comparable to the isomerization rate.[8] Thus, even the alkyltoluene with least tendency to isomerize intermolecularly disproportionates under conditions only slightly more drastic than those required for isomerization.

Discussion

It is reasonable to assume that in the alkylaromatic σ-complex I, the electron deficiency is distributed between the alkyl group and the aromatic ring. For a given aromatic ring the electron deficiency on the alkyl group should increase in the order Me<Et<*i*-Pr<*t*-Bu since this is the order of carbonium ion stability. Furthermore, the greater the electron deficiency on the alkyl group, the more nearly will the α-carbon approach a trigonal configuration, and the weaker the alkyl to aromatic bond should be. All three factors would tend to facilitate a nucleophilic displacement of the aromatic ring by a second aromatic ring. Thus the fact that the relative rates of isomerization[1c] and disproportionation[12] of alkyl aromatics increase in the above order can be rationalized.

Since the above order of alkyl group electron deficiency is the reverse of the order of relative aptitude for intramolecular *vs.* intermolecular isomerization (Table III), the ability of an alkyl group to stabilize a positive charge does not facilitate the alkyl shift as much as it does the alkyl transfer. Therefore it appears likely that some structure such as III which does not involve a positive charge on the alkyl group contributes to the stability of the intermediate in the intramolecular 1,2-shift. This structure is similar to those postulated for Wagner–Meerwein type rearrangements and may be described as an internal electrophilic aliphatic displacement. The contribution of such a structure is consistent with the reported order of relative rates for electrophilic aliphatic substitution[13] (Me < Et < *i*-Pr), and the stereochemistry of electrophilic aliphatic substitution[14] (retention of configuration). The contribution of such a structure appears to conflict with the reported ability of aluminum alkyls to dimerize, Me> Et> *i*-Pr.[15] But since the dimer structure requires aluminum to accommodate four alkyl groups rather than three, the above order may well be a B-strain effect.[16]

Thus the intermolecular mechanism for alkylaromatic positional isomerization bears a resemblance to the mechanism for SN1 solvolyses, and the intramolecular mechanism bears some resemblance to the mechanism for SE2 displacements.

Experimental

The experimental procedures were similar to those used previously.[7-9] The toluene and *o*-xylene and anhydrous hydrogen chloride were commercial grade materials. The *p*-*t*-butyltoluene was obtained by fractionation of commercial material and contained no impurities that could be detected by infrared analysis. The aluminum chloride was Baker and Adams powdered anhydrous reagent grade.

Acknowledgment.—The author is indebted to D. S. Erley of the Dow Spectroscopy Department for the infrared data.

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[Contribution from the School of Chemistry, University of New South Wales, Sydney, Australia]

The Effects of *m*-Substituents on the pK_a Values of Anilines, and on the Stretching Frequencies of the N–H Bonds

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The pK_a values and N–H stretching frequencies of 19 anilines substituted in the 3- and 3,5-positions have been determined and a statistical analysis carried out to determine whether the ΔpK_a–σ_m relationships are significantly different for substituents with $-M$ and $+M$ character. The test is inconclusive, but it is shown that the regression coefficient ρ for all substituents is greater than previously supposed, and that the regression line does not pass through the origin. The relation between pK_a values and N–H frequencies is linear for *m*-substituents.

In the two following papers, the effects of substituents on the pK_a values of 1- and 2-naphthylamines, pyridines, quinolines and isoquinolines will be examined, and in the case of the naphthylamines some unexpected relations between pK_a values and N–H frequencies will be presented. For the purposes of comparison between the relative effects of substituents, especially in the "*meta*" positions in these compounds, upon which with other evidence a new theory of substituent action will be proposed, it was necessary to have an accurate picture of the effects of *m*-substituents on the pK_a values of anilines, and this paper will survey the available evidence and will present new and supplementary data on 22 anilines substituted in the 3- and 3,5-positions.

Results and Discussion

Table I gives the experimental results; pK_a values previously recorded are shown in column 3, and recently published values for the N–H frequencies of substituted anilines are shown in parentheses.

Discussion

pK_a Relationships.—The relation between the ΔpK_a ($= \log K/K_0$) values of *m*- and *p*-substituted anilines and the substituent constants σ originally formulated by Hammett was reinvestigated by Jaffé[1] using a number of dissociation exponents not previously available, and the slope of the regression line was found to be 2.767 with a correlation coefficient of 0.995. The survey of published values shown in Table I reveals considerable variations in the results for aniline and for *m*-substituted compounds, and this observation coupled with the desirability of an accurate estimate of the correlation between pK_a values and N–H stretching frequencies led to the present work. In connection with a general theory of substituent action in aromatic systems involving consideration of the mesomeric moments of substituents to be given in a subsequent paper, it was also desirable to investigate the possibility that *m*-substituents such as NO_2 and CN might show some observable differences from electron donating groups such as OCH_3 and NH_2 in their pK_a–σ_m relationship. There is the further possibility, also postulated by Hine,[2] that differences might be evident between *m*- and *p*-substituents, for, as will be shown, both possibilities exist as a consequence of the theory in question. Only the first of these will, however, be discussed in the present context.

There is no serious disagreement between the experimental results of the present investigation and the mean values (in parentheses) of the published data, as for example: H, 4.59 (4.60), CH_3, 4.70 (4.72), $COOCH_3$, 3.55 (3.56), $COCH_3$, 3.56 (3.59), CN, 2.76 (2.78), OCH_3, 4.21 (4.21), Cl, 3.46 (3.49), F, 3.50 (3.49), the only exception being *m*-NO_2 where the values are 2.47 (2.52). It is not easy to assess a "best" value for any given substituent, for variations in pK_a are wide, and although this external discordance should in general be eliminated by using ΔpK_a values (for internal consistency is usually maintained), there are too few cases where figures for the parent accompany those for the substituted compounds. For the purpose of evaluating the regression coefficients the experimental values have therefore been used, together with the σ_m values recommended by McDaniell and Brown[3] based on the pK_a values of substituted benzoic acids, *viz.*, *m*-NO_2, 0.71; *m*-Cl, 0.373; *m*-F, 0.33; *m*-OCH_3, 0.115; *m*-CH_3, −0.07; *m*-$COCH_3$, 0.376; *m*-$Si(CH_3)_3$, −0.04; *m*-CF_3, 0.42; and *m*-SO_2CH_3, 0.65. For 3,5-disubstituted compounds σ-values are assessed as the sums of the individual constants. There is some uncertainty as to the values for *m*-OC_2H_5, *m*-$COOCH_3$, *m*-CN and *m*-NH_2, mainly owing to uncertainties in the experimental values for the substituted benzoic acids, and in the statistical analysis the substituent *m*-OC_2H_5 has been omitted, and the σ_m-values for *m*-$COOCH_3$ and *m*-CN taken as 0.32 and 0.64, respectively. In the case of *m*-NH_2 it is possible to deduce a σ_m-value from considerations of the following equilibria applying to *m*-aminobenzoic acid

$$NH_3{}^+C_6H_4COOH \overset{K_A}{\rightleftarrows} NH_3{}^+C_6H_4COO^- + H^+$$

TABLE I

pK_a VALUES (H_2O AT 25°) AND N–H STRETCHING FREQUENCIES OF *m*-SUBSTITUTED ANILINES

Substituent	pK_a This research	pK_a Literature	N–H frequencies, cm.$^{-1}$ Sym.	N–H frequencies, cm.$^{-1}$ Asym.
H	4.59	4.51,[a] 4.57,[b] 4.58[c-d-e] 4.59,[f] 4.63,[g-u], 4.63[icc] 4.64,[h] 4.67[dd]	3396 (3395)[z] (3394)[aa]	3481 (3478)[z] (3481)[aa]
m-Cl	3.46	3.33,[j] 3.43,[k] 3.44,[l] 3.47,[m] 3.50,[n] 3.52[o-dd] 3.56,[p] 3.67[b]	3403 (3401)[z]	3491 (3489)[z]
m-F	3.50	3.39,[j] 3.41,[k] 3.67[b]	3404	3492
m-CH_3	4.70	4.66,[d] 4.67,[a-m] 4.71[o] 4.73,[g] 4.74,[e] 4.77,[i] 4.81[dd]	3393	3480
m-C_2H_5	4.70		3395	3479
m-$CH(CH_3)_2$	4.67		3395	3480
m-$C(CH_3)_3$	4.66		3394	3477
3,5-$(CH_3)_2$		4.74[d]	3395	3480
3,5-$[C(CH_3)_3]_2$		4.97[bb-ff]		
m-OCH_3	4.20	4.20,[c] 4.21[o]	3400	3484
m-OC_2H_5	4.18	4.17[c]	3400	3483
m-$COCH_3$	3.56	3.59[dd]	3401	3489
m-$COOCH_3$	3.55	3.55,[q] 3.56[r]	3400	3488
m-CN	2.76	2.75,[cc] 2.81[dd]	3406	3496
m-NO_2	2.47	2.60,[s] 2.62,[b] 2.47,[j-cc] 2.50,[a-w] 2.57,[t] 2.43[v] 2.54,[bb] 2.52[dd]	3407 (3407)[z]	3497 (3495)[z]
3-Cl, 5-OCH_3	3.10		3405	3494
3-OCH_3, 5-NO_2	2.11		3410	3499
3,5-$(OCH_3)_2$	3.82		3402	3487
3,5-Br_2	2.34	2.36[l]	3408	3498
m-NH_2		4.88,[a] 5.0[dd-ee]	3396 (3395)[z]	3481 (3478)[z]
m-CF_3		3.49[b]		
m-$Si(CH_3)_3$		4.64[x]		
m-SO_2CH_3		2.68[y]		

[a] R. Kuhn and A. Wasserman, *Helv. Chim. Acta*, **11**, 3, (1928). [b] J. D. Roberts, R. L. Webb and E. A. McElhill, THIS JOURNAL, **72**, 408 (1950). [c] N. F. Hall and M. R. Sprinkle, *ibid.*, **54**, 3469 (1932). [d] M. Gillois and P. Rumpf, *Bull. soc. chim.*, 112 (1954). [e] R. N. Beale, *J. Chem. Soc.*, 4494 (1954). [f] K. Pedersen, *Klg. Danske. Videnske Selskab*, **14**, 9 (1937). [g] A. L. Bacaralla, E. Grunwald, H. P. Marshall and E. L. Purlee, *J. Org. Chem.*, **20**, 747 (1955). [h] L. A. Flexer, L. P. Hammett and A. Dingwall, THIS JOURNAL, **57**, 2103 (1935). [i] B. Gutbezahl, and E. Grunwald, THIS JOURNAL, **75**, 559 (1953). [j] M. Kilpatrick and C. A. Arenberg, *ibid.*, **75**, 3818 (1953). [k] Estimated from measurements in 30% alcohol; G. M. Bennett, G. L. Brooks and S. Glasstone, *J. Chem. Soc.*, 1825 (1935). [l] J. N. Brönsted and E. Dus, *Z. physik. Chem.*, **A117**, 299, (1925). [m] M. Flurscheim, *J. Chem. Soc.*, **97**, 84 (1910). [n] H. Goldschmidt, *Z. physik. Chem.*, **A99**, 116 (1921). [o] N. F. Hall, THIS JOURNAL, **52**, 5125 (1930). [p] H. Goldschmidt and W. Keller, *Ber.*, **35**, 3534 (1902). [q] C. G. Clear and G. E. K. Branch, *J. Org. Chem.*, **2**, 533 (1938). [r] E. J. Cohn and J. T. Edsall, "Proteins, Aminoacids and Peptides," Reinhold Publ. Corp., New York, N. Y., 1943, p. 99. [s] A. Bryson, *Trans. Faraday Soc.*, **45**, 257 (1949). [t] R. G. Bates and G. Schwarzenbach, *Helv. Chim. Acta*, **37**, 1069 (1954). [u] J. C. James and J. G. Knox, *Trans. Faraday Soc.*, **46**, 257 (1950). [v] E. A. Braude and E. S. Stern, *J. Chem. Soc.*, 1976 (1948). [w] Bell and Bascombe, unpublished results quoted by M. A. Paul and F. A. Long, *Chem. Revs.*, **57**, 9 (1957). [x] R. A. Benkeser and H. R. Krysilk, THIS JOURNAL, **75**, 2421 (1953). [y] F. G. Bordwell and G. D. Cooper, *ibid.*, **74**, 1058 (1952). [z] S. Califano and R. Moccia, *Gazz. chim. ital.*, **86**, 1014 (1956). [aa] W. J. Orville-Thomas, A. E. Parsons and C. P. Ogden, *J. Chem. Soc.*, 1047 (1958). [bb] J. Burgers, M. A. Hoefragel, P. E. Verkade and B. M. Wepster, *Rec. trav. chim.*, **77**, 491 (1958). [cc] M. M. Fickling, A. Fischer, B. R. Mann, J. Packer and J. Vaughan, THIS JOURNAL, **81**, 4226 (1959). [dd] M. J. Vandenbelt, C. Henrich and S. G. Vanden Berg, *Anal. Chem.*, **25**, 726 (1954). [ee] These figures include the statistical factor log 2, hence the pK_a values for structural evaluation are 4.58 and 4.7. From the pK_a values of 4.51 and 4.67 quoted for aniline, the ΔpK_a values for the amino (*m*-NH_2) group are therefore −0.07 and −0.03, respectively. [ff] Extrapolated by the authors from values in 25, 30 and 50% ethanol.

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(1) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

(2) J. Hine, THIS JOURNAL, **81**, 1126 (1959); also H. H. Jaffé, *ibid.*, **81**, 3020 (1959).

(3) H. D. McDaniell and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

$$\mathrm{NH_3^+C_6H_4COOH} \overset{K_B}{\rightleftharpoons} \mathrm{NH_2C_6H_4COOH + H^+}$$

$$\mathrm{NH_3^+C_6H_4COO^-} \overset{K_C}{\rightleftharpoons} \mathrm{NH_2C_6H_4COO^- + H^+}$$

$$\mathrm{NH_2C_6H_4COOH} \overset{K_D}{\rightleftharpoons} \mathrm{NH_2C_6H_4COO^- + H^+}$$

The measured dissociation constants K_1 and K_2 are related to K_A, K_B, K_C and K_D by the relations: $K_1 = K_A + K_B$, $1/K_2 = 1/K_C + 1/K_D$, and $K_A/K_B = K_D/K_C$.[4] Experimental values for pK_1 and pK_2 are 3.04 and 4.79, and on the assumption that pK_B is equal to pK_E where pK_E is the dissociation exponent of the methyl ester of *m*-aminobenzoic acid, the individual exponents may be calculated and have the values $pK_A = 3.20$, $pK_B = 3.56$, $pK_C = 4.64$, and $pK_D = 4.27$. From the pK_a of benzoic acid (4.20) and pK_D we estimate the effect of a *m*-NH_2 group as -0.07 unit. This σ_m-value differs appreciably from the Hammett value -0.161, but is more in keeping with the ΔpK_a values of *m*-amino group in *m*-aminophenol (0.07 and 0.04, refs. *a* and *dd*, Table I), and in *m*-phenylenediamine (Table I).

The regression equations have been obtained for the groups of substituents: (a) NO_2,CN,SO_2CH_3, $COCH_3$, $COOCH_3$, CF_3, CH_3 and C_2H_5 (alkyl substituents included with the −I, −M group since their +I, +M effects unlike those of the halogen group are cumulative); (b) F, Cl, OCH_3, NH_2, 3-OCH_3-5-Cl, 3,5-Br_2; and (c) all the foregoing substituents together with *m*-$Si(CH_3)_3$ and 3-OCH_3-5-NO_2. For the linear regression of ΔpK_a on σ_m, the equation has the form $\Delta pK_a = \sigma\rho + c$, and the values of ρ and c are as follows, r being the correlation coefficient

Group	Type	n	ρ	c	r
a	−I, −M; +I, +M	8	2.79	0.064	0.996
b	−I, +M	6	2.76	.12	.999
c	......	16	2.82	.080	.998

It will be noticed that there are differences in the slopes and intercepts of the lines for the −M and +M groups of substituents, and a determination as to whether these are significant can be made by the *F* test. The result of this test, shown in the appendix, reveals that there is little difference between the probabilities of the data being accommodated on a single regression line or on two separate lines. It is therefore concluded that although the statistical analysis does not enable a distinction to be made between the relative effects of −M and +M groups of substituents in *m*-substituted anilines and benzoic acids, it is possible that such a distinction exists, and that this may be obscured by the relatively small differences involved and by experimental inaccuracies. It will be noticed that in all three equations the lines do not pass through the origin, the intercept in (c) being 0.08 which is rather greater than that deduced by Jaffé,[1] *viz.*, 0.023 based on a pK_a value of 4.58 for aniline. This deviation seems to be significant, for an error of this amount is unlikely for the parent compound aniline.

N–H Frequencies.—Relations between N–H frequencies and physical constants of substituted anilines have been published by Flett,[5] Califano and Moccia,[6] and Whetsel, Roberson and Krell.[7] It is not possible to compare the results of the present research with Flett's values since these were expressed as a graph of NH force constants and σ-values, but agreement is satisfactory with the values of Califano and Moccia, variation of not more than 2 cm.$^{-1}$ being obtained. Nor is direct comparison possible with the results of Whetsel, *et al.*, for these authors measured the first overtones of the N–H stretching frequencies and the combination bands of the N–H bending and stretching frequencies in 0.4 to 1.0% carbon tetrachloride solutions.

The results of the present investigation are graphically shown in Fig. 1 where pK_a values are compared with N–H stretching frequencies. A linear relationship is evident in the asymmetric frequencies with deviations within the limits of experimental error shown by *m*-Cl, *m*-F and 3-Cl-5-OCH_3. In the symmetric frequencies, where linear relations also hold, the deviations for the +M substituents are in some cases beyond the range of experimental error, and are systematic in their variation. This suggests the possibility of separate pK_a–ν relations for the +M and −M substituents as shown by the dotted line in Fig. 1. However, the value for *m*-NH_2 does not lie on this line, nor do the values of the first ν_s overtones determined by Whetsel, Roberson and Krell (ref. 7) show such a trend. Other features observable in the present and in previously published work are: (a) *m*-F and *m*-CF_3 show frequencies greater than the linear relations require; (b) there is no apparent relation between pK_a values and NH frequencies in the series *m*-CH_3, *m*-C_2H_5, *m*-$CH(CH_3)_2$ and *m*-$C(CH_3)_3$, but trends may be obscured by the small differences involved and by experimental inaccuracies. It will be observed that there is some evidence for the Baker–Nathan effect in the pK_a values which form the sequence H < *m*-CH_3 ≈ *m*-C_2H_5 > *m*-$CH(CH_3)_2$ > *m*-$C(CH_3)_3$. It is curious that the ΔpK_a value of 3,5-di-*t*-butylaniline, *viz.*, -0.39 unit, is considerably greater than twice the value for 3-*t*-butylaniline. The decrease in ν_s for *m*-CH_3 revealed in the present work is also observed by Whetsel, *et al.*, in the first overtone, but the further decrease in 3,5-$(CH_3)_2$ found by these authors is not reproduced.

Although the present work does not deal with *p*-substituted anilines, it is of interest to compare the behavior of these in relation to the *m*-substituted compounds, for it is shown in the following paper that distinctive pK_a–ν relations are shown by quinonoid substituted naphthylamines. The work of Califano and Moccia, and Whetsel, Roberson and Krell show that the *p*-substituents NO_2, CN and Cl obey the same linear relation as the *m*-substituents, but the substituents *p*-CH_3, *p*-OCH_3, *p*-NH_2 and *p*-SCH_3 lie on lines passing close to the point representing the parent amine but of different slope. Whetsel, *et al.*, have shown that the results for all substituents can be accommodated on single lines if the frequencies are plotted against

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[4] E. J. Cohn and J. T. Edsall. "Proteins. Aminoacids, and Peptides," Reinhold Publ. Corp., New York, N. Y., 1943, pp. 99, 128.

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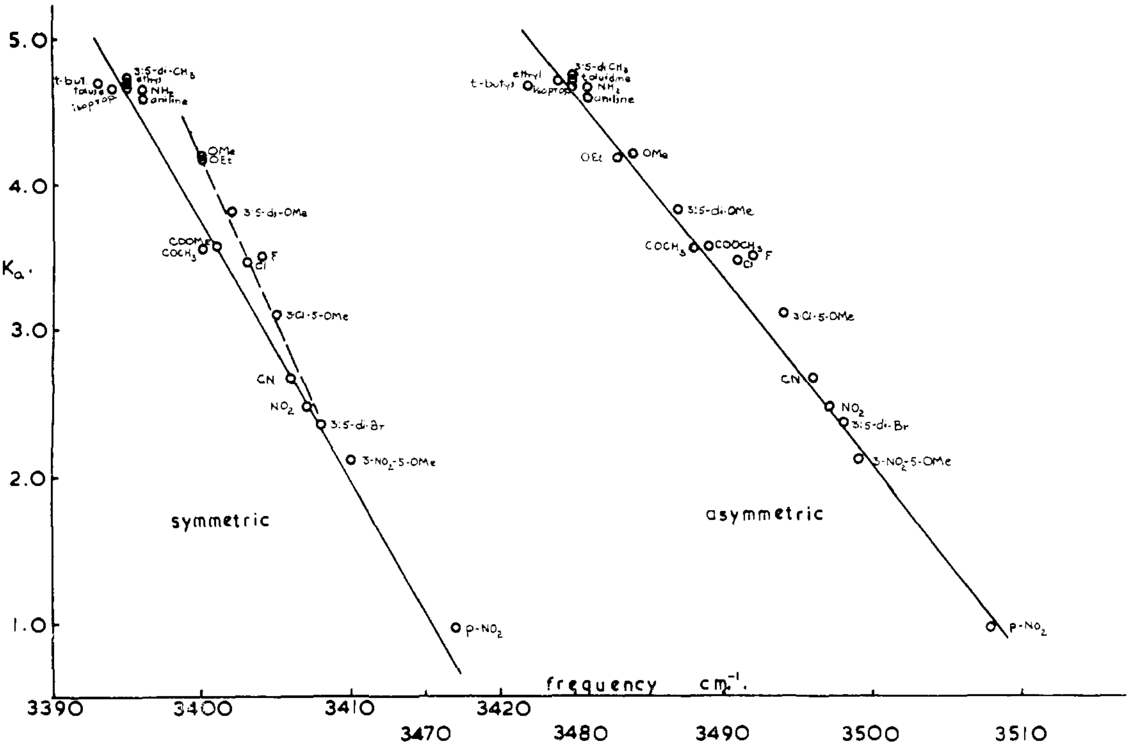

Fig. 1.—Graph of pK_a values and N-H stretching frequencies.

the quantity $\sigma + \sigma^+$, σ^+ being the substituent constants for nuclear substitution evaluated by Brown and Okamoto.[8] This is taken to indicate that mesomeric effects have a significance in determining N–H frequencies which differs from that exercised in the control of acid–base equilibria. Such a conclusion is not unexpected, for N–H frequencies are properties of the bases alone, whereas pK_a values are determined by substituent effects on both the acid and base components of the system, and the relative importance of mesomeric and polar effects in these will not necessarily remain constant as the substituent changes its type.

Experimental

Melting points are not corrected. All substances used in the determination of physical constants were recrystallized or vacuum distilled before use.

m-Toluidine, *m*-chloroaniline, *m*-anisidine, *m*-phenetidine, methyl *m*-aminobenzoate and *m*-nitroaniline were available from stock. *m*-Fluoroaniline was obtained by courtesy of Messrs. Light & Co. *m*-Nitrobenzonitrile was prepared by the method of Bogart and Beans[9] and reduced to *m*-cyanoaniline of m.p. 53–54° (lit.[9] m.p. 53–54°), with hydrochloric acid and stannous chloride.

m-Aminoacetophenone,[10] m.p. 98° (lit.[10] m.p. 98–99°) was used for the preparation of *m*-ethylaniline by the Wolff–Kishner method; 11 g. of *m*-aminoacetophenone hydrazone was heated with potassium hydroxide pellets (25 g.) in a 150-ml. flask until the slight exothermal reaction was over, the mixture treated with water and the *m*-ethylaniline removed with ether. After washing and drying, the ether was removed and the residue distilled *in vacuo*, the fraction at 62° (1.5 mm.), $n^{20}\text{D}$ 1.5556, being collected. *m*-Acetocumidide (m.p. 77–80°) was obtained by courtesy from Dr. M. S. Carpenter[11] and the free amine obtained by hydrolysis with hydrochloric acid. In the same fashion *m*-*t*-butylaniline was prepared from the acetyl derivative, m.p. 101–102°, supplied by Dr. B. M. Wepster.[12] Values for $n^{20}\text{D}$ are 1.5445 and 1.5411 for *m*-cumidine (*m*-isopropylaniline) and *m*-*t*-butylaniline, respectively. The 3,5-disubstituted anilines were prepared as follows: 1,3,5-trinitrobenzene was converted to 3,5-dinitroanisole[13] which was reduced to 3-methoxy-5-nitroaniline of m.p. 119° (lit.[13] m.p. 119°). Replacement of the amino group by chlorine and reduction of the nitro group gave 3-chloro-5-methoxyaniline of m.p. 156° (lit.[14] m.p. 156°). Replacement of the amino group in 3-methoxy-5-nitroaniline by hydroxyl gave 3-methoxy-5-nitrophenol[15] which on methylation and reduction gave 3,5-dimethoxyaniline[16,17] of m.p. 45–46° (lit.[17] m.p. 46°). 3,5-Dibromoaniline and 3,5-dimethylaniline (*s*-xylidine) were prepared by published methods. 3,5-Dibromoaniline had a m.p. of 55–56° (lit.[18] m.p. 55–56°), while 3,5-dimethylaniline was characterized by its acetyl derivative of m.p. 139° (lit.[19] m.p. 140°).

pK_a Determinations.—pK_a values for the reaction $RNH_3^+ \rightleftarrows RNH_2 + H^+$ were determined in aqueous solution by spectrophotometric measurements in the ultraviolet region, since the solubilities of the amines are too low for potentiometric titration. The amines (0.05 mmole) were dissolved and made up to 50 ml. with water; 5-ml. aliquots of this stock solution were diluted to 50 ml. with 2 *N* HCl and 0.02 *N* sodium acetate to secure the amine in the RNH_3^+ and RNH_2 forms, and two buffers of *p*H within 0.4 of the expected pK_a value were used to obtain mixtures of these forms, acetate buffers being used for the range 3.5 to 5.0,

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[10] G. T. Morgan and J. E. Moss, *J. Soc. Chem. Ind.*, **42**, 462T (1923).

[11] M. S. Carpenter, W. M. Easter and T. F. Wood, *J. Org. Chem.*, **16**, 585 (1951).

[12] H. J. Biekart, H. B. Dessens, P. E. Verkade and B. M. Wepster, *Rec. trav. chim.*, **71**, 321 (1952).

[13] H. Vermeulen, *ibid.*, **25**, 12 (1906).

[14] 3-Nitro-5-chloroanisole, m.p. 99°, prepared by the diazotization of 3-nitro-5-methoxyaniline and treatment with cuprous chloride has not been previously described.

[15] Replacement of NH_2 by OH by diazotization and decomposition in 2 *N* H_2SO_4.

[16] S. H. Oakshott and S. G. P. Plant, *J. Chem. Soc.*, 488 (1927).

[17] E. Hope and R. Robinson, *ibid.*, **99**, 1159 (1911).

[18] J. J. Blanksma, *Rec. trav. chim.*, **27**, 42 (1908).

[19] H. L. Haller, E. R. Adams and E. T. Wherry, THIS JOURNAL, **42**, 1840 (1920).

and chloroacetate buffers for the range 2.0 to 3.5. The ionic strength was maintained constant at 0.02 *M* by addition of sodium chloride, the final concentration of the amine being 0.001 *M*. Spectral absorption curves were determined with a Cary recording spectrophotometer (model 11), the ratio RNH_3^+/RNH_2 being determined at intervals of 5 mμ over suitable regions of the absorption curves, and the cell compartment being held at 25 ± 0.2°. *p*H measurements of the buffer solutions were determined with a Cambridge *p*H meter, the glass electrode being initially tested for linearity, and calibrated with a saturated solution of potassium hydrogen tartrate (3.57). Readings were taken on the buffer solutions at 25° before and after the spectrophotometric measurements with repeated recalibrations.

Precision of pK_a Results.—In this paper relating to substituted anilines, and in subsequent papers dealing with substituted naphthylamines and heterocyclic bases, the technique of pK_a measurement was standarized, and an estimate of the precision can be made from consideration of the equation used, *viz.*, $pK_a = pH + \log RNH_3^+/RNH_2$. The quantity $\log RNH_3^+/RNH_2$ was obtained from the relation $RNH_3^+/RNH_2 = (A_b - A/(A - A_a)$ where A_a, A_b and A are the absorbances of the acid, base and buffered solutions. Matched 1-cm. cells were used, the blank differing from the absorbing solution only in the absence of amine. Spectrophotometric measurements were taken in the range 250–400 mμ in which for most systems there is at least one isobestic point, and in which absorbances of the acid species are frequently negligible. In the case of aniline the values of $\log RNH_3^+/RNH_2$ for the buffers 4.74 and 4.25 were $-0.07_7 \pm 0.005$ and $0.40_0 \pm 0.009$ (10 results) giving pK_a values of 4.66 and 4.65. With a correction of −0.06 for ionic strength, the figure of 4.59_5 is obtained with a precision which, allowing ±0.02 for the *p*H measurements and ±0.01 for the log ratios, may be given as within ±0.03 unit. Measurements were rejected unless log ratios were consistent and pK_a values were within 0.03.

Infrared measurements were made with a Perkin–Elmer model 112 recording infrared spectrophotometer using a LiF prism. Spectra were determined in approximately 0.005 *M* solutions of the amines in dried and freshly distilled carbon tetrachloride, gaseous ammonia spectra being interpolated between the records of successive amines. Assignment of frequencies was made by reference to the ammonia bands 3396 and 3472 cm.$^{-1}$, the accuracy being considered to be ±1 cm.$^{-1}$.

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Appendix.—The probability that the sets of data for the −M and +M groups of substituents lie on separate regression lines can be determined by evaluating the variance ratio $F = s^2_{a+b}/s^2$ where s^2 is the residual variance for all 16 substituents with 14 degrees of freedom, and s^2_{a+b} is the combined residual variance of the two separate groups calculated from the equation

$$s^2_{a+b} = \frac{6s^2_a + 4s^2_b}{10}$$

where the number of degrees of freedom is 10. The residual variances are calculated by the equation

$$s^2 = \frac{(\mathrm{I} - r^2)\ \Sigma(\Delta pK_a)^2 - \dfrac{(\Sigma\Delta pK)^2}{n}}{n - 2}$$

r being the correlation coefficient and *n* the sample number.[20] Values of 0.00277 and 0.00409 for s^2 and s^2_{a+b} give $F_{10,14} = s_{a+b}/s^2 = 1.5$ corresponding to a significance level of about 0.25. Such a high level indicates that there is little difference between the probabilities of the ΔpK_a values lying on a single line or being accommodated on two separate lines.

[20] K. A. Brownlee, "Industrial Experimentation," H. M. Stationary Office, London, pp. 32, 59. C. A. Bennett and N. L. Franklin, "Statistical Analysis in Chemistry and the Chemical Industry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 223.

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The Effects of Substituents on the pK_a Values and N–H Stretching Frequencies of 1- and 2-Naphthylamines

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The pK_a values and N–H stretching frequencies of 44 naphthylamines substituted in various ring positions by the groups NO_2, CN, $COOCH_3$, Cl, Br, I, OH, OCH_3 and NH_2 have been measured, interest being devoted chiefly to the compounds in which the groups are in non-quinonoid positions. The results reveal characteristic differences between the effects of substituents in *m*-substituted anilines, 3-substituted 1-naphthylamines and 4-substituted 2-naphthylamines, the most noteworthy feature being shown by the 3-substituted 1-naphthylamines where substituents group themselves into two classes depending on their mesomeric +M or −M characteristics. Similar but smaller effects are observable in the 4-substituted 2-naphthylamines. The σ-values derived satisfy equations of the type $\sigma = a\sigma_I + b\sigma_R$ where σ_I and σ_R are the Taft constants, and the extent of the polar and mesomeric contributions to the substituent effect in *m*-anilines, 3-substituted 1-naphthylamines and 4-substituted 2-naphthylamines can be inferred, and the observed behavior explained. An attempt is made to correlate the results with electronic structure. Relations for compounds with the substituents in the second ring are less clearly defined, but the distinction between the 7-substituted 1-naphthylamines and the 5-substituted 1-naphthylamines is interpreted to indicate smaller intergroup conjugation in the latter. Unexpected relations are shown between pK_a values and N–H frequencies, these being characterized by the non-conformity of the parent amines with the lines given by the various positional series.

Previous communications[1] have described the effects of the groups NO_2 and SO_3^- on the pK_a values of 1- and 2-naphthylamines substituted in the available ring positions, and a tentative interpretation has been offered[2] for these effects in terms of structural changes in the base components of the systems. This theory as applied to the 3-substituted 1-naphthylamines and 4-substituted 2-naphthylamines, for instance, assumed that the inductive effect of the substituent NO_2 on the NH_3^+ pole of the acid was the same as in the similarly constituted *m*-nitroaniline, and that the burden of changes in substitutional effects lay in influences affecting the delocalization of the electrons in the

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[1] A. Bryson, *Trans. Faraday Soc.*, **45**, 257 (1949); **47**, 522 (1951).

[2] A. Bryson, *ibid.*, **47**, 528 (1951).