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Hybridization on Amine Nitrogens and pK_a Values of Some *N*-(4-Nitrophenyl)polymethylenimines

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The ultraviolet and nmr spectra and the ionization constants of a series of *N*-(4-nitrophenyl)polymethylenimines, $4\text{-NO}_2\text{C}_6\text{H}_4\underline{\text{N-(CH}_2)}_n$, with $n = 2$–6, have been determined. The uv and nmr spectra indicate that where $n = 2$ the amine nitrogen is near-sp^3 hybridized, and where $n = 3$–6 hybridization is near-sp^2. Comparison of the pK_a values for the above series with those for *N*-(4-carboxyphenyl)-, *N*-phenyl-, and *N*-methylpolymethylenimines allows a rough estimate of the magnitude of the effect of differing hybridization on pK_a's. This effect leads to base strengthening by *ca.* 2.3 p*K* units, in the case of *N*-(4-nitrophenyl)aziridine, and is believed to account for about 1.0–1.5 of the 3.7–4.2 unit difference between pK_a's of corresponding aniline and 4-nitroaniline derivatives.

Relative basicities of substituted aniline, *N*,*N*-dialkylaniline, and *N*-phenylpolymethyleneimine derivatives are controlled by a variety of factors which often interact in complex manners. These include inductive and mesomeric effects of N and ring substitutents;[1-3] differing solvation stabilization of the free bases,[4,5] or the conjugate anilinium ions;[1,6] steric effects, which might involve changes in the dihedral angle between the lone pair of the amine group and the plane of the ring as a consequence of alkyl-ortho repulsions,[7] as well as increases or decreases in bond-opposition strain on protonation;[8] relief of bond-angle strain on protonation;[8] and, finally, differences in hybridization on the amine nitrogens,[5,9] which influence the amount of orbital overlap and hence the extent of lone-pair charge-delocalization to the ring. Although relatively little attention has been devoted to the latter factor in the extensive literature relating to aromatic amine basicities, the results of some recent studies suggest that hybridization should play an important part in differences between pK_a values of corresponding aniline and nitroaniline derivatives.

Earlier widely held misconceptions[10,11] that the amine nitrogens in aniline and its *N*,*N*-dialkyl derivatives might be sp^2 hybridized have recently been resolved. Bottini and Nash[12] have shown from pK_a and uv spectral investigations and several other groups of workers[13,14] have shown from molecular polarizability studies that the configurations about nitrogen in these amines are more or less pyramidal (*i.e.*, near-sp^3 hybridized in aniline in nonhydroxylic solvents, slightly flattened pyramidal in *N*,*N*-dimethylaniline).[13,15]

The substituents about the amine nitrogens in 4-nitroaniline and its *N*,*N*-dimethyl derivative, on the other hand, are essentially coplanar (*i.e.*, sp^2) in the solid phase or nonhydroxylic solvents as shown by total crystal structure[16] and molecular polarizability determinations.[17] Studies on *p*-carboxyphenylpolymethylenimine ionization constants and *p*-nitrophenylpolymethylenimine reduction rates[9] provide evidence that the same also applies for most $-M$ 4-substituted aniline derivatives in hydroxylic solvents.

A logical consequence of these findings would be that pK_a

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[1] E. Folkers and O. Runquist, *J. Org. Chem.*, **29**, 830 (1964).

[2] M. M. Fickling, A. Fischer, B. R. Mann, J. Packer, and J. Vaughan, *J. Amer. Chem. Soc.*, **81**, 4226 (1959).

[3] A. I. Biggs and R. A. Robinson, *J. Chem. Soc.*, 388 (1961).

[4] C. P. Nash and G. E. Maciel, *J. Phys. Chem.*, **68**, 831 (1964).

[5] J. W. Eastes, M. H. Aldridge, and M. J. Kamlet, *J. Chem. Soc. B*, 922 (1969).

[6] H. K. Hall, Jr., *J. Amer. Chem. Soc.*, **79**, 5441 (1957).

[7] B. M. Wepster in "Progress in Stereochemistry," W. Klyne and P. B. de la Mere, Ed., Vol. II, Butterworths, London, 1958, Chapter 4.

[8] H. C. Brown, R. S. Fletcher, and R. B. Johannesen, *J. Amer. Chem. Soc.*, **73**, 212 (1951); E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, Section 9-4.

[9] W. D. Weringa and M. J. Janssen, *Recl. Trav. Chim. Pays-Bas*, **87**, 1372 (1968).

[10] H. T. Taylor, *Nature*, **181**, 265 (1958).

[11] H. C. Brown and A. Cahn, *J. Amer. Chem. Soc.*, **72**, 2939 (1950).

[12] A. Bottini and C. P. Nash, *ibid.*, **84**, 734 (1962).

[13] M. J. Aroney, R. J. W. Le Fevre, L. Radom, and G. L. D. Ritchie, *J. Chem. Soc. B*, 507 (1968).

[14] C. W. N. Cumper and A. Singleton, *ibid.*, 645 (1968).

[15] The effect of hydrogen bonding should be toward nearer sp^3 hybridization in hydroxylic solvents (see following paper).

[16] T. C. W. Mak and J. Trotter, *Acta Crystallogr.*, **18**, 68 (1965).

[17] M. J. Aroney, K. E. Calderbank, R. J. W. Le Fevre, and R. K. Pierens, *J. Chem. Soc. B*, 561 (1968).

or reactivity changes in going through a Hammett series from positively to negatively 4-substituted aniline derivatives should incorporate important terms attributable to the changing amine nitrogen hybridization. This serves as the basis for some interesting conjecture regarding the many ρ–σ relationships which have been reported for such compounds, since changing conformations about amine nitrogen have never been considered in the standard linear free energy treatments.

The present investigation represents an attempt to unravel the various factors influencing basicities and reactivities of aromatic amines and to assess the magnitudes of effects of changing hybridization. Toward these ends, we have determined the ionization constants as well as the uv and nmr spectra of the *N*-(4-nitrophenyl)polymethylenimines, $4\text{-}NO_2C_6H_4N\text{-}(CH_2)_n$, with $n = 2\text{–}6$. It was anticipated that in this series hybridization on amine nitrogens would change with ring size, with other effects hopefully following established patterns. The reasoning governing our approach toward untangling the interacting factors mentioned in our introductory remarks was that pK_a's would reflect electronic, steric, and solvation effects on both sides of the ionization equilibria, while the spectra should reflect only effects in the free bases.

Results

Ultraviolet and Nmr Spectra.—Listed in Table I, together with comparison results for *N*,*N*-dimethyl- (**1**) and *N*,*N*-diethyl-4-nitroaniline (**2**), are uv spectral data in water for the $[^+R_2N{=}C(1) \rightarrow C(4){=}NO_2^-]$ bands and nmr line positions in acetone-d_6 for the 2,6 protons of *N*-(4-nitrophenyl)aziridine (**3**), -azetidine (**4**), -pyrrolidine (**5**), -piperidine (**6**) and -hexamethylenimine (**7**).

TABLE I

ULTRAVIOLET AND NMR SPECTRAL DATA FOR SOME *N*-(4-NITROPHENYL)POLYMETHYLENIMINES

Compd	$4\text{-}NO_2C_6H_4R$, R =	$\lambda_{max}^{H_2O}$, nm	$\epsilon \times 10^{-3}$	δ^a
1	$(CH_3)_2N\text{-}$	420	19.9	6.72
2	$(C_2H_5)_2N\text{-}$	430	22.9	6.74
3	$(CH_2)_2\text{-}N\text{-}$	325	10.8	7.12
4	$(CH_2)_3\text{-}N\text{-}$	422	17.4	6.32
5	$(CH_2)_4\text{-}N\text{-}$	433	23.5	6.57
6	$(CH_2)_5\text{-}N\text{-}$	425	16.1	6.92
7	$(CH_2)_6\text{-}N\text{-}$	430	22.9	6.72

[a] Chemical shifts in parts per million for the 2,6 protons in acetone-d_6; midpoints of doublets, $J_{HH} \sim 0.10$ ppm; TMS internal standard; determined on Varian HA-100 nmr spectrometer.

From these results, our initial expectation that the three- and four-membered ring compounds would show appreciably more p character in amine nitrogen hybridization appears to have been borne out only in the case of the *N*-(4-nitrophenyl)aziridine (**3**). A 100-nm blue shift for the $[^+R_2N{=}C(1) \rightarrow C(4){=}NO_2^-]$ electronic transition of **3** relative to the other compounds studied[18] implies significantly decreased delocalization of the amine lone-pair electrons to the ring, as would be expected with near-sp^3 hybridization. Markedly enhanced deshielding of the 2 and 6 protons in the nmr[19] (shifted downfield by about 0.4 ppm relative to **1** or **2**) is also consistent with appreciably lessened amine → ring resonance interaction.[20]

With *N*-(4-nitrophenyl)azetidine (**4**), on the other hand, indications of strong "through conjugation," implying near-sp^2 hybridization on the amine nitrogen, were obtained from the uv spectrum, which closely resembled those of the other nitroaniline derivatives studied, and from the chemical shift of the 2,6 protons, which was found further *upfield* than corresponding signals in all the other amines.[19] We regard a planar conformation about nitrogen in a four-membered ring compound as one of the more surprising findings of this investigation and as a good indicator of relative contributions of ring strain and mesomerism to overall free energies in the arylpolymethylenimines.

The sharply decreased ϵ_{max} value for *N*-(4-nitrophenyl)piperidine (**6**) with only minor dispacement in λ_{max} relative to the pyrrolidine (**5**) or the hexamethylenimine (**7**) deserves comment. Such an effect is characteristic of classical steric inhibition of resonance and is readily rationalized as resulting from a twisting of the piperidine group from the ring plane as a consequence of alkyl-ortho repulsions, which would be greater in **6** than in **5** or **7** because of the relative rigidity of the chair form of the six-membered ring.[21] Decreased amine → ring mesomerism, resulting from such a steric inhibition of resonance effect, is also consistent with the 0.2–0.3-ppm downfield shift for the 2,6-proton signal in **6** relative to **1**, **2**, **5**, and **7**,[23] as well as the markedly enhanced rate of disodium disulfide reduction of **6** compared with **1**, **2**, and **5** in aqueous methanol as reported by Weringa and Janssen.[9]

The latter authors[9] have also provided confirmatory information regarding electronic and steric effects in closely related free bases with the following pK_a values for 4-dialkylaminobenzoic acids in 50% ethanol:[24] $Me_2N\text{-}$, 6.01; $Et_2N\text{-}$, 6.19; pyrrolidino, 6.07; piperidino, 5.75. The decreased pK_a for the piperidine compound is, as above, attributed to decreased mesomerism resulting from twisting of the amine plane from the ring plane.[25]

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[18] That λ_{max} values shifted increasingly to the red with increasing polarity in a series of nonhydroxylic solvents, and that shifts were proportional for all compounds (see following paper) implies that we are dealing with corresponding electronic transitions.

[19] Effects are similar, but of smaller magnitudes, for 3,5-proton signals.

[20] I. D. Rae, *Aust. J. Chem.*, **18**, 1807 (1965); **20**, 2381 (1967).

[21] The angle of twist, θ, is calculated to be 33° in **6** from the $\cos^2\theta = \epsilon/\epsilon_0$ relationship[22] (on the assumption that ϵ_0 is the average of the ϵ_{max} values for **5** and **7**). Unsubstituted *N*-phenylpiperidine also shows sharply diminished absorption intensity relative to the corresponding pyrrolidine, probably for analogous reasons.[12] Here the angle of twist (in methanol) is calculated to be about 45°.

[22] E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, 3754 (1955); H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962, Section 15.3.

[23] For comparison with a more frequently cited example of steric inhibition of resonance, the 6-proton signal of *N*,*N*,2-trimethyl-4-nitroaniline is also shifted downfield by about 0.2 ppm relative to the 2,6-proton signal of **1**.

[24] We are dealing here with the $-COOH \rightleftarrows -COO^-$ equilibrium for these compounds. We will have occasion later to discuss pK_a's in the amine protonation equilibrium.

[25] It is a constructive exercise to assume the angle of twist, θ, in 4-piperidinobenzoic acid to be intermediate between that for **6** and *N*-phenylpiperidine,[21] *i.e.*, *ca.* 36–39°, and apply Taft's treatment, $\sigma_R/\sigma_R^0 = \epsilon/\epsilon_0 = \cos^2\theta$ [R. W. Taft and H. D. Evans, *J. Chem. Phys.*, **27**, 1427 (1957)]. If we take for σ_R^0 the value for the $Me_2N\text{-}$ group, -0.83, the $\Delta\sigma_R$ term due to twisting from planarity becomes $+0.29$ to $+0.33$. With a ρ value near 1.0, the decrease in the pK_a for the 4-piperidino relative to the other benzoic acid derivatives is hence also quantitatively accountable for by a straightforward steric inhibition of resonance effect.

TABLE II

DISSOCIATION CONSTANTS OF SOME POLYMETHYLENIMINE DERIVATIVES

	4-$NO_2C_6H_4R$		4-$HOOCC_6H_4R$		C_6H_5R		CH_3R	
R	pK_a[a]	ΔpK_a[b]	pK_a[c]	ΔpK_a[b]	pK_a[d]	ΔpK_a[b]	pK_a[e]	ΔpK_a[b]
$(CH_3)_2N-$	0.65		1.40		4.22[f] 4.39[g]		9.76	
$(CH_3CH_2)_2N-$	1.75	+1.1	2.45	+1.1	5.71[f] 5.85[g] 5.59[h]	+1.5[j]	10.29	+0.5
$\underbrace{(CH_2)_2-N}-$	0.9–1.2[i]	+0.4					7.86	−1.9
$\underbrace{(CH_2)_3-N}-$	0.34	−0.3			4.08[g]	−0.3[j]	10.40	+0.6
$\underbrace{(CH_2)_4-N}-$	−0.42	−1.1	0.39	−1.0	3.71[f] 3.45[g] 3.24[h]	−0.7[j]	10.46	+0.7
$\underbrace{(CH_2)_5-N}-$	2.46	+1.8	2.67	+1.3	4.60[f] 5.22[g] 4.93[h]	+0.7[j]	10.08	+0.3
$\underbrace{(CH_2)_6-N}-$	−0.15	−0.8						

[a] Present investigation, H_2O, 25°. [b] Relative to *N*,*N*-dimethyl derivative. [c] Reference 9, 50% EtOH, 25°. [d] 50% EtOH. [e] Reference 27, H_2O, 25°. [f] Reference 30, 20°. [g] References 4 and 12, 25°. [h] Reference 9, 25°. [i] See Experimental Section regarding uncertainties in determination. [j] Best estimates by comparison of results from corresponding references.

Taken together, the results cited above allow no unequivocal choice of order of amine → ring electron donation among **1**, **2**, **4**, **5**, and **7**; indeed the order may be solvent dependent. However, diminished mesomerism in the aziridine derivative **3** because of more p character in the hybridization on nitrogen and in the piperidine derivative **6** because of alkyl-ortho repulsions seems reasonably well established.

Dissociation Constants.—The pK_a values for **1**–**7** in water at 25.0 ± 0.1° are listed in Table II, together with comparison literature data for some corresponding *N*-(4-carboxyphenyl)-, *N*-phenyl-, and *N*-methylpolymethylenimines. As is seen, the pK_a's for the sp^2-hybridized 4-nitroaniline derivatives vary over a 2.9 p*K* unit range from −0.42 to +2.46, and the 0.9–1.2 value for the sp^3-hybridized aziridinyl derivative **3** falls near the average for all compounds studied.[26] Assessment of a ΔpK_a term, attributable to the difference in hybridization, is therefore impossible from the raw data, and it becomes necessary to eliminate or evaluate some important obtruding effects.

Toward this end, we have also listed ΔpK_a values in Table II, representing differences in pK_a between the polymethylenimine and corresponding dimethylamine derivatives in each series. In the case of the alkylpolymethylenimines (last column), these ΔpK_a's are considered to be measures of combined solvation, inductive, ring-side, and bond-opposition effects on relative amine basicities where no changes in hybridization occur on protonation.[27]

These same effects are believed to be reflected in the three arylpolymethylenimine series, but in addition the ΔpK_a's are here considered to show the effects of differences in amine → ring mesomerism between planar and pyramidally hybridized free bases, as well as I-strain differences between the free bases and their salts caused by possible changes in hybridization on protonation.

The ΔΔpK_a values which are listed in Table III represent differences between ΔpK_a's in the aryl- and the methylpolymethylenimine series, with the common effects presumably cancelling one another out. Hence, they are considered to be rough measures of basicity changes attributable to hybridization effects, either those deriving from differing hybridization in the free bases, or those arising from changing hybridization on protonation. The approximations involved in arriving at these ΔΔpK_a's preclude quantitative intercomparisons, but they do reflect some of the trends which would be anticipated from *a priori* considerations.

TABLE III

ΔΔpK_a VALUES FOR *N*-ARYLPOLYMETHYLENIMINES

R	NO_2-C_6H_4R	HOOC-C_6H_4R	Registry no.	C_6H_5R	Registry no.
$(C_2H_5)_2N-$	+0.6	+0.6	5429-28-7	+1.0	91-66-7
$\underbrace{(CH_2)_2-N}-$	+2.3				
$\underbrace{(CH_2)_3-N}-$	−0.9			−0.9	3334-89-2
$\underbrace{(CH_2)_4-N}-$	−1.8	−1.7	22090-27-3	−1.4	4096-21-3
$\underbrace{(CH_2)_5-N}-$	+1.5	+1.0	22090-24-0	+0.4	4096-20-2

Discussion

Effects on Basicity Attributable to Changing Hybridization.—The base-weakening effect (negative ΔΔpK_a) for the nitrophenylpyrrolidine **5** (and probably for the hexamethylenimine **7**, if comparison data for *N*-methylhexamethylenimine were available) and the base-strengthening effect (positive ΔΔpK_a) for the nitrophenylpiperidine **6**, are fully consistent with Brown's generalizations regarding I strain.[8] The protonation reactions in these instances are $sp^2 \rightarrow sp^3$ transformations; I-strain theory predicts that incursions of bond-opposition strain should lead to $sp^2 \rightarrow sp^3$ transformations being more difficult for five- and seven-membered ring compounds, while relief of bond-opposition strain should make such transformations more facile for six-membered rings. The negative ΔΔpK_a (base weakening) for *N*-(4-nitrophenyl)azetidine confirms the conclusion regarding sp^2 hybridization in the free base and implies that strong bond-

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[26] A rapid acid-catalyzed ring-opening reaction leads to difficulties in measuring the pK_a of **3**. See Experimental Section for information regarding precision of the measurement.

[27] S. Searles, M. Tamres, F. Block, and L. A. Quarterman, *J. Amer. Chem. Soc.*, **78**, 4917 (1956). Particularly to be noted is the −1.9 unit ΔpK_a value for *N*-methylaziridine relative to trimethylamine.

eclipsing strains more than offset effects of the *ca.* 10° relief of bond-angle strain in going to the sp^3 anilinium ion.

The base strengthening in the case of **6** derives from two causes: the I-strain effect noted here and the steric inhibition of resonance effect in the free base noted earlier. The progression of $\Delta\Delta pK_a$ values in Table III from near-sp^3-hybridized *N*-phenylpiperidine to near-sp^2-hybridized *N*-(4-carboxyphenyl)piperidine and **6** suggests that relief of bond-opposition strain is the greater contributer to the observed result.[28]

We have no unequivocal explanation for the negative $\Delta\Delta pK_a$ values for *N*-phenylazetidine and *N*-phenylpyrrolidine.[29] It may be that these have somewhat "flattened pyramidal" configurations about nitrogen (*i.e.*, intermediate hybridization), and that the same considerations apply as with **4** and **5**. Alternatively, some as yet unrecognized effect, possibly involving solvation differences in the free bases such as we have discussed elsewhere,[31] may be operating.

The +2.3 unit $\Delta\Delta pK_a$ value for *N*-(4-nitrophenyl)aziridine in Table III is the term which we attribute to the change from sp^2 to sp^3 hybridization on the amine nitrogen in the free base. It may represent a minimal value, as we have not yet excluded one important base-weakening term, operating only with this single compound among the 4-nitroaniline derivatives studied. This effect, which involves strong solvent association with **3** (but not with **6**, although the latter is a stronger base), will be demonstrated and discussed in the following paper.[32]

It does not follow from the above conclusion that a hypothetical sp^3-hybridized *N*,*N*-dimethyl-4-nitroaniline would show as large a $\Delta\Delta pK_a$ value, since, as Bottini and Nash have suggested for *N*-phenylaziridine,[12] the three-membered ring in **3** may lead to even less orbital overlap with the ring π electrons than is normally the case with an sp^3 lone pair. We do estimate, however, that at least 1.0–1.5 of the 3.7–4.3 unit difference between pK_a's of corresponding aniline and 4-nitroaniline derivatives may be due to the change from sp^3 to sp^2 hybridization. Such effects may help explain the significantly larger ρ values for anilinium ion dissociations than are observed for phenols[2,3] and account in part for the multiplicity of σ values for both donor and acceptor substituents in Hammett-type correlations.[33] These matters will be discussed further in the following paper[32] and a rationale will be offered for the fact that most linear free-energy relationships involving aniline derivatives are indeed linear despite their neglect of the important hybridization term.

Experimental Section

Materials.—All materials were synthesized according to Suhr,[34,35] and recrystallized twice from methanol–water, with the exception of **3**, which was recrystallized from methanol–0.01 *N* aqueous sodium hydroxide to inhibit formation of ring-opened products and/or polymerization. The following melting points and analyses were obtained: *N*-(4-nitrophenyl)aziridine (**3**), mp 81–82° (lit.[34] mp 81.5–82°); *N*-(4-nitrophenyl)azetidine (**4**), mp 118–119° (lit.[34] mp 120–121°); *N*-(4-nitrophenyl)pyrrolidine (**5**), mp 167–168° (lit.[34] mp 166–167°); *N*-(4-nitrophenyl)piperidine (**6**), mp 101–102° (lit.[34] mp 105°); *N*-(4-nitrophenyl)hexamethylenimine (**7**), mp 76–77° (lit.[34] mp 76.3–77°); *N*-(2-hydroxyethyl)-4-nitroaniline, mp 108–110° (lit.[35] mp 111.9–112°).

Anal. Calcd for $C_8H_8N_2O_2$ (**3**): C, 58.53; H, 4.91; N, 17.06. Found: C, 58.21; H, 5.19; N, 17.39. Calcd for $C_9H_{10}N_2O_2$ (**4**): C, 60.65; H, 5.67; N, 15.72. Found: C, 60.33; H, 5.70; N, 15.99. Calcd for $C_{10}H_{12}N_2O_2$ (**5**): C, 62.47; H, 6.30; N, 14.58. Found: C, 62.21; H, 6.38; N, 14.89. Calcd for $C_{11}H_{14}N_2O_2$ (**6**): C, 64.05; H, 6.86; N, 13.58. Found: C, 63.96; H, 6.70; N, 13.83. Calcd for $C_{12}H_{16}N_2O_2$ (**7**): C, 65.42; H, 7.34; N, 12.72. Found: C, 65.66; H, 7.36; N, 12.99.

Uv Studies and Measurement of pK_a's.—Except for the measurements with **3**, which are discussed below, absorption spectra were obtained at 25.0 ± 0.1°, using 1-cm quartz cells with a Cary Model 14 recording spectrophotometer provided with a thermostated cell jacket. Previously described precautions were taken to guard against photochemical transformations.[36] Beer's law was applicable in all cases at the concentrations studied. Working solutions containing 1% methanol in the desired solvents were prepared from methanolic stock solutions and were in the range $2\text{–}8 \times 10^{-5}$ *M*.

To obtain spectra of the free bases, aliquot portions of the stock solutions were diluted into 1% sodium hydroxide; spectra of the anilinium ions were obtained by diluting into concentrated hydrochloric acid. pK_a's were determined at $\lambda_{max}^{1\%\ NaOH}$ and calculated from the equation

$$pK_a = pH\ (\text{or } H_0) - \log\,[(A - A_1)/(A_2 - A)] \qquad (1)$$

where A is the absorbance of the solution of acidity corresponding to H_0 or pH, A_1 is the absorbance in concentrated acid, and A_2 is the absorbance in 1% sodium hydroxide.

Spectral data and average values for pK_a's of **1**–**7**, determined at three acidities for each compound, are listed in Tables I and II; the precisions, except in the case of **3**, were ±0.03 p*K* unit. Arnett and Mach[37] have shown that tertiary anilines in sulfuric acid; these values were used in the pK_a determinations of the tertiary amines.[38]

Uv Studies and pK_a Measurements on *N*-(4-Nitrophenyl)aziridine (3).—Because of rapid formation of ring-opened products [probably *N*-(2-hydroxyethyl)-4-nitroaniline accompanied by polymerization products][39] upon protonation of **3**, it was not possible to determine the pK_a of the corresponding aziridinium ion as above.

The accuracy of this pK_a determination was dependent on the accuracy with which we could determine the initial equilibrium concentration of the free amine upon addition to buffer. It was

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[28] Another possible obtruding effect has not been excluded. Alkyl-ortho repulsions should tend toward destabilization of the anilinium ions. Relative to the dimethylanilinium ions, the effects should be base weakening in the case of the six-membered ring compounds (rigidity of the chair form), and base strengthening in the case of the three- and four-membered ring compounds. If these were taken into account, the $\Delta\Delta pK_a$ for **6** would be more positive, that for **3** less positive, and that for **4** more negative.

[29] The wide discrepencies in the reported data for the *N*-phenylpolymethyleneimines[4,9,12,30] (Table II) make the $\Delta\Delta pK_a$ values in this series somewhat suspect.

[30] G. Baddely, J. Chadwick, and H. T. Taylor, *J. Chem. Soc.*, 451 (1956).

[31] The discussion[5] involved the size of the water cluster solvating aniline as compared with its *N*-mono- and *N*,*N*-dialkyl derivatives. As applicable here, the argument might be that the constrained four- and five-membered rings allow closer approach or approach by a larger solvating cluster, with correspondingly greater free base stabilization.

[32] M. J. Kamlet, R. R. Minesinger, E. G. Kayser, M. H. Aldridge, and J. W. Eastes, *J. Org. Chem.*, **36**, 3852 (1971).

[33] H. van Bekkum, P. E. Verkade, and B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, **78**, 85 (1959).

[34] H. Suhr, *Justus Liebigs Ann. Chem.*, **689**, 109 (1965).

[35] H. Suhr, *ibid.*, **687**, 175 (1965).

[36] M. J. Kamlet and L. A. Kaplan, *J. Org. Chem.*, **22**, 576 (1957).

[37] E. M. Arnett and G. W. Mach, *J. Amer. Chem. Soc.*, **86**, 2671 (64).

[38] As no values for H_0'', corresponding to secondary anilines, appear in the literature, values for H_0'' used in the pK_a calculation for *N*-(2-hydroxyethyl)-4-nitroaniline[39] were taken to be midway between those on the H_0' and H_0''' scales.

[39] The composition of the final product mixture formed on protonation of **3** and subsequent ring-opening appears to be variable and is probably concentration and pH dependent. While the spectrum corresponds closely to that of *N*-(2-hydroxyethyl)-4-nitroaniline, $\lambda_{max}^{1\%\ NaOH}$ 405 nm (ϵ 18,400), it is not solely the latter compound, as the apparent pK_a of one final reaction solution was measured to be −0.3, while the pK_a of an independently synthesized sample of *N*-(2-hydroxyethyl)-4-nitroaniline was observed to be −0.12.[38] Reactions at spectrophotometric concentrations preclude product isolation; however, such concentrations may favor production of *N*-(2-hydroxyethyl)-4-nitroaniline over polymeric species.

therefore necessary to obtain spectrophotometric data early in the reaction to obtain accurate extrapolation of optical densities back to zero time. The free aziridine appears to be sufficiently stable in 0.1 *N* NaOH to allow static measurements of optical density and extinction coefficient. No significant change in absorption was observed over a period of 20 min. However, at pH's near the pK_a of the ion, reaction is quite rapid and rapid-mixing techniques were necessary.

A spring-loaded rapid-mixing syringe, as designed originally by Gordon and Thompson[40] and modified by Burlinson and Kaplan,[41] was mounted atop the cell compartment of the Cary Model 14 spectrophotometer. A standard 2-ml hypodermic glass syringe with a 2-in no. 20 stainless steel needle was fitted to the end of a brass housing. The glass plunger was attached to a spring-loaded brass plunger within the housing. The syringe could be cocked and set to deliver rapidly any required volume up to 2 ml. The brass syringe holder was mounted vertically, directly above the mouth of the uv cell and at such a height that the tip of the needle was below the surface of the liquid in the absorption cell. The needle was bent slightly where it entered the cell to avoid the light path. A specially constructed 2.00-cm absorption cell with a wide and deep neck to accommodate the volume change upon injection was used. The syringe was calibrated by weight of water delivered, and found to deliver a volume increment to a precision of 0.500 ± 0.004 ml.

Our procedure consisted of monitoring the decrease with time (typical half-lives were 5–30 sec) in optical density at the wavelength of maximum absorption of the aziridine (325 nm) and, for a separate identical sample, the increase in optical density of the ring-opened product at its wavelength of maximal absorption (403 nm).[39] The completely reacted solution had an absorption tail extending to somewhat below 325 nm; it was therefore necessary to correct the observed absorbance at 325 nm for product to obtain the optical density due to free **3** only. At any given time, the observed optical density at 325 nm minus [the ratio of optical densities of the final product solution at 325 and 403 nm multiplied by the observed optical density (at 403 nm)] corresponded to the optical density due to the free aziridine [Az].

Since the total analytical concentration of species ([Az] + [AzH$^+$] + ring-opened product) was fixed, a plot of product optical densities at 403 nm *vs.* the corrected optical densities for free aziridine (at 325 nm) at corresponding times showed linear regression. When extrapolated back to zero product absorbance, *i.e.*, zero time, such a plot gave the initial optical density of free aziridine at the particular pH, from which the initial equilibrium concentration of aziridine could be calculated.[42]

The original formal concentration of **3** (= [Az] + [AzH$^+$]) being known, the difference between this and the initial equilibrium concentration of aziridine [Az] at the particular pH represents the initial equilibrium concentration of aziridinium ion [AzH$^+$]. With this data, the pK_a could be calculated from the equation

$$\text{p}K_a = \text{pH} - \log [\text{Az}]/[\text{AzH}^+] \qquad (2)$$

To test the reliability of this method in furnishing the extinction coefficient of free aziridine by an extrapolated plot, a run was made at a pH of 4.00, which was sufficiently basic to assure essentially completely unprotonated **3** at zero time, and allowed reaction to proceed at a conveniently measurable rate (half-life about 6 min). The extrapolated extinction coefficient for free **3** was 10,960, compared with a statically determined value of 10,750 in 1% NaOH.

Because of extremely short reaction times below a pH of 2.20 (half-lives less than 5 sec), it was possible to obtain data only on *ca.* 2–6% protonated aziridine solutions even with the fast-mixing technique (spectrophotometer pen response and turbulence in the absorption cell preclude accurate data in the first 3–4 sec after mixing). Table IV lists pertinent data used in estimating the pK_a value for *N*-(4-nitrophenyl)aziridine in water at 25°. Because of the inherent uncertainties involved in calculating a pK_a from data at only 2–6% protonation, we have not taken an average of the results, but report only that there is a high probability that the pK_a for **3** falls between 0.9 and 1.2.

Table IV

Determination of pK_a of *N*-(4-Nitrophenyl)aziridine

pH	([Az] + [AzH$^+$]),[a] × 10^{-5} *M*	ϵ_{max} (corr)[b]	[Az],[c] × 10^{-1} *M*	[Az]/[AzH$^+$]	pK_a
2.20	5.11	10,127	4.81	16.0	1.0
2.50	4.64	10,506	4.53	41.2	0.9
2.70	5.06	10,524	4.95	45.0	1.0
2.70	4.92	10,569	4.84	60.5	0.9
2.80	4.83	10,455	4.79	36.2	1.2

[a] Initial formal concentration of **3**. [b] Extrapolated extinction coefficient at 325 nm, corrected for tail of band due to ring-opened species. [c] Calculated using 10,750 as the molar extinction coefficient of free aziridine.

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[40] R. Thompson and G. Gordon, *J. Sci. Instrum.*, **41**, 480 (1964).

[41] N. Burlinson and L. A. Kaplan, U. S. Naval Ordnance Laboratory Report NOLTR 69-53, May 13, 1969.

[42] At the pH values in question, the ring-opened product was 99+% in the unprotonated form.[39]