# Hydrogen Bonding by Hydroxylic Solvents to Aromatic Amines. Effects on Spectra and Relative Basicities of Some *N*-(4-Nitrophenyl)polymethylenimines

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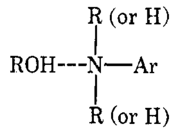
Linear interrelationships are found between the solvent shifts of the uv absorption maxima for near-sp$^2$ hybridized $4\text{-NO}_2\text{C}_6\text{H}_4\underbrace{\text{N-(CH}_2)}{}_n$, $n = 3$, 4, and 5, regardless of solvent type, *i.e.*, hydroxylic or nonhydroxylic. The solvent shifts for *N*-(4-nitrophenyl)aziridine ($n = 2$), which is near-sp$^3$ hybridized on the amine nitrogen, maintain the above linear interrelationships in nonhydroxylic media but deviate markedly in hydroxylic solvents; *i.e.*, the bathochromic shifts are all markedly smaller than expected. This indicates strong hydrogen bonding by hydroxylic solvents to the sp$^3$-hybridized amine in contrast to the absence of such solvent association with the sp$^2$-hybridized amines and would account, at least partially, for the anomalously low basicity observed for *N*-(4-nitrophenyl)aziridine. Displacements of nmr chemical shifts in going from nonhydroxylic to hydroxylic solvents appear to confirm these conclusions.

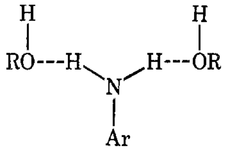
In the preceding paper,[1] uv and nmr spectra and p$K_a$'s of some *N*-(4-nitrophenyl)polymethylenimine derivatives, $4\text{-NO}_2\text{C}_6\text{H}_4\underbrace{\text{N-(CH}_2)}{}_n$, with $n = 2$–6, were compared with data for *N*,*N*-dimethyl- (**1**) and *N*,*N*-diethyl-4-nitroaniline (**2**). From the uv and nmr spectra it was concluded that *N*-(4-nitrophenyl)aziridine (**3**) was near-sp$^3$ hybridized at the amine nitrogen, while *N*-(4-nitrophenyl)azetidine (**4**), -pyrrolidine (**5**), and piperidine (**6**), as well as **1** and **2**, were near-sp$^2$ hybridized.[2]

The following p$K_a$'s were reported: **1**, 0.65; **2**, 1.75; **3**, $0.9 < \text{p}K_a < 1.2$; **4**, 0.34; **5**, −0.42; **6**, 2.46. It came as somewhat of a surprise to us that, despite the difference in hybridization on the amine nitrogens (which, from *a priori* considerations, would have suggested that **3** should be a significantly stronger base),[3] the p$K_a$ value for the aziridine was near the average for the nitroaniline derivatives studied. We therefore undertook to reexamine whether, in unraveling the various complex interacting phenomena contributing to the amine basicities, we had failed to take into account some important base-weakening effect on **3**. A specific solvent-association effect seemed a likely possibility.

We have mentioned[4] that two types of hydrogen bonding contribute to the total solvation picture involving aniline derivatives and hydroxylic solvents.[5–8] Type A, referred to as hydrogen bonding *by* solvent *to* substrate, leads toward ground-state delocalization of the electron pair on nitrogen, hence serving as a hypsochromic influence on the K band in the uv spectrum.[5] Such solvation had been considered to be increasingly significant the greater the base strength of the amine, and should be favored by sp$^3$ hybridization. Type B, referred to as hydrogen bonding *to* solvent *by* substrate, serves toward charge concentration on the nitrogen, a bathochromic influence,[6–8] and would be expected to represent a greater proportion of total solvation with the more acidic sp$^2$-hybridized amines. Either type of solvation should lower the free energy of the amine, and hence the anilinium ion p$K_a$; the type-A hydrogen bond, involving the better donor and acceptor, would be expected to have a significantly larger effect. Important base weakening by type-A hydrogen bonding has been suggested[4,9] in the cases of aniline and its *N*-alkyl and *N*,*N*-dialkyl derivatives.



type A



type B

**Uv Spectra.**—To test for type-A hydrogen bonding in the cases of **1** and **3–6**, we have determined their uv spectra in a series of 31 solvents, both hydroxylic and nonhydroxylic. Positions of the maxima are listed in Table I, together with values of $-\Delta\nu_{\max}$, the bathochromic shifts (in kilokaisers) for each compound in each solvent relative to the spectrum of the same compound in cyclohexane. Plotted in Figure 1 are $-\Delta\nu_{\max}$ values for **1**, **3**, **4**, and **6** as functions of the corresponding $-\Delta\nu_{\max}$ values for *N*-(4-nitrophenyl)pyrrolidine (**5**), the least basic amine in the series.

It is seen that, in the plots for **1**, **4**, and **6**, bathochromic shifts for both hydroxylic (filled data points) and nonhydroxylic solvents (open data points) fall on the same straight lines which extend over a range of 4.3 kK (*ca.* 65 nm) between cyclohexane and water. Correlation is excellent; with the piperidine **6**, for example, least-squares analysis leads to the equation

$$\Delta\nu(6) = 0.005 + 1.018\Delta\nu(5) \qquad (1)$$

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[1] J. W. Eastes, M. H. Aldridge, R. R. Minesinger, and M. J. Kamlet, *J. Org. Chem.*, **36**, 3847 (1971).

[2] The numbering system is the same as in the preceding paper.[1] Numbers from **3** to **6** correspond to the size of the polymethylenimine ring.

[3] A referee has suggested that based on p$K_a$ = *ca.* 6 for *N*-phenylaziridine [from the $\Delta\nu_{\text{O-D}}$ of hydrogen-bonded CH$_3$OD: T. Kagiya, Y. Sumida, and T. Inoue, *Bull. Chem. Soc. Jap.*, **41**, 767 (1968)], and assuming only modest conjugative interaction for the 4-nitro substituent, **3** would be predicted to have a p$K_a$ near 3.

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

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

[6] J. H. P. Utley, *J. Chem. Soc.*, 3252 (1963); B. D. Pearson, *Proc. Chem. Soc.*, 78 (1962).

[7] R. R. Minesinger, E. G. Kayser, and M. J. Kamlet, *J. Org. Chem.*, **36**, 1342 (1971).

[8] M. J. Kamlet, *Israel J. Chem.*, **1**, 428 (1963).

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

TABLE I

ULTRAVIOLET SPECTRA OF SOME *N*-(4-NITROPHENYL)POLYMETHYLENIMINES

$4\text{-}NO_2C_6H_4R$

**1**, $R = -N(CH_3)_2$
**2**, $R = -N(C_2H_5)_2$
**3**, $R = -\underline{N-(C}H_2)_2$
**4**, $R = -\underline{N-(C}H_2)_3$
**5**, $R = -\underline{N-(C}H_2)_4$
**6**, $R = -\underline{N-(C}H_2)_5$

| Solvent | Compd | $\lambda_{max}$, nm | $\nu_{max}$, kK | $-\Delta\nu_{max}$, kK[a] |
|---|---|---|---|---|
| $C_6H_{12}$ | **1** | 356.0 | 28.09 | |
| | **3** | 312.3 | 32.02 | |
| | **4** | 355.0 | 28.17 | |
| | **5** | 363.8 | 27.49 | |
| | **6** | 359.4 | 27.82 | |
| $CCl_4$ | **3** | 317.3 | 31.52 | 0.50 |
| | **4** | 364.9 | 27.40 | 0.77 |
| | **5** | 372.5 | 26.85 | 0.64 |
| | **6** | 368.5 | 27.14 | 0.68 |
| EtOEt | **1** | 369.5 | 27.06 | 1.03 |
| | **3** | 319.0 | 31.35 | 0.67 |
| | **4** | 367.6 | 27.20 | 0.97 |
| | **5** | 377.4 | 26.50 | 0.99 |
| | **6** | 371.2 | 26.94 | 0.88 |
| $(CH_3)_3CNH_2$ | **3** | 322.5 | 31.08 | 0.94 |
| | **5** | 384.0 | 26.04 | 1.45 |
| | **6** | 378.0 | 26.46 | 1.36 |
| $CH_3COOC_2H_5$ | **3** | 324.5 | 30.82 | 1.20 |
| | **4** | 379.2 | 26.37 | 1.80 |
| | **5** | 386.8 | 25.83 | 1.66 |
| | **6** | 382.0 | 26.18 | 1.64 |
| Tetrahydropyran | **3** | 324.8 | 30.79 | 1.23 |
| | **5** | 385.7 | 25.93 | 1.56 |
| | **6** | 382.0 | 26.18 | 1.64 |
| $Cl_2C{=}CHCl$ | **3** | 323.6 | 30.90 | 1.12 |
| | **5** | 386.9 | 25.85 | 1.64 |
| | **6** | 382.5 | 26.14 | 1.68 |
| Dioxane | **1** | 380.6 | 26.27 | 1.82 |
| | **3** | 324.8 | 30.79 | 1.23 |
| | **4** | 379.0 | 26.39 | 1.78 |
| | **5** | 387.8 | 25.79 | 1.70 |
| | **6** | 382.5 | 26.14 | 1.68 |
| $CH_3CCl_3$ | **3** | 324.5 | 30.82 | 1.20 |
| | **5** | 387.8 | 25.79 | 1.70 |
| | **6** | 383.3 | 26.09 | 1.73 |
| $C_6H_6$ | **3** | 326.0 | 30.67 | 1.35 |
| | **5** | 389.0 | 25.71 | 1.78 |
| | **6** | 384.5 | 26.01 | 1.81 |
| $(CH_3)_3COH$ | **3** | 318.2 | 31.43 | 0.59 |
| | **5** | 390.2 | 25.63 | 1.86 |
| | **6** | 385.7 | 25.93 | 1.89 |
| Tetrahydrofuran | **3** | 327.5 | 30.53 | 1.49 |
| | **5** | 390.6 | 25.60 | 1.89 |
| | **6** | 386.1 | 25.90 | 1.92 |
| $(CH_3)_2CHOH$ | **3** | 320.5 | 31.20 | 0.82 |
| | **4** | 385.1 | 25.97 | 2.20 |
| | **5** | 392.0 | 25.51 | 1.98 |
| | **6** | 387.3 | 26.82 | 2.00 |
| $CH_3CH_2OH$ | **1** | 386.8 | 25.85 | 2.24 |
| | **3** | 321.2 | 31.13 | 0.89 |
| | **4** | 385.7 | 25.93 | 2.24 |
| | **5** | 393.0 | 25.45 | 2.04 |
| | **6** | 388.6 | 25.73 | 2.09 |
| $CH_3\text{–}CO\text{–}CH_3$ | **1** | 390.2 | 25.63 | 2.46 |
| | **3** | 330.0 | 30.30 | 1.72 |
| | **4** | 390.1 | 25.63 | 2.54 |
| | **5** | 396.5 | 25.22 | 2.27 |
| | **6** | 392.5 | 25.48 | 2.34 |
| $CH_3OH$ | **1** | 390.3 | 25.62 | 2.47 |
| | **3** | 321.5 | 31.10 | 0.92 |
| $CH_3OH$ | **4** | 390.0 | 25.64 | 2.53 |
| | **5** | 397.1 | 25.18 | 2.31 |
| | **6** | 392.8 | 25.46 | 2.36 |
| $CHCl_3$ | **3** | 327.3 | 30.55 | 1.47 |
| | **5** | 399.8 | 25.01 | 2.48 |
| | **6** | 395.0 | 25.32 | 2.50 |
| $ClCH_2CH_2Cl$ | **3** | 331.6 | 30.16 | 1.86 |
| | **5** | 400.0 | 25.00 | 2.49 |
| | **6** | 395.8 | 25.27 | 2.55 |
| $CH_3OCH_2CH_2OH$ | **3** | 328.5 | 30.44 | 1.58 |
| | **4** | 392.0 | 25.51 | 2.66 |
| | **5** | 399.0 | 25.06 | 2.43 |
| | **6** | 395.3 | 25.30 | 2.52 |
| $CH_2Cl_2$ | **1** | 393.0 | 25.45 | 2.64 |
| | **3** | 330.0 | 30.30 | 1.72 |
| | **5** | 400.5 | 24.97 | 2.52 |
| | **6** | 396.0 | 25.25 | 2.57 |
| $CH_3CN$ | **3** | 330.5 | 30.26 | 1.76 |
| | **5** | 401.5 | 24.91 | 2.50 |
| | **6** | 396.5 | 25.22 | 2.60 |
| $ClCH_2CHCl_2$ | **3** | 333.5 | 29.98 | 2.04 |
| | **5** | 401.8 | 24.89 | 2.60 |
| | **6** | 397.5 | 25.16 | 2.66 |
| Dimethylformamide | **1** | 398.9 | 25.07 | 3.02 |
| | **3** | 336.2 | 29.74 | 2.28 |
| | **5** | 405.8 | 24.64 | 2.85 |
| | **6** | 402.5 | 24.84 | 2.98 |
| $C_6H_5CH_2CH_2OH$ | **3** | 329.5 | 30.35 | 1.67 |
| | **5** | 410.0 | 24.39 | 3.10 |
| | **6** | 405.5 | 24.66 | 3.16 |
| Sulfolane | **3** | 338.5 | 29.54 | 2.48 |
| | **5** | 411.1 | 24.32 | 3.17 |
| | **6** | 406.5 | 24.60 | 3.22 |
| $C_6H_5CH_2OH$ | **3** | 328.8 | 30.41 | 1.61 |
| | **5** | 412.5 | 24.24 | 3.25 |
| | **6** | 406.6 | 24.59 | 3.23 |
| $C_6H_5OCH_2CH_2OH$ | **3** | 331.2 | 30.19 | 1.83 |
| | **4** | 405.0 | 24.69 | 3.48 |
| | **5** | 412.2 | 24.26 | 3.23 |
| | **6** | 407.2 | 24.56 | 3.26 |
| $HOCH_2CH_2OH$ | **3** | 327.0 | 30.58 | 1.44 |
| | **4** | 405.0 | 24.69 | 3.48 |
| | **5** | 412.8 | 24.22 | 3.27 |
| | **6** | 408.0 | 24.51 | 3.31 |
| $HOCH_2CH_2CN$ | **3** | 329.4 | 30.36 | 1.66 |
| | **4** | 410.0 | 24.39 | 3.78 |
| | **5** | 415.8 | 24.05 | 3.44 |
| | **6** | 411.5 | 24.30 | 3.52 |
| $CF_3CH_2OH$ | **1** | 413.3 | 24.20 | 3.89 |
| | **3** | 309.0 | 32.36 | −0.34 |
| | **4** | 415.9 | 24.04 | 4.13 |
| | **5** | 422.2 | 23.69 | 3.80 |
| | **6** | 419.4 | 23.84 | 3.98 |
| $H_2O$ | **1** | 422.0 | 23.70 | 4.39 |
| | **2** | 430.0 | 23.26 | |
| | **3** | 323.5 | 30.91 | 1.11 |
| | **4** | 422.0 | 23.70 | 4.47 |
| | **5** | 431.7 | 23.16 | 4.33 |
| | **6** | 422.8 | 23.65 | 4.17 |

[a] Bathochromic shift relative to spectrum in cyclohexane.

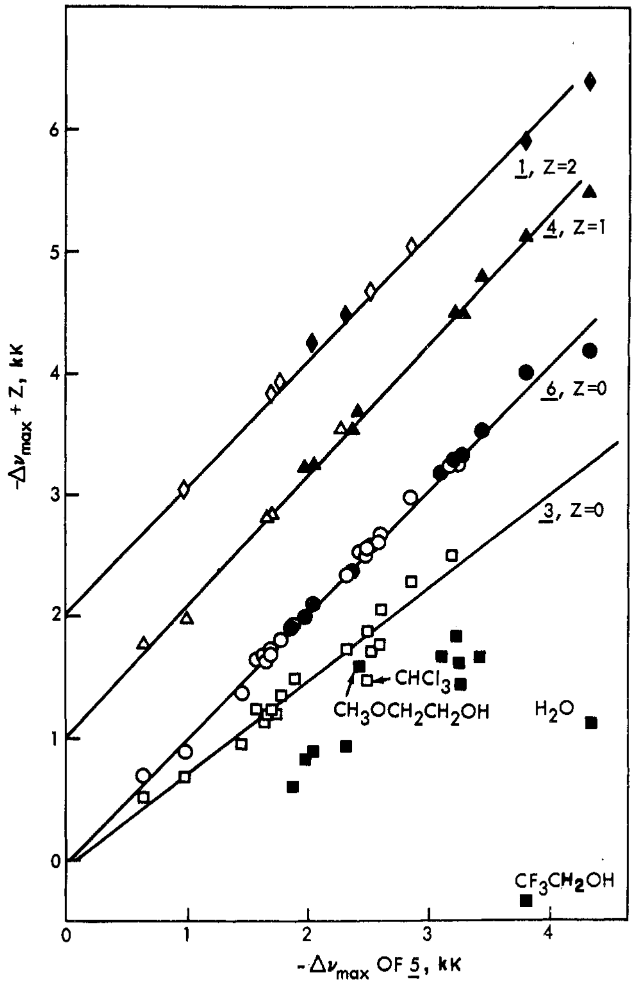

Figure 1.—Spectral shifts in various solvents plotted against corresponding shifts for *N*-(4-nitrophenyl)pyrrolidine (**5**): open data points, nonhydroxylic solvents; filled data points, hydroxylic solvents. The plots for 1 and 4 are displaced upward by 1.0 and 2.0 kK, respectively.

with *r*, the correlation coefficient, = 0.997 and *s*, the standard deviation, = 0.07 kK (*ca.* 0.5–1.0 nm). The plots for **1** and **4** show equally good linearity.[10]

A completely different type of situation obtains in the case of *N*-(4-nitrophenyl)aziridine (**3**). The $-\Delta\nu_{max}$ values for **3** in the nonhydroxylic solvents again show good linearity with corresponding $-\Delta\nu_{max}$ values for **5**, the correlation equation being

$$\Delta\nu(3) = 0.059 + 0.772\Delta\nu(5) \qquad (2)$$

with $r = 0.989$ and $s = 0.095$ kK. Here, however, the ROH solvents do not follow the trend established for the nonhydroxylic media. The data points for 10 of the 11 alcohols and for water fall off the plot by between *ca.* 6 and 30 standard deviations, and always in the direction of lower $-\Delta\nu_{max}$ values (less strongly bathochromic displacements). We take these strong deviations from the linearity observed in the other instances to be manifestations of the hypsochromic influences of type-A hydrogen bonding *by* these ROH solvents *to* **3**. The effect is so strong for **3** in trifluoroethanol that, despite the markedly more polar character of this solvent, the net result is a 3-nm *hypsochromic* shift relative to the spectrum in cyclohexane.

As rough quantitative measures of these hydrogen-bonding effects *by* the various solvents *to* **3**, we have calculated $\Delta\Delta\nu_{max}$ values, *i.e.*, the differences between observed $-\Delta\nu_{max}$ values and values calculated from eq 2. These are listed in Table II together with $\sigma^*$ values for R in ROH.[11]

TABLE II

$\Delta\Delta\nu_{max}$ VALUES FOR *N*-(4-NITROPHENYL)AZIRIDINE IN VARIOUS HYDROXYLIC SOLVENTS

| Solvent ROH | $\sigma^*$ of R | $-\Delta\nu_{max}$ obsd, kK | $-\Delta\nu_{max}$ (eq 2), kK | $\Delta\Delta\nu_{max}$, kK |
|---|---|---|---|---|
| $(CH_3)_3COH$ | −0.30 | 0.59 | 1.38 | 0.79 |
| $(CH_3)_2CHOH$ | −0.19 | 0.82 | 1.47 | 0.65 |
| $CH_3CH_2OH$ | −0.10 | 0.89 | 1.51 | 0.62 |
| $CH_3OH$ | 0.00 | 0.92 | 1.72 | 0.80 |
| $C_6H_5CH_2CH_2OH$ | +0.08 | 1.67 | 2.33 | 0.66 |
| $CH_3OCH_2CH_2OH$ | +0.20 | 1.58 | 1.81 | 0.23 |
| $C_6H_5CH_2OH$ | +0.22 | 1.61 | 2.45 | 0.84 |
| $HOCH_2CH_2OH$ | +0.22 | 1.44 | 2.46 | 1.02 |
| $C_6H_5OCH_2CH_2OH$ | +0.30 | 1.83 | 2.43 | 0.60 |
| $N{\equiv}CCH_2CH_2OH$ | +0.46 | 1.66 | 2.60 | 0.94 |
| HOH | +0.49 | 1.11 | 3.28 | 2.17 |
| $CF_3CH_2OH$ | +0.92 | −0.34 | 2.87 | 3.21 |

It is evident that the data follow no quantitative Taft-type $\rho$–$\sigma^*$ relationship[11] (possibly because of steric factors and varying size of the solvating cluster), but the trend does seem to be toward higher $\Delta\Delta\nu_{max}$ values (stronger solvation) the more acidic the ROH compound. It also appears that solvents capable of *intra*molecular hydrogen bonding (*e.g.*, $CH_3OCH_2CH_2OH$, $C_6H_5OCH_2CH_2OH$) show lower $\Delta\Delta\nu_{max}$ values than might be expected from their $\sigma^*$'s.[12]

**Nmr Spectra.**—We have also examined the nmr spectra of **1** and **3–6** in a number of solvents to ascertain whether a similar specific solvation effect involving only **3** is discernible by means of this probe. We had mentioned in our previous paper[1] that the nmr chemical shifts for the 2,6 protons are reasonably sensitive indicators of amine → ring mesomerism,[13] the greater the electron supply by the amine nitrogen, the less being the deshielding of the 2,6 protons by the 4-nitro group, and the lower the downfield shift. By extension of this reasoning, constraining the electron pair on the amine nitrogen in a type-A hydrogen bond should lead to less delocalization of charge to the ring, and therefore an increase in the downfield shift for the 2,6 protons.

A similar downfield shift as we go from nonhydroxylic to hydrogen-bonding solvents should also be observed for the *N*-methylene protons of **3**. The rational here would be that a type-A hydrogen-bonded amine nitrogen should be more effective at inductive electron withdrawal than its nonassociated counterpart.

Nmr spectral data for **1** and **3–6** in acetone-$d_6$, 11% $D_2O$-$CD_3COCD_3$, 20% $D_2O$-$CD_3COCD_3$, and trifluoroethanol are given in Table III. The results are

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[10] Linearity was also observed in plots of $-\Delta\nu_{max}$ for **1**, **2**, and **4–6** *vs.* corresponding values with hydroxylic and nonhydroxylic solvents for 4-nitrotoluene, which appears to exclude specific solvation effects involving the amine groups in these nitroaniline derivatives. This will be discussed in greater detail in a subsequent paper.

[11] R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, Chapter 13.

[12] It is also comment worthy that, of the nonhydroxylic solvents, chloroform shows the greatest deviation from the observed linearity. This may be because of the small amounts of ethanol stabilizer in Spectrograde chloroform. Small amounts of moisture in the other nonhydroxylic solvents may also account for the slightly greater scatter (and lower correlation coefficient) in the plot for **3** as compared with **1**, **4**, and **6**.

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

TABLE III
NMR CHEMICAL SHIFTS FOR
*N*-(4-NITROPHENYL)POLYMETHYLENIMINES
IN VARIOUS SOLVENTS

| Compd | $CD_3COCD_3$, δ, ppm | $CD_3COCD_3$/$D_2O$, 8/1, Δδ, ppm[a] | $CD_3COCD_3$/$D_2O$, 8/2, Δδ, ppm[a] | $CF_3CH_2OH$, Δδ, ppm[a] |
|---|---|---|---|---|
| 2,6 PROTONS[b] | | | | |
| 1 | 6.74 | 0.00 | +0.01 | −0.12 |
| 3 | 7.12 | +0.05 | +0.11 | +0.03 |
| 4 | 6.32 | +0.02 | ...[c] | −0.10 |
| 5 | 6.57 | +0.03 | +0.03 | −0.12 |
| 6 | 6.92 | 0.00 | +0.01 | −0.18 |
| *N*-Methylene Protons | | | | |
| 1 | 3.13 | 0.00 | +0.01 | −0.08 |
| 3 | 2.23 | +0.03 | +0.08 | +0.08 |
| 4 | 4.04[d] | +0.01 | ...[c] | ...[e] |
| 5 | 3.42[d] | +0.02 | +0.01 | −0.07 |
| 6 | 3.47[d] | 0.00 | +0.02 | −0.06 |

[a] Displacements relative to spectra in acetone-$d_6$. [b] Midpoint of doublet; $J_{HH}$ = *ca.* 10 cps. [c] Insoluble. [d] Triplet. [e] Obscured by solvent absorption.

presented in terms of δ values relative to TMS internal standard in the acetone-$d_6$ solvent and Δδ values (displacements relative to line positions in acetone-$d_6$) for the hydrogen-bonding solvents.

The data show the expected trends. As $D_2O$ is added by increments to the deuterioacetone, both the 2,6 and the *N*-methylene proton signals of **1** and **4–6** show slight downfield shifts, but no consistent trends beyond experimental precision; with **3**, however, the downfield shifts are progressive, beyond experimental error, and unmistakable. The effects are more clearly shown in going from deuterioacetone to trifluoroethanol. Here, both sets of signals are shifted upfield in the cases of the $sp^2$-hybridized nitroaniline derivatives, but downfield only in the case of **3**.

These findings seem to offer strong corroborative evidence for the conclusions drawn from the uv studies. To evaluate the significance of the 0.11 ppm Δδ for **3** in going from deuterioacetone to 20% $D_2O$, the downfield displacement in the chemical shift for the 6 proton in *N*,*N*,2-trimethyl-4-nitroaniline relative to the 2,6-proton signal of **1** is 0.19 ppm. Hence, the hydrogen-bonding effect is of the same order of magnitude as is an effect resulting from significant steric inhibition of resonance.[14]

## Conclusions

Both the uv and the nmr results serve as strong evidence that, of the nitroaniline derivatives studied, only the pyramidally hybridized aziridine derivative **3** undergoes significant type-A hydrogen bonding by hydroxylic solvents, despite the fact that **6** is a stronger base in water than **3** by 1.3–1.6 p*K* units. It is tempting to conclude, therefore, that hybridization on the amine nitrogen is a factor which influences type-A hydrogen bonding more strongly than "intrinsic" basicity.

The above comparison is not completely fair without qualification, however, since the p$K_a$ of **3** in water already incorporates the base-weakening effect of this solvent stabilization of the free amine. The fairer test would involve relative p$K_a$'s of **3** and **6** in a nonhydroxylic solvent. Unfortunately, such a comparison is precluded by the rapid acid-catalyzed ring-opening reaction of **3**, which makes measurement of its basicity extremely difficult.[1]

It would be valuable, therefore, to be able to evaluate the extent of the base weakening by this solvation effect for **3** and other pyramidally hybridized aromatic amines in water. Little information toward this end is available; estimates in the case of near-$sp^3$-hybridized aniline and its *N*,*N*-dialkyl derivatives have ranged from several tenths to about 1.0 p*K* unit,[4,9] and the three-membered ring in **3** might make the value somewhat greater.[15] How much greater, however, is at present impossible to assess, and we must leave the quantitative aspects of this problem involving **3** unresolved.

These, and our earlier findings regarding hybridization effects on amine basicities,[1] lead to some interesting speculation regarding Hammett-type $\rho$–$\sigma$ correlations and other linear free-energy relationships for aromatic amines. At one end of a Hammett series, *i.e.*, with positively substituted aniline derivatives, we have near-$sp^3$ hybridization (base strengthening) and strong free base solvation (base weakening). At the other end, with the negatively substituted aniline derivatives, we have near-$sp^2$ hybridization (base weakening) and little or no solvent stabilization of the free amine. Individually, these base-strengthening and base-weakening effects could account for respectable proportions of the 5.0 unit difference between 4-methoxy- and 4-nitroanilinium ion p$K_a$'s. *That ionization constants in the aniline or dialkylaniline series show good* $\rho$–$\sigma$ *correlation may therefore be an accidental consequence of the fact that the hydrogen-bonding and hybridization effects tend to just about cancel one another out.*[16,17] The multiplicity of $\sigma$ values which have been noted for both donor and acceptor substituents in other Hammett-type correlations[18] may arise from situations where such extraneous effects do not quite offset one another (*e.g.*, as would be the case for most reactions in nonhydroxylic solvents).

## Experimental Section

Preparations, physical properties, and analyses for the materials used here were given in the preceding paper.[1] Ultraviolet absorption spectra were determined on a Cary Model 14 recording spectrophotometer with matched 1-cm silica cells. Concentrations were 3–5 × $10^{-5}$ *M*. Previously described precautions were taken to guard against photochemical transformations.[19] Nmr spectra were determined on a Varian HA-100 spectrometer, using internal TMS as a reference standard.

**Registry No.**—**1**, 100-23-2; **2**, 2216-15-1; **3**, 30855-79-9; **4**, 31947-44-1; **5**, 10220-22-1; **6**, 6574-15-8.

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[14] The angle of twist of the dimethylamine group in *N*,*N*-2-trimethyl-4-nitroaniline is *ca.* 40° (unpublished information).

[15] Overlap between the amine lone pair and the ring $\pi$ system is probably less here than in normally $sp^3$-hybridized amines with *ca.* 109° valence angles.[1]

[16] The reasoning here might be considered circuitous on the basis that the anilinium ion p$K_a$'s provide part of the information used to derive the $\sigma^-$ values for the $-M$ substituents in the Hammett equation. The same conclusion can be derived, however, by comparing p$K_a$'s of anilinium ions and phenols, where analogous changes in hybridization and solvation on oxygen are unlikely.

[17] Another possibility, that hybridization and solvation on the amine nitrogens also vary progressively with $\sigma$ has not been ruled out. This would require, however, that we go from near-$sp^3$ hybridization in aniline to $sp^{>3}$ hybridization in *p*-hydroxy- or *p*-methoxyaniline, and we consider this possibility the less likely.

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# Nucleophilic Substitution at an Acetylenic Carbon. Kinetics of the Reaction between Bromoacetylene and Triethylamine in Dimethylformamide[1]

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Isolation of ethynyltriethylammonium bromide and chloride was achieved in the reaction between triethylamine and the respective monohaloacetylenes (**1**) in dry ether. The kinetics of the same reaction was studied in dimethylformamide (DMF). Because of the ready decomposition of **1** in air, a conductometric method of following the formation of **2** in a closed, oxygen-free system was devised. This conductance method could be used for kinetics in the range $[HC{\equiv}CBr]_0 = 0.002\text{–}0.004\ M$ and gave consistent rates for $[(C_2H_5)_3N]_0 < 0.4\ M$. Higher concentrations of triethylamine, which lowered the dielectric constant of the medium, also reduced the rate of salt formation. The activation parameters for this second-order reaction are $\Delta H^{\ddagger} = 11.8$ kcal/mol and $\Delta S^{\ddagger} = -43$ eu. Several reaction paths to **2** can be discounted easily, but a choice between paths a *vs.* c and i in Scheme I cannot be made.

Although there is considerable interest in the properties of the haloalkynes, no kinetic study on any of the parent compounds HC≡CX has been carried out.[2,3] Undoubtedly, the proclivity of these simple halides to burn, explode, or decompose on contact with oxygen may have been a factor. In our exploration of the scope of nucleophilic substitution at an acetylenic carbon,[2] we now examine process 1. When this

$$\underset{\mathbf{1}}{HC{\equiv}CBr} + (C_2H_5)_3N \longrightarrow \underset{\mathbf{2}}{HC{\equiv}CN(C_2H_5)_3{}^+\,Br^-} \xrightarrow{(C_2H_5)_3N}$$

$$\underset{\mathbf{3}}{[HC{\equiv}CN(C_2H_5)_2]} + \underset{\mathbf{4}}{(C_2H_5)_4N^+Br^-} \qquad (1)$$

work was started, the chemistry of ynamines was just being developed. Now, these are familiar reagents,[4] although their salts are still rare.[5] The first results on process 1 were, in fact, incidental to a study of the dehydrobromination of 1,2-dibromoethylene by triethylamine in DMF.[6] In this study we isolated **2** and obtained the kinetics of and restricted the mechanistic alternatives in reaction 1.

## Experimental Section[1b]

Purified DMF,[6] bp 58° (30 mm), was redistilled over Linde 13X Molecular Sieves directly into a special solvent reservoir, in which it could be stored and from which it could be dispensed through Teflon tubing and syringe needles, always under dry nitrogen. An ir spectrum of the purified DMF (0.1 mm) showed no detectable water absorption (<0.05%). An nmr (neat) spectrum had no foreign peaks. The specific conductance at 25° was well below $10^{-8}$ ohm$^{-1}$ cm$^{-1}$ (lit.[7] $0.4\text{–}2.7 \times 10^{-7}$ ohm cm$^{-1}$), which was the limit of measurement of our conductance bridge. Triethylamine, purified as described previously,[6] was checked and stored in the same way as DMF. Diethylamine was dried over potassium hydroxide, then fractionally distilled under nitrogen.

**Bromoacetylene (1).**[8]—This substance is dangerous and may burn or explode on contact with air; it was prepared, transferred, and stored under dry nitrogen.[6] The bromoacetylene generator was connected to a line which consisted of a bubbler containing aqueous potassium hydroxide, a column (2.5 × 30 cm) of calcium chloride, four U-traps, a receiver, and a bubbler (air seal). 1,2-Dibromoethylene was added dropwise to a solution of ethanolic sodium hydroxide and brought to reflux temperature. The monobromoacetylene was carried into the line by a stream of nitrogen and purified by trap-to-trap distillation, until it was finally condensed into the flask at −78° containing the solvents (15 g of DMF or 45 ml of ethyl ether).

For kinetic runs, the solution of **1** (*ca.* 1.2 *M*) in DMF was diluted *ca.* 10 times with DMF under nitrogen and stored in Dry Ice. For preparative runs, the ether solution was mixed directly with triethylamine under nitrogen.

**Chloroacetylene (1′).**[8]—Chloroacetylene is even more dangerous than bromoacetylene, because it is as reactive and much more volatile. It was generated from *cis*-1,2-dichloroethylene in essentially the same way as described above.

**Reaction between Bromoacetylene and Diethylamine.**—Bromoacetylene was introduced into a flask containing diethylamine (8 ml) 6 in anhydrous ether (45 ml) at −78°. This flask was brought to ∼25°, venting occasionally to relieve excess pressure. After the solution was stirred magnetically for 24 hr, the white solid was filtered off under nitrogen, and the filtrate was concentrated under nitrogen to give a yellow oil (∼1 ml). The ir spectrum of the solid precipitate was identical with that of authentic diethylamine hydrobromide. As for the liquid product, since it was unstable and decomposed during distillation,

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(1) (a) Supported in part by the National Institutes of Health, Grant GM 7021; (b) Abstracted from the Ph.D. thesis of R. T., Illinois Institute of Technology, 1970.

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