Nuclear Magnetic Resonance in Amino-group of Aniline Derivatives

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(Received March 28, 1961)

The association of aniline molecules by their weak hydrogen bonds was suggested by several authors[1,2]. However, the association is still not well ascertained. Nuclear magnetic resonance measurements of aniline derivatives have not yet been made and are expected to give valuable information about the intermolecular hydrogen bond of these compounds and, in connection with the work on dimethyl phenols[3], about the effects of the ortho-methyl group on the proton resonance chemical shift of the amino-group. Thus this paper presents the study of the hydrogen bond of the amino-group by NMR measurements.

Experimental

All the NMR measurements were carried out with a Varian NMR spectrometer at a radio frequency of 56.4 Mc./sec. and at a temperature of 20°C. The compounds investigated were aniline, *o*-, *m*- and *p*-toluidines and 2, 3-, 2, 4-, 2, 5-, 2, 6- and 3, 4-dimethylanilines. These were all guaranteed grade reagents and purified by distillation immediately before making solutions. The solvents used were carbon tetrachloride and acetone. These were purified with a Podobielniak fractional distillator. Solutions with concentrations of between 0.01 and 1 mol. fractions were made for all liquid aniline derivatives. 3, 4-Dimethyl aniline is solid and the concentrations of the solutions measured were up to saturated solution. The chemical shifts from water as an external reference were determined by the side band technique. Corrections for bulk diamagnetic susceptibility of the solutions were made. The values of the volume susceptibility were obtained by applying Pascal's rule and appropriate extrapolations. Their values were 0.676 for aniline, 0.70 for all toluidine isomers and 0.68 for all dimethyl aniline isomers.

Results and Discussion

The concentration dependence of the amino proton resonance for carbon tetrachloride solutions are shown in Fig. 1a and those for acetone solutions in Fig. 1b. Pure aniline derivatives investigated give amino proton resonance at $+1.7\sim+1.9$ p. p. m. The resonance fields are remarkably higher than those of hydroxyl proton resonance in phenols. Figure 2 shows an example of the concentration dependence of the chemical shifts for dimethyl aniline isomers. The resonance of the amino protons in carbon tetrachloride solutions was a sharp single absorption while that in acetone solutions was generally broad, especially in dilute solutions.

In Fig. 1, curves for the amino protons in various aniline derivatives investigated are observed to fall in a rather narrow field range and apparently there is no notable feature connecting the relative position of the methyl group to the amino group. This fact is remarkably in contrast with the hydroxyl proton resonance of dimethyl phenol isomers[3]. In

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[1] E. Fischer, *Z, Naturforsch.*, **9a**, 90 (1954); A. E. Lutskii, *Zhur. Obshchei. Khim.*, **26**, 2299 (1956).

[2] J. C. Dearden and W. F. Forbes, *Can. J. Chem.*, **38**, 896 (1960).

[3] I. Yamaguchi, This Bulletin, **34**, 774 (1961).

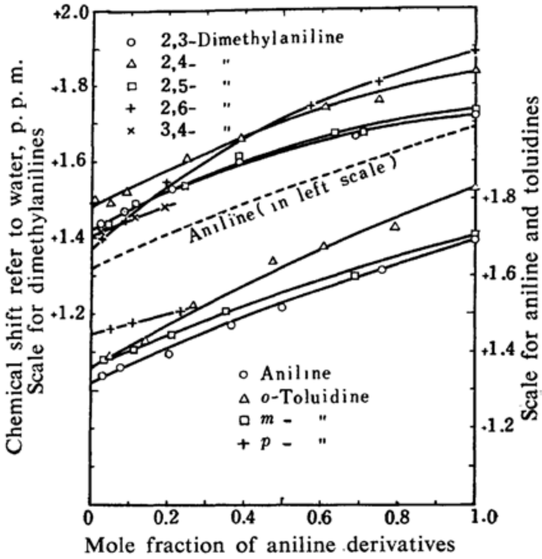

Fig. 1a. Concentration dependence of amino proton chemical shift for aniline derivatives in carbon tetrachloride solution.

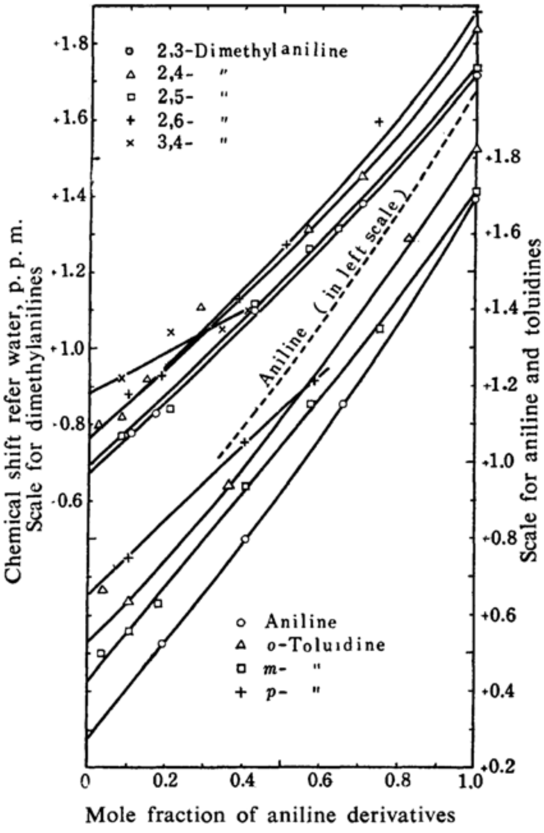

Fig. 1b. Concentration dependence of amino proton chemical shift for aniline derivatives in acetone solution.

this narrow range, the curves for dimethyl aniline isomers appear at the highest field side, those for toluidine isomers at the middle and that for aniline at the lowest side. This order seems to correspond exactly to the order of the base strength of these compounds. The cause of this arrangement of the shifts would mainly be the inductive effect of the methyl groups. In each group of the isomers, the curves for compounds with ortho- or para-methyl group appear at a higher field than those with the meta-methyl group. This result suggests that the mesomeric effect of the methyl group also has an important role to the chemical shift of the amino protons.

Dodd and Stephenson[4] showed a correlation between the basicity of amines and the NH frequency shift in the infrared absorption spectrum caused by hydrogen bond formation between amines and acetone or pyridine. Thus it seems to be natural to expect some correlations between basicity and hydrogen bond shift of proton resonance spectrum of an aniline. Several authors[5,6] pointed out that the basicity of aniline derivatives is strongly dependent on the position and the inductive and mesomeric effects of a substituent in the ring. For example, among *m*- and *p*-toluidines and aniline the base strength of *p*-toluidine is the strongest and that of aniline is the weakest, and this fact was ascribed to the inductive and mesomeric effects of the methyl group. However, the effect of an ortho-substituent on the basicity is not simple because of the additional specific ortho effect[5].

The base strengths of aniline derivatives were reported by several authors[5,7]. Although the pK_a value of a compound reported in one paper is slightly different from that in another, due partly to the solvent and concentration used, the order of the magnitude of the pK_a values is almost the same. The following is the increasing sequence of the pK_a values of aniline derivatives: 3, 4-diMe-, *p*-Me-, 2, 4-diMe-, 3, 5-diMe-, *m*-Me-, 2, 3-diMe-anilines, aniline, 2, 5-diMe-, *o*-Me- and 2, 6-diMe-anilines. The order of the values of the chemical shift in carbon tetrachloride solutions seems to correlate approximately with that of the base strengths of the compounds although some lack of accordance between the two orders is observed. Qualitatively, the factor which

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[4] R. E. Dodd and G. W. Stephenson, "Hydrogen Bonding", Ed. by Hadzi, Pergamon Press, New York (1959), p. 177.

[5] R. N. Beale, *J. Chem. Soc.*, **1954**, 4494.

[6] M. Gillois and P. Rumph, *Bull. soc. chim. France*, **1954**, 112.

[7] N. F. Hall and M. R. Sprinkle, *J. Am. Chem. Soc.*, **54**, 3469 (1932); G. Thomson, *J. Chem. Soc.*, **1946**, 1113; van Helden et al., *Rec. trav. chim.*, **73**, 39 (1954); B. M. Wepster, ibid., **76**, 357 (1957).

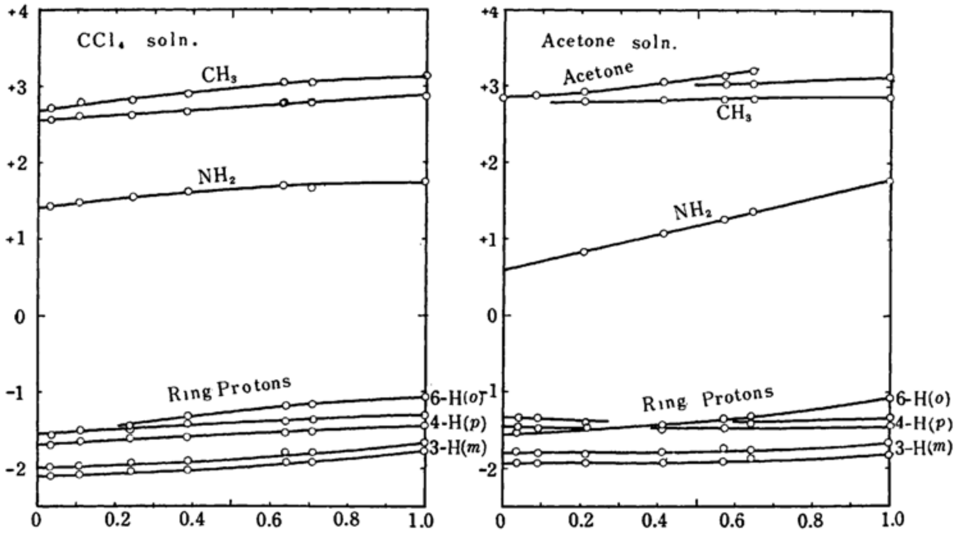

Fig. 2. Concentration dependence of chemical shift for 2,5-dimethyl aniline in carbon tetrachloride and acetone solutions.

determines the base strength of an amine is the charge density on the nitrogen atom[8] and not that on the proton in the amino group. The effective charge density on the nitrogen atom, which has lone pair electrons as well as valence electrons, may be affected in a complicated way rather by changes in the structural and chemical circumstances of the amino-group than by the electronic effect of substituents. Therefore the slight lack of accordance between the order of the proton resonance chemical shifts and that of the base strengths may be observed.

For carbon tetrachloride solutions, the slope of the concentration dependence curve for the amino protons is considerably small and is nearly the same as, but slightly smaller than, that for methyl protons in toluidine and dimethylaniline isomers. The positive slope of the curves is caused by the magnetic anisotropy effect of the aromatic rings in the solutions[9]. If the slope of the curves for methyl protons is assumed to arise merely from the anisotropic effect and if the amino protons are assumed to be affected by the same anisotropic field as that for methyl protons, the curves for the amine protons which are subtracted by the anisotropic effect can be obtained. These curves have a negative slope which might be an indication of a dissociation process of hydrogen bonds on dilution. The association of aniline molecules by intermolecular hydrogen bonds is not well ascertained, although it is, with less confidence, pointed out by several authors with physicochemical measurements[1] and infrared studies[2]. If a hydrogen bond with the same order of strength as an OH hydrogen bond exists between solute molecules, the slope would be more concentration dependent. The slopes which were observed are much smaller than those of dissociation processes of the OH hydrogen-bonded systems. This difference in the NMR behavior between the system might be partly due to the difference between the effective charge in the electronic shielding of the OH group and that of the amino group on formation of hydrogen bonds. It is unfortunate that the data available for estimation of bond energies of the N–H···N hydrogen-bonded systems as well as NMR data for amino protons are very scarce, and at the present stage, no decisive conclusion on the extent of the hydrogen bonding for aniline derivatives can be drawn from the NMR shift data. However, from the knowledge of the NMR measurements so far made with the OH hydrogen-bonded systems, it may be said that the hydrogen-bonded association of aniline derivatives occurs and the strength of it is fairly weak.

For acetone solutions, the effect of the hydrogen bond formation between the solute and the solvent is remarkable and the dilution shifts are large compared with those for carbon tetrachloride solutions. The order of the magnitude of the chemical shifts of the amino protons in acetone solutions is almost the same as that for carbon tetrachloride solutions.

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[8] See for example: G. W. Wheland, "Resonance in Organic Chemistry", John & Wiley. New York (1955).

[9] A. A. Bothner-By and R. E. Glick, *J. Chem. Phys.*, 26, 1651 (1957).

TABLE I. CHEMICAL SHIFTS, DILUTION SHIFTS AND Δ VALUE OF NH_2 PROTON IN ANILINE DERIVATIVES (IN p. p. m.)

Compound	Pure *p*-cresol	CCl_4 soln.		Acetone soln.		Δ
		Concn.=0	$\delta_1-\delta_0$	Concn.=0	$\delta_1-\delta_0$	
Aniline	+1.69	+1.33	0.36	+0.28	1.41	1.05
o-Toluidine	+1.82	+1.37	0.45	+0.53	1.29	0.84
m-Toluidine	+1.71	+1.37	0.34	+0.44	1.27	0.93
p-Toluidine	—	+1.44	—	+0.66	—	0.78
2,3-Dimethyl aniline	+1.72	+1.42	0.30	+0.67	1.05	0.75
2,4-Dimethyl aniline	+1.84	+1.48	0.36	+0.78	1.06	0.70
2,5-Dimethyl aniline	+1.73	+1.43	0.30	+0.68	1.05	0.75
2,6-Dimethyl aniline	+1.88	+1.38	0.50	+0.76	1.08	0.62
3,4-Dimethyl aniline	—	+1.5	—	+0.9	—	0.6

bond formation of a compound, Δ value*, proposed by the present author[10] is listed in Table I for the aniline derivatives investigated. The values of the chemical shift and the dilution shifts for the amino protons in carbon tetrachloride and acetone solutions are also listed in Table I. The magnitudes of the Δ value are about 1 and this value suggests the weakness in the ability of hydrogen bond formation of the compounds. This value nearly corresponds to the ability of 2,6-di-*tert*-butyl-*p*-cresol[10]. The Δ values for aniline and *m*-toluidine are large while that of 2,6-dimethyl aniline is remarkably small. With the data of the dilution shift for carbon tetrachloride solutions, the extent of the hydrogen bond formation of the aniline derivatives is clearly dependent on the existence of the ortho-methyl group.

Among the curves of the amino proton resonance for carbon tetrachloride solutions the behavior of the curves for 2,*x*-dimethyl anilines (x=3,4 and 5) are peculiar as indicated by their small dilution shifts compared with that of 2,6-dimethyl aniline. The value is even smaller than that of *o*-toluidine. Considering the behavior of the curves by subtracting the anisotropic effect of the rings in the solution medium, this peculiarity apparently means that 2,*x*-dimethylanilines (x =3,4 and 5) associate to a higher extent than *o*-toluidine does. However, this intrerpetation can not be accepted from the standpoint of the Δ values of these compounds. This discrepancy may possibly be caused by an additional effect of the *x*-(meta- or para-) methyl group on the amino proton resonance and this effect counterbalances the effect of the ortho-methyl group.

The ring proton spectra for dimethyl aniline isomers show slight concentration dependence. The displacement of the ortho-proton resonance line to a lower field on dilution is observed. The displacement is more remarkable for acetone solutions than for carbon tetrachloride solutions. This inclination is opposed to the behavior of the ortho-proton curves for phenol derivatives[3,11]. On association of aniline derivatives, the charge migration from the ring to the amino group would not be so much as for phenol derivatives because, possibly, the hydrogen bonding is very weak. However, the proton in the amino group is attracted by the proton-accepting group and this results the change in the electrostatic field at the ortho-proton[12]. In this way, the association would cause the displacement of the resonance field of the ortho-proton to a higher field. In acetone solutions, a weak hydrogen bond between the acetone and the ortho-proton would form and the displacement of the ortho-proton resonance to a lower field on dilution is observed as in the case of dimethyl phenols in acetone solution[3].

Summary

Concentration dependenec of the chemical shift of amino protons in aniline derivatives in carban tetrachloride and acetone solutions were measured. The chemical shift of the amino proton in aniline derivatives is revealed to be clearly dependent on the existence of the ortho-methyl group. In carbon tetrachloride solutions, the concentration dependence of the resonance lines is slight, suggesting that the association of the solute molecules by hydrogen bonding is very weak. In acetone solutions, the dependence suggests hydrogen bond formation between solute and acetone. The base strength of aniline derivatives appeared to have no direct correlation with the

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[10] I. Yamaguchi, This Bulletin, 34, 451 (1961).

* Δ is defined as the difference between the chemical shift of a hydnogen-bonded proton at infinite dilution for carbon tetrachloride solution and that for an acetone solution.

[11] I. Yamaguchi, This Bulletin, 34, 353 (1961).

magnitude of the chemical shift of amino proton in these compounds. The ring proton spectra of dimethyl aniline are slightly concentration dependent. The resonance in the ortho-protons appears to be displaced to a lower field on dilution and this tendency was ascribed to the change in the electrostatic field at the proton arising from the N–H bond moment change by hydrogen bond formation.

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