402. *Spectra of Arylammonium Ions.*

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The intensities of weak electronic absorption bands in solutions of arylammonium ions, including tri-*N*-methylanilinium ion, are essentially insensitive to the ionic strength of the solution and to the nature of the solvent. These intensities remain difficult to reconcile with present theory.

It has long been recognized [1,2] (sometimes under the title of " Waterman's effect ") that the electronic spectra of aromatic and heteroaromatic molecules are virtually unaffected by the attachment of an $-NH_3^+$ group, whereas in the corresponding amines the spectra are shifted towards the red and greatly intensified. Sklar [3] accordingly concluded that purely inductive, as opposed to mesomeric effects could be neglected in the theory of substitutional spectral shifts.

It is not surprising that there should be a marked difference in effectiveness between the two types of perturbation,[4] but it has proved difficult to understand why $-NH_3^+$ groups should have no significant effect. This is especially so in the case of the 2600 Å system of benzene and the 3200 Å system of naphthalene, which are intrinsically very weak and depend upon perturbations, ordinarily provided by certain vibrations, for their intensities. The perturbation provided by a whole electronic charge close to the ring should be large, and in reaction kinetics it shows up clearly in the strong *meta*-directing properties of the $-NH_3^+$ group.[5] Consequently, it is hardly surprising that calculations [by Prof. D. P. Craig and one of us (I. G. R.); unpublished because so unsuccessful] of the intensity of the 2600 Å system of $C_6H_5{\cdot}NH_3^+$ consistently predict large enhancements

[1] Ramart-Lucas and Wohl, *Compt. rend.*, 1933, **196**, 1804.
[2] Harberts, Heertjes, van der Hulst, and Waterman, *Bull. Soc. chim. France*, 1936, **3**, 643.
[3] Sklar, *J. Chem. Phys.*, 1939, **7**, 984.
[4] Goodman, Ross, and Shull, *ibid.*, 1957, **26**, 474.
[5] Ingold, *Chem. Rev.*, 1934, **15**, 225.

relative to benzene; yet the standard types of molecular wave-function are quite well suited for calculations of the π-electron polarizability of benzene [6,7]—a closely related quantity. The model used in the calculations on the anilinium ion was a benzene ring with a charge $+e$ located at the observed C–N bond distance, but it was consistently found that even a charge as small as $0{\cdot}1e$ should measurably alter the spectrum (whose intensification is roughly proportional to the square of the perturbing charge).

This disagreement between calculation and experiment caused us to reconsider the validity of the model. A free-ion spectrum cannot be studied alone; the amines are weak bases and their spectra have all been recorded in aqueous acid solutions of strength 0·01M or more. It seemed possible, therefore, that the full effect of a positively charged substituent might be heavily reduced by an oppositely charged ionic atmosphere or by solvation of the $-NH_3^+$ group. If so, then the intensity should vary with ionic strength, nature of the cations present, and polarity of the solvent.

Spectra in the literature are insufficient to resolve this question, so we examined closely those of anilines and naphthylamines in a variety of solvents, concentrating on the two band systems cited above since they, especially, should be sensitive to changes in molecular environment. As a preliminary, the spectrum of benzene was investigated in water, 4M-hydrochloric acid, and 4M-sodium chloride and found to be identical in all three media.

The substances studied (references are to previous measurements of their acid solution spectra) were aniline,[2,8,9] *N*-methylaniline, di-*N*-methylaniline,[8,10] tri-*N*-methylanilinium chloride, and 1- [9] and 2-naphthylamine.[9,10] The ions added were H^+, K^+, Na^+, Li^+, Cl^-, ClO_4^-, SO_4^{2-}, selected because their absorptions are not too intense in the regions of interest. Representative spectra are shown in the Figure along with the molar extinction coefficient, ε, of the strongest peak and the f value (omitted for the naphthylamines because a stronger transition underlies the 3200 Å system).

The spectra are clearly insensitive to environment, the small variation observed being not far beyond the accuracy of the measurements (determined largely by purity), and in any event nowhere exceeding 5%. Particularly significant are the results on the previously unstudied quaternary salt, tri-*N*-methylanilinium chloride, which is stable in neutral solutions. Its spectrum is virtually the same in water, aqueous solutions of high ionic strength, methanol, and hexane containing just enough methanol to allow it to form a 0·002M-solution.

Among the other amines, a close search was made for specific ionic interactions. The most marked were in acid–salt mixtures of relatively low H^+ concentration and could safely be attributed to activity effects and the presence of traces of free base. At acid concentrations above 0·1M, variations of intensity did not exceed 3%, generally increasing slightly with increasing salt molarity up to 4M. At constant molarity, substitution of ClO_4^- for Cl^- had no effect, and SO_4^{2-} (from observations on 1-naphthylamine only) caused a slight decrease in intensity. Partial replacement of H^+ by alkali-metal ions only very slightly (<3%) altered the intensity.

N-Methylation of anilinium ion increased the intensity by approximately 6% for each methyl group added. Some intensification is expected as the mass of the substituent is increased (the f value for hexachlorobenzene is twice that of benzene), but the methylation effect is probably partly due to interaction of the methyl groups with the ring (*e.g.*, *via* hyperconjugation).[11]

This work thus emphasizes the generality of the original experimental result; the intensities of the spectra of arylammonium ions persistently remain unexpectedly low. Polysubstitution also has no demonstrable effect, as is shown by earlier work on the

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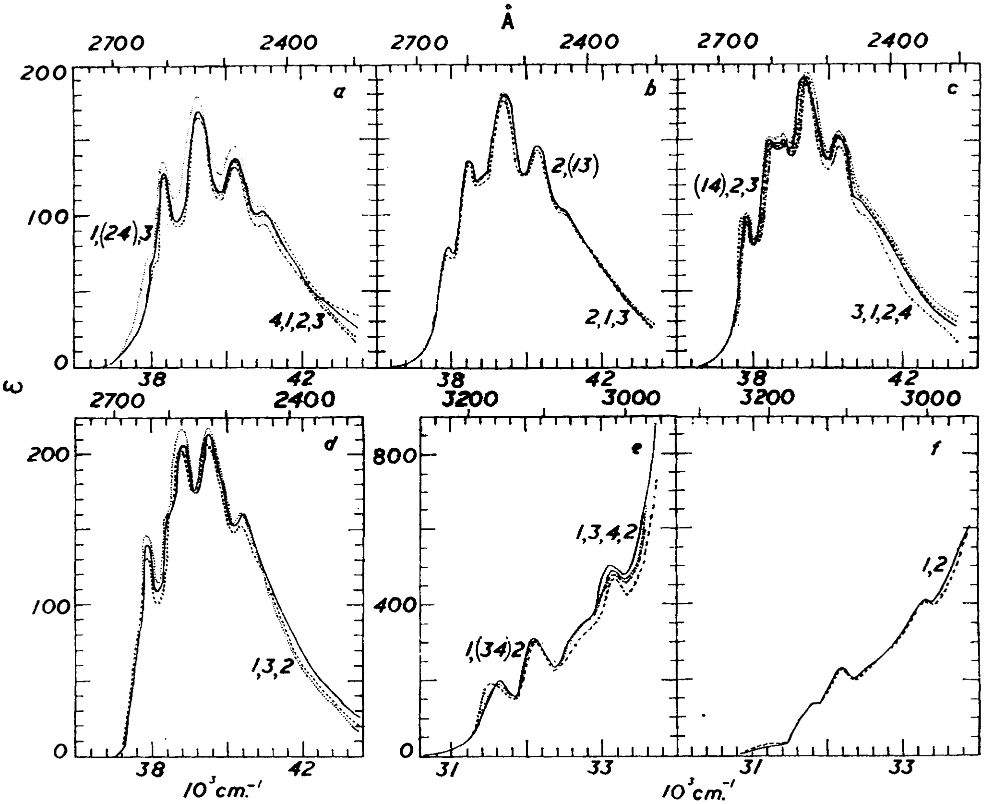
[6] Bolton, *Trans. Faraday Soc.*, 1954, **50**, 1265.
[7] Ross and Yates, unpublished calculations.
[8] Wohl, *Bull. Soc. chim. France*, 1939, **6**, 1312.
[9] Ramart-Lucas, *ibid.*, 1950, **17**, 262.
[10] Moede and Curran, *J. Amer. Chem. Soc.*, 1949, **71**, 852.
[11] Jones, *ibid.*, 1945, **67**, 2127.

phenylenediamines[12–15] (which, for the *meta*-compound, we checked). We are forced to assume then that the rôle of the solvent, whose presence is virtually unavoidable, is relegated to that of a polarizable medium surrounding the absorbing species, but we feel it must be necessary to take into account its bulk dielectric properties, as well probably as its ability to solvate the charged positions of the ring in a more specific manner, when setting up a model for a calculation. The activation by NH_3^+ of the *meta*-position towards electrophilic attack must then be seen as a co-operative effect, specifically involving the attacking ion, and thus as a property of the activated complex.

Absorption spectra of arylammonium ions.



Values of $\varepsilon_{max.}$ in parentheses.

(*a*) Aniline. (1) 10N-HCl (181 at 39,300 cm.$^{-1}$); (2) 1N-HCl (169; $f = 0{\cdot}0023$); (3) 0·1N-HCl (166); (4) 0·1N-HCl (170).

(*b*) *N*-Methylaniline. (1) 1N-HCl (181 at 39,450 cm.$^{-1}$; $f = 0{\cdot}0026$); (2) 0·1N-HCl (177); (3) 0·1N-HCl + 0·9N-NaCl (182).

(*c*) Di-*N*-methylaniline. (1) 1N-HCl (191 at 39,400 cm.$^{-1}$; $f = 0{\cdot}0028$); (2) 0·1N-HCl (192); (3) 0·1N-HCl + 0·9N-NaCl (188); (4) 0·1N-HCl + 0·9N-LiCl (197).

(*d*) Tri-*N*-methylanilinium chloride. (1) 10N-HCl (218 at 40,500 cm.$^{-1}$); (2) water (214; $f = 0{\cdot}0031$); (3) 4N-NaCl (207).

(*e*) 1-Naphthylamine. (1) 1N-HCl (502 at 33,200 cm.$^{-1}$); (2) 0·1N-HCl (465); (3) 0·1N-HCl + 0·9N-NaCl (490); (4) 0·1N-$HClO_4$ (480).

(*f*) 2-Naphthylamine. (1) 1N-HCl (405 at 33,600 cm.$^{-1}$); (2) 0·1N-HCl (402).

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[12] Biquard, *Bull. Soc. chim. France*, 1936, **3**, 909.

[13] Lanning and Cohen, *J. Biol. Chem.*, 1951, **189**, 111.

[14] Maschka, Stein, and Trauer, *Monatsh.*, 1954, **85**, 188.

[15] Anderson and Steedly, *J. Amer. Chem. Soc.*, 1949, **71**, 852.

EXPERIMENTAL

Spectra were measured with a Uvispek spectrophotometer, and some of them checked with a Cary Model 11 instrument. Cell lengths were 2 cm. and concentrations about 0·002M. Some measurements with 5 cm. cells and correspondingly diluted solutions revealed no deviations from Beer's law.

Materials.—The substances are prone to oxidation and because the absorption bands studied are very weak, impurity concentrations of 0·01% or lower could detectably affect the spectra. The criteria of purity are thus much more stringent than those required for measurements of the same accuracy upon the free bases. The purification procedures were therefore repeated till the intensities agreed to within 1%.

Aniline, *N*-methylaniline, and di-*N*-methylaniline were obtained from commercial products, each of which, after a preliminary distillation, was fractionated at 760 ± 1 mm. in a 5-foot spinning-band column. The boiling range was less than 0·1°. They were stored over potassium hydroxide, and immediately before use were repeatedly distilled over zinc powder at a pressure of nitrogen of 10^{-4} mm. till colourless. Solutions were made up by weight, and remained spectroscopically stable for several hours. Tri-*N*-methylanilinium chloride was made from the iodide by ion exchange on a chloride resin (Amberlite IRA/400) and recrystallized from ethyl acetate. Each repurification cycle included further passages through the resin. The salt is deliquescent; a concentrated stock solution was analysed by titration of the chloride. 1-Naphthylamine was refluxed with water to remove the 2-isomer and distilled in nitrogen at 5 mm. The base is unstable, but the hydrochloride, purified by recrystallization from a 1 : 1 mixture of ethanol and concentrated hydrochloric acid, can be preserved in an inert atmosphere. 2-Naphthylamine was prepared by hydrolysing the purified *N*-acetyl derivative; the hydrochloride was recrystallized from concentrated hydrochloric acid. Inorganic chemicals were of Analytical Reagent grade.

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