chloride was dried (MgSO<sub>4</sub>) and concentrated to give, as a clear yellowish oil, 123 mg (100%) of 2-methoxy-2-phenylpropanal (14): NMR (DDCl<sub>3</sub>)  $\delta$  9.50 (s, 1 H, CHO), 7.33 (s, 5 H, C<sub>6</sub>H<sub>5</sub>), 3.27 (s, 3 H, OCH<sub>3</sub>), 1.63 (s, 3 H, CH); IR (neat) 2820, 2690, 1735 cm<sup>-1</sup>. Further purification by preparative GLC (SE-30, 145 °C) did not alter the spectral properties reported above for unpurified material.

(S)-2-Methoxy-2-phenylpropanal (14). As with racemic material, 730 mg (2.7 mmol) of (2R,3S)- and (2R,3R)-1,3-diphenyl-2-hydroxy-3-methoxy-1-butanones (12 and 13) in a ratio of 74.8:25.2 gave, after 6 h at 0 °C with periodic acid, 424 mg (96%) of crude (S)-2-methoxy-2-phenylpropanal (14), which was used without purification in the chromium trioxide oxidation.

2-Methoxy-2-phenylpropionic Acid (15). To 200 mg (1.22 mmol) of 2-methoxy-2-phenylpropanal (14) in 15 mL of acetone at 0 °C was added 140 mg of concentrated sulfuric acid followed by 122 mg (1.3 equiv) of chromium trioxide. The mixture was stirred at 0 °C for 30 min and then diluted with methylene chloride and extracted twice with 10% sulfuric acid. The 2-methoxy-2-phenylpropionic acid (15) was then extracted twice with 50 mL of 1 M sodium hydroxide. The basic solution was acidified to pH 2 at 0 °C and extracted three times with 50 mL of methylene chloride. Drying (MgSO<sub>4</sub>) and concentration afforded 138 mg (63%) of dense colorless oil 15: NMR (DDCl<sub>4</sub>)  $\delta$  10.1 (br, 1 H, OH), 7.2–7.6 (m, 5 H, C, H), 3.30 (s, 3 H, OCH), 1.80 (s, 3 H, CH<sub>3</sub>); IR (neat) 1710 cm<sup>-1</sup>.

(+)-(S)-2-Methoxy-2-phenylpropionic Acid (15). As with the racemic material, 424 mg of (S)-14 was converted to 418 mg (90%) of (+)-(S)-15,  $[\alpha]^{25}_{D}$ +6.28° (c 1.6, CH<sub>3</sub>OH). The acid 15 was purified further by column chromatography using hexaneethyl acetate-acetic acid 80:19:1, which raised the specific rotation to  $[\alpha]^{25}_{\rm D}$  +6.98° (c 1.1, CH<sub>3</sub>OH) [lit.<sup>15b</sup>  $[\alpha]^{25}_{\rm D}$  26.0 (CH<sub>3</sub>OH)]. (+)-(S)-Methyl 2-Methoxy-2-phenylpropionate (16). In a refluxing solution of sulfuric acid (50 mg) and methanol (30 mL), 300 mg (1.66 mmol) of (+)-(S)-15  $[\alpha]^{25}_{\rm D}$  +6.98°, was converted to the methyl ester (+)-(S)-16. The methanol was diluted with methylene chloride and extracted with 10% sodium hydroxide. The organic layer was dried (MgSO<sub>4</sub>) and concentrated, affording 306 mg (95%) of (+)-(S)-16:  $[\alpha]^{25}_{\rm D}$  +2.98° (c 1.0, CH<sub>3</sub>OH); NMR (DCDl<sub>3</sub>)  $\delta$  7.2-7.6 (m, 5 H, C<sub>6</sub>H<sub>5</sub>), 3.70 (s, 3 H, CO<sub>2</sub>CH<sub>3</sub>), 3.27 (s, 3 H, OCH<sub>3</sub>), 1.77 (s, 3 H, CH<sub>3</sub>); IR (neat) 2810, 1730, 1260 cm<sup>-1</sup>. Using a chiral shift reagent,<sup>16</sup> the CO<sub>2</sub>CH<sub>3</sub> singlet exhibited a doublet at 284 Hz and 272 Hz; integration indicated an optical purity of 22%.

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**Registry No.** (±)-1, 70774-47-9; (+)-1, 63257-41-0; (-)-1, 63257-42-1; (±)-2, 70774-48-0; (-)-2, 63257-44-3; (±)-2a, 91899-74-0; 3, 66364-97-4; 4, 70729-30-5; (±)-5, 70397-72-7; (+)-5, 66365-00-2; (-)-5, 66364-98-5; (±)-6, 91899-75-1; (±)-6-d, 91899-76-2; (±)-7, 67737-73-9; 12, 91899-77-3; (±)-12, 92007-86-8; 13, 91899-78-4; (±)-13, 92007-87-9; (±)-14, 92007-88-0; (R)-14, 91899-79-5; (S)-14, 66221-50-9; (±)-15, 92007-85-7; (R)-15, 24190-08-7; (S)-15, 24190-10-1; (R)-16, 24190-11-2; (S)-16, 26164-23-8; 17, 91899-80-8; Mg(ClO<sub>4</sub>)<sub>2</sub>, 10034-81-8; LiClO<sub>4</sub>, 7791-03-9; CF<sub>3</sub>CO<sub>2</sub>H, 76-05-1; CISO<sub>3</sub>H, 7790-94-5; HClO<sub>4</sub>, 7601-90-3; ZnCl<sub>2</sub>, 7646-85-7; AlCl<sub>3</sub>, 7446-70-0; CuCl<sub>2</sub>, 7447-39-4; BCl<sub>3</sub>, 10294-34-5; AgO<sub>2</sub>CCF<sub>3</sub>, 2966-50-9; AgBF<sub>4</sub>, 14104-20-2; AgNO<sub>3</sub>, 7761-88-8; BF<sub>3</sub>, 7637-07-2; HCl, 7647-01-0; HOAc, 64-19-7; AcCl, 75-36-5.

## Proximate Charge Effects. 6.<sup>1</sup> Anion-Cation-Zwitterion Triplets in Solution

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The reaction of *p*-nitrophenol with tetra-*n*-butylammonium taurinate in 95.3 mol % dioxane-water was found to give an anion-cation-zwitterion triplet which then dissociates to a zwitterion and to an ion pair. The equilibrium constants for the formation of this triplet,  $K_{\rm f}$ , and for dissociation,  $K_{\rm d}$ , were found to be  $K_{\rm f} = 3.57 \ {\rm L}^{1/2} \ {\rm mol}^{-1/2}$  and  $K_{\rm d} = 1.73 \times 10^{-7} \ {\rm mol} \ {\rm L}^{-1}$ .

Ion pairs, triplets, and higher aggregates of electrolytes in nonpolar solvents have been known for some time.<sup>2</sup> The driving force for their formation is principally the Coulomb force attraction of oppositely charged particles. Zwitterions (dipolar ions) have a net neutral charge, yet it appears plausible that electrostatic forces at their (oppositely) charged ends might, in nonpolar solvents, prove, in some cases, to be sufficient to cause self association into zwitterion pairs or association with ion pairs to form anion-cation-zwitterion triplets. We wish to report evidence for the existence of the latter entity with the zwitterion being taurine (<sup>+</sup>H<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub><sup>-</sup>) and the ion pair being tetra-*n*-butylammonium *p*-nitrophenoxide ([*n*-Bu]<sub>4</sub>N<sup>+</sup> *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>O<sup>-</sup>) in 95.3 mol % dioxane-water solvent. Anion-Cation-Zwitterion Triplet Formation and Dissociation. In connection with an investigation of the kinetics of the aminolysis of p-nitrophenyl esters by tetra-*n*-butylammonium taurinate, I, it became necessary to measure the equilibrium constant for the acid-base reaction between p-nitrophenol and I in 95.3 mol % dioxane-water solvent (eq 1).

$$p \cdot \text{NO}_2\text{C}_6\text{H}_4\text{OH} + \text{H}_2\text{NCH}_2\text{CH}_2\text{SO}_3^- + (n \cdot \text{Bu})_4\text{N}^+ \approx p \cdot \text{NO}_2\text{C}_6\text{H}_4\text{O}^- + (n \cdot \text{Bu})_4\text{N}^+ + {}^+\text{H}_3\text{NCH}_2\text{CH}_2\text{SO}_3^- (1)$$

Acid-base reactions of 2,4-dinitrophenol and amines in aqueous dioxane had been studied by Pearson & Vogelsong<sup>3</sup> and found to obey the equilibrium law

$$K = \frac{[\mathbf{B}\mathbf{H}^+\mathbf{A}^-]}{[\mathbf{A}][\mathbf{B}]} \tag{2}$$

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Table I. The Equilibrium  $p \cdot NO_2C_6H_4OH + H_2NCH_2CH_2SO_3^- + (n \cdot Bu)_4N^+ \Rightarrow p \cdot NO_2C_6H_4O^- + (n \cdot Bu)_4N^+ + ^+H_3NCH_2CH_2SO_3^- in 95.3 mol \%$ Dioxane-Water at 25.0 °C

	[PNP] <sup>a</sup>	[TBAT] <sup>6</sup>	$A/\epsilon^{c}$	$K_3^d$	K4e				
	8.695	33.57	0.787	303	3.81				
	8.695	83.93	1.85	329	3.85				
	8.695	167.9	3.21	355	3.73				
	8.695	419.7	5.78	479	3.66				
	9.999	37.45	1.01	308	4.12				
	9.999	93.61	2.23	313	3.91				
	9.999	187.2	3.90	349	3.61				
	9.999	468.1	6.70	506	3.92				
	17.39	33.57	1.21	232	4.17				
	17.39	83.93	2.59	214	3.69				
	17.39	167.9	4.92	242	3.82				
	17.39	419.7	9.61	301	3.76				
	20.00	37.45	1.49	223	4.27				
	20.00	93.61	3.20	210	3.86				
	20.00	187.2	5.83	227	3.82				
	20.00	468.1	11.12	274	3.65				

<sup>a</sup> Stoichiometric *p*-nitrophenol concentration,  $M \times 10^5$ . <sup>b</sup>Stoichiometric concentration of tetra-n-butylammonium taurinate,  $M \times 10^5$ . <sup>c</sup> p-Nitrophenoxide concentration, obtained spectroscopically at 408 nm,  $M \times 10^5$ . <sup>d</sup> Equilibrium constant for eq 3, L mol<sup>-1</sup>. <sup>e</sup> Equilibrium constant, eq 4, mol<sup>1/2</sup> L<sup>-1/2</sup>.

If a neutral acid and a neutral base yield an ion pair in a poorly ionizing solvent, then in our case (eq 1), the product might be an anion-cation-zwitterion triplet and the equilibrium law ought to be

$$K_{3} = \frac{[p - \text{NO}_{2}\text{C}_{6}\text{H}_{4}\text{O}^{-}...^{+}\text{H}_{3}\text{NCH}_{2}\text{CH}_{2}\text{SO}_{3}^{-}...(n - \text{Bu})_{4}\text{N}^{+}]}{[p - \text{NO}_{2}\text{C}_{6}\text{H}_{4}\text{OH}][\text{H}_{2}\text{NCH}_{2}\text{CH}_{2}\text{SO}_{3}^{-}...(n - \text{Bu})_{4}\text{N}^{+}]}$$
(3)

The term in the numerator of this expression can be determined experimentally from the absorbance of *p*-nitrophenoxide at 408 nm, the two terms in the denominator then being the stoichiometric concentrations of p-nitrophenol and tetra-n-butylammonium taurinate less the above. Column 4 in Table I lists equilibrium constants,  $K_3$ , calculated by using eq 3. It is clear that these  $K_3$  values are far from constant, changes in both acid and base concentration causing large changes in  $K_3$ . One difficulty with eq 3 is that it does not take into account possible self-association of the p-nitrophenol. Self-association of phenols in nonpolar solvents has been observed<sup>4-9</sup> in a variety of phenols, though not in o-nitro-substituted phenols. Hence, the applicability of eq 2 to the work of Pearson and Vogelsong was due to the fact that they used an o-nitrophenol, 2,4-dinitrophenol, which did not associate. Taking account of *p*-nitrophenol self-association in our system and choosing an aggregation number of two (see below for a justification of this), we get

$$K_{4} = \frac{[p - NO_{2}C_{6}H_{4}O^{-}...^{+}H_{3}NCH_{2}CH_{2}SO_{3}^{-}...(n - Bu)_{4}N^{+}]}{[(p - NO_{2}C_{6}H_{4}OH)_{2}]^{1/2}[H_{2}NCH_{2}CH_{2}SO_{3}^{-}...(n - Bu)_{4}N^{+}]}$$
(4)

Values for the equilibrium constant,  $K_4$ , calculated with eq 4 are listed in column 5, Table I. The large changes in the previous equilibrium constant  $(K_3)$  with changes in

p-nitrophenol concentration have vanished, suggesting that we now have the correct molecularity for p-nitrophenol. There are, however, still unacceptable variations in the values of the equilibrium constants with changes in tetra-n-butylammonium taurinate concentration.

The ion pairs formed from acid-base reactions in nonionizing solvents,<sup>3,10</sup> were found not to dissociate to free ions to an observable extent. However, in the present case, there is another kind of dissociation that is possible, namely the dissociation of the anion-cation-zwitterion triplet to an ion pair and a zwitterion (eq 5). This dis-

$$\frac{1}{n}(p-\mathrm{NO}_{2}\mathrm{C}_{6}\mathrm{H}_{4}\mathrm{O}\mathrm{H})_{n} + \mathrm{H}_{2}\mathrm{NC}\mathrm{H}_{2}\mathrm{C}\mathrm{H}_{2}\mathrm{SO}_{3}^{-}...(n-\mathrm{Bu})_{4}\mathrm{N}^{+} \rightleftharpoons$$

$$p-\mathrm{NO}_{2}\mathrm{C}_{6}\mathrm{H}_{4}\mathrm{O}^{-}...^{+}\mathrm{H}_{3}\mathrm{NC}\mathrm{H}_{2}\mathrm{C}\mathrm{H}_{2}\mathrm{SO}_{3}^{-}...(n-\mathrm{Bu})_{4}\mathrm{N}^{+} \rightleftharpoons$$

$$^{+}\mathrm{H}_{3}\mathrm{NC}\mathrm{H}_{2}\mathrm{C}\mathrm{H}_{2}\mathrm{SO}_{3}^{-} + p-\mathrm{NO}_{2}\mathrm{C}_{6}\mathrm{H}_{4}\mathrm{O}^{-}...(n-\mathrm{Bu})_{4}\mathrm{N}^{+} (5)$$

sociation is plausible even in a poorly dissociating solvent, because it does not cause any increase in charge separation. The existence of the second equilibrium, the dissociation of the anion-cation-zwitterion triplet,  $K_{\rm d}$ , should explain the changes in the equilibrium constant,  $K_4$ , with changes in amine concentration.

To solve for  $k_f$  and  $k_d$  in eq 5, we need

$$K_{\rm f} = \frac{\left[p \cdot \mathrm{NO}_2 \mathrm{C}_6 \mathrm{H}_4 \mathrm{O}^- \dots^+ \mathrm{H}_3 \mathrm{NC} \mathrm{H}_2 \mathrm{C} \mathrm{H}_2 \mathrm{SO}_3^- \dots (n \cdot \mathrm{Bu})_4 \mathrm{N}^+\right]}{\left[\frac{\mathrm{PNP} - A/\epsilon}{n}\right]^{1/n} [\mathrm{TBAT} - A/\epsilon]}$$
(6)

which is obtained from eq 5;

$$K_{\rm d} = \frac{[p \cdot \rm NO_2C_6H_4O^-...(n \cdot Bu)_4N^+][^+H_3\rm NCH_2\rm CH_2\rm SO_3^-]}{[p \cdot \rm NO_2\rm C_6\rm H_4O^-...^+H_3\rm N\rm CH_2\rm CH_2\rm SO_3^-...(n \cdot Bu)_4\rm N^+]}$$
(7)

also, from eq 5;

$$\frac{A}{\epsilon} = [p \cdot NO_2C_6H_4O^-...^+H_3NCH_2CH_2SO_3^-...(n \cdot Bu)_4N^+] + [p \cdot NO_2C_6H_4O^-...(n \cdot Bu)_4N^+] (8)$$

which expresses the fact that absorbance at 408 nm is a measure of all the *p*-nitrophenoxide present, where PNP =

the stoichiometric concentration of p-nitrophenol

TBAT = the stoichiometric concentration of tetra-*n*-butylammonium taurinate (I)

n = the aggregation number of *p*-nitrophenol

 $A/\epsilon$  = the absorbance at 408 nm divided by the extinction coefficient of p-nitrophenoxide at 408 nm

Combining eq 6-8 leads to eq 9, which contains only  $K_{\rm f}$ ,  $K_{d}$ , n, and experimentally measured quantities. This is

$$\frac{A/\epsilon}{\left[\left(\frac{\text{PNP} - A/\epsilon}{n}\right)^{1/n} (\text{TBAT} - A/\epsilon)\right]^{1/2}} = K_{\text{f}}\left[\left(\frac{\text{PNP} - A/\epsilon}{n}\right)^{1/n} (\text{TBAT} - A/\epsilon)\right]^{1/2} \pm (K_{\text{f}}K_{\text{d}})^{1/2}$$
(9)

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**Figure 1.** The error in the slope,  $K_t$ , of eq 9 as a function of the *n* value [% error = (standard deviation of the slope/slope) × 100].



Figure 2. Plot of

$$\frac{A/\epsilon}{\left[\left(\frac{\text{PNP} - A/\epsilon}{2}\right)^{1/2} (\text{TBAT} - A/\epsilon)\right]^{1/2}} \times 10^2 \text{ (y axis) vs.}$$
$$\left[\left(\frac{\text{PNP} - A/\epsilon}{2}\right)^{1/2} (\text{TBAT} - A/\epsilon)\right]^{1/2} \times 10^3 \text{ (x axis)}$$

a linear equation and, if *n* is known, a plot of the left hand term vs. the first square root term on the right should yield a straight line having slope  $K_{\rm f}$  and intercept =  $(K_{\rm f}K_{\rm d})^{1/2}$ .

To obtain n, the aggregation number of p-nitrophenol from our data, we evaluated the slope,  $K_i$ , of the above equation for values of n ranging from 1 to 3 in 0.1 increments. The error in this slope was calculated for each nvalue. The results are shown in Figure 1, where this error is plotted against the n values. The results show that a minimum is observed at an n value of 2.0.

Using this aggregation number, we now calculated  $K_{\rm f}$  and  $K_{\rm d}$  with eq 9. The values are

$$K_{\rm f}$$
 = 3.57 ± 0.075 L<sup>1/2</sup> mol<sup>1/2</sup>

$$K_{\rm d} = 1.73 \pm 0.17 \times 10^{-7} \text{ mol } \text{L}^{-1}$$

The fit of the data is depicted in Figure 2.<sup>22</sup>

The cation-anion-zwitterion triplet dissociation constant,  $K_d$ , in this solvent is quite small. Thus, when the total *p*-nitrophenoxide concentration is  $7.9 \times 10^{-6}$  M (the first entry in Table I), 14.4% of it is in the form of the taurine zwitterion and the tetra-*n*-butylammonium *p*nitrophenoxide ion pair, and at our highest *p*-nitrophen $\nu$ 

oxide concentration,  $1.1 \times 10^{-4}$  M (last entry in Table I), only 3.9% of it has dissociated. The stability of the triplet in this instance is no doubt a consequence of the preference of the *p*-nitrophenoxide ion for the H bond donor taurine over the tetra-*n*-butylammonium cation. This preference can be observed in the ion pair dissociation constants of quaternary and other ammonium picrates measured by Fuoss and Kraus.<sup>11-14</sup> They found that, in benzene, chlorobenzene, ethylene chloride, and nitrobenzene solvents, the hydrogen bonding ammonium picrates had ion pair dissociation constants which were  $10^2-10^5$  smaller than those of the corresponding quaternary ammonium picrates.

Association between p-Nitrophenol and Tetra-nbutylammonium Taurinate (I). There is evidence<sup>10</sup> for acid-base association in nonpolar solvents which would lead to equilibrium expressions originating from the hydrogen-bonded complex. These possible schemes and their associated equilibrium constants are

$$p \cdot \operatorname{NO}_2 \operatorname{C}_6 \operatorname{H}_4 \operatorname{OH}_{\ldots} \operatorname{H}_2 \operatorname{NCH}_2 \operatorname{CH}_2 \operatorname{SO}_3^{-} \dots (n \cdot \operatorname{Bu})_4 \operatorname{N}^+ \stackrel{H_5}{\longleftrightarrow} \\ p \cdot \operatorname{NO}_2 \operatorname{C}_6 \operatorname{H}_4 \operatorname{O}^- \dots^+ \operatorname{H}_3 \operatorname{NCH}_2 \operatorname{CH}_2 \operatorname{SO}_3^{-} \dots (n \cdot \operatorname{Bu})_4 \operatorname{N}^+ (10) \\ K_5 = \frac{A/\epsilon}{(223)^{-} (223)^{-} (123)^{-} (11)}$$

$$P-NO_2C_6H_4OH...H_2NCH_2CH_2SO_3^{-}...(n-Bu)_4N^{+} \stackrel{K_6}{\longleftrightarrow}$$

$$^{+}\text{H}_{3}\text{NCH}_{2}\text{CH}_{2}\text{SO}_{3}^{-} + p \cdot \text{NO}_{2}\text{C}_{6}\text{H}_{4}\text{O}^{-}...(n \cdot \text{Bu})_{4}\text{N}^{+}$$
 (12)

$$K_6 = \frac{(A/\epsilon)^2}{(\text{PNP} - A/\epsilon)}$$
(13)

$$p \cdot \operatorname{NO}_2C_6H_4OH...H_2\operatorname{NCH}_2CH_2SO_3^-...(n \cdot \operatorname{Bu})_4\operatorname{N}^+ \xleftarrow{K_{\mathfrak{f}}} \\ p \cdot \operatorname{NO}_2C_6H_4O^-...^+H_3\operatorname{NCH}_2CH_2SO_3^-...(n \cdot \operatorname{Bu})_4\operatorname{N}^+ \xleftarrow{K_{\mathfrak{d}}} \\ ^+H_3\operatorname{NCH}_2CH_2SO_3^- + p \cdot \operatorname{NO}_2C_6H_4O^-...(n \cdot \operatorname{Bu})_4\operatorname{N}^+ (14)$$

$$\frac{A/\epsilon}{(\text{PNP} - A/\epsilon)^{1/2}} = K'_{\text{f}}(\text{PNP} - A/\epsilon)^{1/2} \pm (K'_{\text{f}}K'_{\text{d}})^{12} \quad (15)$$

The  $K_5$  and  $K_6$  values calculated from our data exhibited large variations in equilibrium constant value with changes in acid and base concentration. The slope calculated from eq 15 had a negative value and an extremely poor correlation coefficient. These results alone lead to the conclusion that a hydrogen-bonded complex between p-nitrophenol and taurinate is not an important species in this solvent. Rivetti and Tonellato<sup>15</sup> observed that, in benzene solvent, the absorption maximum of p-nitrophenol shifted from 305 to 320 nm on addition of imidazole. They interpreted this as evidence for the presence of a strong hydrogen-bonded association between the *p*-nitrophenol hydrogen and an imidazole nitrogen. To test for this possibility in our solvent, we added fairly large concentrations of amine to p-nitrophenol and observed the effect on the absorption maximum of the *p*-nitrophenol (308 nm) and on the absorption maximum of the p-nitrophenoxide (408 nm). Table II shows that addition of tetra-n-butylammonium taurinate produces no observable shift of either maximum; a very large (0.16 M) concentration of benzylamine being required to produce an observable effect. We conclude again that *p*-nitrophenol-taurinate association does not play a role in 95.3 mol % dioxane-water.

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Table II. Absorption Maximum of p-Nitrophenol and p-Nitrophenoxide<sup>o</sup> in the Presence of Tetra-n-butylammonium Taurinate (TBAT) or Benzylamine (BA) in 95.3 mol % Dioxane-Water

			λ <sub>max</sub> , nm	
$[PNP]^b$	[TBAT] <sup>c</sup>	$[BA]^d$	$\overline{p-NO_2}$ - C <sub>6</sub> H <sub>4</sub> OH	<i>p</i> -NO <sub>2</sub> - C <sub>6</sub> H <sub>4</sub> O <sup>-</sup>
$5.00 \times 10^{-5}$	0	0	308	
$1.00 \times 10^{-4}$	$3.74 \times 10^{-4}$	0	308	408
$1.00 \times 10^{-4}$	$9.36 \times 10^{-4}$	0	308	408
$1.00 \times 10^{-4}$	$18.7 \times 10^{-4}$	0	308	408
$1.00 \times 10^{-4}$	$46.8 \times 10^{-4}$	0	308	408
$1.08 \times 10^{-4}$	0	0.168	308	
$1.08 \times 10^{-4}$	0	1.68	312	

<sup>a</sup> The  $\lambda_{max}$  of a solution  $(2 \times 10^{-3} \text{ M})$  of tetra-*n*-butylammonium *p*-nitrophenoxide in this solvent is 408 nm. <sup>b</sup> Stoichiometric concentration of *p*-nitrophenol. <sup>c</sup> Stoichiometric concentration of tetra-*n*-butylammonium taurinate. <sup>d</sup> Stoichiometric concentration of benzylamine.

In connection with the results listed in Table II, it is worth noting that, whereas benzylamine and taurinate anion have comparable basicities in water,<sup>16</sup> benzylamine produces no observable *p*-nitrophenoxide in 95.3 mol % dioxane-water even at very high concentrations of benzylamine. There is evidently an enormous difference<sup>17</sup> between  $K_{\rm f}$  and  $K_{\rm BA}$  (eq 16) in a poorly ionizing solvent,

$$p \cdot \text{NO}_2\text{C}_6\text{H}_4\text{OH} + \text{C}_6\text{H}_5\text{CH}_2\text{NH}_2 \xleftarrow{\text{K}_{BA}} \\ p \cdot \text{NO}_2\text{C}_6\text{H}_4\text{O}^-\dots^+\text{H}_3\text{NCH}_2\text{C}_6\text{H}_5$$
(16)

even though both reactions involve the same amount of charge generation (two new charges). The difference reflects the preference for anion-cation-zwitterion formation from an ion pair over ion pair formation from neutral species.

The Spectrum of p-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>O<sup>-</sup> as a Function of Aggregation. Changes in the position of the absorption maximum with aggregation state have been observed and used in the elucidation of ion pair structure and equilibria.<sup>2c</sup> In the present case, the absorption maximum never varied from its value of 408 nm. In an effort to observe the pure ion pair, we prepared *p*-nitrophenoxide from *p*-nitrophenol and tetra-*n*-butylammonium hydroxide. The spectra of solutions prepared in this way did not differ from *p*-nitrophenoxide solutions prepared from *p*-nitrophenol and high concentrations of tetra-*n*-butylammonium taurinate (i.e., pure triplets). The molar absorptivity of *p*-nitrophenoxide at 408 nm of solutions prepared by these two methods differed by less than 0.2%.

We conclude that the small amount of water present in our solvent system and available for hydrogen bonding to p-nitrophenoxide, blurs the spectroscopic difference between the ion pair and the internally hydrogen-bonded anion-cation-zwitterion triplet. This makes it possible to use the absorbance at 408 nm as a measure of *all* the p-nitrophenoxide present.

**Conclusion.** A new state of aggregation in solution, an anion-cation-zwitterion triplet, is described. The equi-

librium constant for the formation of this triplet from p-nitrophenol and tetra-*n*-butylammonium taurinate in 95.3 mol % dioxane-water was measured,  $K_{\rm f} = 3.57 \ {\rm L}^{1/2} \ {\rm mol}^{1/2}$ . The equilibrium constant for the dissociation of this triplet into an ion pair and a zwitterion was measured,  $K_{\rm d} = 1.73 \times 10^{-7} \ {\rm mol} \ {\rm L}^{-1}$ . p-Nitrophenol was found to exist as a dimer in 95.3 mol % dioxane-water.

It appears plausible that the family of charged aggregated species in solution may include not only ion pairs and higher aggregates, anion-cation-zwitterion triplets and higher aggregates, but also zwitterion pairs and higher aggregates. All these species are probably common in biological systems. The study of their formation and dissociation may shed light on such areas as membrane structure and assembly, nerve cell function and the mechnism of the assembly and dissassembly of native protein conformations.

## **Experimental Section**

**Materials.** 1,4-Dioxane (Baker Analyzed Reagent) was passed through a column of activated alumina and stored under nitrogen,  $n^{20}{}_{\rm D}$  1.4229 (lit.<sup>18</sup>  $n^{20}{}_{\rm D}$  1.4224). The 95.3 mol % dioxane-water was then prepared by weight using the above and deionized water. The aqueous dioxane was deaerated with CO<sub>2</sub> free nitrogen, stored in the dark and used within 3 days. **Taurine** (Aldrich) was recrystallized from water. **Benzylamine** was dried over KOH and distilled,  $n^{20}{}_{\rm D}$  1.5441 (lit.<sup>19</sup>  $n^{20}{}_{\rm D}$  1.5438). *p*-Nitrophenol was recrystallized from 2% aqueous HCl and dried at 78 °C in vacuo, mp 113–114 °C (lit.<sup>20</sup> mp 115–115.6 °C). **Tetra-n-butyl-ammonium bromide** (Eastman) was recrystallized from ethyl acetate-ether, mp 118–119 °C (lit.<sup>21</sup> mp 118.5 °C).

An aqueous tetra-*n*-butylammonium hydroxide solution was prepared by adding 2.95 g (0.00256 equiv) of  $Ag_2O$  to a solution of 7.408 g (0.00230 mol) of tetra-*n*-butylammonium bromide in 95 mL of water. The mixture was stirred for 20 min in the dark and filtered, and the filtrate was diluted to 100.0 mL. Titration of an aliquot with HCl showed it to be 0.2024 N.

**Tetra-***n***-butylammonium taurinate** (TBAT) was prepared as follows. To 95.0 mL of a 0.2024 N aqueous solution of tetra*n*-butylammonium hydroxide was added 2.456 g (0.01962 mol) of taurine. The water was removed at room temperature in vacuo, the brown solid residue dissolved in 50 mL methylene chloride, decolorized with charcoal, and filtered, and the filtrate evaporated to dryness at room temperature in vacuo to yield a white oil. Trituration of this oil with hexane caused crystallization to a highly hydroscopic white solid: 5.5 g (78%); mp 116–118 °C. A sample of this material was titrated with HCl to give an equivalent weight of 377.0 (calcd  $M_r = 366.6$ ).

Equilibrium Constants. Solutions of p-nitrophenol and tetra-n-butylammonium taurinate in 95.3 mol % dioxane-water were prepared by weight and diluted to the concentrations listed in Table I. The solutions were equilibrated in a thermostated bath at 25.0 °C and their spectra were determined in the thermostated cuvette holder of a Cary 17 or a Perkin-Elmer 402 UV-visible spectrophotometer. The molar absorptivity of tetra-n-butylammonium p-nitrophenoxide was determined by dissolving a weighed amount of *p*-nitrophenol in a solution of standardized tetra-n-butylammonium hydroxide in 95.3 mol % dioxane-water. The molar absorptivity at 408 nm was found to be  $25\,092$  L mol<sup>-1</sup>. The molar absorptivity of the tetra-*n*-butylammonium-2-ammoniumethyl sulfonate-p-nitrophenoxide triplet was determined by dissolving a weighed amount of p-nitrophenol in solutions of tetra-n-butylammonium taurinate of successively higher cncentrations till a maximum absorbance at 408 nm was

<sup>(16)</sup> The  $pK_b$  of benzylamine is 4.65 [Robinson, R. A.; Kiang, A. K. Trans. Faraday Soc. 1956, 52, 327] and the  $pK_b$  of taurinate is 4.94 [King, E. J. J. Am. Chem. Soc. 1953, 75, 2204].

<sup>(17)</sup> From the lack of any *p*-nitrophenoxide color produced by even 0.33 M benzylamine, we estimate the value of  $K_{BA}$  to be less than  $1.2 \times 10^{-2}$  L mol<sup>-1</sup>. This is not directly comparable to the  $K_f$  value,  $3.57 \text{ L}^{1/2} \text{ mol}^{1/2}$ , because of the different dimensions of the two constants. A meaningful comparison would be to compare the concentration of *p*-nitrophenoxide produced by  $2 \times 10^{-4}$  M *p*-nitrophenol and  $4.7 \times 10^{-3}$  M taurinate (last entry Table I) with the amount of *p*-nitrophenoxide produced by  $2 \times 10^{-4}$  M *p*-nitrophenoxide and  $4.7 \times 10^{-3}$  M benzyl amine. The values are  $1.1 \times 10^{-4}$  M *p*-nitrophenoxide and  $<1.1 \times 10^{-8}$  M *p*-nitrophenoxide.

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<sup>(19)</sup> Vogel, A. I. J. Chem. Soc. 1948, 1825.

<sup>(20)</sup> Carrick, L. L. J. Phys. Chem. 1921, 25, 633.

<sup>(21)</sup> Reynolds, M. B.; Kraus, C. A. J. Am. Chem. Soc. 1948, 70, 1709. (22) A referee has pointed out that the application of a nonlinear least-squares calculation to eq 9 will yield both the equilibrium constants and the aggregation number, n. The values obtained by the Gauss-Newton method were  $K_f = 3.28 \pm 0.087$ ,  $K_d = (1.93 \pm 1.14) \times 10^{-7}$ , and  $n = 1.89 \pm 0.032$ .

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reached. This highest concentration of tetra-n-butylammonium taurinate was  $2.88 \times 10^{-2}$  M and it gave a molar absorptivity for p-nitrophenoxide of  $25\,048$  L mol<sup>-1</sup>.

The equilibrium constant,  $K_3$ , was calculated from the expression

$$K_3 = \frac{A/\epsilon}{[\text{PNP} - A/\epsilon][\text{TBAT} - A/\epsilon]}$$

The equilibrium constant,  $K_4$ , was calculated by using the expression

$$K_4 = \frac{A/\epsilon}{[(PNP - A/\epsilon)1/2]^{1/2}[TBAT - A/\epsilon]}$$

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**Registry No.** Tetra-*n*-butylammonium bromide, 1643-19-2; tetra-n-butylammonium hydroxide, 2052-49-5; tetra-n-butylammonium taurinate, 91900-05-9; taurine, 107-35-7; p-nitrophenol, 100-02-7; benzylamine, 100-46-9.

## S-Substituted Thiacyclobutenium Salts<sup>1</sup>

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Treatment of 3-phenyl- or 3-(2-naphthyl)-2H-thietes with trimethyl- or triethyloxonium tetrafluoroborate or with methyl trifluoromethanesulfonate yields colorless S-alkylthiacyclobutenium salts. They react with cyanide ion to give both ring opened and dealkylated products. Repetition of previously reported syntheses of 4methyl-1,2-diphenylthiacyclobutenium perchlorate and 2-methyl-1,4-diphenylthiacyclobutenium perchlorate gave instead 4-methyl-2-phenylbenzo-1-thiopyrylium perchlorate and 2-methyl-4-phenylbenzo-1-thiopyrylium perchlorate, respectively. These thiopyrylium salts also were synthesized independently.

The synthesis of S-substituted thiacyclobutenium salts **1a** and **1b** by cyclization of  $\beta$ -phenylthic ketones has been described.<sup>3</sup> The purported salt **1a** had a melting or decomposition point (212 °C) identical with that reported for the thiopyrylium salt  $2^{4,5}$  In the reported <sup>1</sup>H NMR



spectra of 1a and 1b in trifluoroacetic acid, the absorption of the methine proton on carbon-2 was not observed. Moreover, the ultraviolet spectrum attributed to 1a was essentially identical with that reported for  $2.4^{5}$  The only other thiacyclobutenium salt reported previously is 3, in which the carbon-carbon double bond is part of an aromatic system.<sup>6</sup> Several thiacyclobutenium structures, however, have been suggested as intermediates.<sup>5,7</sup>

## **Results and Discussion**

Alkylation of Thietes. A different method than that used for the synthesis of the alleged structures 1a and 1b was adopted as a general way of preparing thiacyclobutenium salts. 3-Arylthietes, e.g., 4 and 5, are much more stable<sup>8</sup> than alkyl-substituted thietes or the unsubstituted thiete,<sup>9</sup> and they can be alkylated with triethyl- or trimethyloxonium tetrafluoroborate in methylene chloride at 0 °C. The sulfonium salts obtained are hygroscopic and difficult to isolate. They yield ring opened and dealkylated products on treatment with tetraethylammonium cyanide. The ring-opened 4-(methylthio)- or 4-(ethylthio)-3-butenonitriles were obtained in about 25% yield and the dealkylated products, thietes 4 and 5, were obtained in about 50% yield.

$$\begin{array}{c} Ar \\ Ar \\ S \\ Ar = Ph \\ Ar = 2 - naphthyl \\ R = Me, Et \end{array}$$

The trifluoromethanesulfonate (triflate) salts, 6 and 7, prepared by alkylation with methyl triflate, were less hy-

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