

Table VI. Vaporization Heats of Azo Compounds, kcal mol<sup>-1</sup>

Compound	$\Delta H_v$ (uv)	$\Delta H_v$ (other)
Azoisopropane (1)	8.63	8.33, <sup>a</sup> 9.00 <sup>b</sup>
Azo- <i>n</i> -propane (2)	9.45	9.82 <sup>a</sup>
Azo- <i>tert</i> -butane (3)	9.47	7.81 <sup>b</sup>
2,3-Diazabicyclo[2.2.1]heptene-2 (4)	10.5	10.0, <sup>b</sup> 10.6 <sup>c</sup>
1,4-Dimethyl-2,3-diazabicyclo-[2.2.2]octene-2 (5)	16.70	

<sup>a</sup> Reference 13. <sup>b</sup> Determined in this laboratory using a modified isoteniscope. <sup>c</sup> C. Steel, unpublished result.

higher temperatures. An alternative explanation would say that the apparent curve is actually two straight lines and that a solid phase transition occurs at their intersection with a  $\Delta H$  of about 1.3 kcal mol<sup>-1</sup>. Despite the problem with 4, the average value of  $\Delta H_v$

does not differ greatly from the other determinations as shown in Table VI.

The heat of vaporization apparatus consisted of a quartz cell connected *via* a graded seal and sealing constriction to a 10/30 joint. After the compound was degassed and sealed in the cell under high vacuum, the cell was placed into a thermostated silicone oil bath fitted with quartz end windows. The whole assembly, which had a volume of about 200 ml, was placed in the cell compartment of a Cary 17 spectrometer. The temperature was regulated by a Bayley Controller and monitored by a thermistor and wheatstone bridge. Temperature control was better than 0.03°.

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## Molecular Structure of Ion Pairs from Electric Dipole Moments. I. Potassium *p*-Toluenesulfonate and Lithium Chloride in Octanoic Acid<sup>1</sup>

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**Abstract:** Measurements of the permittivity of dilute solutions in octanoic acid at 25° led to the following electric dipole moments: for LiCl ion pairs,  $\mu$  6.78 D (as compared with 7.12 D in the gas phase); for potassium *p*-toluenesulfonate (KTs) ion pairs,  $\mu$  4.8 D. It was found that  $2\text{LiCl} \rightleftharpoons (\text{LiCl})_2$ ;  $K = 183 \pm 20$ ;  $\mu$  for  $(\text{LiCl})_2 \sim 0.0$ . Analysis of the dipole moment of KTs establishes a symmetrical structure in which the K<sup>+</sup> ion sits on, or very near, the symmetry axis of the Ts<sup>-</sup> ion, adjacent to the plane defined by the oxygen atoms. In carrying out this analysis, the noncentric tosylate ion is treated as a point dipole superposed on a point charge and the position of this *electric center* is precisely defined. The polarizability is divided into two parts which are treated as point polarizabilities, one of which is located at the electric center. The K-O distance is evaluated as 3.15 Å.

In spite of the importance of ion pairing in the chemistry of electrolytic solutions,<sup>2-4</sup> relatively little is known about the molecular structure of the ion pairs. For ion pairs involving radical anions, it is clear from esr spectra that the cation attaches itself to the anion at specific sites.<sup>4,5</sup> For ion pairs formed from ions with stable electron configurations, it is often assumed that the binding takes place so as to bring the centers of ionic charge to a closest approach.<sup>2,3,6</sup> For ions such as Li<sup>+</sup>, Cl<sup>-</sup>, (CH<sub>3</sub>)<sub>4</sub>N<sup>+</sup>, or ClO<sub>4</sub><sup>-</sup>, which have centric charge distributions, the center of ionic charge is well defined by symmetry. However, for unsymmetrical ions such as anilinium<sup>+</sup> or *p*-toluenesulfonate<sup>-</sup> (Ts<sup>-</sup>), the position of the center of charge is open to some ambiguity. One would like to choose the position so that the electric field of the ion is that of an ionic charge

superposed on a dipole of predictable magnitude and direction. (Electric moments higher than the dipole moment will be neglected.) If such a choice were objectively possible, then the measured dipole vector for the ion pair, in combination with the dipole vectors of the constituent ions, would enable us to find the radius vector joining the centers of ionic charge and thus to deduce the molecular structure of the ion pair.

**LiCl in Octanoic Acid.** Specifically, we have measured electric dipole moments for LiCl and KTs in octanoic acid. The latter solvent was chosen because of its relatively good solvent action for electrolytes, coupled with a low dielectric permittivity ( $\epsilon$  2.48 at 25°). LiCl was chosen to provide a control experiment. The dipole moment of LiCl in the gas phase is 7.12 D.<sup>7,8</sup> Our experimental result in octanoic acid, calculated according to Onsager's theory,<sup>9,10</sup> is 6.78 D. The reasonable agreement between the two values indicates that in spite of the hydrogen-bonded solvent structure, accurate dipole moments for ion pairs can

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

(2) G. H. Nancollas, "Interactions in Electrolyte Solutions," Elsevier, Amsterdam, 1966.

(3) C. W. Davies, "Ion Association," Butterworths, Washington, D. C., 1962.

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

(5) A. Hudson and G. R. Luckhurst, *Chem. Rev.*, **69**, 191 (1969).

(6) R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience, New York, N. Y., 1959.

(7) A. J. Hebert, R. W. Breivogel, Jr., and K. Street, Jr., *J. Chem. Phys.*, **41**, 2368 (1964).

(8) A. J. Hebert, F. J. Lovas, C. A. Melendres, C. D. Hollowell, T. L. Story, Jr., and K. Street, Jr., *J. Chem. Phys.*, **48**, 2824 (1968).

(9) L. Onsager, *J. Amer. Chem. Soc.*, **58**, 1486 (1936).

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

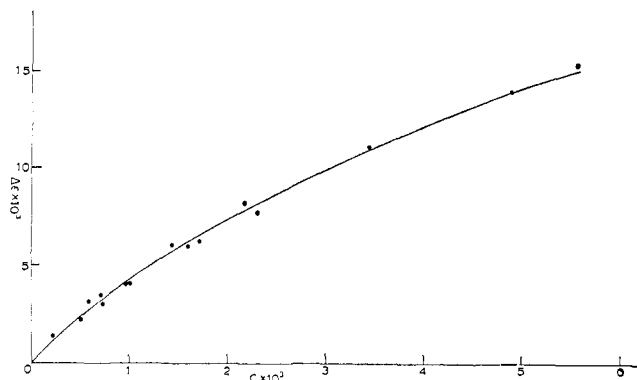


Figure 1. Dielectric increment,  $\Delta\epsilon$ , as a function of LiCl concentration,  $c$ , in octanoic acid. Circles represent the experimental points. Solid line represents calculated  $\Delta\epsilon$  as a function of  $c$  according to the scheme  $2\text{LiCl} \rightleftharpoons (\text{LiCl})_2$  ( $K = 183$ ).

be obtained. Evidently, the LiCl ion pairs in octanoic acid are not "freezing" solvent dipoles and remain structurally very similar to LiCl molecules in the gas phase.

As shown in Figure 1, the plot of  $\epsilon$  vs. LiCl concentration shows downward curvature, suggesting that the polar LiCl ion pairs exist in equilibrium with less polar ion-pair aggregates. The data are consistent with the model,  $2\text{LiCl} \rightleftharpoons (\text{LiCl})_2$ . The dipole moment of the  $(\text{LiCl})_2$  double ion pairs is close to zero, and the association constant is  $183 \pm 20 M^{-1}$ .

**The Structure of Potassium *p*-Toluenesulfonate.** For KT's, the dipole moment determined in octanoic acid is 4.81 D. In analyzing this result, we shall assume that dipole correlation effects, *i.e.*, "freezing" of solvent dipoles around the ion pairs, may be neglected.

We begin by comparing the experimental dipole moment with predictions based on the dipole moments of model substrates. Figure 2 shows two plausible structures for the ion pairs of KT's: structure a is unsymmetrical, with the cation interacting strongly with only one of the three oxygen atoms; structure b is symmetrical, with the cation interacting equally with all three oxygen atoms. Other structures are of course conceivable; for instance, structures in which a cation interacts strongly with two oxygen atoms are often found in crystalline sulfates.<sup>11</sup> But for the present purpose, structures a and b will suffice.

The experimental dipole moment  $\mu_{\text{IP}}$  may be resolved into a moment  $\mu_-$  due to the *p*-toluenesulfonate ion, plus a moment  $\mu_{q,\alpha}$  due to the ionic charges and their mutual polarization. The value of  $\mu_-$  may be estimated with good accuracy from the experimental dipole moment, 5.04 D, of *p*-toluenesulfonyl chloride<sup>12</sup> and a small correction (0.5 D, added vectorially) to account for the electronegativity difference between oxygen and chlorine.<sup>13</sup> The result is  $\mu_- = 5.2$  D, pointing from the center of the oxygen atoms toward the sulfur atom.<sup>14</sup>

The magnitude of  $\mu_{q,\alpha}$  cannot be estimated precisely because good empirical models do not exist. However,

(11) R. W. G. Wyckoff, "Crystal Structures," Vol. 3, 2nd ed, Interscience, New York, N. Y., 1965.

(12) A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman, San Francisco, Calif., 1963.

(13) L. Pauling, "The Nature of Chemical Bond," Cornell University Press, Ithaca, N. Y., 1944.

(14) We are using the physicists' convention in which the dipole vector points from the negative pole to the positive pole.

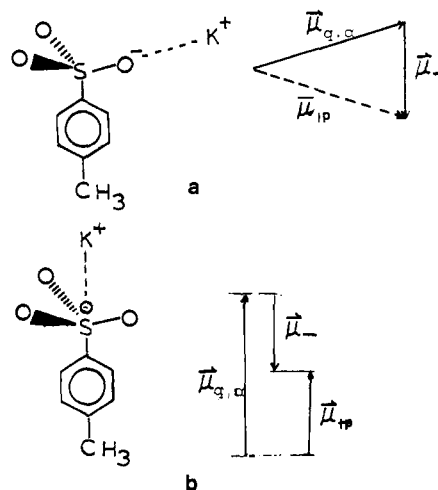


Figure 2. Plausible structures and the corresponding dipole moment diagrams for potassium *p*-toluenesulfonate ion pairs.

one would expect that  $\mu_{q,\alpha}$  for KT's is of similar magnitude to the dipole moments of KCl (10.3 D) and KBr (10.4 D).<sup>7,8</sup> If this be granted, structure a in Figure 2 must be ruled out because the vector equation,  $\mu_{q,\alpha} = \mu_{\text{IP}} - \mu_-$ , cannot be solved with any acceptable value of  $\mu_{q,\alpha}$ . Indeed, were it not for the possibility of error in  $\mu_{\text{IP}}$  and  $\mu_-$ , the equation would have no solution at all, since it implies that  $\mu_{\text{IP}}$  for structure a cannot be less than 4.90 D (when  $\mu_{q,\alpha} = 1.75$  D), while the experimental value is 4.81 D. Allowing for possible error, values of  $\mu_{q,\alpha}$  as high as 2.5 D can be accommodated, but this figure is clearly less than the expected magnitude of 10 D.

On the other hand, if we assume structure b,  $\mu_-$  and  $\mu_{q,\alpha}$  will oppose each other and  $\mu_{q,\alpha}$  is evaluated as 10.0 D, which is precisely the expected magnitude. There is little doubt, therefore, that structure b is essentially correct. Most likely, the potassium ion sits precisely on the symmetry axis of the *p*-toluenesulfonate ion. However, structures in which it sits slightly off the axis are also possible.

**The Electrical Centers of Noncentric Ions.** The foregoing suggests that simple, naive notions involving the vector addition of model dipoles may be sufficient to establish the structure of ion pairs within useful limits. In the following, we shall try to give a more rigorous treatment.

Böttcher<sup>15</sup> has suggested a model in which the charge distribution and polarizability of the real ion are represented as a single charge, dipole, and isotropic polarizability which are all collapsed onto a single point. We shall call this point the *electrical center* of the ion. An ion pair is represented as a pair of such electrical centers interacting at the appropriate distance. Because the polarizability of each ion is represented as a point polarizability, the electrical centers of the ions in the ion pair are identical with those in the free ions.

Böttcher's model has been tested for ion pairs formed from ions with centric charge distributions and is remarkably successful at reproducing experimental dipole moments for such ion pairs as LiCl, *n*-Bu<sub>4</sub>NBr, and *n*-Bu<sub>4</sub>NClO<sub>4</sub>.<sup>16,17</sup>

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

(16) K. Bauge and J. W. Smith, *J. Chem. Soc.*, 4244 (1964).

In applying Böttcher's model, there is a fundamental ambiguity concerning the dipole moment of the ionic charge distribution. For an uncharged molecule, the dipole moment is a constant characteristic of the molecule, but for an ion the dipole moment varies with the origin of the coordinate system, that is, with the site chosen for the electrical center.<sup>15, 17, 18</sup> For instance, the dipole moment of a centric ion such as  $n\text{-Bu}_4\text{N}^+$  is zero only if the electrical center is placed at the geometrical center of the ion, which is of course the site that one would naturally choose.

We wish to place the electrical center of *any* ion, be it centric or noncentric, such that the dipole moment of the ionic charge distribution is predictable from dipole moments of similarly constituted uncharged molecules. That is, we wish to make  $\mathbf{u}_{\text{ion}}$  be the dipole moment of a hypothetical molecule, identical with the ion, from which the ionic charge has been removed.

Let the ion be represented as a system of localized point charges  $q_i$ , which may be partial charges, some of which are positive and others negative. Let  $\mathbf{r}_i$  denote the radius vector from the electrical center to  $q_i$ . The center of positive charge is then defined by eq 1, in which  $Q_p$  is the sum total of the positive point charges and  $\mathbf{r}_p$  is the radius vector from the electrical center to the center of positive charge. The center of negative charge is defined analogously by eq 2. The ionic

$$\sum_{\text{pos}} q_i \mathbf{r}_i = \mathbf{r}_p \sum_{\text{pos}} q_i = \mathbf{r}_p Q_p \quad (1)$$

$$\sum_{\text{neg}} q_i \mathbf{r}_i = \mathbf{r}_n \sum_{\text{neg}} q_i = \mathbf{r}_n Q_n \quad (2)$$

charge is  $Q_p + Q_n$ .

We wish to place the center of charge so that for a cation  $\mathbf{u}_+$  is defined by eq 3 and for an anion  $\mathbf{u}_-$  is defined by eq 4. Reflection will show that this is

$$\mathbf{u}_+ = |Q_n|(\mathbf{r}_p - \mathbf{r}_n) \quad (3)$$

$$\mathbf{u}_- = |Q_p|(\mathbf{r}_p - \mathbf{r}_n) \quad (4)$$

precisely the way one would define the dipole moment if the charge were absent. A necessary and sufficient condition is that the electrical potential ( $\varphi_+$  due to a cation or  $\varphi_-$  due to an anion) at an arbitrary point P at some distance  $r$  from the electrical center be given by eq 5. The geometry of this problem is shown in

$$\varphi_+ = \frac{Q_p + Q_n}{r} + \frac{|Q_n|(r_p + r_n) \cos \theta}{r^2} \quad r_p = 0 \quad (5a)$$

$$\varphi_- = \frac{Q_p + Q_n}{r} + \frac{|Q_p|(r_p + r_n) \cos \theta}{r^2} \quad r_n = 0 \quad (5b)$$

Figure 3, and the solution is derived in the Appendix. The result is as follows: for a cation, the electrical center must be placed at the center of positive charge; for an anion, it must be placed at the center of negative charge. This result is valid regardless of the magnitudes of  $Q_p$  and  $Q_n$  and of the manner in which the point charges are dispersed in the ion.

(17) E. Grunwald, S. Highsmith, and T.-P. I, "Ions and Ion Pairs in Organic Reactions," Vol. 2, M. Szwarc, Ed., Wiley-Interscience, New York, N. Y., 1974, Chapter 5.

(18) H. Fröhlich, "Theory of Dielectrics," Oxford University Press, London, 1949.

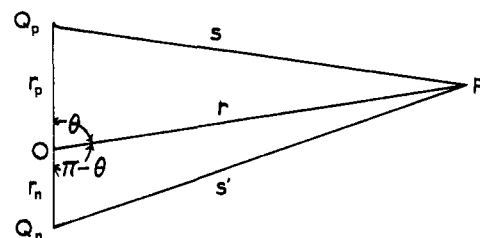


Figure 3. Electrical center of an ion.

The dipole moments  $\mathbf{u}_+$  and  $\mathbf{u}_-$  as defined in (3) and (4) can be predicted from known moments of uncharged model compounds, provided the following condition is satisfied. The ionic charge, located at the electrical center, will polarize the ion. Since this polarization is absent in the uncharged model compound, the vector sum of charge-induced moments in the ion must be zero or very small. In Böttcher's model this requirement is met by hypothesis, since the polarizability is treated as a point located at the electrical center. Noncentric real ions are not so accommodating; we shall allow for this complication by introducing a suitable second point polarizability located at a physically plausible site off the electrical center.

In free ions, charge-induced dipole interactions are very important.<sup>19</sup> However, in ion pairs the induced moments are distinctly smaller, and it is a reasonable first approximation, in locating the electrical center, to neglect them.

Thus for *p*-toluenesulfonate ion, the electrical center will lie at the center of negative charge. Because each oxygen atom in the  $\text{SO}_3^-$  group has a formal charge of  $-1$ , the center of negative charge will be determined largely by the oxygen atoms and will lie on the central axis of the ion, approximately in the plane defined by the three oxygen atoms. (Induced moments will tend to displace the electrical center toward the geometrical center.) The dipole vector  $\mathbf{u}_-$  is conveniently estimated from the dipole moment of *p*-toluenesulfonyl chloride, as described in the preceding section.

The preceding analysis suggests that the binding site of the ions in an ion pair can be modified merely by the introduction of a polar substituent, because such a substituent will displace the electrical center of the given ion. For example, the introduction of a *p*-nitro group in the benzenesulfonate ion will shift the electrical center from near the plane of the sulfonate oxygen atoms into the benzene ring. It is therefore conceivable that the ion pairs of potassium *p*-nitrobenzenesulfonate will have a structure in which the potassium ion is close to only two rather than three sulfonate oxygen atoms and sits, as nearly as possible, over the plane of the benzene ring. Research along these lines is currently in progress.

**Dipole Analysis for Potassium *p*-Toluenesulfonate.** In this section we wish to apply a modified Böttcher's model in order to calculate the distance between the electrical centers of  $\text{K}^+$  and  $\text{Ts}^-$  in KTs ion pairs. The result will be compared with K-O and K-S distances determined by X-ray crystallography in potassium ethylsulfate<sup>20</sup> and potassium  $\alpha$ -hydroxybenzyl-

(19) See, for example, J. I. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, **92**, 5986 (1970).

(20) (a) J. A. J. Jarviz, *Acta Crystallogr.*, **6**, 327 (1953); (b) M. R. Truter, *ibid.*, **11**, 680 (1958).

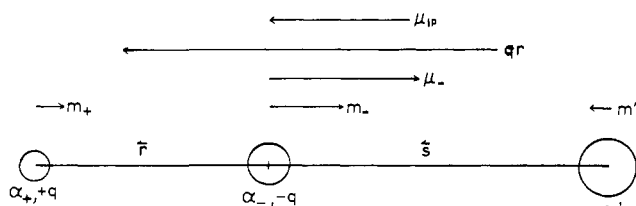


Figure 4. Vector diagram of electric moments for potassium *p*-toluenesulfonate ion pairs.

sulfonate,  $\text{KO}_3\text{SCH}(\text{OH})\text{C}_6\text{H}_5$ .<sup>21</sup> These are the most closely related crystal structures available.<sup>11</sup>

The specific model used is shown in Figure 4. The potassium ion is represented as a polarizable point charge ( $+q$ ,  $\alpha_+$ ). The  $\text{Ts}^-$  ion is represented as an electrical center ( $-q$ ,  $\alpha_-$ ,  $\mathbf{u}_-$ ) and an auxiliary point polarizability ( $\alpha'$ ). The vector  $\mathbf{r}$  denotes the distance between the electrical centers, and the vector  $\mathbf{s}$  denotes the distance between  $\alpha_-$  and  $\alpha'$ . The positive direction is from the negative to the positive center.  $\mathbf{m}_+$ ,  $\mathbf{m}_-$ , and  $\mathbf{m}'$  denote the induced moments. According to Figure 4, the dipole moment of the ion pair is given by eq 6. Note that all vectors are parallel. In the

$$\mathbf{u}_{\text{IP}} = q\mathbf{r} + \mathbf{u}_- + \mathbf{m}_+ + \mathbf{m}_- + \mathbf{m}' \quad (6)$$

following, explicit vector notation will therefore be dropped; positive values will denote that the given dipole is pointing in the positive  $\mathbf{r}$  direction.

Following Böttcher,<sup>22</sup> the induced moments are given by eq 7. The expression for  $\alpha'$ , eq 7c, does not

$$m_+ = \alpha_+ \left[ \frac{-q}{r^2} + \frac{2\mathbf{u}_-}{r^3} + \frac{2m_-}{r^3} + \frac{2m'}{(r+s)^3} \right] \quad (7a)$$

$$m_- = \alpha_- \left[ \frac{-q}{r^2} + \frac{2m_+}{r^3} + \frac{2m'}{s^3} \right] \quad (7b)$$

$$m' = \alpha' \left[ \frac{q}{s^2} - \frac{q}{(r+s)^2} + \frac{2m_+}{(r+s)^3} + \frac{2m}{s^3} \right] \quad (7c)$$

include a term for interaction with  $\mathbf{u}_-$  because the estimation of  $\mathbf{u}_-$  by means of uncharged model compounds automatically includes self-polarization effects that do not involve the ionic charge.

In solving eq 7 for  $\mathbf{r}$ , the following numerical data were used:  $q = 4.803 \times 10^{-10}$  esu; for  $\text{K}^+$ ,  $\alpha_+ = 1.05 (\text{\AA})^3$ ; <sup>23</sup> for  $\text{Ts}^-$ ,  $\mu_- = -5.20$  D (estimated from the dipole moment of *p*-toluenesulfonyl chloride, as described before). Because of the elongated shape of the  $\text{Ts}^-$  ion, the total polarizability  $[16.84 (\text{\AA})^3]$ <sup>24</sup> was separated into two point polarizabilities. At the electrical center,  $\alpha_-$  was taken to be  $5.80 (\text{\AA})^3$ , which is the polarizability of sulfate ion.<sup>23</sup> The remainder of the polarizability,  $\alpha' = 11.04 (\text{\AA})^3$ , was placed at a distance  $s = 4.58 \text{\AA}$  from the electrical center, intended to be half-way between the 1-carbon atom of the benzene ring and the center of the hydrogen atoms of the 4-methyl group.

The results of the calculation which fit the experimental dipole moment of 4.81 D are as follows:  $r =$

(21) T. Kuroda, T. Ashida, Y. Sasada, and M. Kakudo, *Bull. Chem. Soc. Jap.*, **40**, 1377 (1967).

(22) Reference 15, Chapter 5, Section 26.

(23) K. Fajans and G. Joos, *Z. Phys.*, **23**, 1 (1924).

(24) B. J. Berkowitz and E. Grunwald, *J. Amer. Chem. Soc.*, **83**, 2956 (1961).

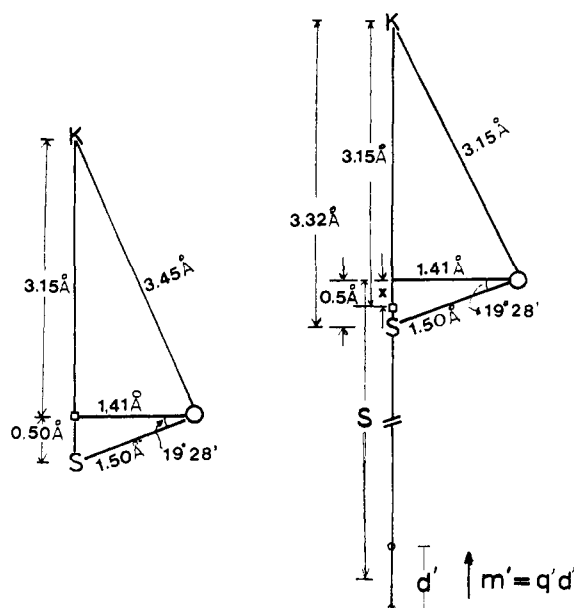


Figure 5. Interatomic and interionic distances for potassium *p*-toluenesulfonate ion pairs: (□) represents the electrical center.

$3.15 \text{\AA}$ ;  $qr = 12.88$  D;  $m_+ = -0.96$  D;  $m_- = -2.65$  D;  $m' = 0.74$  D;  $\mu_- = -5.20$  D.

For  $\text{K}^+$ , the electrical center is at the geometrical center of the ion. For  $\text{Ts}^-$ , the electrical center is, in first approximation, at the center of the triangle defined by the three oxygen atoms. Adopting an S-O bond distance of  $1.50 \text{\AA}$ <sup>11</sup> and tetrahedral bond directions about sulfur, and introducing  $r = 3.15 \text{\AA}$ , we arrive, in first approximation, at an S-K distance of  $3.65 \text{\AA}$  and an O-K distance  $3.45 \text{\AA}$  in the  $\text{KTs}^-$  ion pair (Figure 5a).

To a better approximation, we must allow for the induced moment  $\mathbf{m}$  (Figure 4), whose effect will be to move the center of negative charge (and hence the electrical center) toward the benzene ring. Let the induced dipole be represented as a pair of induced monopoles  $q'$  separated by a distance  $d'$ . Then  $\mathbf{m}' = q'd'$ , and the distance  $x$  between the center of the oxygen atoms ( $(-3)4.803 \times 10^{-10}$  esu of charge) and the center of negative charge is given by eq 8.

$$(3)4.803 \times 10^{-10}x = q'(s + (d'/2)) \quad (8)$$

Unfortunately, the magnitude of  $d'$  can be estimated only very approximately. The polarizability  $\alpha'$  is due mainly to the benzene ring and hence involves some delocalized electrons. However, the major contribution to  $\alpha'$  is made by localized electrons. It seems plausible to assume that the mean charge displacement  $d'$  is of the same magnitude as the covalent radius of a carbon atom in the benzene ring, or  $0.70 \text{\AA}$ .<sup>13</sup> Thus  $q' = 1.43 \times 10^8 m'$ . Substituting in (8), and letting  $(s + (d'/2)) \approx s = 4.58 \text{\AA}$ , we find that  $x$  is related to  $m'$  according to (9).

$$x (\text{\AA}) = 0.45m' (\text{D}) \quad (9)$$

find that  $x = 0.33 \text{\AA}$ . Thus, as shown in Figure 5b, the S-K distance is  $3.32 \text{\AA}$  and the O-K distance is  $3.15 \text{\AA}$ . We believe that these values are as close to the "true" distances as the present approach permits. For comparison, in crystalline  $\text{KO}_3\text{SOEt}$ , the shortest S-K distance is  $3.60 \text{\AA}$  and the near-neighbor O-K distances range from  $2.80$  to  $3.20 \text{\AA}$ .<sup>20</sup> In crystalline  $\text{KO}_3\text{SCH}$

(OH)C<sub>6</sub>H<sub>5</sub>, the shortest S–K distance is 3.40 Å and the near-neighbor O–K distances range from 2.73 to 3.27 Å.<sup>21</sup> The O–K distances in these compounds are more relevant because the K<sup>+</sup> ion does not sit on the three-fold axis of the SO<sub>3</sub> group in these crystals. The agreement of these distances with the O–K distance of 3.15 Å deduced for KT<sub>2</sub> ion pairs from the dipole moment is quite satisfactory.

### Concluding Remarks

It seems fair to say that no method of structure determination is truly exact because all methods involve theoretical models with subjective assumptions. This is particularly true for methods involving ions and ion pairs in liquid solution where the quantitative determination of structure and size is beset with difficulties.<sup>25</sup> In view of this, we believe that the approach we have outlined, in spite of its subjective assumptions, is scientifically sound and pragmatically successful.

### Experimental Section

**Materials.** Reagent grade lithium chloride was recrystallized twice from distilled water and dried *in vacuo* at 100°. Potassium *p*-toluenesulfonate was prepared and purified as described by Crampton.<sup>26</sup> Octanoic acid was purified by collecting a center portion during vacuum distillation with a head temperature of about 100°. Repeated crystallization was not sufficient to purify octanoic acid as shown by the appearance of an absorption peak at 248 nm when LiCl was dissolved in it. Solutions of LiCl in distilled solvent showed no such absorption; thus it was used as a criterion of purity. Relevant physical properties of octanoic acid at 25° are as follows:  $d = 0.9066$ ;  $n_D = 1.4261$ ;<sup>27</sup> and  $\epsilon_0 = 2.4812$ .

**Measurements.** Solutions were prepared with special care to minimize access of atmospheric moisture, and handled and stored in a drybox. The salts were weighed out on a microbalance with an accuracy of better than 0.25%. The complex admittance of the solutions  $Y = G + j\omega C$  was measured with a General Radio type 1615 A transformer ratio arm bridge and guarded three-terminal cells. Full details have been described in a previous paper from this laboratory.<sup>10</sup> The conductance  $G$  was in the range 1–8 nmho for different solvent batches and did not increase appreciably upon addition of LiCl or KT<sub>2</sub>. The capacitance  $C$  was about 45 pF and could be measured with a precision of  $\pm 0.002$  pF, which corresponds to  $\pm 1 \times 10^{-4}$  in  $\epsilon$ . (The air capacitance of the cells was about 18 pF.) Values of  $\epsilon_0$  for the pure solvent, determined in four separate cells that were equilibrated side by side in the dry nitrogen thermostat, showed a standard deviation of  $4 \times 10^{-4}$ . We believe that this figure, rather than  $1 \times 10^{-4}$ , is a realistic estimate of the accuracy of  $\Delta\epsilon$  ( $=\epsilon_{\text{solution}} - \epsilon_{\text{solvent}}$ ) for the salt solutions. The magnitudes of  $\Delta\epsilon$  ranged from 0.001 to 0.02.

We estimate from the conductance that the concentration of free ions is less than  $5 \times 10^{-9}$  M. According to the Debye–Falkenhagen theory,<sup>28,29</sup> the contribution of the free ions to  $\epsilon$  is correspondingly less than  $14 \times 10^{-4}$  but probably greater than the estimated accuracy of  $4 \times 10^{-4}$ . On the other hand, the contribution of the free ions to  $\Delta\epsilon$  is probably less than  $4 \times 10^{-4}$ , and we decided not to take it into account.

**Results for LiCl.** Measurements were made on 14 solutions in which the LiCl concentration ranged from 0.2 to 6 mM. The results are plotted in Figure 1; it can be seen that the relationship of  $\Delta\epsilon$  to  $c$  shows distinct downward curvature. Following previous workers,<sup>18,30</sup> we assumed that the LiCl ion pairs exist in equilibrium with nonpolar or less polar double ion pairs (eq 10–12). On



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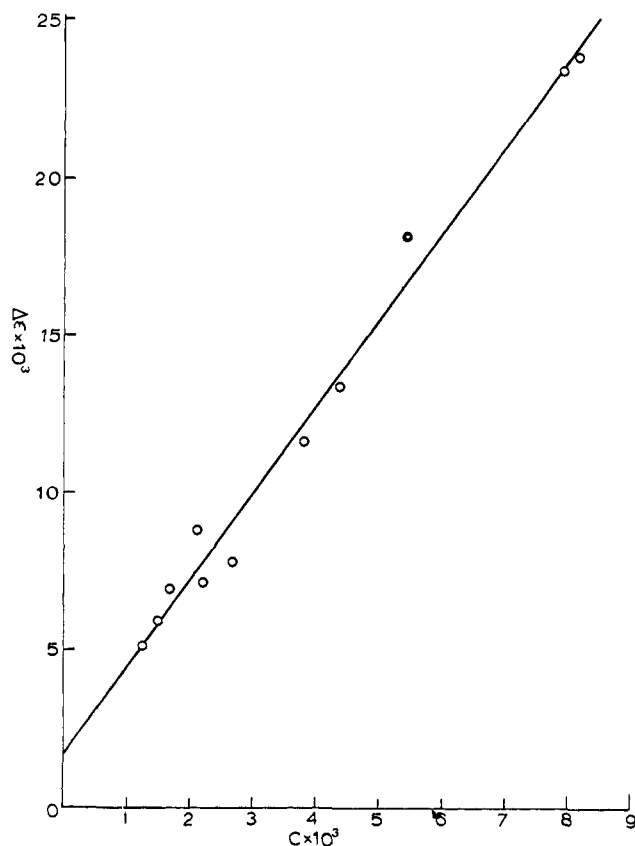


Figure 6. Dielectric increment,  $\Delta\epsilon$ , as a function of KT<sub>2</sub> concentration,  $c$ , in octanoic acid. Open circles represent the experimental points. The solid line represents the least-squares line.

$$K = c_2/c_1^2 \quad c_1 + 2c_2 = c \quad (11)$$

$$\Delta\epsilon = S_1c_1 + S_2c_2 \quad (12)$$

fitting the data to this scheme by nonlinear least-squares methods we obtained the following parameters:  $S_1 = 5.47 \pm 0.05$ ;  $S_2 = 0.0$ ;  $K = 183 \pm 20$ ; standard error of fit of  $\Delta\epsilon = 3 \times 10^{-4}$ . The fit is well within the experimental error of  $4 \times 10^{-4}$ .

**Results for KT<sub>2</sub>.** Values of  $\Delta\epsilon$  vs.  $c$  clearly fell on a straight line. However, the linear relationship had a small positive intercept, as shown in Figure 6. Curve fitting by the method of least squares gave the equation,  $\Delta\epsilon = (1.7 \pm 0.5) \times 10^{-3} + (2.74 \pm 0.11)c$ , with a standard error of fit of  $9 \times 10^{-4}$ . Attempts to fit the data to the scheme of eq 10–12 or to other schemes that require the data to pass through the origin led to worse fit. We therefore concluded that the solute exists simply in the form of KT<sub>2</sub> ion pairs whose dipole moment we computed from the slope.

Linear relationships with unexplained nonzero intercepts are not without precedent for solutions in nonaqueous solvents. In other work we noted that plots of  $\Delta\epsilon$  vs.  $c$  for *p*-nitrophenol and for dibenzo-crown-6 in octanoic acid likewise gave small positive intercepts. Maryott<sup>30</sup> similarly observed a small positive intercept for  $\Delta\epsilon$  vs.  $c$  of several ion pairs in benzene, and Kay, *et al.*,<sup>31</sup> observed a small positive intercept in the plot of the relative change in viscosity vs. concentration in methanol.

Returning to the data for KT<sub>2</sub>, because of the nonzero intercept the accuracy of the dipole moment may be lower than one would expect from the statistical error of the slope.

**Calculation of Dipole Moment.** Dipole moments were calculated from the slope, or *molar dielectric increment*  $S$ , according to Onsager's theory. Methods of calculation varying slightly in detail have been described by different workers.<sup>10,32–34</sup> We used

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method B of Grunwald and Effio.<sup>10</sup> As pointed out by these workers,<sup>16</sup> the Onsager theory is likely to give an accurate result for the dipole moment of the solute (subscript 2) in self-associated solvents (subscript 1) if  $\mu_2^2/V_2 \gg \mu_1^2/V_1$ , where  $V$  denotes the molar volume. This condition is satisfied in the present case.

$V_2$  and the molar refraction  $R_2$  used in the calculation were as follows: for LiCl,  $V_2 = 10.4 \text{ cm}^3/\text{mol}$  and  $R_2 = 9.37 \text{ cm}^3/\text{mol}$ ; for KTs,  $V_2 = 121.0 \text{ cm}^3/\text{mol}$  and  $R_2 = 46.34 \text{ cm}^3/\text{mol}$ . These values were measured in acetic acid.<sup>35</sup>

### Appendix

Refer to Figure 3. The electrical center 0 is placed at an arbitrary point joining the positive point charge  $Q_p$  to the negative point charge  $Q_n$ . We are interested in the potential  $\varphi$  at any point P. It is assumed that the distances  $s$ ,  $r$ ,  $s'$  are substantially greater than  $r_p$  and  $r_n$ . The potential  $\varphi$  is given by eq 13. On applying the law

$$\varphi = (Q_p/s) + (Q_n/s') \quad (13)$$

of cosines we evaluate  $s$  and  $s'$  according to eq 14. On

$$s = (r^2 + r_p^2 - 2rr_p \cos \theta)^{1/2} \quad (14a)$$

$$s' = (r^2 + r_n^2 + 2rr_n \cos \theta)^{1/2} \quad (14b)$$

expanding in power series and neglecting terms of

(35) L. E. Mayer and C. D. Brown, unpublished results, 1970.

order  $(r_p/r)^2$ ,  $(r_n/r)^2$ , and higher, we obtain eq 15. On

$$s^{-1} = r^{-1}(1 + (r_p/r) \cos \theta + \dots) \quad (15a)$$

$$(s')^{-1} = r^{-1}(1 - (r_n/r) \cos \theta + \dots) \quad (15b)$$

substituting these expressions in eq 13, we obtain eq 16.

$$\varphi = \frac{Q_p + Q_n}{r} + \frac{(Q_p r_p + |Q_n| r_n) \cos \theta}{r^2} \quad (16)$$

To obtain eq 5a for cations, we rewrite eq 16 in the form of eq 17a. It thus becomes clear that the electrical center must be placed so that  $r_p = 0$ . To obtain eq 5 for anions, we similarly write eq 17b and place the elec-

$$\varphi_+ = \frac{Q_p + Q_n}{r} + \frac{|Q_n|(r_p + r_n) \cos \theta}{r^2} + \frac{(Q_p - |Q_n|)r_p \cos \theta}{r^2} \quad (17a)$$

$$\varphi_- = \frac{Q_p + Q_n}{r} + \frac{Q_p(r_p + r_n) \cos \theta}{r^2} + \frac{(|Q_n| - Q_p)r_n \cos \theta}{r^2} \quad (17b)$$

trical center so that  $r_n = 0$ .

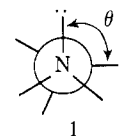
## Photoelectron Spectra of Hydrazines. III. Evidence for Similar Lone Pair-Lone Pair Dihedral Angles for Acyclic Hydrazines

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**Abstract:** The photoelectron spectra of 22 alkylated hydrazines (including six monoalkyl and nine tetraalkyl) having Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, and *t*-Bu alkyl substituents are reported. Calculations by the INDO method on the five methylated hydrazines, using a lone pair-lone pair dihedral angle ( $\theta$ ) of  $90^\circ$  correlate well with the observed IP's for these compounds (least squares (LS) line has standard deviation of 42 meV). Assuming  $\theta = 90^\circ$  for all compounds, and using a simple method to estimate the change in IP caused by replacement of methyl by another alkyl group, the plot of observed *vs.* calculated ( $\theta = 90^\circ$ ) IP for all the alkylhydrazines studied has a slope of 0.98 and an intercept of 0.15 eV, and the standard deviation is 78 meV. Since the calculations indicate a change of  $\geq 30$  meV for each degree change in  $\theta$  within  $\pm 30^\circ$  of the crossover point of the symmetric and antisymmetric lone pair MO's, it is argued that only rather small changes in  $\theta$  can be resulting from changes in alkyl substitution in these acyclic hydrazines.

The photoelectron spectra (pes) of hydrazines are of particular interest because of the presence of two "lone pair" orbitals on nitrogen, which would ionize at the same potential except for interactions of these orbitals with other orbitals and with each other. With adjacent lone pairs, one would expect the principal interaction to be the lone pair-lone pair interaction, which should be strongly dependent upon the dihedral angle between the lone pairs,  $\theta$  (see 1).<sup>1</sup> Both we<sup>2</sup> and Rademacher<sup>3</sup> have recently described pes of hydrazines



which demonstrate that this is the case. Rademacher proposed a method to evaluate the angle  $\theta$ , using the pes splitting  $\Delta$  ( $IP_2 - IP_1$ , where  $IP_1$  and  $IP_2$  are the first and second ionization potentials, attributable to "lone pair" ionizations).<sup>3</sup> To accurately describe the effects of conformation on the observed splittings, it is necessary to evaluate the magnitude of other effects, such as substitution pattern and changes in substituent groups, upon the pes. A convenient starting point for such an

(1) For a discussion of electron pair interactions in saturated molecules, see R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971).

(2) (a) S. F. Nelsen and J. M. Buschek, *J. Amer. Chem. Soc.*, **95**, 2011 (1973); (b) *ibid.*, **95**, 2013 (1973).

(3) P. Rademacher, *Angew. Chem.*, **85**, 410 (1973).