color of the reaction mixture changed to yellow during this addition. The mixture was warmed at reflux for 1 hr and filtered hot; the solid product was washed with chlorobenzene and with ether and dried at 90° (0.1 mm) to give 7.4 g (94% yield) of yellow powder, **17** (X = I), mp 300–304° dec.

Anal. Calcd for $C_{37}H_{30}I_2P_2$: C, 56.22; H, 3.83; I, 32.11; P, 7.84. Found: C, 56.57; H, 4.16; I, 31.77; P, 7.65.

Evaporation of the filtrate to dryness gave 3.3 g of slightly yellow triphenylphosphine, mp 78–80°, having a P^{31} nmr signal at +6.3 ppm (an authentic sample of triphenylphosphine melted at 80–81° and had a P^{31} nmr signal at +6.0 ppm).

Compound **17** (X = I) was also prepared by addition of I_2 to a solution of **5** in chlorobenzene. Working-up of the product gave a 99% yield of yellow solid, mp 302–304°, having an infrared spectrum essentially identical with that obtained for the product prepared from diiodotriphenylphosphine and **5**.

Acknowledgments. We thank R. F. Jansen for obtaining most of the infrared and nmr spectra, C. H. Dungan for help with high-resolution nmr determinations, J. D. Downing for assistance in synthesis, and D. W. Grisley, Jr., J. S. Driscoll, M. M. Crutchfield, and H. I. Weingarten for helpful advice.

Solvation of Anilinium Salts

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Abstract: Nuclear magnetic resonance spectra have been obtained for several anilinium salts in a variety of solvents. It has been found that the charge on nitrogen in quaternary anilinium salts reduces the electron densities around the rings, the effect decreasing with distance, and it is concluded that pure inductive effects decrease with distance. For primary anilinium salts in polar media, the spectra are nearly independent of the anion and the NH_3^+ substituent has an influence on the ring carbon densities comparable to that of hydrogen. In nonpolar media the nmr spectra of primary anilinium salts vary with the nature of the accompanying anion, and NH_3^+ has a small deshielding effect on the ring hydrogens. The addition of exactly 4 equiv of methanol to a $CDCl_3$ solution of *p-n*-butylanilinium salt changes the nmr spectrum to that observed in pure methanol. Salts of secondary and tertiary anilines behave in a manner intermediate between the primary and quaternary salts described above. The effects which most satisfactorily account for these results are: (1) hydrogen bonding of solvent molecules to ammonium groups; and (2) in nonpolar media, formation of intimate ion pairs in which the *centers of charge are juxtaposed.* Investigation of the nmr spectra of model systems for intimate ion pairs such as aniline oxides and BF_3 adducts of anilines reveals that substituent dipoles which are not in conjugation with aromatic rings exert only a small effect on the ring electron densities.

The chemical shift of hydrogen has been ascribed to a sum of terms each arising from a different effect: electron currents on atoms,[1,2] in bonds,[3–8] and around rings.[1,2,4] Solvent effects in chemical shifts have been treated by various workers in terms of anisotropic shielding[9] by solvents, dispersion forces,[10] and electric fields.[11]

The idea that charge influences chemical shift originally came from electronegativity correlations by Dailey and Schoolery[12] and by Narasimhan and Rogers.[13] It was suggested on the basis of ring hydrogen shifts observed in cyclic aromatic species that in systems which have the same ring current and a common solvent for all substances studied, the differences in chemical shifts observed for the ring protons are probably chiefly caused by the charge distribution around the ring.[14] The shifts due to charge among the ring hydrogens are given by eq 1, where z is the charge on

$$\delta(H_i) - \delta(H_{C_6H_6}) = 10z(C_i) \qquad (1)$$

carbon i and $\delta(H_i)$ and $\delta(H_{C_6H_6})$ are shifts of hydrogen on carbon i and in benzene, respectively, both in the same medium. This idea was tested by several workers,[15–17] and the general conclusion is that although π-electron densities dominate the chemical shifts, other effects contribute also and care should be exercised to take account of them. Relationships similar to (1) for aromatic ^{13}C[18] and ^{19}F[19] shifts have also been reported.

It was of interest to measure charge distributions with the nmr method in compounds whose ring carbon

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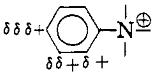
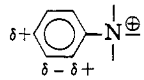
Table I. Nmr Parameters for  [a]

X	Y	Solvent	τ_o[b]	τ_m	τ_{NCH_3}	τ_{OCH_3}	J_o[c]	J_m[d]	$J_{m'}$[e]	J_p
NO_2	$N(CH_3)_2$	Acetone	3.220	1.912	7.228		9.53	3.40	2.30	0.22
NO_2	NH_2	Acetone	3.258	1.981			9.05	2.88	2.66	0.18
NO_2	$ND_3^+Cl^-$	D_2O, D^+	2.538	1.948			9.05	2.88	2.66	0.18
NO_2	$NH_3^+CF_3CO_2^-$	CF_3CO_2H	2.143	1.506			8.72	3.44	1.36	0.20
NO_2	$N(CH_3)_2OD^+Cl$	D_2O	1.415	1.619	6.099		9.13	3.79	1.23	0.28
CH_3O	NH_2	CCl_4	3.499	3.278		6.274	8.73	3.45	1.75	0.30
CH_3O	$ND_3^+Cl^-$	D_2O	2.690	3.045		6.301	8.81	2.89	2.61	0.36
CH_3O	$ND_3^+CF_3CO_2^-$	D_2O	2.673	2.017		6.343	9.05	3.04	2.68	0.45
CH_3O	$N(CH_3)_2OD^+Cl^-$	D_2O	2.290	2.984	6.189	6.248	9.02	3.25	2.54	0.53
CH_3O	$N(CH_3)_3^+I^-$	D_2O	2.336	2.976	6.455	6.254	9.31	3.46	2.86	0.19

[a] At 33°, J in hertz, 5% concentration. [b] ±0.003 ppm. [c] ±0.02 Hz. [d] m = 2,6; C_1-Y. [e] m' = 3,5; C_1-Y.

atoms were suspected of having very different charges. One such group of compounds consists of anilinium salts. In the anilinium salts, there should be a major effect on the charges around the rings due to the positive charge on nitrogen. Since here the nitrogen atom is not conjugated with the aromatic system, the effect of the N^+ substituent on the charges of the different carbon atoms must be transmitted mainly by the inductive effect. The question arises as to whether the inductive effect of a substituent on an aromatic ring decreases with distance (I) or alternates around the ring (II).


I


II

In this work are reported the chemical shifts of hydrogens in anilinium salts. It will be shown that the results for quaternary anilinium salts are indeed a measure of the inductive effect of an N^+ substituent. On the other hand, the chemical shifts for aromatic hydrogens in the salts of primary, secondary, and tertiary amines are strongly affected by solvents and anions. The results obtained in this work provide some insight into the mode of solvation of ammonium ions and the structure of intimate ion pairs.

Ion pairs have been detected by molecular weight and conductance studies.[20] Intimate ion pairs in solvolysis reactions have been differentiated from solvent-separated ion pairs kinetically.[21] Hogen-Esch and Smid have recognized intimate and solvent-separated ion pairs with a combination of ultraviolet spectroscopic and conductance methods.[22]

Ion pairing in salts of metal complexes has been detected with nmr techniques by Larson and Wahl[23] and by LaMar.[24,25] Using similar methods, Buckson and Smith have measured association constants for tetrabutylammonium salts in nitrobenzene.[26]

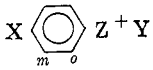
Results and Discussion

The chemical shifts and coupling constants of selected anilinium salts, aniline oxide salts, and anilines are listed in Table I.

Analysis for the A_2B_2 cases (*para*-substituted reagents) was accomplished as described in the Experimental Section. Since the A_2B_2 pattern is symmetrical about its center, it is not possible to assign *a priori* the chemical shift of a particular ring proton. The chemical shifts of the aromatic hydrogens listed in this work were obtained on the basis of the known effects of substituents on the chemical shifts of aromatic hydrogens,[27a-d] and on the basis of the existence of small long-range couplings between methyl hydrogens of methyl or methoxy substituents and the aromatic hydrogen *ortho* to the substituent. The coupling constants $J(CH_3, H_m)$ have not been observed in this work and are probably too small to resolve.

Chemical shifts of the aromatic hydrogens in derivatives of *para*-substituted anilines, p-$YC_6H_4N\!<^+$, where the N^+ substituent is NH_3^+, $N(CH_3)_2^+OH$, $N(CH_3)_2O$, and $N(CH_3)_3^+$, are listed in Table II.

Table II. Chemical Shifts in Anilinium Salts and Related Compounds[a]



X	Z, Y	Solvent	τ_o	τ_m	$\tau_o - \tau_m$
Cl	$N(CH_3)_3$, I	CH_3OH	2.108	2.462	−0.273
Cl	NH_3, Cl	CH_3OH	2.480	2.450	0.030
Cl	H	CH_3OH	2.510	2.510	0.000
Cl	NH_3, Cl	DMSO	2.510	2.510	0.000
Cl	$N(CH_3)_2BF_3$	DMSO	2.590	2.530	0.060
CH_3O	NH_3, Cl	CH_3OH	2.664	2.985	−0.321
CH_3O	ND_3, Cl	D_2O, DCl	2.738	3.091	−0.353
CH_3O	NH_3, Cl	DMSO	2.632	2.969	−0.337
CH_3O	ND_3, CF_3CO_2	D_2O, CF_3CO_2D	2.672	3.017	−0.344
CH_3O	H	CH_3OH	2.603	3.123	−0.320
CH_3O	$N(CH_3)_3$, I	CH_3OH	2.116	2.816	−0.700
CH_3O	$N(CH_3)_2OH$, Cl	CH_3OH	2.290	2.984	−0.694
CH_3	NH_3, Cl	CH_3OH	2.720	2.720	0.000
CH_3	NH_3, Cl	DMSO	2.670	2.670	0.000
CH_3	$N(CH_3)_2O$	CH_3OH	2.833	2.833	0.000
CH_3	$N(CH_3)_2O$	CH_2Cl_2	2.840	2.840	0.000
CH_3	H	CH_3OH	2.790	2.830	0.040
CH_3	$N(CH_3)_3$, I	CH_3OH	2.220	2.648	−0.428
NO_2	NH_3, Cl	CH_3OH, HCl	2.405	1.815	0.590
NO_2	ND_3, Cl	D_2O, DCl	2.538	1.948	0.603
NO_2	NH_3, CF_3CO_2	CF_3CO_2H	2.143	1.506	0.637
NO_2	H	DMSO	2.503	1.723	0.780
NO_2	$N(CH_3)_2OH$, Cl	D_2O	1.415	1.619	−0.204

[a] At 33°, 0.2 M.

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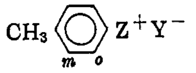
Table III. Effect of N-Alkylation on Chemical Shifts in *p*-Toluidinium Salts[a]

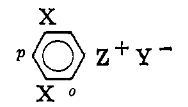


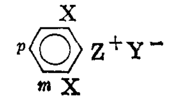
Solvent	Z	Y	τ_o	τ_m	$\tau_o - \tau_m$	τ_{CCH_3}	τ_{NCH_3}
CH_3OH	NH_3	Cl	2.720	2.720	0.000	7.645	
CH_3OH	NH_3	I	2.750	2.750	0.000	7.630	
CH_3OH	NH_2CH_3	Cl	2.860	2.860	0.000	7.645	6.980
CH_3OH	NH_2CH_3	I	2.670	2.670	0.000	7.650	6.980
CH_3OH	$NH(CH_3)_2$	Cl	2.513	2.627	−0.114	7.620	6.755
CH_3OH	$NH(CH_3)_2$	I	2.505	2.595	−0.090	7.650	6.750
CH_3OH	$N(CH_3)_3$	I	2.220	2.648	−0.428	7.585	6.292
CH_3OH	$N(CH_3)_2OH$	Cl	2.073	2.461	−0.388	7.770	5.973
DMSO	NH_3	Cl	2.670	2.670	<0.04	7.820	
DMSO	NH_3	I	2.780	2.780	<0.04	7.800	
DMSO	$N(CH_3)_3$	I	2.195	2.635	−0.440	7.651	6.370
DMSO	$N(CH_3)_2OH$	Cl	2.145	2.635	−0.490	7.650	6.107
D_2O	NH_3	Cl	2.720	2.720	<0.04	7.820	
D_2O	NH_3	I	2.870	2.870	<0.04	7.820	
D_2O	NH_2CH_3	Cl	2.800	2.800	<0.04	7.820	7.095
D_2O	$NH(CH_3)_2$	Cl	2.730	2.730	<0.04	7.810	6.910
D_2O	$NH(CH_3)_2$	I	2.720	2.720	<0.04	7.805	6.900
D_2O	$N(CH_3)_3$	I	2.408	2.632	−0.224	7.650	6.420
D_2O	$N(CH_3)_2OH$	Cl	2.379	2.733	−0.344	7.799	6.258

[a] 0.05 *M* at 33°.

The effects of N-alkylation on the nmr spectra of *p*-toluidinium salts are shown in Table III. A comparison of the nmr data for *meta*- and *ortho*-substituted anilines is listed in Table IV.

Table IV. Chemical Shifts in Disubstituted Anilinium Salts[a]

Solvent	X	Z	Y	τ_o	τ_p	$\tau_o - \tau_p$
						
CH_3OH	CH_3	NH_3	Cl	3.080	2.940	0.160
CH_3OH	Cl	NH_3	Cl	2.763	2.620	0.143
CH_3OH	Cl	$N(CH_3)_3$	I	2.010	2.370	−0.360
CH_3OH	CH_3	$N(CH_3)_3$	I	2.500	2.780	−0.280
D_2O	CH_3	$N(CH_3)_3$	I	2.730	2.900	−0.170
D_2O	CH_3	NH_3	Cl	3.110	2.980	0.130



Solvent	X	Z	Y	τ_m	τ_p	$\tau_m - \tau_p$
CH_3OH	CH_3	NH_3	Cl	2.825	2.825	0.000
CH_3OH	CH_3	NH_3	Br	2.780	2.780	0.000
CH_3OH	Br	NH_3	Cl	2.068	2.952	−0.884
CH_3OH	Br	NH_3	Br	2.144	2.936	−0.792
DMSO	Br	NH_3	Cl	2.050	3.050	−1.000
DMSO	Br	NH_3	Br	2.148	3.032	−0.884
DMSO	CH_3	NH_3	Cl	2.830	2.830	0.000
DMSO	CH_3	NH_3	Br	2.850	2.850	0.000

[a] 0.05 *M* at 33°.

Measurement of the rate of NH exchange of these anilines in 60% sulfuric acid solution was attempted using the methods of Meiboom and co-workers.[28, 29] The rate of NH exchange in salts of secondary and tertiary anilines under our experimental conditions was found to be too fast to study by the nmr method.

Molecular weight determinations of *p*-anisidinium, *p*-toluidinium, and *p*-chloroanilinium chlorides, respectively (0.02 *M* in methanol), show the salts to consist of free ions under these conditions.

Inspection of Tables I–III reveals that the nmr spectra of quaternary and primary anilinium salts are very different. The hydrogens *ortho* to the N^+ substituent in quaternary anilinium salts and in the salts of N,N-dimethylaniline N-oxides are deshielded with respect to the *meta* hydrogens in all cases studied. Although the absolute magnitudes of the two shifts in different solvents varied, the difference between them changed by only small increments.

Quaternary Salts. If variations in the chemical shifts of the aromatic hydrogens in *quaternary anilinium salts* reflect mainly differences in electron densities around the ring, then these data provide a measure of the inductive effect of an N^+ substituent on electron densities at the different carbon atoms. The nmr spectrum of N,N,N-trimethylanilinium iodide is too complicated to analyze so the two-ring deuterated salts listed in Table V were prepared and the ring hydrogen shifts determined (see Table V). Assuming that deuterium substitution has only a negligible effect on these ring hydrogen shifts, the derived charges, *z*, around the quaternary salt are

z_1	z_2	z_3	z_4	z_N
+0.08	+0.06	+0.03	+0.04	+0.7

The charges on nitrogen and C_1 were obtained in the following way. The change in the shift of NCH_3 proceeding from a tertiary amine to a quaternary salt is about −1.0 ppm.[14] In these experiments, the shift of NCH_3 changes from τ 7.01 in dimethylaniline to 6.33 in the quaternary salts. The increment in shift corresponds to a charge of +0.7 on nitrogen. Suming up this with the other charges leaves +0.08 on C_1.

Altogether the inductive effect of N^+ on the charges around the aromatic ring decreases with the distance from N^+ and does not alternate.

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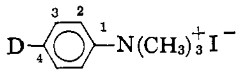
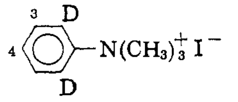
(29) E. G. Grunwald, A. Loewenstein, and S. Meiboom, *ibid.*, **27**, 630 (1957).

Table V. The Nmr Parameters for Deuteriated Quaternary Ammonium Salts 0.2 *M* in Methanol

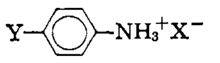
Salt	τ_o	τ_m	τ_p	J_o, Hz
	2.074	2.370		9.0 ($J_{2,3}$)
		2.367	2.310	7.0 ($J_{3,4}$)

These results reveal the N$^+$ substituent in *quaternary anilinium salts* to be a powerful electron-withdrawing group.[30] Musher[31] and Buckingham[32] have treated the effect of electric fields on the chemical shifts of protons. By employing a variety of internal dielectric constants, neither the absolute values for the ring hydrogen chemical shifts in the quaternary anilinium salts nor the differences between them can be predicted on the basis of these models. Apparently the effect of the N$^+$ substituent in altering the electron densities around the aromatic ring is transmitted through the π and the σ electrons and not just through space.

Primary Salts. In contrast to the data for quaternary anilinium salts, the single common feature of the results for all the primary anilinium salts studied under a wide variety of conditions is that the *NH_3^+ substituent has a very small influence on the chemical shifts of the aromatic hydrogens* (see Tables II–IV). Table VI shows that the chemical shift differences $\tau_o - \tau_m$ for primary anilinium salts (Y = NH_3) closely resemble the corresponding values for the compounds where Y = H. In these latter salts, the influence of the NH_3^+ substituent on the ring hydrogen chemical shifts is comparable to that of hydrogen. The effect persists in a wide variety of polar solvents including water, methanol, dimethyl sulfoxide, dioxane, trifluoroacetic acid, and sulfuric acid. When the number of alkyl groups on nitrogen in the anilinium salts increases, the deshielding effect of the N$^+$ substituent on the ring hydrogens progressively increases from no effect for the primary salts to the maximum effects for the quaternary salts listed in Table III; the chemical shifts for the N-methyl hydrogens parallel those for the ring hydrogens.

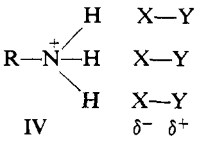
The consistent pattern of results found for the primary anilinium salts suggests that the underlying explanation of the results described above must be common to all the primary salts in all the polar solvents used. Two effects may be chiefly responsible for the small inductive influence exerted by NH_3^+; they concern (A) ion pairing, and (B) the solvation shell around NH_3^+.

(A) Ion pairing. In high concentration solutions, the salts may exist as ion pairs in which the centers of charge are juxtaposed (III). The effect of N$^+$ on the ring hydrogen shifts will be counterbalanced by that of the accompanying anion.[33]



III

(B) Solvation Shell around NH_3^+. The ammonium substituent may be attached to a shell of oriented solvent molecules, XY, which shields it from one side only (IV), the remaining volume being occupied by the aromatic part of the salt. A large part of the positive charge usually assigned to nitrogen is located on the NH hydrogens. The effect of these positive charges on the chemical shifts of the aromatic hydrogens is counterbalanced by the negative ends of the solvent dipoles. In this manner the positive charge is dispersed into the solvent and the NH_3^+ group has a minor influence on the shifts of the ring hydrogens.



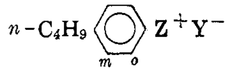
IV

Thus two effects may be responsible for the small influence of the NH_3^+ group on the ring shifts. It is not possible at this point to assess their relative importance because both models can be employed to predict the same phenomenon—that substitution on nitrogen will increase the effective charge on nitrogen and hence decrease the ring hydrogen shifts.

Anilinium Salts and Derivatives Thereof in Nonpolar Media. In order to evaluate the relative importance of the two models proposed above, some anilinium salts soluble in nonpolar media were prepared and their nmr spectra determined under a variety of conditions. Salts of *p*-*n*-butylaniline and N-substituted derivatives were found to be soluble in several nonpolar solvents.

The molecular weight measurements listed in Table VI show that all salts studied in deuteriochloroform are associated to varying degrees, trimers for the primary salts and dimers for the tertiary salts.

Table VI. Anilinium Salts in Deuteriochloroform[a]



Z	Y	Concn, *M*	τ_o	τ_m	τ_{NH}	τ_{NCH_2}	Mol wt
NH	Cl	0.05	2.50	2.72	−0.67		557
NH_3	Br	0.05	2.46	2.72	+0.13		690
NH_3	I	0.05	2.42	2.70	+0.92		860
NH_3	CH_3SO_4	0.05	2.59	2.81			
$NH(CH_3)_2$	Br	0.05	2.24	2.62		7.17	
$NH(Bu)_2$	Cl	0.10	2.44	2.76	−1.34	6.93	600
$NH(Bu)_2$	Br	0.10	2.42	2.76	−0.86	6.79	690
$N(CH_3)_3$	I	0.05	2.26	2.74		6.14	600

[a] At 33°.

In all those cases where the NH chemical shift could be observed, it was found to be very sensitive to the nature of the accompanying anion, thus demonstrating that the anion must be near -N$^+$ (see Table VI). Hence, the salts most likely exist as intimate ion pairs in deuteriochloroform, and this conclusion is independent of the state of aggregation of the ion pairs.

For the primary salts, the NH shifts are approximately a monotonic function of the crystallographic radii of the anions Cl,$^-$ Br,$^-$ I$^-$,[34] and of the corresponding

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[30] G. Fraenkel, *J. Chem. Phys.*, **39**, 1614 (1963).

[31] J. I. Musher, *ibid.*, 37, 34 (1962).

[32] A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960).

[33] Ion pairs in which the two centers of charge are arranged differently from III would be predicted to yield nmr spectra unlike those reported here.

[34] L. Pauling, "Nature of Chemical Bond," 2nd ed, Cornell University Press, Ithaca, N. Y., 1948.

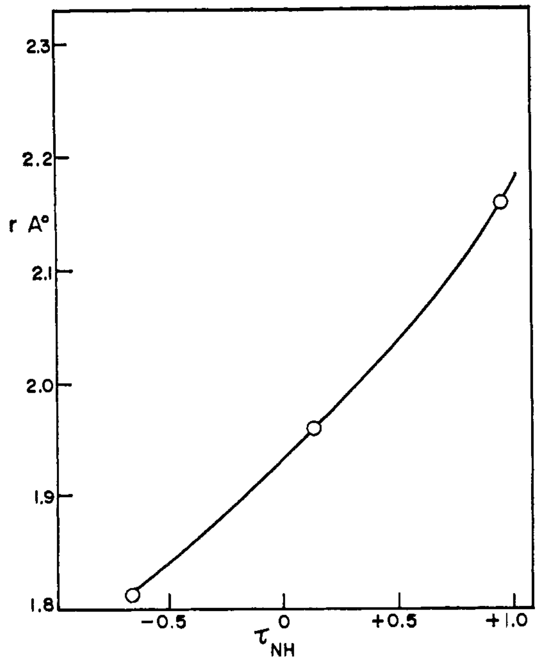


Figure 1. Plot of ionic radii of Cl^-, Br^-, and I^- *vs.* NH shifts in corresponding *p-n*-butylanilinium salts, 0.05 *M* in $CDCl_3$.

electronegativities of these elements[35] (see Figures 1 and 2). These relationships strongly support the view that the NH hydrogens are hydrogen bonded to the anions.

The chemical shifts of the aromatic hydrogens for these *p-n*-butylanilinium salts also vary among the different salts in deuteriochloroform. The chemical shifts of the hydrogens *meta* to N^+ remain relatively constant, whereas the values of τ_o change markedly from salt to salt. The *ortho* hydrogen chemical shifts, τ_o, is at a minimum in the quaternary salts and increases (becomes more positive) with decreasing substitution on nitrogen.

Among the primary salts, the chemical shifts of the aromatic hydrogens depend on the nature of the accompanying anions whereas those for other salts are nearly independent of the anions. The aromatic hydrogen chemical shifts in these salts determined in deuteriochloroform are independent of concentration, within the range 0.025 to 0.5 *M*.

An experiment was carried out in deuteriochloroform to estimate the rate of anion exchange between two different salts in the same solution. A solution 0.025 *M* in both *p-n*-butylanilinium chloride and the iodide was prepared in deuteriochloroform. At temperatures down to −30°, the nmr spectrum yielded for the aromatic hydrogens a single A_2B_2 pattern whose analysis is listed in Table VII. The chemical shifts, τ_o and τ_m, for this sample are exactly the average of those observed independently for pure *p-n*-butylanilinium chloride and the iodide 0.05 *M* in deuteriochloroform. This experiment demonstrates that the shifts for the two salts in the above mixture are averaged out owing to fast anion–cation exchange.[36]

In a second experiment, the nmr spectrum of *p-n*-butyl-N,N-dimethylanilinium bromide in deuteriochloroform was obtained as a function of temperature. At −33°, the N-methyl resonance consisted of an equal doublet with separation of 5.0 cps due to J_{NHCH_3}. With increasing temperature, the doublet progressively collapsed to a single line by 60°. However, using carbon tetrachloride as the solvent, the N-methyl resonance signal always consisted of a singlet. Thus the NH exchange rate was slower for this salt in deuteriochloroform than in carbon tetrachloride.

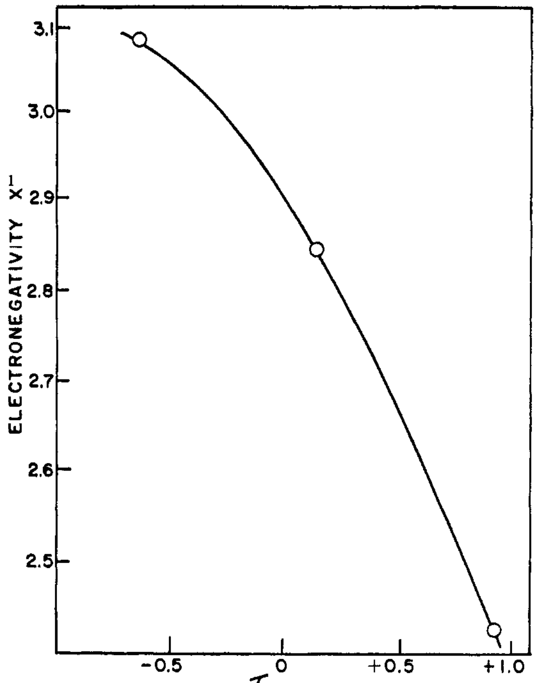
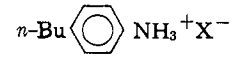


Figure 2. Electronegativity of X^- in *p-n*-butylanilinium salts *vs.* NH shift. Salts are 0.05 *M* in $CDCl_3$.

Table VII. The Chemical Shifts of Pure and Mixed Anilinium Salts in Deuteriochloroform[a]



X	Concn, *M*	τ_0	τ_m
Cl^-	0.050	2.50	2.72
I^-	0.050	2.42	2.70
Cl^- I	0.025 0.025	2.46	2.71

[a] At 33°.

In summary, the results obtained with deuteriochloroform as the solvent are: (a) the chemical shifts τ_m are relatively invariant; (b) the NH chemical shifts depend on the nature of the anion and the cation in all cases observed; (c) the *ortho* hydrogen shifts depend on the anions in the primary salts; (d) the chemical shifts τ_o are independent of the anions in tertiary and quaternary salts, and depend on the extent of substitution on the nitrogen; (e) τ_o and τ_m are independent of the salt concentration for all salts studied.

A wide variety of salts were studied in deuteriochloroform. Similar experiments were carried out with other nonpolar solvents: methylene chloride, ether, and carbon terachloride (see Table VIII). Due to solubility problems the variety of salts studied in these media was

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(35) W. Gordy and W. Thomas, *J. Chem. Phys.*, **24**, 439 (1956).
(36) Reference 2, Chapter 10.

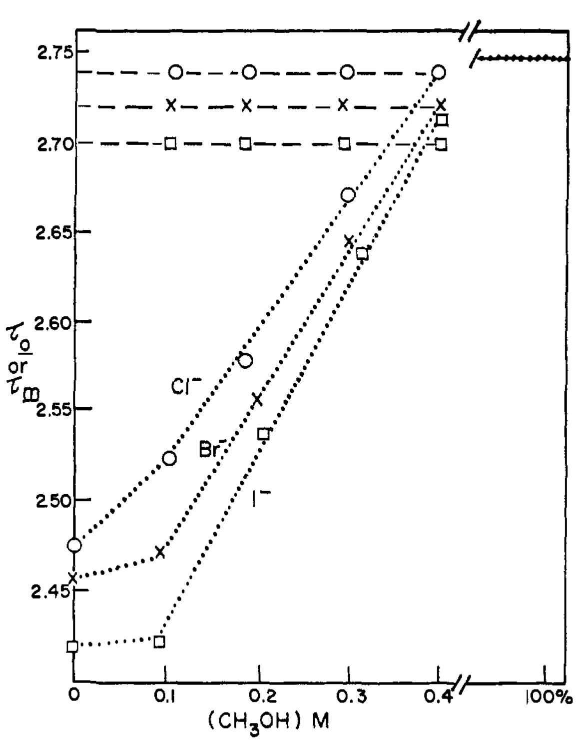
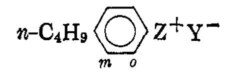


Figure 3. Effect on the aromatic hydrogen shifts in *p*-*n*-butylanilinium salts (0.05 *M* in CDCl$_3$) of adding methanol.

restricted; however, the same general trends found for the deuteriochloroform solutions operate here also.

Table VIII. The Chemical Shifts of Anilinium Salts in Nonpolar Media[a]



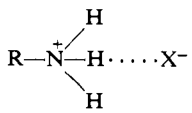
Solvent	Z	Y	Concn, *M*	τ_0	τ_m	τ_{NCH_2}	τ_{NH}
CCl$_4$	NH(CH$_3$)$_2$	Br	0.05	2.05	2.73	6.75	
CCl$_4$	NHBu$_2$	Cl	0.10	2.39	2.81		−1.05
CCl$_4$	NHBu$_2$	Br	0.10	2.39	2.81		−1.50
CH$_2$Cl$_2$	NH(CH$_3$)$_2$	Br	0.05	2.46	2.66		
CH$_2$Cl$_2$	NHBu$_2$	Cl	0.10	2.46	2.72		
CH$_2$Cl$_2$	NHBu$_2$	Br	0.10	2.42	2.78		
CH$_2$Cl$_2$	N(CH$_3$)$_3$	I	0.05	2.37	2.74	6.22	
Et$_2$O	NHBu$_2$	Cl	0.05	2.38	2.90		
Et$_2$O	NHBu$_2$	Br	0.05	2.31	2.79		

[a] At 33°.

Altogether these results show that the anilinium salts in nonpolar media exist as aggregates of intimate ion pairs in which the centers of charge are juxtaposed. In this way the anion counterbalances the influence of N$^+$ on the ring hydrogen shifts. The effect of substitution on nitrogen is to increase the average distance between the centers of charge and thus decrease the influence of the anion on the ring shifts, thereby lowering the values of τ_o. Nothing is known about the arrangement of the ion pairs within the aggregates.

A suitable model for an intimate ion pair is a molecule with a dipolar substituent attached to, but not in conjugation with, a benzene ring. Examples of such compounds are BF$_3$ adducts of anilines and aniline oxides. As is seen in Table III, these substituents have only a small influence on the ring shifts.

It is suggested from the manner in which the NH shifts vary with anions that the NH hydrogens are hydrogen bonded to the gegenions (V). This is the



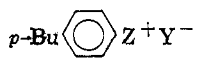
V

first time that the structure of an intimate ion pair has been determined.

In this section it is shown that anilinium salts in nonpolar media exist as intimate ion pairs with juxtaposed centers of charge.

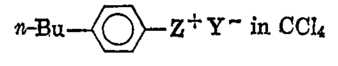
Effects of Polar Cosolvents on the Nmr Spectra of Anilinium Salts in Nonpolar Media. Having established tentatively that anilinium salts in nonpolar media exist as intimate ion pairs, it was of interest to study the effect on the nmr spectra of adding small amounts of polar substances to the nonpolar solutions. If the cosolvent could compete with the anion for an interaction site at NH$^+$, effects should be observed in the nmr spectra of the salts. The results of these experiments are illustrated in Figure 3 and Tables IX and X. It is seen that addition of polar substances to ion aggregates of anilinium salts produces changes in the *ortho* hydrogen chemical shifts while the *meta* shifts remain relatively stationary. The changes in τ_o are all upfield shifts. They are most pronounced for the primary salts and decline with substitution on nitrogen. In tertiary and quaternary salts, the changes which attend the addition of polar cosolvents are smaller and sometimes too small to measure. The largest effects

Table IX. Ring Shifts of Anilinium Salts in CDCl$_3$ Containing Polar Cosolvents



Concn, *M*	Z	Y	Cosolvent	Cosolvent concn, *M*	τ_0	τ_m
0.05	NH$_3$	CH$_3$SO$_3$	...	...	2.59	2.81
0.05	NH$_3$	CH$_3$SO$_3$	CH$_3$OH	0.05	2.63	2.81
0.05	NH$_3$	CH$_3$SO$_3$	CH$_3$OH	0.10	2.64	2.81
0.05	NH$_3$	CH$_3$SO$_3$	CH$_3$OH	0.20	2.81	2.81
0.05	NH$_3$	Br	...	...	2.46	2.72
0.05	NH$_3$	Br	Acetone	0.15	2.46	2.72
0.05	NH$_3$	Br	DMSO	0.15	2.46	2.72
0.05	NH$_3$	Br	Ethylene glycol	0.10	2.48	2.74
0.05	NH(CH$_3$)$_2$	Br	...	...	2.24	2.62
0.05	NH(CH$_3$)$_2$	Br	CH$_3$OH	0.05	2.26	2.62
0.05	NH(CH$_3$)$_2$	Br	CH$_3$OH	0.10	2.27	2.62
0.05	NH(CH$_3$)$_2$	Br	CH$_3$OH	0.15	2.29	2.62
0.10	NHBu$_2$	Cl	...	...	2.44	2.76
0.10	NHBu$_2$	Cl	CH$_3$OH	0.10	2.45	2.76
0.10	NHBu$_2$	Cl	CH$_3$OH	0.20	2.47	2.76
0.10	NHBu$_2$	Cl	CH$_3$OH	0.30	2.48	2.76
0.10	NHBu$_2$	Br	...	...	2.42	2.76
0.10	NHBu$_2$	Br	CH$_3$OH	0.10	2.44	2.76
0.10	NHBu$_2$	Br	CH$_3$OH	0.20	2.45	2.76
0.05	N(CH$_3$)$_3$	I	...	...	2.26	2.74
0.05	N(CH$_3$)$_3$	I	CH$_3$OH	0.05	2.26	2.74
0.05	NHBu$_2$	Br	...	...	2.42	2.76
0.05	NHBu$_2$	Br	DMSO	0.05	2.42	2.76
0.05	NHBu$_2$	Br	DMSO	0.10	2.43	2.76
0.05	NHBu$_2$	Br	DMSO	0.15	2.44	2.76

Table X. Ring Shifts of Anilinium Salts Containing Polar Substances

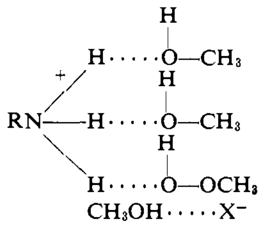


Z	Y	Salt concn, *M*	Cosolvent	Cosolvent concn, *M*	τ_0	τ_m
$NH(CH_3)_2$	Br	0.05	...	...	2.03	2.73
$NH(CH_3)_2$	Br	0.05	MeOH	0.05	2.13	2.73
$NH(CH_3)_2$	Br	0.05	MeOH	0.10	2.21	2.73
$NH(CH_3)_2$	Br	0.05	MeOH	0.15	2.27	2.73
$NH(CH_3)_2$	Br	0.05	DMSO	0.05	2.06	2.73
$NH(CH_3)_2$	Br	0.05	DMSO	0.10	2.08	2.73
$NH(CH_3)_2$	Br	0.05	Dioxane	0.15	2.03	2.73
$NHBu_2$	Cl	0.10	...	...	2.39	2.81
$NHBu_2$	Cl	0.10	MeOH	0.20	2.41	2.81
$NHBu_2$	Br	0.10	...	...	2.39	2.81
$NHBu_2$	Br	0.10	MeOH	0.10	2.47	2.81
$NHBu_2$	Br	0.20	MeOH	0.20	2.51	2.81

were observed for hydroxylic solvents, and more minor changes occurred on addition of dimethyl sulfoxide, acetone, dioxane, ethyl acetate, tetramethylene sulfone, and ether.

The results with the primary salts in methanol in deuteriochloroform merit further discussion. Addition of methanol to these solutions changes τ_o to a maximum obtained at *4 equiv of methanol/equiv of salt* for primary salts (see Figure 3). Thereafter τ_o does not change on further addition of methanol up to 100% methanol. In fact, the τ_o maxima closely resemble the shifts found for anilinium salts in pure methanol.

These data strongly imply that in the primary salts there are four sites which interact with single methanol molecules; three are NH hydrogens and the fourth is the gegenion. It is suggested that the nature of the interaction is hydrogen bonding. In such a model the negative ends of the hydrogen bonds counter the effect of N^+ on the ring hydrogen shifts, and the gegenion is displaced from the ammonium groups (VI).



VI

Discussion

The origin of ring hydrogen shifts in aromatic compounds[1-14] is discussed in the introductory section. Even though a variety of effects contribute to these shifts, empirically the shifts behave in a relatively simple manner. The ring shifts in a number of *para*-disubstituted benzenes correlate linearly with substituent parameters, *S*,[27] derived from the data.

$$\delta(H_X) = S(o\text{-X}) + S(m\text{-X})$$

In the present work, the anilinium salts also fall into this pattern; $S(o\text{-}NH_3^+)$ for all polar media studied is found to be 0.0 ± 0.01 ppm.

In this research it has been found that the ring hydrogen shifts in anilinium salts vary with substitution on nitrogen, solvents, and, in certain cases, anions. It is proposed that the effects observed here are most simply accounted for by two chemical interactions which perturb the influence of the ammonium substituent on the ring hydrogen shifts. They are (1) ion pairing and (2) hydrogen bonding.

(1) In the intimate ion pairs of salts in deuteriochloroform, the accompanying anion is hydrogen bonded to an NH hydrogen and counterbalances to different degrees the effect of N^+ on the ring shifts.

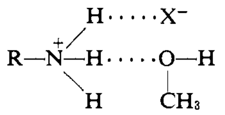
(2) It is suggested that the changes in the ring hydrogen shifts which attend the addition of the first 4 equiv of methanol/equiv of salt in $CDCl_3$ are best explained by hydrogen bonding of methanol to the three NH hydrogens and the anion, thus dispersing the charge ascribed to nitrogen. This latter arrangement very likely resembles the environment of the salts in pure hydrogen-bonding solvents. The very small values of $S(o\text{-}NH_3^+)$ and $S(m\text{-}NH_3^+)$ in polar solvents are chiefly ascribed to hydrogen bonding.

In terms of the solvation model, the effect of increasing the degree of substitution on nitrogen would be to sterically hinder hydrogen bonding at NH^+, localizing the positive charge on nitrogen and thus bringing about increased deshielding of the aromatic hydrogens as well as the N-alkyl hydrogens. The latter trend has been observed in this work (see Table III). Similar results have been obtained for the chemical shifts of hydrogens in alkylammonium salts (see Table XI).[14]

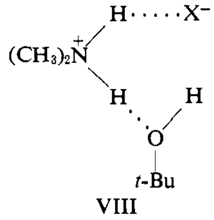
Table XI. Chemical Shift Increments for Alkylated Ammonium Bromides in Water (0.1 *M*) at 33°

Alkylammonium cation	$\tau_{NCH_3^+} - \tau_{NCH_3}$
$CH_3NH_3^+$	−0.36
$(CH_3)_2NH_2^+$	−0.44
$(CH_3)_3NH^+$	−0.70
$(CH_3)_4N^+$	−1.00

Between the extremities of intimate ion pairs and hydrogen-bonded ammonium solvates described under 1 and 2, respectively, intermediate situations may be envisaged where both the anion and a methanol molecule are hydrogen bonded to the same ammonium group (VII). This may take place in solutions of anilinium salts in chloroform containing a small amount of methanol. In fact, Grunwald and Cocivera[37] have suggested a similar structure for methylammonium salts in *t*-butyl alcohol (VIII) based on proton-exchange rates.



VII



VIII

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(37) E. Grunwald and M. Cocivera, *J. Am. Chem. Soc.*, **87**, 2070 (1965).

The nmr spectra of solvent-separated ion pairs in hydrogen-bonding solvents would be expected to be very similar to those of free ion solvates described above. Marple and Fritz found electrolytes to be associated as ion pairs in *t*-butyl alcohol.[38] The nmr spectra of anilinium salts in *t*-butyl alcohol are independent of the anions[39] and quite similar to the results obtained with methanol. Hence these salts most likely exist as solvent-separated ion pairs in *t*-butyl alcohol.

In the preceding discussion it is not necessary to stipulate the mechanism by which the charge on nitrogen or an anion alters the chemical shift of the ring hydrogens. As noted above, calculated chemical shifts due to the electric field in quaternary anilinium salts are quite different from those observed. It is more likely that the charge on nitrogen alters the electron densities around the ring by the inductive effect. Thus the ring hydrogen shifts should reflect the charges on carbon. It is suggested that the chemical interactions of intimate ion pairing and hydrogen bonding reduce the effective charge on nitrogen, and hence also its inductive influence on the ring carbon electron densities.

In summary, it has been found that certain salts in nonpolar media exist as intimate ion pairs with juxtaposed centers of charge. However, the addition of polar cosolvents to these solutes causes the ammonium groups to be surrounded by a shell of hydrogen-bonded cosolvent molecules. This cation solvation markedly reduces the inductive effect of N^+ on the ring carbon electron densities. The effect of hydroxylic solvents on the inductive influence of NH_3^+ must be mainly attributed to hydrogen bonding.

Recently Condon[40] has discussed the influence of hydration on the basicity of amines. His conclusions are entirely in accord with those reported here.

Examples of phenomena which may be understood in terms of the ion pair and the solvation shell models follow. Taft,[41] Deno,[42] and Arnett[43] have suggested that variations in hydrogen bonding of NH^+ hydrogens to solvent may be responsible for the finding that primary, secondary, and tertiary aromatic amines *fit different* acidity functions.

Several authors[44–47] have studied the effect of ammonium and amine oxide substituents on the rates of reactions or on reaction equilibria. Roberts[44] and Willi[47] derived σ constants for ammonium groups using different chemical systems. Within each system N-alkylation increases the σ value of an ammonium substituent at a particular position, *meta* or *para*. For any particular ammonium substituent σ_m always exceeds σ_p. For the hydrolysis in basic solution of substituted methyl benzoates, Wepster[45] found rate constants of 8.6×10^{-3}, 335, and 203 M^{-1} sec^{-1} for unsubstituted, *m*-$N(CH_3)_2O$, and *p*-$N(CH_3)_2O$ methyl benzoates, respectively. All these results lead to the conclusion that the inductive effect of the ammonium group decreases with distance and increases with substitution on nitrogen.

On the basis of the forgoing information, it might be expected that anilinium salts would be more reactive to electrophilic substitution than N,N,N-trimethylanilinium salts. Ridd and co-workers[48] reported that anilinium salts undergo nitration both at the *meta* and *para* positions. The rate constants for nitration at the *meta* and *para* positions in anilinium salts are 179×10^{-8} and 220×10^{-8} M^{-1} sec^{-1}, respectively, and the corresponding values for N,N,N-trimethylanilinium salts are 4.76×10^{-8} and 1.15×10^{-8} M^{-1} sec^{-1}, respectively. Similar results were obtained for the nitration of benzylammonium salts.

Bishop and Craig[49] have discussed the inductive effect of NH_3^+ in terms of a perturbation of the energy levels of the benzene molecule by the NH_3^+ group. Their calculated charge distribution is unlike any of the charge distributions obtained in the present work. The model suggested is not in accord with the physical and chemical results mentioned above.

Experimental Section

Chemicals. Diethyl ether, methyl alcohol, ethyl acetate, chloroform, acetone, benzene, *p*-dioxane, and *t*-butyl alcohol came from the Mallinckrodt Chemical Co.; methyl, ethyl, *n*-propyl, and *n*-butyl iodides, 2,6-dibromoaniline, 2,6-dimethylaniline, 3,5-dimethylaniline, 4-chloroaniline, 4-bromoaniline, 4-nitroaniline, *p*-toluidine, *p*-anisidine, and trifluoroacetic acid came from Eastman Organic Chemicals; *n*-amyl iodide, *n*-amyl bromide, *n*-amyl chloride, di-*n*-octylamine, *n*-octyl iodide, and *p*-*n*-butylaniline, K and K Rare Chemicals; hydrogen iodide, hydrogen chloride, hydrogen bromide, and argon, Matheson Coleman and Bell; deuteriochloroform, Merck Sharp and Dohme; *n*-butyllithium, Foote Mineral; trimethyl phosphate, Ethyl Corp.; dimethyl sulfoxide, Crown Zellerbach; methanesulfonic acid, Pennsalt Chemicals; lithium aluminum hydride, Metal Hydrides; tri-*n*-butyl phosphate, Commercial Solvents Corp.; methylene chloride, Motor Kool Products; tetramethylene sulfone, Phillips Petroleum Co.; D_2O, Columbia Chemical Co.

Purification of Solvents. Diethyl ether was distilled from methylmagnesium bromide. Pentane was distilled from lithium aluminum hydride.

4-Deuterio-N,N-dimethylaniline. 4-Bromo-N,N-dimethylaniline (40 g, 0.2 mole) was dissolved in 100 cc of freshly distilled anhydrous ether in a dry 250-cc erlenmeyer flask. The flask was placed in a (nitrogen atmosphere) drybox. An equal amount of *n*-butyllithium (0.2 mole) in hexane was carefully added dropwise with a gas-tight Hamilton syringe. The solution was left in the drybox for 2 hr, and the organolithium compound precipitated. The flask was removed from the drybox, and the reaction mixture was slowly hydrolyzed by adding the minimum amount of deuterium oxide required to dissolve the precipitate. The ether layer was separated and dried over anhydrous sodium sulfate. After the removal of solvents, the oily residue was purified by fractional distillation under vacuum at 61°(5 mm), 14.0 g, 56% yield.

2,6-Dibromo-N,N-dimethylaniline. 2,6-Dibromoaniline (50 g, 0.2 mole) and trimethyl phosphate (20 g, 0.4 mole) were gently heated in a 250-cc round-bottomed flask equipped with an efficient water-cooled condenser. When a vigorous exothermic reaction commenced at 65°, heating was discontinued. After the reaction subsided, two layers were present, and the solution was gently refluxed for 2 hr. It was cooled to room temperature, 20% sodium hydroxide solution (50 cc) was added to the mixture, and the solution was again refluxed for another hour. The mixture was then poured into a 250-cc beaker and allowed to cool to room temperature. The oily layer was poured off from the solid sodium phos-

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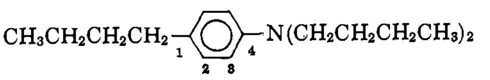
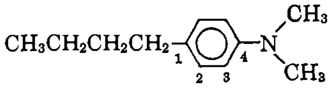
(48) M. Brickman, S. Johnson, and J. H. Ridd, *Proc. Chem. Soc.*, 228 (1962).

(49) D. M. Bishop and D. P. Craig, *Mol. Phys.*, **6**, 139 (1963).

Table XII. Nmr Parameters for Alkylated Anilines

Structure	τ_1	τ_2	τ_3	τ_4	$J_{(2,3)}$, Hz
	7.90	3.19	3.65	7.10	8.50
	7.50	3.09	3.41	7.17	8.80

phate, and water was added to the solid. The aqueous solution was extracted with two 10-cc portions of ether. The combined oil and ether extracts were dried over sodium hydroxide pellets, and the ether was evaporated. The residue was treated with an equal volume of acetic anhydride and stored overnight. Then ether (30 cc) was added to the solution, followed by 10 cc of 33% aqueous HCl and 15 cc of water to dissolve the base. The aqueous acid layer was separated, treated with 25% sodium hydroxide solution to free the base, and extracted with three 15-cc portions of ether, and the ether extracts were dried over sodium hydroxide pellets. The solvent was removed by evaporation, and the residue was distilled under vacuum at 110° (5 mm), 27 g, 48% yield.

2,6-Dideuterio-N,N-dimethylaniline. 2,6-Dibromo-N,N-dimethylaniline (28 g, 0.1 mole) was dissolved in 100 cc of freshly distilled anhydrous pentane in a 250-cc erlenmeyer flask, previously dried by flaming in a current of helium. The flask was transferred to the drybox, and *n*-butyllithium (0.2 mole) in hexane was carefully added dropwise to the solution with a gas-tight Hamilton syringe. The precipitation of 2,6-dilithio-N,N-dimethylaniline salt occured within 2 hr. The reaction flask was removed from the drybox, and the precipitate was carefully hydrolyzed by adding the stoichiometric amount of deuterium oxide. After the solvents were removed by evaporation, the product was distilled under vacuum at 59° (5 mm), 31 g, 26% yield.

4-*n*-Butyl-N,N-di-*n*-butylaniline. 4-*n*-Butylaniline (30 g, 0.2 mole) and tri-*n*-butyl phosphate (37 g, 0.14 mole) was placed in a 250-cc round-bottomed flask equipped with an efficient water-cooled condenser and gently heated until an exothermic reaction commenced. After this vigorous reaction subsided, the solution was refluxed for 2 hr and cooled down to room temperature. A 20% solution of sodium hydroxide (50 cc) was introduced into the flask, and the reaction mixture was refluxed for another hour. The solution was cooled and extracted with three 15-cc portions of ether. The etheral extracts were dried over sodium hydroxide pellets and reduced in volume to approximately 20 cc by evaporation. The residue was distilled under vacuum at 210° (2 mm), 17 g, 32% yield. 4-*n*-Butyl-N,N-di-*n*-butylaniline was identified by its nmr spectrum in CCl_4 as listed in Table XII.

4-*n*-Butyl-N,N-dimethylaniline. 4-*n*-Butylaniline (30 g, 0.2 mole) and trimethyl phosphate (20 g, 0.14 mole) were used to prepare 4-*n*-butyl-N,N-dimethylaniline in the same manner as 4-*n*-butyl-N,N-di-*n*-butylaniline. 4-*n*-Butyl-N,N-dimethylaniline was distilled under vacuum at 185° (2 mm), 16 g, 46% yield. The nmr parameters are listed in Table XII.

Amine Salts. Amine salts were prepared by dissolving the free amines in CCl_4 or ether and adding the pure acids. The precipitated salts were recrystallized from the mixtures of ethyl acetate and methyl alcohol or ethyl acetate and dioxane. Anisidinium bromide, for example, was prepared as follows. Anisidine (22 g, 0.2 mole) was dissolved in 50 cc of ether in a 125-cc erlenmeyer flask. Dry hydrogen bromide gas was bubbled into the flask, and a white precipitate formed instantly. The filtered salt was recrystallized from a mixture of ethyl acetate and methanol until a constant melting point was obtained.

Quaternary amine salts were prepared from tertiary amines and alkyl halides in refluxing ether. The precipitated salts were filtered and recrystallized from mixtures of ethyl acetate and dioxane.

Nmr Spectroscopy. Two nmr spectrometers were used in this study; the Varian A-60 high resolution nmr spectrometer was equipped with a Hewlett-Packard wide-range oscillator, 200 CD, a Hewlett-Packard Model 522 digital counter, and a variable temperature probe. The Varian HR-60 nmr spectrometer was equipped with a Hewlett-Packard Model 522 digital counter, a Hewlett-Packard wide-range audiooscillator 200 CDR, and a heteronuclear decoupler Model HD-60, NMR Specialties.

In order to obtain a maximum signal-to-noise ratio, the field gradients were adjusted between each sweep. Spectra were recorded only when the half-width of the benzene or tetramethylsilane lines was 0.15 Hz or less.

The nmr spectra were calibrated by the method of audio side-band modulation. Audio frequencies were counted for 10 sec with accuracy of 0.2% or better.

The chemical shifts of easily recognizable solvent signals were accurately measured with respect to tetramethylsilane in separate experiments, and the solvent resonance signals were used as secondary standards for most samples. All shifts in this paper are reported on the τ^{50} scale with an accuracy of $\tau \pm 0.002$.

In the cases of CCl_4, $CDCl_3$, ether, and deuterium oxide, a minimum amount of benzene or dioxane was added as a secondary standard. The exact separations between these secondary standards and tetramethylsilane in each solvent were measured individually. For the internal calibration of nmr spectra of compounds in methanol, dimethyl sulfoxide (DMSO), and methylene chloride, the $C^{13}H$ side bands in the solvent absorption were also used.

Analysis of Nmr Spectra. Analysis of A_2X_2, A_2B_2, and A_2B systems, respectively, was accomplished by Pople's method[51] in conjunction with the aid of the computer programs NMRIT and NMREN, written by Swalen.[52]

Osmometer. The Mechrolab Model 203A vapor pressure osmometer was used in this work for determining apparent molecular weights of salts in solution.

Ultraviolet Spectrometer. All ultraviolet spectra were determined with the Cary Model 14 spectrometer. Measurements were made on the salt solutions to ensure that the salts had not dissociated. Such was the case for all data reported herein.

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(50) G. V. D. Tiers, "Characteristic Nmr 'Shielding Values' for Hydrogen in Organic Structures," Minnesota Mining and Manufacturing Co., St. Paul, Minn., 1958.

(51) Reference 2, Chapter 6.

(52) We are indebted to Dr. J. D. Swalen of IBM Research Laboratory of San Jose, Calif., for giving us these programs.