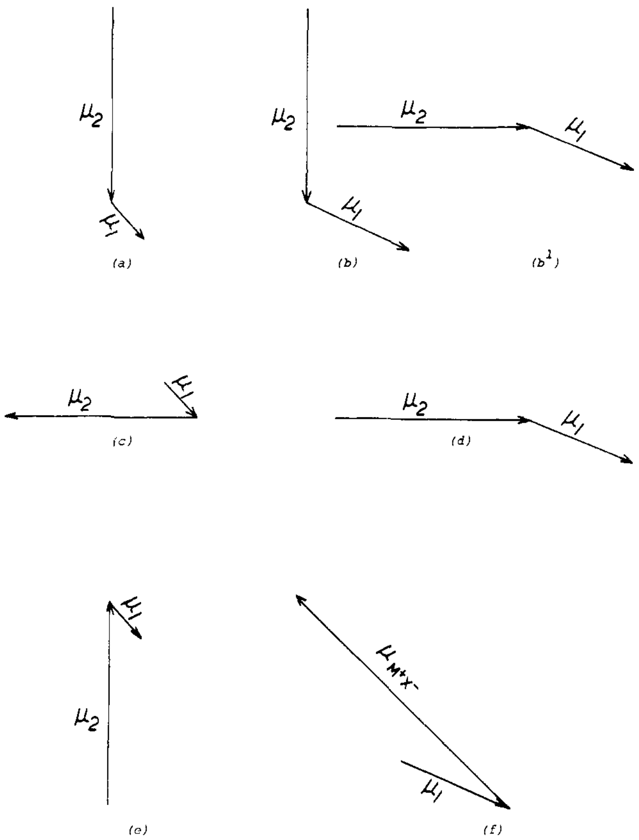

Figure 3. Vector diagrams of dipole orientations of μ_1 and μ_2 for the various models shown in Figure 1.

cult, however, because the stoichiometry of the solvation complexes is not known, the accuracy of $\mu_{2,\mathrm{solv}}$ is relatively low, and the shape of the acetic acid molecule is too unsymmetrical for its polarizability and induced moments to be represented credibly by a single isotropically polarizable electrical center. Our approach in the following will therefore be more qualitative.

Models for Solvated Ion Pairs. In discussing the hydrogen-bonded structure of liquid acetic acid, it is necessary to consider both the cis and the trans conformation of the carboxyl group (Figure 1).[18] The cis conformation has a dipole moment of ~1.4 D, which makes an angle of 112° with respect to the OH-bond direction. The trans conformation has a dipole moment of ~3.9 D, which is nearly parallel to the OH-bond direction. The two conformations generate two families of models for the solvation complexes.

The models to be considered will be called monodentate-to-cation (Figures 1a, 1b, and 1b′), monodentate-to-anion (Figures 1c and 1d), and bidentate (Figures 1e and 1f). In the monodentate-to-cation models, the solvent molecule acts as a ligand. In the monodentate-to-anion models, the solvent molecule acts as a hydrogen-bond donor. In the bidentate model involving *cis*-AcOH, the structure is cyclic. The bidentate model involving *trans*-AcOH corresponds to a solvent-separated ion pair.

As for any process involving ring formation, the cyclic bidentate complex involving *cis*-AcOH will form only if certain geometrical requirements are met. As indicated in Figure 2, the directions of preferred coordination are roughly parallel, approaching each other only slightly. Hence the distance between the two points of van der Waals contact, 2.8 ± 0.1 Å according to measurements using CPK space-filling molecular models, should match the distance between the binding sites in the ion pairs. For simple ion pairs such as the alkali halides, the latter distance would be essentially equal to the distance between the ionic centers. Hence the geometrical requirements for cyclic bidentate complex formation will be most nearly met if the interionic distance in the alkali halide ion pair is ca. 2.8 Å.

Vector diagrams of the dipole orientations of μ_1 and μ_2 in the various models are indicated in Figure 3. These diagrams neglect the creation of induced moments by mutual polarization, which would normally reduce the dipole moment of the solvation complex. According to the vector diagrams, we expect $\mu_{2,\mathrm{solv}}$ to be greater than μ_2 for the models in Figures 1a, 1b, and 1d. (See also Figure 1.) We expect $\mu_{2,\mathrm{solv}}$ to be less than μ_2 for the models in Figures 1e and (probably) 1c. For the solvent-separated ion pair in Figure 1f, the distance between the ionic centers is greatly increased. Hence a greatly enlarged vector $\mu_{M^+X^-}$ takes the place of μ_2, and we expect $\mu_{2,\mathrm{solv}}$ to be greater than μ_2 even though the directions of μ_1 and $\mu_{M^+X^-}$ roughly oppose each other.

On the basis of these considerations, if $\mu_{2,\mathrm{solv}} > \mu_2$, there are numerous models that could fit. On the other hand, if $\mu_{2,\mathrm{solv}}$ is about 1-2 D less than μ_2, then of the models that have been considered, the cyclic bidentate model e is the only one that will fit. If at the same time the geometrical requirements for ring formation are met by the ion pair, then the cyclic bidentate model is strongly indicated.

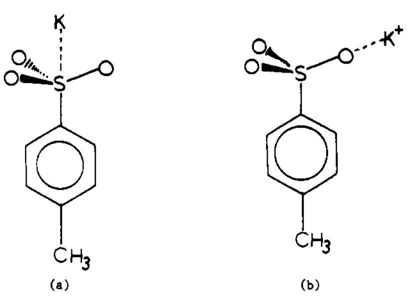

Figure 4. Plausible models of ion-pair structure for potassium *p*-toluenesulfonate: (a) axial structure, (b) corner structure.

Structure of Solvation Complexes. For the alkali halides listed in Table III, interionic distance in the isolated ion pair is 2.02 Å for LiCl, 2.67 Å for KCl, and 2.82 Å for KBr.[19] The latter values are close to the estimated 2.8 ± 0.1 Å distance that is considered optimum for cyclic bidentate solvation, and we note that $\mu_{2,\mathrm{solv}}$ is appropriately less than μ_2 by 1-2 D. We infer that the solvation complexes of KCl and KBr have structures similar to that modeled in Figure 1e.

On the other hand, for LiCl the interionic distance is too small for strain-free cyclic bidentate solvation. At the same time, the Li^+ ion, owing to its small size and high charge density, is a strong Lewis acid toward oxygen bases. Since $\mu_{2,\mathrm{solv}}$ for LiCl is greater than μ_2 by 1-2 D, we believe that the monodentate-to-cation model 1a is indicated. The model in Figure 1b is less probable, owing to the high μ_1 for *t*-AcOH.

For *unsolvated* KTs in previous work,[20] we considered two kinds of ion-pair structure, shown in Figure 4. The axial structure in Figure 4a has a predicted dipole moment of ~5 D, which is in good agreement with the experimental $\mu_2 = 4.8$ D in octanoic acid.[20] The corner structure in Figure 4b has a predicted $\mu_2 \sim 10$ D. For KTs in acetic acid, as shown in Table III, $\mu_{2,\mathrm{solv}} = 8.6$ D for $m = 1$. This result can be explained by two different kinds of solvated structure. If the basic axial structure in Figure 4a remains intact (by analogy with Crown complexes of KTs[17]), then the large enhancement of μ_2 owing to solvation requires solvation by *trans*-AcOH, according to the models in Figures 1b or 1b′. Alternatively, the ion pair could rearrange to the polar corner structure in Figure 4b, which then becomes solvated according to the cyclic bidentate model in Figure 1e. It is relevant in this connection that the nearest-neighbor K^+O^- distance in potassium sulfonate crystals is 2.8-3.2 Å. According to Figure 2, 2.8 ± 0.1 Å would be the optimum distance for bidentate cyclic solvation. It is also relevant that $\mu_{2,\mathrm{solv}}$ is 1-2 D less than $\mu_2 \sim 10$ D predicted for the polar corner structure in Figure 4b.

Regarding the structure of solvated *p*-toluidinium *p*-toluenesulfonate, it is clear from the large enhancement of the dipole moment that solvation plays a prominent role. In this case the models for cation solvation are different from those of Figure 1 because the cation now can function as hydrogen-bond donor. We prefer not to speculate about detailed structures until further work has been done.

References and Notes

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