Interionic Structure of N-Ethyl-N,N-dimethylanilinium Benzenesulfonate Ion Pairs from Electric Dipole Moments¹

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Electric dipole moments are measured for N-ethyl-N,N-dimethylanilinium benzenesulfonate ion pairs with polar substituents in either phenyl ring. The solvent is octanoic acid ($\epsilon_0 = 2.46$). The interionic geometry is deduced by dipole vector analysis for ion pairs with 4-phenyl substituents, ring positions being numbered so that the NR_3^+ and SO_3^- groups are attached at 1-positions. Coordinate axes are defined as follows. The x axis is identified with the 1,4-phenyl axis in the anion, the positive x direction being taken from position 4 to 1. The y axis is defined so that the dipole vector μ_0' of the unsubstituted ion pair lies in the x,y plane. On that basis, the angle between the positive direction of μ_0' and the x axis is 42°. On the same basis, the 1,4-phenyl axis of the cation lies in the x,z plane, and the angle between the x axis and a line drawn from cation ring position 1 to 4 is 32°. Dipole vector analysis for the *m*-nitrobenzenesulfonate ion pair shows that rotation of the *m*-nitrophenyl ring about the x axis produces a nearly symmetrical or random angular distribution. The dielectric cells used in the present measurements employ an improved design.

The interionic geometry of ion pairs in solution has been studied by nuclear magnetic²⁻¹⁰ and electron spin^{11,12} resonance, by infrared,^{7,10} Raman,¹⁰ and fluorescence⁷ spectroscopy, and by analysis of electric dipole moments.^{13–15} The present work extends previous measurements¹⁴ of electric dipole moments (μ) in octanoic acid ($\epsilon_0 = 2.46$) for a series of substituted N-ethyl-N,N-dimethylanilinium benzenesulfonate ion pairs (Figure 1). In the earlier work,¹⁴ Y and X' were H, and X was a series of substituents with known dipole vectors. It was thus possible to determine, by dipole vector analysis, the angle θ between the dipole vector μ_0 in the unsubstituted ion pair and the 1,4-phenyl axis in the anion. The latter axis is a convenient reference because the charge distribution of the benzenesulfonate ion has, in addition to the negative charge, a dipole moment of 4.58 ± 0.1 D parallel to the phenyl axis (Figure 1).²

We now report data for a series of ion pairs in which both X and Y are variable. These data permit us to deduce the direction of the 1,4-phenyl axis in the cation relative to that in the anion. We also report the dipole moment of the m-nitrobenzenesulfonate ion pair (Figure 1, $X' = NO_2$). This permits us to deduce the average of the angular distribution of the phenyl plane in the anion about its 1,4 axis.

Results

Results are listed in Table I. The method of measurement is the same as before,¹⁴ but the dielectric-cell design was improved to make the cell more sturdy. The calculation of dipole moments followed previous practice.¹⁴

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TABLE I: Electric Dipole Moments (D) for N-Ethyl-N,N-dimethylanilinium Benzenesulfonate Ion Pairs in Octanoic Acid at 25.0 °C

Y	X	Χ′	$d\epsilon/dc_2$	μ _{IP}	μ_{Y}^{a}	μ _X ^b
Br	CH ₃	Н	$4.91 \pm 0.24^{\circ}$	6.51 ± 0.16	-2.1	-0.56
NO_2	Cl	Н	6.50 ± 0.17^{d}	7.46 ± 0.11	-4.39	1.69
CF_3	CH ₃	н	4.81 ± 0.25^{d}	6.46 ± 0.19	-2.96	-0.56
NO ₂	Br	н	5.68 ± 0.17^{d}	6.98 ± 0.10	-4.39	1.7
NO_2	CH_3	Н	4.60 ± 0.16	6.30 ± 0.09	-4.39	-0.56
Н	CH ₃	Н	7.13 ± 0.25 ^e	7.83 ± 0.16	-0.4	-0.56
Н	NO_2	Н	15.12 ± 0.24^{e}	11.36 ± 0.11	-0.4	3.99
н	Cl	Н	9.40 ± 0.18^{e}	8.96 ± 0.13	-0.4	1.69
Н	Н	NO_2	$12.31 \pm 0.33^{\circ}$	10.25 ± 0.15		

 ${}^{a}\mu_{Y}$ includes the cation dipole of -0.4 D, shown in Figure 1, and is positive if directed from N⁺ to Y. For the present substituents, $\mu_Y =$ $-0.4 - \mu_{C_6H_5Y}$. ${}^{b}\mu_X$ is positive if directed from X to SO₃⁻. The magnitude of $\mu_X = \mu_{C_6H_5X}$. 'Molar dielectric increment. Linear intercept of ϵ vs $c_2 = 0.003$. d Same as footnote c, except intercept = 0.001. e Reference 14.

The data for the ion pairs with para substituents will now be used to deduce the direction of the 1,4-phenyl axis in the cation relative to that in the anion. The axes of the Cartesian coordinate system are defined as follows. The x axis is the 1,4-phenyl axis in the anion. The y axis is defined so that the dipole vector μ_0' lies in the x,y plane. The vector $\mu_0' = \mu_0 - \mu_{cat}$, where μ_0 is the dipole vector of the unsubstituted ion pair, and μ_{cat} is the 0.4-D dipole vector of the unsubstituted cation (Figure 1).¹⁶ The direction of the 1,4-phenyl axis then is that of the dipole vector $\mu_{\rm Y}$, which in turn is the vector sum of the 0.4-D intrinsic dipole of the cation, plus the dipole moment of the p-Y substituent. The latter is identified with the known dipole moment¹⁷ of C_6H_5Y .

Let α,β,γ denote the direction angles of μ_{Y} (and hence of the 1,4-phenyl axis in the *cat*ion) with respect to x,y,z, respectively. Let μ denote the dipole vector of the substituted ion pair, and let μ_x, μ_y, μ_z denote the components of μ . Let $\mu_0' \cos \theta$ denote the x component of μ_0' , and let μ_X denote the dipole vector assignable to the 4-substituent in the anion. The components of μ then are expressed by eqs 1 and μ^2 by eq 2.

$$\mu_x = \mu_0' \cos \theta + \mu_X + \mu_Y \cos \alpha \tag{1a}$$

$$\mu_{\nu} = \mu_0' \sin \theta + \mu_V \cos \beta \tag{1b}$$

$$\mu_z = \mu_Y \cos \gamma \tag{1c}$$

$$\mu^{2} = (\mu_{0}')^{2} + \mu_{X}^{2} + \mu_{Y}^{2} + 2\mu_{X}\mu_{0}'\cos\theta + 2\mu_{Y}(\mu_{0}'\cos\theta\cos\alpha + \mu_{X}\cos\alpha + \mu_{0}'\sin\theta\cos\beta)$$
(2)

⁽¹⁶⁾ In the previous work,¹⁴ μ_0 rather than μ_0' defined the x,y plane. (17) McClellan, A. L. *Tables of Experimental Dipole Moments*; Freeman: San Francisco, 1963; Vol. 1; Ibid. Rahara Enterprises: El Cerrito, CA, 1974; Vol. 2.



Figure 1. Structural formula and ionic dipole vectors.



Figure 2. Fit of eqs 1 and 2. The solid line is (calculated μ) = (observed μ).

Equation 2 is convenient for least-squares calculation. μ , μ_X , and μ_Y are experimental variables and μ_0' , $\cos \theta$, $\cos \alpha$, and $\cos \beta$ are parameters of fit. The results, by weighted nonlinear least squares, are $\mu_0' = 8.19 \pm 0.15$ D, $\cos \theta = 0.74 \pm 0.03$, $\cos \alpha = 0.85 \pm 0.03$, and $\cos \beta = 0.00 \pm 0.04$. Accordingly $\mu_0 = 7.94$ D, $\theta = 42 \pm 3^\circ$, $\alpha = 32 \pm 5^\circ$, and $\beta = 90 \pm 3^\circ$. μ_0 and θ are in good agreement with previous results,¹⁴ which had been based on ion pairs with para substituents only in the anions. The new results for α and β indicate that the 1,4-phenyl axis in the cation lies in the x,z plane and is inclined at a 32° angle with respect to the 1,4-phenyl axis in the anion. The interionic geometry is depicted in Figure 3.

The results obtained for α and β strike us as plausible. Space-filling molecular models show that if the N-ethyl group is rotated so that its CH₃ structure approaches the surface of the phenyl group in the cation, an inclination between the 1,4-phenyl axes of 32° for α and 90° for β will allow close approach of the ionic charge centers and good meshing of the van der Waals surfaces.

The fit of the data to eq 2 is respectable, as shown in Figure 2. However, the number of fitting parameters is relatively large, and when allowance is made for them, the error of fit is 1.6 times the experimental error of the data. The intrinsic accuracy of the parameters α and β thus is lower than the stated precision and may in fact be only semiquantitative.

Separate infrared spectral studies¹⁸ indicate that, in octanoic acid, the present ion pairs form hydrogen-bonded complexes of the type COOH····OSO₂Ph. However, the dipole moments reported in Table I are similar in magnitude to dipole moments measured in the aprotic solvents chlorobenzene and anisole,¹⁸ suggesting that hydrogen bonding with octanoic acid does not greatly affect the apparent dipole moments of these ion pairs. It may of course affect the interionic structures, but the basic assumption of our treatment, that *p*-phenyl substituents have negligible effect on interionic structure, probably remains correct.

Returning to the analysis of dipole moments, the result obtained for the *m*-nitrobenzenesulfonate ion pair gives information about the angular distribution of the *m*-nitrophenyl ring about the x axis.¹⁶ If one assumes that the meta substituent does not perturb the interionic geometry, the dipole moment of the ion pair measures the ensemble average of the angular distribution, as follows. Let ϕ denote the angle between the y axis and the projection of the dipole due to the *m*-nitro substituent onto the y,z plane (Figure



Figure 3. Vector diagram of interionic geometry.



Figure 4. Rotation of the *m*-nitrophenyl ring about the x axis. $\phi = 0$ when the phenyl plane lies in the x,y plane. The component of the phenyl-NO₂ dipole in the y,z plane is 3.45 D.

4), and let μ_x , μ_y , and μ_z denote the components of the overall moment μ for the *m*-nitro ion pair. It then follows (by applying parameters obtained in the preceding analysis) that $\mu_x = 7.74$ D, $\mu_y = (5.49 - 3.45 \cos \phi) D$, and $\mu_z = (-0.21 + 3.45 \sin \phi)$ D. Accordingly $\mu^2 = (102.0 - 37.9 \cos \phi - 1.4 \sin \phi)$. By comparison, the experimental $\mu^2_{obs} = 105.1 \pm 3.1$. The difference between the two expressions evaluates the ensemble average of $(\cos \phi + 0.04 \sin \phi)$. The result is $\langle \cos \phi \rangle + 0.04 \langle \sin \phi \rangle = -0.08 \pm 0.08$, where $\langle \rangle$ denotes the ensemble average. Thus $\langle \cos \phi \rangle$ is small and, within the experimental error, could be zero. Accordingly, the angular distribution of the *m*-nitrophenyl ring in the *y*,*z* plane is nearly symmetrical and could be random.

Experimental Section

Materials. Commercial "Gold Label" octanoic acid was purified by drying over $MgSO_4$ and then distilling at reduced pressure. Purity was checked by measuring the dielectric constant of the solvent in each series of measurements.

The N-ethyl-N,N-dimethylanilinium p-benzenesulfonate salts with Y = Br, X = CH₃; Y = H, X = CH₃; Y = H, X = NO₂; and Y = H, X = Cl were taken from previous work.¹⁴ The salts with Y = NO₂, X = Cl, Br, or CH₃ were synthesized by Dr. Nayan Amin at Brandeis University by the Menschutkin reaction of 4-nitro-N-methyl-N-ethylaniline¹⁹ with methyl (4-X)benzenesulfonate in tetramethylene sulfone. The reaction mixtures were heated for 17 h at temperatures in the range 100–120 °C. The salt with Y = NO₂, X = Cl was recrystallized from ethyl acetate/ether: mp 155–6 °C. The salt with Y = NO₂, X = Br was recrystallized first from ethyl acetate/ether and then from ethanol/ether: mp 172–4 °C. The salt with Y = NO₂, X = CH₃ was recrystallized first from ethyl acetate and then from ethanol/ether: mp 184–6 °C. The proton NMR spectra of the salts were consistent with expectation and showed no bands attributable to impurities.

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Figure 5. Cross section of the modified dielectric cell.

N,N-Dimethyl-4-(trifluoromethyl)aniline was prepared from 4-(trifluoromethyl)aniline and formaldehyde by sodium borohydride reduction.¹⁹ A slurry of 4.4 g (0.027 mol) of 4-(trifluoromethyl)aniline, 6 g (0.16 mol) of sodium borohydride, and 50 mL of tetrahydrofuran (THF) was made in a beaker. A solution was prepared by adding first 8.3 mL of 35% aqueous formaldehyde and then 7 mL of 3 M sulfuric acid to 50 mL of THF in a 500-mL round-bottom flask equipped with a stirrer and condenser and sitting in a water bath. The slurry was then added dropwise to the flask, allowing the reaction mixture to cool between each addition. After half the slurry had been added, another 7 mL of 3 M sulfuric acid was added. On completion of the reaction, solid KOH was added to raise the pH to 11. The organic layer was separated, combined with ether extracts of the aqueous layer, washed with saturated NaCl solution, dryed over magnesium sulfate, and rotary evaporated to yield a crude product consisting of white crystals. The crude product was recrystallized twice from ethanol/water and dried under vacuum to yield 2 g of the pure amine: mp 69-70 °C. The proton NMR spectrum was consistent with expectation.

N,N-Dimethyl-N-ethyl-4-(trifluoromethyl)anilinium ptoluenesulfonate was prepared by the Menschutkin reaction of the above with ethyl p-toluenesulfonate in anhydrous toluene. After refluxing for 4 days, anhydrous diethyl ether was added to precipitate the crude quaternary ammonium salt. Pure salt was obtained by recrystallizing twice from ethanol/diethyl ether/ethyl acetate. The pure dry salt melted at 244-6 °C; its proton NMR spectrum was consistent with expectation and showed no bands attributable to impurities.

N,N-Dimethyl-N-ethylanilinium 3-nitrobenzenesulfonate was prepared by the Menschutkin reaction of methyl 3-nitrobenzenesulfonate²⁰ (1 g) with N-methyl-N-ethylaniline¹⁹ (3 g) in 10 mL of dry toluene. The reaction mixture was warmed gently and stirred for 30 min, after which time a white precipitate appeared. Anhydrous diethyl ether (15 mL) was added and the flask was refrigerated to improve the precipitation of salt. After vacuum-drying, recrystallization from ethanol/diethyl ether and drying yielded 0.25 g of pure crystals melting at 122–3 °C. The proton NMR spectrum was consistent with expectation.

Since organic quaternary ammonium salts tend to be hygroscopic, the following indication of stability may be of interest. The 3-nitrobenzenesulfonate salt was stored in a desiccator under nitrogen, in accordance with our common practice. After 2 years of such storage, and 1.5 years after completion of the dielectric experiments, the melting point of the leftover portion of the present salt was 115-17 °C.

Capacitance Cells. Measurements of capacitance and conductance were made at 20 kHz on a calibrated¹⁴ General Radio audiofrequency bridge, Model 1615A, as described previously.¹⁴ However, the stainless steel concentric-spherical dielectric cell was redesigned so as to make the mounting of the inner low-voltage electrode and the electrical connection to it more robust.

The improved design is shown in Figure 5. The support tube D for the inner electrode is made of Kel-F and screws tightly into the electrode ball C. The latter is pulled snugly against a Teflon spacer F by screwing a stainless steel flange G on to the support until it bottoms out against the O-ring seat E. (Initially the support tube was made of Teflon, but that was found to be too soft. Kel-F is harder and adequately inert.)

To make an electrical connection to the low-voltage electrode, a guarded wire is threaded through the support tube, the final 6 mm of the guard and 3 mm of the insulation are removed, and the exposed inner conductor is threaded through, and soldered to, a hole in a small stainless steel bar. The bar fits into a notch in the bottom of the support tube and is held in place by a spring-loaded round-head screw whose head makes electrical contact to the electrode. One must make sure in this procedure that the guard wire extends into the electrode ball and that it does not short against the inner conductor. To secure the electrical connection after assembly, the I-shaped flange G consists of two halves which, after assembly, are screwed tightly together via the screws H, thus compressing the Kel-F support tube and clamping the fragile wire in place.

As before, the cell capacitances were interpreted by the equation, $C_{exp} = a + \epsilon C_0$, where C_{exp} is the measured capacitance and *a* is a small correction term, specific for each cell, due to imperfect guarding of the inner "low-voltage" conductor on passing through the outer "high-voltage" part of the dielectric cell. C_0 is the corrected cell capacitance under vacuum, and ϵ is the dielectric constant of the fluid in the cell. Owing to the rigid cell construction, the correction term (*a*) for each cell remained constant as long as the cell remained assembled. After disassembly and reassembly, *a* was redetermined to a precision of 0.002 pF by measurements using benzene ($\epsilon = 2.275$ at 25 °C) and air.

Cleaning. The cells were cleaned after each experiment with six rinses of pure methanol. The methanol was introduced with a syringe into the rear filling tube (Figure 5) so that the cavity filled from the bottom. The liquid was removed the same way. After rinsing, the whole cell was immersed in methanol overnight, to allow octanoic acid and other substances that might have crept inside the threaded bore of the low-voltage electrode to be replaced by methanol. After one additional rinse, the residual methanol was then removed by evacuation of the cells in a desiccator overnight. This procedure gave clean cells that were free from "electrode polarization", without any need for disassembly. After cleaning and drying, the cells were checked by measuring their air capacitances.

Measuring Procedures. The solutions examined were in the concentration range 0.2–4.0 mM. The most concentrated solutions had to be stirred, typically for 1 h, in order for the salt to dissolve.

In a representative experiment, four or six cells were brought to constant temperature side by side in a dry-nitrogen thermostat. Half the cells were filled with the given solution, and the others were filled with pure solvent. The cells generally took about 2 h to come to a steady capacitance after immersion in the 25 °C thermostat. The standard deviation of [ϵ (solution) – ϵ (solvent)] for an experiment was usually less than 0.001.

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