The Influence of Hydration on Base Strength.
II. Aliphatic Amines and N-Substituted Anilines

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Empirical equations are presented for correlating the base strengths of aliphatic amines and N-substituted anilines in terms of Taft's substituent constants (σ^*) and in terms of the number of hydrogens attached to nitrogen in the ammonium ion (n). Apart from a statistical correction, the number n is used as a measure of the net effect of hydration of amine and ammonium ion by hydrogen bonding. Various mathematical functions of n are used to estimate the effect and give values about 6 pK units for the contribution of hydration to the base strength of tertiary amines to about 11 pK units in the case of NH_4^+. The value for tertiary amines agrees with an estimate based on electrostatics. The effect of hydration shows a small dependence on the nature of the substituents attached to nitrogen, determined by σ^*. In the case of aniline and N-monosubstituted anilines, a previously unsuspected factor (resonance-augmented hydration of the free base) may be base weakening by about 1.6 pK units. The inductive effect of the phenyl group in anilines appears to be base weakening by only 0.37 pK unit, instead of 3, as had been supposed. Resonance and effects of hydration are then each responsible for a reduction in base strength of 2–3 pK units.

In paper I of this series,[1] the effects of hydration of amine and ammonium ion on the equilibrium

$$R_1R_2R_3NH^+ + H_2O \rightleftharpoons R_1R_2R_3N + H_3O^+ \qquad (1)$$

and possible influences of the substituents, R_i, on the hydration energy, were considered. A general equation was presented for relating the net hydration energy (defined as the difference between the hydration energies of ammonium ion and amine) to the nature and number of the substituents. This was estimated as 4–8 pK units for the first water molecule, from electrostatic considerations, and it was suggested that the effect should be smaller for additional water molecules because of charge dispersal and repulsive interactions between the dipoles of two or more water molecules. In this paper, empirical estimates of net hydration energies are made from the base strengths of aliphatic amines; and the apparent dependence of net hydration energy on the nature and number of substituents is compared with the form of the equation presented earlier. Finally, an empirical extension to aromatic amines is made.

Aliphatic Amines. The base strengths of aliphatic amines having regular[2] substituents are well correlated by either of the following empirical equations (2 and

3). These equations are equivalent to within 0.01 unit for $n = 1, 2, 3$, or 4.

$$pK_a = 9.61 + (10.92 - 0.778n) \log n -$$
$$(3.38 - 0.08n)\sum_{i=1}^{3}\sigma_i^* - \log (n/s) \quad (2)$$

$$pK_a = 4.39 + 6.7066\ldots n - 1.63n^2 +$$
$$0.1433\ldots n^3 - (3.38 - 0.08n)\sum_{i=1}^{3}\sigma_i^* - \log (n/s) \quad (3)$$

In these equations, pK_a is, as usual, the negative logarithm of the thermodynamic equilibrium constant for reaction 1; n is the number of hydrogens attached to nitrogen in the ammonium ion; $\Sigma\sigma_i^*$ is a sum of substituent constants devised by Taft,[3] one for each of the groups R_1, R_2, and R_3 attached to nitrogen in the amine; and s is a statistical factor designating the number of equivalent basic sites in the amine.[4]

The origins and meanings of eq. 2 and 3 are as follows. Hall[5] showed that the base strengths of aliphatic amines are well correlated by means of Taft's σ^* constants, but that three separate equations are needed, as follows: for primary amines

$$pK_a = 13.23 - 3.14\Sigma\sigma^* \qquad (4a)$$

for secondary amines

$$pK_a = 12.13 - 3.23\Sigma\sigma^* \qquad (4b)$$

for tertiary amines

$$pK_a = 9.61 - 3.30\Sigma\sigma^* \qquad (4c)$$

Ammonia is in a class by itself and was not correlated.

The success of Hall's correlation tends to discredit steric strain[6] and "polarstriction"[7] as factors determining the base strengths of amines, and to support the idea that solvation of the ammonium ion by hydrogen bonding to the oxygen of a water molecule stabilizes the ion in aqueous solution and thus tends to increase base strength under these conditions.[8] The extent of hydrogen bonding is supposed to be directly related to the number of hydrogens attached to nitrogen in the ammonium ion, and would be greatest for ammonia itself and least for a tertiary amine.

The largest deviations from eq. 4a, b, and c are found mostly with amines having substituents with large steric requirements, and are such as to make the base

(1) F. E. Condon, *J. Am. Chem. Soc.*, **87**, 4481 (1965).

(2) A "regular" substituent was defined in paper I of this series as one for which the effect on pK_a is wholly an inductive or direct field effect. Steric effects, resonance interaction with the electron pair on nitrogen, and effects of hydrophilic groups within the substituent are absent.

(3) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 536 ff.

(4) S. W. Benson, *J. Am. Chem. Soc.*, **80**, 5151 (1958).

(5) H. K. Hall, Jr., *ibid.*, **79**, 5441 (1957).

(6) H. C. Brown, *ibid.*, **67**, 374, 378 (1945).

(7) S. R. Palit, *J. Phys. Colloid Chem.*, **51**, 1028 (1947).

(8) (a) A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1293 (1949); (b) R. G. Pearson, *J. Am. Chem. Soc.*, **70**, 204 (1948); (c) R. G. Pearson and F. V. Williams, *ibid.*, **76**, 258 (1954).

weaker than calculated. They can be explained qualitatively as a result of steric hindrance to solvation.[5] Hall wisely refrained from using such data in evaluating the constants for the eq. 4a, b, and c.[9]

Equations 2 and 3 are results of an attempt by this author to combine Hall's three equations (eq. 4) into one in a way that would take quantitative account of the number of hydrogens attached to nitrogen in the ammonium ion and the corresponding degree of stabilization by hydrogen bonding. For eq. 2, a "log n" term was introduced in order to maintain consistency with the definitions of pK_a and σ^*. Then it was found by trial and error that a two-term coefficient, $9.92 - 0.778n$, was needed to generate the three leading terms in eq. 4a, b, and c, and an additional term, 13.71, for the case of ammonia itself. The required statistical term,[4] $-\log (n/s)$, was added and was counterbalanced by changing the two-term coefficient to $(10.92 - 0.778n)$. Finally, as the coefficients of $\Sigma\sigma^*$ in Hall's equations (eq. 4) differ regularly by 0.08, on the average, the two-term coefficient, $3.38 - 0.08n$, was constructed purely empirically for the combined eq. 2.

For eq. 3, the statistical term for monobasic amines was added to each of the eq. 4a, b, and c so as to give: for primary amines

$$pK_a = 13.71 - 3.14\Sigma\sigma^* - \log (n/s) \quad (5a)$$

for secondary amines

$$pK_a = 12.43 - 3.23\Sigma\sigma^* - \log (n/s) \quad (5b)$$

for tertiary amines

$$pK_a = 9.61 - 3.30\Sigma\sigma^* - \log (n/s) \quad (5c)$$

and for ammonia itself

$$pK_a = 14.31 - 3.06\Sigma\sigma^* - \log (n/s) \quad (5d)$$

The last equation follows from substituting $n = 4$ into eq. 2. Next, the power series in n, $f(n) = cn + dn^2 + en^3$, was constructed; and the constants in this function were evaluated by requiring that the differences in $f(n)$ for $n = 1, 2, 3$, and 4 correctly reproduce the differences in the leading terms of eq. 5a, b, c, and d. The coefficient for $\Sigma\sigma^*$ in eq. 3 was constructed in the same way as for eq. 2.

Equations 2 and 3 generate Hall's three equations with one small difference: the coefficient for $\Sigma\sigma^*$ in eq. 4b becomes 3.22 instead of 3.23. This makes a difference of no more than 0.03 unit in calculated pK_a values of secondary amines.

In addition, eq. 2 and 3 yield for the pK_a of ammonia, 9.21, which is the experimental value.[5] It may be noted that this result was a coincidence of the development of eq. 2, but a required result in the development of eq. 3.

The correlation by eq. 2 and 3 is shown in Figure 1. The effects of hydration on pK_a are tentatively identified with the first "log n" term in eq. 2 and with the power series (cubic) in n in eq. 3; but it is shown subsequently that these terms must be modified by addition of a term in $\Sigma\sigma^*$, which measures structural

effects on the net hydration energy. The quantities measured by the first "log n" term in eq. 2 and by the terms of the power series in n in eq. 3 will be referred to as the "raw net hydration energies."[10]

Equation 2 is of particular interest because it does the same job as eq. 3 with one less constant; and because its logarithmic term for the "raw net hydration energy" is consistent with the definitions of pK_a and σ^*. It does not, however, provide absolute values for the "raw net hydration energies" but provides only values relative to that for a tertiary amine. The first "log n" term vanishes when $n = 1$ (3° amine) and takes on the values 2.82, 4.10, and 4.70, when $n = 2, 3$, and 4, respectively. These are the differences between the leading term in eq. 5c and those in eq. 5b, a, and d, respectively, and will be referred to as "relative raw net hydration energies" (that is, relative to that for a tertiary amine).[11]

The power series in n in eq. 3, then, is simply an extrapolation formula for estimating the "raw net hydration energy" for a tertiary amine. Other methods of extrapolation deserve equal consideration, therefore, in addition to the estimate based on electrostatics made in paper I of this series. Two other extrapolation formulas are contained in the following expressions (eq. 6 and 7). The "log $(n + 1)$" term in eq. 6 and the

$$pK_a = 2.77 + (25.64 - 3.12n + 0.21n^2) \log (n + 1) -$$
$$(3.38 - 0.08n)\sum_{i=1}^{3}\sigma_i^* - \log (n/s) \quad (6)$$

$$pK_a = 3.40 + 6.21\sum_{j=0}^{n-1}(1/2.2)^j -$$
$$(3.38 - 0.08n)\sum_{i=1}^{3}\sigma_i^* - \log (n/s) \quad (7)$$

new summation term appearing in eq. 7 reproduce approximately the differences in the leading terms of eq. 5a, b, c, and d and provide an extrapolation to the "raw net hydration energy" for a tertiary amine.

The several values for the "raw net hydration energies" provided by eq. 2, 3, 6, and 7 (and the estimate based on electrostatics) are assembled in Table I. The latter estimate was for a tertiary amine only; and to it have been added the "relative raw net hydration energies" (the differences in the leading terms of eq. 5a, b, c, and d).

The several estimates are similar but not identical. The "raw net hydration energy" for a tertiary amine appears to be about 6 pK units with an uncertainty of about 0.8 unit.

Further interpretation leads to refinement of the "raw net hydration energies." Rearrangement of eq. 3 gives eq. 8. The rearrangement is mandatory; for without it, the effects of hydration would appear to

(9) E. Folkers and O. Runquist, *J. Org. Chem.*, **29**, 830 (1964), have arrived at somewhat different values of the constants in eq. 4a, b, and c by utilizing all the data. As the objective here, however, is to evaluate hydration effects apart from steric complications, it is assumed that eq. 4a, b, and c correctly represent the base strengths of amines with "regular" substituents.[2]

(10) Each term in an equation for pK_a represents a contribution to the standard free energy change for reaction 1, $\Delta G°$, in pK units, since $pK_a = \Delta G°/2.303RT$.

(11) Folkers and Runquist[9] have presented a single equation for correlating the base strengths of aliphatic amines, which is equivalent to the following.

$$pK_a = 9.76 + 1.12n - 3.23\Sigma\sigma^*$$

That is, they have suggested the hydration effect is directly proportional to n. In their treatment, however, they have ignored the statistical factor; their proportionality "constant" has an uncertainty of 12.5% (1.12 ± 0.14), and they were forced arbitrarily to set $n = 0$ in the case of tertiary aliphatic amines.
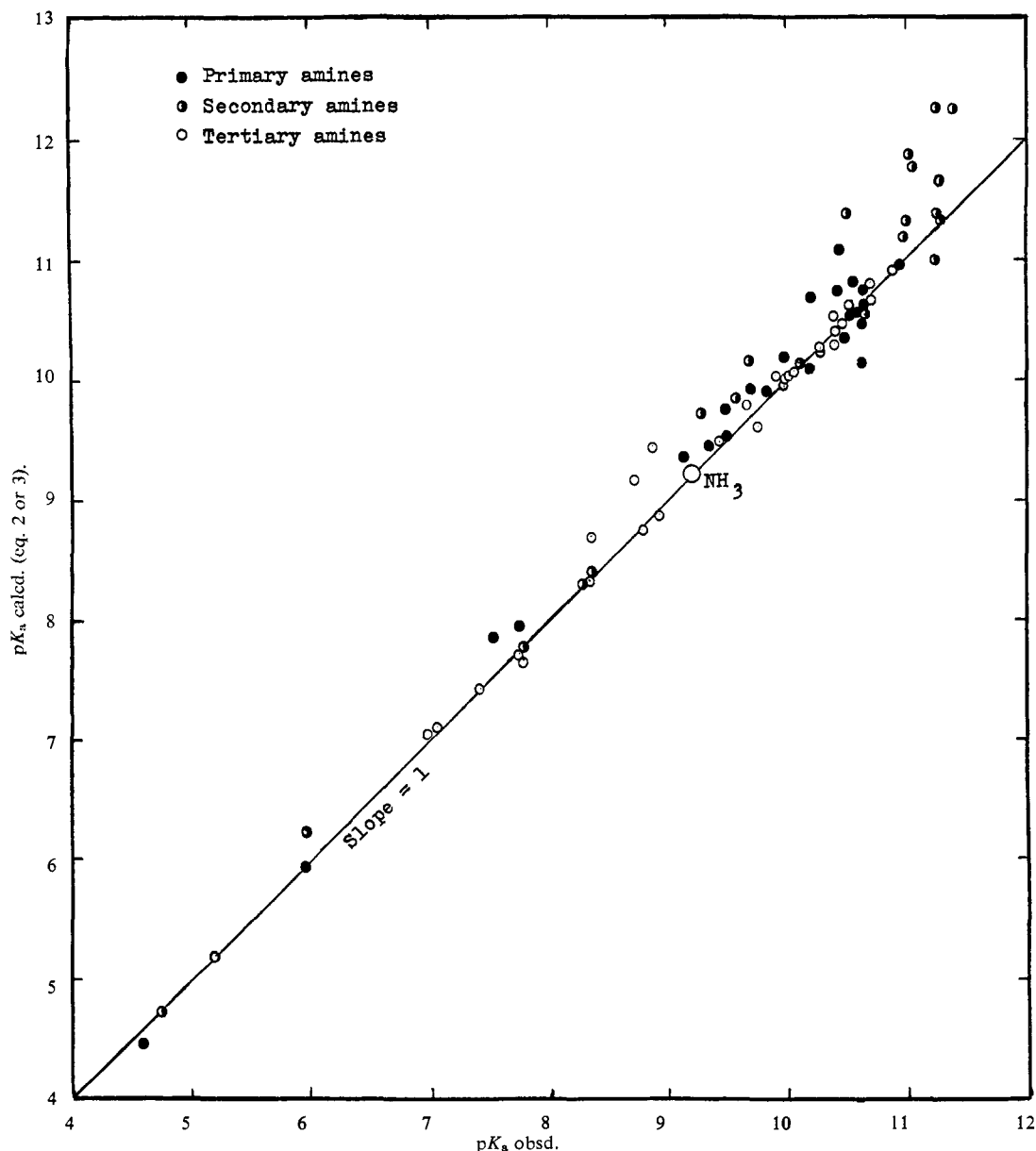
Figure 1. Correlation of base strengths of aliphatic amines (listed in ref. 5).

$$pK_a = 4.39 + 6.7066\ldots n - 1.63n^2 +$$

$$0.1433\ldots n^3 + 0.08n\sum_{i=1}^{3}\sigma_i^* -$$

$$3.38\sum_{i=1}^{3}\sigma_i^* - \log(n/s) \quad (8)$$

depend on the origin of the scale of the substituent constants, σ^*. Such a dependence is inadmissible, since the origin of the scale is arbitrary.[12]

(12) Suppose, for example, that the substituent constants were all relative to $\sigma_H = 0$, instead of $\sigma_{Me} = 0$. A new scale of constants then would be defined by the relationship $\sigma\dagger = \sigma^* - 0.49$, inasmuch as $\sigma^*_H = 0.49$; and in each of the eq. 5 (or 4), $\Sigma\sigma^* = \Sigma\sigma\dagger + 1.47$. With this substitution, one obtains for tertiary amines

$$pK_a = 4.76 - 3.30\Sigma\sigma\dagger - \log(n/s) \quad (5c')$$

and for secondary amines

$$pK_a = 7.68 - 3.23\Sigma\sigma\dagger - \log(n/s) \quad (5b')$$

and similarly modified eq. 5a' and 5d'. The differences in the leading terms, which are attributed to hydration effects, now are 2.92, 4.33, and 5.05 pK units, instead of 2.82, 4.10, and 4.70 pK units.

The interpretation of eq. 8 is as follows. The leading term, 4.39, represents the intrinsic pK_a of tri-

Table I. Effects of Hydration on Base Strengths of Aliphatic Amines. The "Raw[a]" Net Hydration Energies" (pK Units)

n (class)	Rela-tive (eq. 2)	"Cubic" (eq. 3)	"Log $(n+1)$" (eq. 6)	$6.21\sum_{j=0}^{n-1}\left(\dfrac{1}{2.2}\right)^{j}$ (Eq. 7)	Electro-statics
1 (3°)	0[b]	5.22	6.84	6.21	6.03 ± 2.01[c]
2 (2°)	2.82	8.04	9.66	9.03	8.85 ± 2.01
3 (1°)	4.10	9.32	10.94	10.31	10.13 ± 2.01
4 (NH₃)	4.70	9.92	11.55	10.89	10.73 ± 2.01

[a] For refinement, add $0.08n\Sigma\sigma^*$. (See text.) [b] Arbitrary zero. [c] The spread is for values of the "internal" dielectric constant between 1 and 2.[1]

methylamine in the absence of hydration effects. The effects of hydration on the pK_a of any particular

amine are measured by the "net hydration energy" expression (eq. 9). The effects of structural changes

$$\delta pK_h = 6.7066\ldots n - 1.63n^2 +$$
$$0.1433\ldots n^3 + 0.08n\sum_{i=1}^{3}\sigma_i^* \quad (9)$$

(with trimethylamine as a basis) are measured by the second term in $\Sigma\sigma^*$; the reaction constant, $\rho^* = 3.38$, is the same for all amines. The last term is the statistical factor described earlier.

Rearranged forms of eq. 6 and 7 may be given a similar interpretation. They provide values of 2.77 and 3.40, respectively, for the intrinsic pK_a of trimethylamine, and correspondingly different expressions for the effects of hydration (eq. 10 and 11).

$$\delta pK_h = (25.64 - 3.12n + 0.21n^2)\log(n + 1) +$$
$$0.08n\sum_{i=1}^{3}\sigma_i^* \quad (10)$$

$$\delta pK_h = 6.21\sum_{j=0}^{n-1}\left(\frac{1}{2.2}\right)^j + 0.08n\sum_{i=1}^{3}\sigma_i^* \quad (11)$$

The expression (eq. 9) is identical in form with that derived in paper I of this series, which was based on the proposal that effects of charge dispersal and interactions between the dipoles of two or more bound water molecules might be accommodated by a power series in $n - 1$. The constant, 0.08, appearing in front of $\Sigma\sigma^*$ may therefore be identified as the difference between reaction constants for hydration of ammonium ion and amine. Except for this correspondence, however, there is no reason for preferring eq. 9 over alternative expressions, such as (10) and (11).

The effects of structure on the "net hydration energy," $0.08n\Sigma\sigma^*$, vary from -0.031 to $+0.67$ pK unit among the 77 amines correlated by Hall.[5] The remaining parts of the expressions 9, 10, and 11 are evaluated in Table I.

Averaging and dividing each average by n gives 6.1, 4.5, 3.4, and 2.7 for the hydration effect per water molecule, when n is 1, 2, 3, and 4, respectively. This decreasing dependence on n may be attributed to charge dispersal and repulsive interactions between the dipoles of two or more bound water molecules.

Finally, it should be noted that hydration by other mechanisms, such as dipole–dipole interactions, have not been considered here. Their contributions to the pK_a differences observed may be quite small, however, because of the shielding provided by hydrogen-bonded water molecules.

N-Substituted Anilines. Folkers and Runquist[9] have shown that the base strengths of N-substituted anilines can be correlated by means of Taft's σ^* constants, but that each class of amine requires a different straight line plot of pK_a against $\Sigma\sigma^*$, indicating different degrees of hydration of primary, secondary, and tertiary anilinium ions. Their equation for N-substituted anilines (combining hydration and structural effects) may be written as eq. 12 in which $\sigma^* = 0.60$ for the

$$pK_a = 6.15 + 1.12n - 3.23\sum_{i=1}^{3}\sigma_i^* \quad (12)$$

phenyl group[3] is to be used. In their treatment, however, they have ignored the statistical factor[4] and

possible effects of steric inhibition of resonance in such bases as N-*t*-butylaniline, N-*t*-amylaniline, and N-methyl-N-*t*-butylaniline.[13]

Equations 2 and 3 of this paper are unsatisfactory for correlating the base strengths of N-substituted anilines. In the first place, the σ^* value of 0.60 for the phenyl group would not be suitable, because of the strong electron-withdrawing resonance interaction with the amino group. Even with a special, exalted value of σ^* for the phenyl group, however, the equations prove to be unsatisfactory, because *the difference in the pK_a values of secondary and tertiary N-substituted anilines attributable to hydration effects is only about half as great as the corresponding difference in the pK_a values of secondary and tertiary aliphatic amines.* These differences were taken care of in the approximate treatment of Folkers and Runquist by an arbitrary use of $n = 0$ for the aliphatic tertiary amines.[9]

Consequently, an equation of the same form as eq. 2 was developed for the N-substituted anilines. From data tabulated by Folkers and Runquist and by methods used by Hall[5] and by Folkers and Runquist, but omitting data for bases in which steric inhibition of resonance may be a factor, the following equations were found. For nine N-monosubstituted anilines

$$pK_a = 6.22 - 3.03\sum_{i=1}^{2}\sigma_{al}^* \quad (13a)$$

with a standard deviation of 0.144 pK_a unit; and for ten N,N-disubstituted anilines

$$pK_a = 5.36 - 3.19\sum_{i=1}^{2}\sigma_{al}^* \quad (13b)$$

with a standard deviation of 0.341 pK_a unit.

In these equations, the symbol σ_{al}^* means that only the σ^* values for the aliphatic substituents are to be used. As the phenyl group is a constant substituent throughout the series, its σ^* value was arbitrarily taken as 0.

A decrease of 0.16 unit in ρ^* is indicated on going from the disubstituted anilines to the monosubstituted anilines. Linear extrapolation gives $\rho^* = 2.87$ for aniline itself. Since for aniline, $pK_a = 4.65$, and $\Sigma\sigma_{al}^* = 0.98$, we may write for aniline

$$pK_a = 7.46 - 2.87\sum_{i=1}^{2}\sigma_{al}^* \quad (13c)$$

On introducing the statistical factor and a ρ^* that is linearly dependent on n, these equations become, for aniline

$$pK_a = 7.94 - (3.35 - 0.16n)\sum_{i=1}^{2}\sigma_{al}^* - \log n \quad (14c)$$

for N-monosubstituted anilines

$$pK_a = 6.52 - (3.35 - 0.16n)\sum_{i=1}^{2}\sigma_{al}^* - \log n \quad (14a)$$

and for N,N-disubstituted anilines

$$pK_a = 5.36 - (3.35 - 0.16n)\sum_{i=1}^{2}\sigma_{al}^* - \log n \quad (14b)$$

(13) (a) G. Vexlearschi and P. Rumpf, *Compt. rend.*, **229**, 1152 (1949); (b) T. C. van Hoek, P. E. Verkade, and B. M. Wepster, *Rec. trav. chim.*, **77**, 559 (1958).
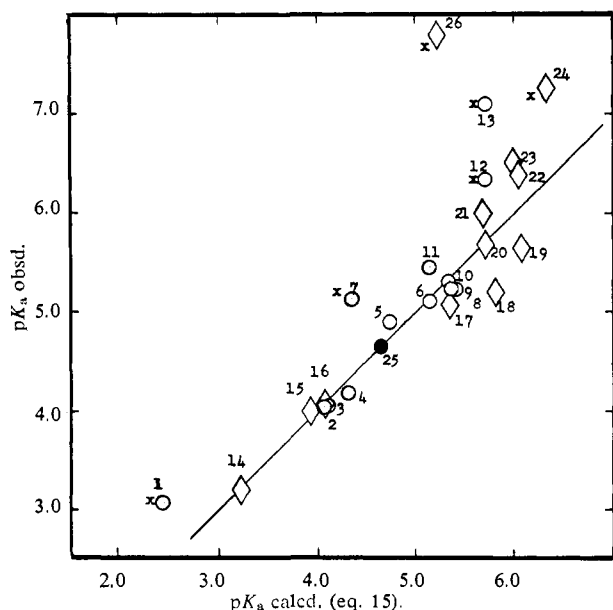
Figure 2. Correlation of base strengths of N-substituted anilines: ●, aniline; ○, N-monosubstituted anilines; ◇, N,N-disubstituted anilines; ×, data not used in evaluation of constants for eq. 15. Substituents or identity: 1, HC≡CCH₂; 2, C₆H₅CH₂; 3, HOCH₂-CH₂; 4, H₂C=CHCH₂; 5, CH₃; 6, CH₃CH₂; 7, CH₃CH=CHCH₂; 8, sec-C₄H₉; 9, n-C₃H₇; 10, i-C₃H₇; 11, n-C₄H₉; 12, t-C₅H₁₁; 13, t-C₄H₉; 14, N-phenylmorpholine; 15, C₆H₅CH₂, C₆H₅CH₂; 16, HOCH₂CH₂, HOCH₂CH₂; 17, CH₃, CH₃; 18, N-phenylpiperidine; 19, n-C₃H₇, n-C₃H₇; 20, CH₃, n-C₃H₇; 21, CH₃, CH₃CH₂; 22, CH₃CH₂, n-C₃H₇; 23, CH₃CH₂, CH₃CH₂; 24, benzoquinuclidine; 25, aniline; 26, CH₃, t-C₄H₉.

Finally, representing each of the leading terms in eq. 7a, b, and c by $A + (B + Cn) \log n$,[14] and solving the three resulting equations for A, B, and C, gave (for aniline and N-substituted anilines)

$$pK_a = 5.36 + (0.75 + 1.55n) \log n -$$
$$(3.35 - 0.16n)\sum_{i=1}^{2}\sigma_{ai}^* - \log n \quad (15)$$

Equation 15 was used to calculate pK_a values of aniline and the 25 N-substituted anilines listed by Folkers and Runquist.[9] The results are compared with the experimental values in Figure 2, where the numbering is that used by Folkers and Runquist.

Bases in which steric inhibition of resonance is probably a factor have pK_a values higher than calculated by eq. 15, as would be expected. These are N-t-butylaniline (12), N-t-amylaniline (13), N-methyl-N-t-butylaniline (26), and benzoquinuclidine (24). The pK_a values of N-propargylaniline (1) and N-crotylaniline (7) also appear to be anomalous and were not used in evaluating the constants for eq. 15. Excluding these, the root mean square (standard) deviation for the remaining 20 compounds is 0.26 pK_a unit.

Estimation of the absolute net hydration energies of the anilines is complicated by resonance effects. As suggested in Figure 3, the free bases on the one hand may suffer a diminished hydration compared to aliphatic amines because of withdrawal of the electron pair on nitrogen into the ring.[15] On the other hand,

(14) A form $A + Bn + Cn^2$ might have been used, but the extrapolation it provides serves no purpose here.
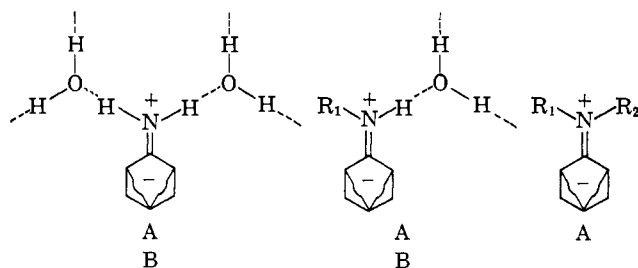(15) Cf. L. Pauling and D. Pressman, J. Am. Chem. Soc., 67, 1003 (1945).

Figure 3. Schematic representation of hydration of anilines (cf. Figure 1, ref. 1) suggesting: A, diminished hydration because of withdrawal of the electron pair from nitrogen; and B, augmented hydration energy because of positive charge on nitrogen.

those having at least one hydrogen on the nitrogen may be more strongly hydrated than corresponding aliphatic amines because of a substantial positive charge centered on the nitrogen.[16] These phenomena would be absent, however, in the anilinium ions, which may be assumed to be hydrated like the corresponding aliphatic ammonium ions.

It is impossible to estimate the importance of the phenomenon designated by A in Figure 3. It would have the effect of increasing the net hydration energy (that is, the difference between the hydration energies of anilinium ion and amine) and of increasing base strength, therefore, relative to the aliphatic amines. The phenomenon designated by B in Figure 3 would have the opposite effect; and the available data indicate its magnitude is 1.6–1.7 pK units, as will now be shown.

Use of $\sigma^* = 0.60$ for phenyl in eq. 9, 10, or 11 permits an estimate of the "raw net hydration energies" of anilines, in the absence of the resonance effects depicted in Figure 3. The values based on eq. 9 are presented in Table II. Use of eq. 10 or 11 would give somewhat different values, of course, but with the same differences between the values for primary, secondary, and tertiary amines. As the conclusions to be drawn are based on these differences, they are independent of which equation is used.

Table II. "Raw Net Hydration Energies" for Anilines (pK Units)

	$n = 1$	2	3
Calcd. (eq. 9)	$5.27 + A$	$8.14 + A$	$9.46 + A$
Obsd. (eq. 15 and 16)	$5.27 + A$	$6.43 + A$	$7.85 + A$
$\delta\delta pK_h$, "aniline hydration effect,"	0	1.71	1.61

It is assumed (i) that the result for N,N-disubstituted anilines is correct, except for the effect designated by A in Figure 3; and (ii) that the differences in the leading terms of eq. 14a, b, and c correctly represent the differences in the "raw net hydration energies" of primary, secondary, and tertiary anilines (just as it was assumed that the differences in the leading terms of eq. 5a, b, c, and d represent the differences in the "raw net hydration energies" of ammonia, primary, secondary, and tertiary aliphatic amines). Then it is seen

(16) The dipole moments of aliphatic and aromatic amines are not much different; but in the anilines, the nitrogen is at the positive end of the dipole, while in aliphatic amines, it is most likely at the negative end. The reversal of polarity requires substantial charge development, and the effect on hydration appears to be considerable. For supporting evidence, see W. D. Kumler and C. W. Porter, ibid., 56, 2449 (1934).

Table III. Effects of Substitution of Phenyl for Hydrogen on pK_a Values of Amines

	Based on calcd. pK_a values			Based on actual pK_a values		
	RNH$_2$	RNHMe	RNMe$_2$	RNH$_2$	RNHMe	RNMe$_2$
pK_a for R $=$ H	9.21	10.15	10.55	9.21	10.62	10.64
Statistical effect	+0.12	0.18	0.30	0.12	0.18	0.30
Inductive effect	−0.37	−0.37	−0.37	−0.37	−0.37	−0.37
Net hydration effect ($-A$)	−2.07	−2.97	−2.85	−2.07	−2.97	−2.85
Net pK_a for R $=$ C$_6$H$_5$ ($-A$)	6.89	6.99	7.63	6.89	7.46	7.72
pK_a for R $=$ C$_6$H$_5$	4.65	4.74	5.36	4.65	4.89	5.07
Mesomeric effect ($+A$)	−2.24	−2.25	−2.27	−2.24	−2.57	−2.65

that the "raw net hydration energies" of aniline and N-monosubstituted anilines are, respectively, 1.61 and 1.71 pK units smaller than expected, and these differences may be attributed to the phenomenon designated by B in Figure 3, now called the "aniline hydration effect."

The "aniline hydration effect" is a previously overlooked, base-weakening factor in anilines and N-monosubstituted anilines, which is not present in N,N-disubstituted anilines. It helps to account for some apparent anomalies in the base strengths of N-substituted anilines.[17] Compare, for example, the net change in pK_a on going from trimethylamine (9.76) to dimethylamine (10.64) with the net change in pK_a on going from N,N-dimethylaniline (5.07) to N-methylaniline (4.89). Both are changes observed on replacing a methyl by hydrogen; but the first is an increase of 0.88 pK unit, the second is a decrease of 0.18 pK unit. The difference in these changes, amounting to 1.06 pK units, may be attributed largely to resonance-augmented hydration of the N-methylaniline.

Equation 15 may be rewritten as follows (eq. 16).

$$pK_a = 0.09 - A +$$

(net hydration energy for anilines)

$$\left[5.27 + A + (0.75 + 1.55n)\log n + 0.16n\sum_{i=1}^{2}\sigma_{\mathrm{al}}{}^* \right] -$$

$$3.35\sum_{i=1}^{2}\sigma_{\mathrm{al}}{}^* - \log n \quad (16)$$

Here eq. 9 has been adopted for estimating the "raw net hydration energy" for tertiary anilines. Use of eq. 10 and 11 would give the values 6.89 and 6.26, respectively, for the first term in the bracketed expression for the net hydration energy, and the values $(-1.53 - A)$ and $(-0.90 - A)$, respectively, for the leading term on the right, which represents the "intrinsic" pK_a of N,N-dimethylaniline in the absence of hydration effects. Both the intrinsic pK_a and the net hydration energy for anilines remain unknown to the extent of the quantity A, the resonance-diminished hydration energy of the free bases, represented by A in Figure 3.

Comparison of eq. 8 and 16 reveals that the reaction constant, ρ^*, relating pK_a to $\Sigma\sigma_{\mathrm{al}}{}^*$, is essentially the same for the anilines as for the aliphatic amines (-3.35 vis-à-vis -3.38), as it should be.

(17) B. M. Wepster, *Rec. trav. chim.*, **71**, 1171 (1952).

Effects of Replacement of Hydrogen by Phenyl. Wepster[17] considered the problem of evaluating the inductive and mesomeric effects of the phenyl group in aromatic amines and came to the conclusion that each was responsible for a reduction in base strength of 3 pK units. His treatment ignored the statistical effect, however, and did not recognize the hydration effects described here. Taking these into account leads to somewhat different conclusions, as shown in Table III.

The most striking difference is in the magnitude of the inductive effect, which we must conclude is responsible for a reduction of only 0.37 pK unit. Since $\sigma^*{}_{\mathrm{H}} = 0.49$, $\sigma^*{}_{\mathrm{C_6H_5}} = 0.60$, and $\rho^* = -3.38$, the inductive effect of replacing hydrogen by phenyl must be only $-3.38 \times 0.11 = -0.37$ pK unit.

Each net hydration effect shown in Table III was calculated as the difference between the net hydration energy for the aniline from eq. 16 and the net hydration energy for the aliphatic amine from eq. 9. Clearly, the difference is independent of the choice of these expressions rather than (10) or (11), for example. It remains unknown, however, by the quantity A, which represents the resonance-diminished hydration of anilines suggested by Figure 3.

After the pK_a of each aliphatic amine is modified by the statistical effect, the inductive effect, and the net hydration effect of replacement of hydrogen by phenyl, there remains a difference from the pK_a of the aromatic amine, which is attributable to the mesomeric effect. Two sets of estimates of this difference are made in Table III, one based on the pK_a values calculated by eq. 8 and 16, the other based on the actual pK_a values. The former estimate is independent of possible anomalies due to unknown causes. (The actual pK_a of methylamine, for example, is significantly higher than the calculated.)

The mesomeric effect remains unknown by the quantity A. Approximate agreement is indicated, however, with Wepster's estimate of 3 pK units.