

as indicating that as structure III is increased in importance, structure II decreases in importance (*i.e.*, negative charge from X accumulates on both C and O). This result is in accord with charge density relationships obtained by HMO calculations.<sup>94</sup>

Similar results are obtained for  $-\text{SO}_2\text{X}$  substituents. In Fig. 3 a line of slope 2.0 is drawn between the two substituents  $\text{CH}_3$  and  $\text{CF}_3$ ,<sup>95</sup> for which eq. 2b is expected to hold approximately. Deviations for  $\text{X} = -\text{R}$  sub-

(94) Reference 8b and unpublished results.

(95) The  $\sigma_I$  value of +0.84 for the  $-\text{SO}_2\text{CF}_3$  substituent has been communicated to the authors by Dr. W. A. Sheppard.

stituents are apparent in Fig. 3. It is of interest that the magnitudes of the deviations for a given X in  $-\text{COX}$  and  $-\text{SO}_2\text{X}$  are similar. A consequence is the fact that corresponding  $\sigma_I$  values are quite generally about +0.40 more positive in the latter series (implying the equivalent of about 0.5 electronic unit more positive charge on S than C).

The present results illustrate in an apparent unambiguous manner how a given (but arbitrary) position in the molecule must be specified in order that the terms resonance and inductive effects of substituents can have even an approximate utility.

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## The Protonation of Benzyldeneaniline and its *p*- and *p'*-Dimethylamino Derivatives<sup>1</sup>

BY RICHARD L. REEVES AND WENDELL F. SMITH

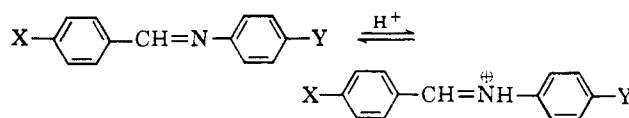
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The spectra of a number of substituted benzyldeneanilines and their conjugate acids have been measured in either water or 50% ethanol. Protonation of the azomethine nitrogen gives a bathochromic shift of the  $\text{N} \rightarrow \text{V}_1$  absorption band, contrary to previously reported results. The mono-acid of *p*-dimethylaminobenzyldeneaniline (Ib) exists almost entirely as the anilinium form, whereas that of benzyldene-*p'*-dimethylaminoaniline (Ic) is a tautomeric mixture containing approximately 70–85% of the ammonium form. Hydrolysis half-times for the mono-acids are in the millisecond range, with the exception of that of Ib, which is more stable. The spectral results for the compounds studied are interpreted in the light of simple molecular orbital calculations.

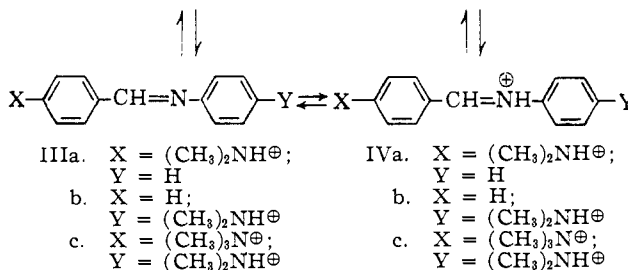
### Introduction

In recent years several publications have appeared on the structure of the conjugate acid of *cis*- and *trans*-azobenzene<sup>2,3</sup> and on the position of protonation of 4-aminoazobenzene and its derivatives.<sup>4</sup> Protonation of benzyldeneaniline (Ia), which is isoconjugate with azobenzene, and its two *p*-dimethylamino derivatives Ib and Ic has, however, remained a relatively unexplored subject.

The long-wave-length absorption maxima of benzyldeneaniline and several of its derivatives are reported to undergo a hypsochromic shift upon conversion to the corresponding conjugate acids.<sup>5,6</sup> In contrast to this observation, protonation of azobenzene<sup>7</sup> and the Schiff base Id<sup>8</sup> causes a bathochromic shift of the same band. The known rapid rates of hydrolysis of Schiff bases in general<sup>8–12</sup> make the reported spectra obtained in highly acid solution<sup>5,6</sup> appear suspect. Accordingly, we have obtained spectra of the conjugate acids of benzyldeneaniline and a number of its derivatives, using the flow technique described previously,<sup>8</sup> and have measured the hydrolysis rates in the pH range where the mono-acid is the predominant species. From our interpretation of the spectral results we have assigned the position of protonation in the mono-acid cations of the *p*- and *p'*-dimethylamino derivatives Ib and Ic. We also have interpreted some of the experimental results in the light of



- |   |  |
|---|--|
| Ia. X = Y = H   | IIa. X = Y = H                           |
| b. X = $(\text{CH}_3)_2\text{N}$ ; Y = H                                | b. X = $(\text{CH}_3)_2\text{N}$ ; Y = H |
| c. X = H; Y = $(\text{CH}_3)_2\text{N}$                                 | c. X = H; Y = $(\text{CH}_3)_2\text{N}$  |
| d. X = $(\text{CH}_3)_2\text{N}^\oplus$ ; Y = OH                        |  |
| e. X = $(\text{CH}_3)_2\text{N}^\oplus$ ; Y = OCH <sub>3</sub>          |  |
| f. X = $(\text{CH}_3)_2\text{N}^\oplus$ ; Y = CH <sub>3</sub>           |  |
| g. X = $(\text{CH}_3)_2\text{N}^\oplus$ ; Y = $(\text{CH}_3)_2\text{N}$ |  |
| h. X = $(\text{CH}_3)_2\text{N}^\oplus$ ; Y = H                         |  |



LCAO-MO (linear combination of atomic orbitals-molecular orbital) theory. The method has been previously applied in some detail to the interpretation of the electronic absorption spectrum of compound Ia.<sup>7,13</sup> The calculations have now been extended to include the alternant hydrocarbon ion isoconjugate with Ib and Ic.

The spectrum of the mono-acid cation of 4-aminoazobenzene is best interpreted in terms of an equilibrium mixture of the tautomeric azonium and ammonium ions.<sup>4</sup> Ricketts and Cho<sup>14</sup> interpret their spectral data on the mono-acid cations of benzyldene-*p'*-phenylazoaniline (I, X = H, Y = PhN=N-) and *p*-dimethylaminobenzyldene-*p'*-phenylazoaniline (I, X =  $(\text{CH}_3)_2\text{N}$ -, Y = PhN=N-) as involving a tautomeric mixture resulting from protonation at both the azo and the azomethine nitrogens. The results of Weinstein and McInnich<sup>15</sup> on hydrogen-

(1) Throughout this paper, *p*-substituents will refer to the benzyldene ring and *p'*- to the aniline ring.

(2) (a) H. H. Jaffé and R. W. Gardner, *J. Am. Chem. Soc.*, **80**, 319 (1958);

(b) S.-J. Yeh and H. H. Jaffé, *ibid.*, **81**, 3279 (1959).

(3) F. Gerson, E. Heilbronner, A. van Veen and B. M. Wepster, *Helv. Chim. Acta*, **43**, 1889 (1960).

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(5) G. Smets and A. Delvaux, *Bull. soc. chim. Belges*, **56**, 106 (1947).

(6) (a) N. Ebara, *Bull. Chem. Soc. Japan*, **33**, 534 (1960); (b) **34**, 1151 (1961).

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(8) R. L. Reeves, *J. Am. Chem. Soc.*, **84**, 3332 (1962).

(9) (a) A. V. Willi and R. E. Robertson, *Can. J. Chem.*, **31**, 361 (1953);

(b) A. V. Willi, *Helv. Chim. Acta*, **39**, 1193 (1956).

(10) B. Kastening, L. Holleck and G. A. Melkonian, *Z. Elektrochem.*, **60**, 130 (1956).

(11) O. H. Wheeler and P. H. Gore, *J. Org. Chem.*, **26**, 3298 (1961).

(12) E. H. Cordes and W. P. Jencks, *J. Am. Chem. Soc.*, **84**, 832 (1962).

(13) W. F. Smith, *Tetrahedron*, in press (1963).

(14) J. A. Ricketts and C. S. Cho, *J. Org. Chem.*, **26**, 2125 (1961).

(15) J. Weinstein and E. M. McInnich, *J. Am. Chem. Soc.*, **82**, 6064 (1960).

TABLE I  
 PREPARATION OF SCHIFF BASES

Com- pound	Reacn. solvent	Recrystn. solvent	M. p., °C.	Carbon, %		Hydrogen, %		Nitrogen, %		Chlorine, %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
Ia	Benzene	<i>n</i> -Heptane	51–52	86.2	86.6	6.1	6.2	7.7	7.7	..	..
Ib	Ethanol	Ethanol	98–99	80.3	80.0	7.2	6.9	12.5	12.4	..	..
Ic	None	Ligroin	97.5–98.5	80.3	80.3	7.2	7.3	12.5	12.8	..	..
Id	AcOH	Water	216 dec.	66.1	66.4	6.6	6.7	9.6	9.7	12.2	12.3
Ie	Ethanol	MeOH- <i>i</i> -PrOH	187.5–188.5	67.0	66.5	6.9	6.6	9.1	9.4	11.6	11.9
If	Ethanol	EtOH-H <sub>2</sub> O	175–176	70.7	70.5	7.3	7.2	9.7	10.1	12.3	12.7
Ig	Water	Ethanol	236–238	68.0	67.6	7.6	7.5	13.2	13.1	..	..
Ih	AcOH	Ethanol	180 dec.	52.5	52.2	5.2	5.4	7.7	7.3	34.7 <sup>a</sup>	34.3 <sup>a</sup>

<sup>a</sup> As the iodide.

bonded complex formation between *p*-nitrophenol and a series of substituted benzylideneanilines in carbon tetrachloride indicate that complex formation occurs at the azomethine nitrogen for both compounds Ib and Ic.

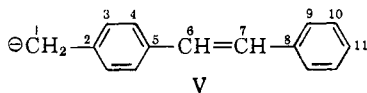
### Experimental

**Materials.**—The Schiff bases Ia–Ih were prepared by warming equimolar amounts of the appropriate amine and aldehyde in a solvent (Table I), cooling the solution, and removing the precipitated product by filtration. All the products were solids. The solvents from which they were recrystallized are given in Table I, with the melting points and analyses.

**Ultraviolet Spectra.**—The spectra of the solubilized Schiff bases in aqueous acid solutions were obtained by the flow technique described previously.<sup>8</sup> The ionic strength of each solution was 0.05 after mixing, and was adjusted by additions of potassium chloride to the buffer solution. The acid dissociation constants were determined from the change in spectrum with acidity. The *p*H of each effluent from the flow apparatus was measured with a glass electrode. The hydrogen-ion activities were converted to concentrations by the relationship  $-\log m_{H^+} = -\log a_{H^+} - 0.08$ .<sup>16</sup> The studies in 50% (by volume) ethanol–water mixtures were made by mixing equal volumes of a solution of the Schiff base in absolute ethanol with standardized aqueous hydrochloric acid in the flow machine.

The solutions of hydrogen chloride in ethylene chloride were prepared by bubbling the gas through the solvent, titrating an aliquot with tetra-*n*-butylammonium hydroxide in 90% benzene–methanol, and diluting the stock solution immediately to the desired acid concentrations. The absorption maximum of the long-wave-length peak of IIc exhibited a medium effect in acidic ethylene chloride, shifting progressively to longer wave lengths with increasing acid concentrations. Because Ic was not stable in acidic ethylene chloride, 0.49 ml. of a solution of Ic in ethylene chloride was injected from a calibrated Cornwall hypodermic syringe into 4.0 ml. of the acidic solvent in a 1-cm. quartz cell and the change in optical density at the absorption maximum then measured as a function of time. The time between mixing and the beginning of the record was measured with a stopwatch and the plot of density *vs.* time was extrapolated to zero time. The absorption maxima at each acidity were determined in separate runs by mixing in the same way and rapidly scanning the spectrum on a Cary recording spectrophotometer.

**Molecular Orbital Calculations.**—Schiff bases Ib and Ic and their respective anilium ions IIB and IIC are isoconjugate with the alternant hydrocarbon ion V. The perturbation treatment



of Coulson and Longuet-Higgins<sup>17</sup> was applied to compound V in order to interpret the spectral shifts of Ib and Ic upon protonation. A Hückel molecular orbital calculation was first carried out on V, all Coulomb integrals being set equal to  $\alpha$ , all resonance integrals to  $\beta$ , and overlap being neglected. From the resulting eigenvectors atom–atom, bond–atom and bond–bond polarizabilities were calculated according to eq. 64, 65 and 67 of reference 17 on an IBM 1620 computer.

### Results

**Absorption Spectra.**—The spectra of benzylideneaniline and its conjugate acid in 50 volume % ethanol are shown in Fig. 1. The spectral data for all the

benzylideneanilines studied here and their conjugate acids are recorded in Table II.

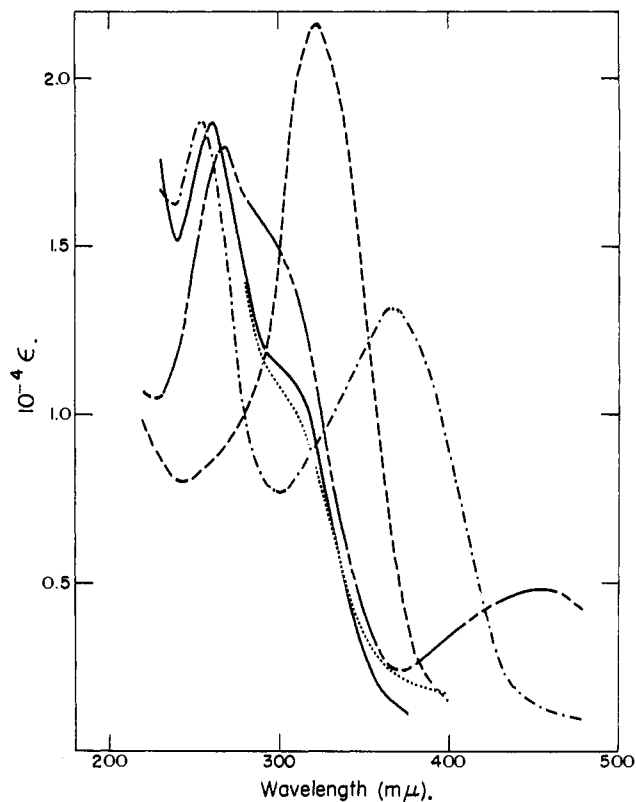


Fig. 1.—Absorption spectra of some N-benzylideneanilines and their conjugate acids: —, Ia in 50% ethanol; ---, Ia in 0.05 N HCl (50% ethanol); - · - ·, Ic in 50% ethanol; · · · ·, Ic in 0.05 N HCl (50% ethanol); · · · · ·, Ig in aq. *p*H 3.54 buffer.

The low stabilities of the conjugate acids in aqueous or partially aqueous solutions are indicated by the hydrolysis half-times given in the last column. These rates were determined by the steady-state flow method.<sup>8</sup> The spectral data for the first four structures entered in the table show that protonation of azomethine nitrogen results in a bathochromic shift of the long-wave-length peak with an increase in the extinction coefficient. The spectral change associated with protonation of the *p*-dimethylamino derivative Ib is similar to that found on protonation of the Schiff bases containing only azomethine nitrogen, and it is concluded that the conjugate acid of Ib exists almost entirely as the anilium form IIB in 50% ethanol. Low concentrations of the ammonium form of the mono-acid might not be detected since the absorption of this species is characterized by a shoulder rather than a peak (*vide infra*). *p*-Dimethylaminobenzylideneaniline (Ib) differs from the other Schiff bases studied here in that the extinction coefficients of both the free base and the conjugate acid are several times as large

(16) I. Feldman, *Anal. Chem.*, **28**, 1859 (1959).

(17) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc. (London)*, **A191**, 39 (1947).

TABLE II  
SPECTRAL AND STABILITY DATA FOR SUBSTITUTED  
BENZYLIDENEANILINE AT 25°

Structure	Solvent	$\lambda_{\max}$ , m $\mu$ <sup>a</sup>	$\epsilon \times 10^{-4}$	$t_{1/2}$ , msec. <sup>b</sup>
Ia	50% EtOH	305 <sup>c</sup>	1.1	
Ia	0.05 N HCl in 50% EtOH			31
Id	Water	323	2.2	
Id	0.05 N aq. HCl	367	2.1	60
Ie	Water	332	1.3	
Ie	0.15 N aq. HCl	370	1.6	42
If	Water	325	1.1	
If	0.10 N aq. HCl	343	1.9	51
Ig	Water	370	1.4	
Ig	pH 3.54 buffer	300 <sup>c</sup>	1.0	44
Ib	50% EtOH	358	3.4	
Ib	0.05 N HCl in 50% EtOH		8.2	9400
Ic	50% EtOH	368	1.3	
Ic	0.05 N HCl in 50% EtOH	455, 270 <sup>c</sup>		10
Ic	CICH <sub>2</sub> CH <sub>2</sub> Cl	380	1.4	
Ic	2.3 $\times 10^{-4}$ N HCl in CICH <sub>2</sub> CH <sub>2</sub> Cl	484, 280		

<sup>a</sup> Observed absorption maximum for the longest-wave-length peak. <sup>b</sup> Calcd. from the observed pseudo-first-order rate constant, measured at the acidity where the spectrum of the conjugate acid was obtained. <sup>c</sup> A shoulder on a peak falling at shorter wave lengths.

as those of the remaining derivatives. Even more interesting is the relative stability of the anilium form of Ib toward hydrolysis. The unusual stability of Ib in mildly acid solution has been noted previously<sup>9a</sup> and ascribed to the fact that Ib is probably present as the ammonium form in acid solution. Our data now show this interpretation to be unlikely.

The table shows that the effect of electron-donating substituents in the *p*-position of the aniline ring is to decrease the energy of the N  $\rightarrow$  V<sub>1</sub> transition in both the free base and the conjugate acids. This supports the conclusion obtained from previous MO calculations.<sup>13</sup>

The spectral changes associated with protonation of the *p*'-dimethylamino derivatives Ic and Ig stand in marked contrast to those for the *p*-dimethylamino derivatives and the other Schiff bases. Progressive acidification of solutions of Ig to pH 3.5 results in diminution of the strong peak at 370 m $\mu$  and an increase in absorption in the region of 300 m $\mu$ , with an isosbestic point at 320 m $\mu$ . At pH 2.5 and at higher acidity the absorption at 300 m $\mu$  decreases with a shift away from the isosbestic point, suggesting that significant concentrations of di-acid IVc are present at pH 2.5 and below. From the *pK*<sub>a</sub> of Ig (4.48, Table IV) the concentration of mono-acid at pH 3.5 is calculated to be 90% of the total Ig present. The absence of an absorption peak in the acid form of Ig at wave lengths longer than 370 m $\mu$  and the similarity of the absorption curve to that of benzylideneaniline free base (Fig. 1) lead to the conclusion that the mono-acid of Ig has the ammonium structure IIIc. Further support for this assignment is found from the value of the *pK*<sub>a</sub> and from the MO calculations (*vide infra*).

The spectrum of benzylidene-*p*'-dimethylaminoaniline (Ic) changed progressively with increasing acidity with an isosbestic point in the range of 10<sup>-4</sup> to 10<sup>-2</sup> N HCl in 50% ethanol. It remained essentially unchanged in going from 0.025 N to 0.05 N acid. From the estimated *pK*<sub>a</sub> of the mono-acid (~3.5) it was calculated that Ic should be completely converted to mono-acid in 0.05 N acid. The low

stability of Ic mono-acid (Table II) prevented the measurement of meaningful spectra at significantly higher acidities to determine the acidity at which the concentration of di-acid becomes important. On proceeding from free base to mono-acid, the same decrease in the 368-m $\mu$  peak and increase in absorption in the 300-m $\mu$  region is observed with Ic as with Ig. In addition, however, the spectrum of Ic mono-acid shows absorption at 455 m $\mu$  (Fig. 1). The optical density of the long-wave-length peak is rather high to be assigned as an n  $\rightarrow$   $\pi^*$  transition of the mono-acid cation IIIb.<sup>7,18</sup> Also, the observed red shift of the peak upon increasing the HCl concentration in ethylene chloride (Table III) further militates against its

TABLE III  
EFFECT OF ACIDITY ON THE LONG-WAVE-LENGTH ABSORPTION  
MAXIMUM OF Ic IN ETHYLENE CHLORIDE

Ic concentration = 1 $\times 10^{-4}$ M					
10 <sup>4</sup> (HCl), M	$\lambda_{\max}$ , m $\mu$	Density at absorption max.	10 <sup>4</sup> (HCl), M	$\lambda_{\max}$ , m $\mu$	Density at absorption max.
0	470	0.025	2.3	484	0.765
0.30	470	.117	4.5	494	.610
.43	470	.198	9.1	505	.403
.91	474	.618	24	515	.213
			1500	(470-515)	.013

assignment as an n  $\rightarrow$   $\pi^*$  transition since one should expect a progressive blue shift with increasing solvent polarity for such a transition.<sup>19</sup> We therefore assign this absorption to a low concentration of the anilium form of the mono-acid IIIc, in equilibrium with the ammonium form of the mono-acid IIIb. It is not possible to determine exactly the position of the tautomeric equilibrium IIIc  $\rightleftharpoons$  IIIb without knowing the extinction coefficients of the two species.

We can place some limits on the concentration of IIIc from the facts that (1) the ammonium form of the mono-acid has negligible absorption in the visible region of the spectrum, and (2) the extinction coefficients of the long-wave-length band are greater in the anilium salts by factors of 1.2-2.4 than in the free bases (Table II). From this it can be estimated that about 15-30% of the mono-acid of Ic is present in equilibrium as the anilium form.

In an attempt to determine the effect of solvent polarity on the position of the tautomeric equilibrium IIIc  $\rightleftharpoons$  IIIb, the spectrum of Ic was examined at a number of acidities in ethylene chloride. It was hoped that a less polar solvent would bring our results more into line with the predictions of the MO calculations (*vide infra*) and the results found in the non-polar solvent, carbon tetrachloride.<sup>15</sup> We found that acidification of solutions of Ic in this solvent did give rise to appreciable absorption in the region of 450-515 m $\mu$  but that the absorption passed through a maximum with increasing acidity (Table III). Clearly the dissociation constants for the di-acid and the mono-acid are too close to permit the isolation of pure mono-acid in this solvent. Qualitatively, however, the optical density of the 470-515 m $\mu$  band at the acidity where maximum absorption occurs appears higher than in 50% ethanol, indicating that a higher proportion of IIIc is probably present in the equilibrium mixture of mono-acids in ethylene chloride than in the more polar solvents. We believe the shift in absorption maximum of the long-wave-length band with increasing acidity (Table III) is due to changes in the dielectric constant

(18) J. W. Sidman, *Chem. Rev.*, **58**, 689 (1958).

(19) (a) H. McConnell, *J. Chem. Phys.*, **20**, 700 (1952); (b) G. J. Bealey and M. Kasha, *J. Am. Chem. Soc.*, **77**, 4462 (1955).

of the solvent with increasing ion concentrations<sup>20</sup> and not to the presence of more than one absorbing species.

**Acid Dissociation Constants.**—The  $pK_a$ 's of the solubilized benzylideneanilines Id–Ig were measured on flowing solutions, as described previously,<sup>8</sup> and are recorded in Table IV.

TABLE IV

ACID DISSOCIATION CONSTANTS FOR *p*-TRIMETHYLAMMONIUM-BENZYLIDENEANILINES AT 25°

Structure	$\sigma^a$	$pK_a$
Ig	−0.600	4.49 ± 0.03 <sup>b</sup>
Id	−.357	2.11 ± .04 <sup>b</sup>
Ie	−.268	1.93 ± .10 <sup>b</sup>
If	−.170	1.85 ± .06 <sup>b</sup>

<sup>a</sup> Values taken from H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).  
<sup>b</sup> 95% confidence.

The constants are equilibrium-concentration quotients and refer to dilute aqueous solutions of ionic strengths 0.05 at 25°. The concentrations of the acidic and basic species were determined spectrophotometrically and  $[H^+]$  was calculated from *pH* measurements by use of the appropriate activity coefficient.<sup>16</sup> The substituents are listed in the order of decreasing electron-donating ability. Further extension of the series to weaker electron-donating substituents (less basic Schiff bases) would have increased the error and would have required working in a region of acidity where the measurement and interpretation of acidity are difficult and where variable or high ionic strength would have been required. A Hammett plot of  $\log K_a$  vs.  $\sigma$  gave a linear plot for compounds Id, Ie and If of slope  $\rho = 1.5$ . The  $pK_a$  for Ig is clearly not correlated by the same Hammett parameters that correlate the other members of the series.

**Molecular Orbital Calculations.**—We were interested in examining the predicted direction of the shift of the  $N \rightarrow V_1$  absorption maximum upon protonation of benzylideneaniline in the light of simple MO theory. Benzylideneaniline is isoconjugate with stilbene, which is an alternant hydrocarbon. The change in transition energy associated with a change in the Coulomb integral,  $d\alpha_r$ , on atom *r* is, to a first approximation, given by the equation<sup>21</sup>

$$\Delta E \cong (c_{m+1,r}^2 - c_{m,r}^2)d\alpha_r \quad (1)$$

where *m* is the index of the highest occupied orbital, the *c*'s are LCAO coefficients, and *E* represents the transition energy. For an alternant hydrocarbon  $c_{m,r}^2 = c_{m+1,r}^2$  and a shift is not predicted upon perturbation of atom *r*. However, Coulson has shown<sup>21</sup> that when overlap is included, a change in  $\Delta E$  is predicted, the sign of which is the same as that of  $d\alpha_r$ . Denoting by *z* the difference in Coulomb integral between  $\text{>>NH}^+$  and  $\text{>>C}$  and by *x* the difference in

Coulomb integral between  $\text{>>N}$  and  $\text{>>C}$ , then since  $(z - x) < 0$ , a bathochromic shift ( $\Delta E < 0$ ) is predicted upon protonation of benzylideneaniline.

Application of eq. 1 to compounds Ib and Ic gives:  $\Delta E(\text{Ib} \rightarrow \text{Iib}) \cong (c_{m+1,7}^2 - c_{m,7}^2)d\alpha_7 = 0.016(z - x)$ ; and  $\Delta E(\text{Ic} \rightarrow \text{Iic}) \cong (c_{m+1,6}^2 - c_{m,6}^2)d\alpha_6 = 0.235(z - x)$ , the effect of the amino nitrogen canceling to a first approximation. The much larger bathochromic shift predicted for Ic  $\rightarrow$  Iic is a result of the fact that atom 6 (the azomethine nitrogen) is unstarred, and therefore  $c_{m,6} = 0$  as *m* is the non-bonding molecular orbital.

(20) (a) Y. H. Inami, H. K. Bodenseh and J. B. Ramsey, *J. Am. Chem. Soc.*, **83**, 4745 (1961); (b) J. T. Denison and J. B. Ramsey, *J. Chem. Phys.*, **18**, 770 (1950).

(21) C. A. Coulson, *Proc. Phys. Soc.*, **A65**, 933 (1952).

In the case of Ib  $\rightarrow$  Iib, atom 7 (the azomethine nitrogen) is starred; since  $c_{m+1,7} \cong c_{m,7}$ , only a small shift is predicted.

The ratio of the calculated shifts,  $\Delta E(\text{Ib} \rightarrow \text{Iib})/\Delta E(\text{Ic} \rightarrow \text{Iic})$ , is only  $\sim 0.07$ , whereas experimentally the ratio is  $\sim 0.94$  in polar solvents. Clearly other factors must be considered in determining the effect on the eigenvalues of a perturbation of atom *r*. The change in energy of a MO resulting from perturbation of Coulomb and resonance integrals can be represented according to eq. 2.<sup>17</sup>

$$d\epsilon_i = \sum_r c_r^2 d\alpha_r + 2 \sum_{r < s} c_r c_s d\beta_{rs} \quad (2)$$

A change in Coulomb integral  $d\alpha_t$  on atom *t* will affect the Coulomb integral of the *r*th atom, according to the equation

$$d\alpha_r \cong (\pi_{r,t}/\pi_{r,r})d\alpha_t \quad (3)$$

where  $\pi_{r,t}$  is the atom–atom polarizability of *r* with respect to *t*, and  $\pi_{r,r}$  is the self-atom polarizability of atom *r*. Similarly, the resonance integral of the *r*th bond will be affected according to eq. 4

$$d\beta_{rs} \cong (\pi_{rs,t}/\pi_{rs,rs})d\alpha_t \quad (4)$$

in which  $\pi_{rs,t}$  is the bond–atom polarizability of bond *rs* with respect to atom *t*, and  $\pi_{rs,rs}$  is the bond–bond self-polarizability of bond *rs*. Substitution of 3 and 4 into 2 gives

$$d\epsilon_i \cong \left[ \sum_r c_r^2 \frac{\pi_{r,t}}{\pi_{r,r}} + 2 \sum_{r < s} c_r c_s \frac{\pi_{rs,t}}{\pi_{rs,rs}} \right] d\alpha_t \quad (5)$$

The change in transition energy upon protonating the anil nitrogen will then be given by

$$\Delta E \cong \left\{ \left[ \sum_r (c_{m+1,r}^2 - c_{m,r}^2) \frac{\pi_{r,t}}{\pi_{r,r}} \right] + \left[ 2 \sum_{r < s} (c_{m+1,r} c_{m+1,s} - c_{m,r} c_{m,s}) \frac{\pi_{rs,t}}{\pi_{rs,rs}} \right] \right\} (z - x) = (Q + P)(z - x) \quad (6)$$

where *Q* and *P* represent the terms within brackets. It is found by substitution of the appropriate values that for Ib  $\rightarrow$  Iib,  $Q = -0.054$ ,  $P = 0.105$  and  $\Delta E = 0.051(z - x)$ ; for Ic  $\rightarrow$  Iic,  $Q = 0.269$ ,  $P = 0$  and  $\Delta E = 0.269(z - x)$ . In the case of Ic  $\rightarrow$  Iic, the *P* term vanishes since atom *t* is an unstarred atom (no. 6) and, according to a theorem of Jaffé,<sup>22</sup> the bond orders of all bonds are independent of the Coulomb integrals of all unstarred atoms. The ratio of  $\Delta E(\text{Ib} \rightarrow \text{Iib})/\Delta E(\text{Ic} \rightarrow \text{Iic})$  is now  $\sim 0.19$ , a threefold improvement over the previous ratio. The remaining discrepancy probably lies in solvent–solute interactions, since the shifts will also depend upon differences in dipole moments of the ground and excited states of the anils and their corresponding anilium ions and the interaction of these dipoles with the surrounding dielectric.<sup>23</sup>

The  $N \rightarrow V_1$  transition energy for stilbene is  $-1.09\beta$ ,<sup>24</sup> whereas that of *V* is  $-0.618\beta$ . Protonation of the dimethylamino group in Ib or Ic, giving IIIa and IIIb, respectively, should, by the arguments just given, result in a hypsochromic shift, since IIIa and b are isoconjugate with stilbene.

## Discussion

The spectral results clearly show and the MO calculations predict that protonation of the azomethine nitrogen in diaryl Schiff bases gives a bathochromic shift of the  $N \rightarrow V_1$  absorption band. The similar bathochromic shift in this band accompanying protonation of the *p*-dimethylamino derivative Ib shows that the conjugate acid of this Schiff base exists almost ex-

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(23) E. G. McRae, *J. Phys. Chem.*, **61**, 562 (1957).

(24) W. Maier, A. Saupe and A. Englert, *Z. physik. Chem. (Frankfurt)*, **10**, 273 (1957).

clusively as the anilium ion IIb in polar solvents. On the other hand, the large hypsochromic shift of the  $N \rightarrow V_1$  band accompanying protonation of the solubilized  $p'$ -dimethylamino derivative Ig, the close resemblance of the absorption curve of the conjugate acid to that of benzyldeneaniline free base and the absence of any band in the curve of the mono-acid at longer wave lengths than the  $N \rightarrow V_1$  band in the free base all indicate that the mono-acid exists as the ammonium form IIIc. The MO calculations predict a hypsochromic shift in this band upon forming the ammonium ion. In addition, the large deviation of the acid dissociation constant of the mono-acid of Ig from the Hammett relationship that correlates the  $pK_a$ 's of the conjugate acids of Id, Ie and If indicates that the measured  $pK_a$  for Ig mono-acid involves a different acidic species from the others. Since the position of protonation of Id-If is unambiguously at the azomethine nitrogen, the assignment of the ammonium form to the conjugate acid of Ig becomes compelling. In order for the  $pK_a$  for the mono-acid of Ig to fit the same Hammett plot as the acid forms of Id-If, an "exalted"  $\sigma$ -value for  $p'-(\text{CH}_3)_2\text{N}-$  of  $-2.6$  would be required. Such a large negative value is not reasonable in the light of all other experience with the electronic effects of this substituent.

Having thus established the spectral features to be expected for the two possible conjugate acids of  $p'$ - and  $p'$ -dimethylamino Schiff bases from the spectra of the mono-acids of Ib and Id-If on the one hand and of Ig on the other, we can interpret the observed absorption curve of the mono-acid of benzyldene- $p'$ -dimethylaminoaniline (Ic) as being due to a mixture of both the anilium ion and the ammonium ion in equilibrium, where the latter form appears to predominate.

The present spectral and kinetic data on the benzyldeneanilines and their conjugate acids leave little doubt that the previously reported spectra of benzyldeneaniline conjugate acids<sup>5,6</sup> are incorrect. The apparent hypsochromic shifts of the long-wave-length bands observed by these workers upon protonation of benzyldeneaniline and the substituted benzyldeneanilines, and the failure of the substituents to influence the absorption maxima of the "conjugate acids"<sup>6</sup> can be explained if it is concluded that the reported spectra are those of hydrolysis products. Similar considerations apply to the spectral data of Ricketts and Cho<sup>14</sup> on the "conjugate acids" of Schiff bases of 4-aminoazobenzene. These workers report identical absorption maxima (320 and 495  $m\mu$ ) for the mono-acid cations of benzyldene- $p'$ -phenylazoaniline,  $p'$ -dimethylaminobenzylidene- $p'$ -phenylazoaniline and 1-methyl-4-carboxystyrylcarboxaldehyde- $p'$ -phenylazoanil. The facts that these absorption maxima are not altered by substitution and are identical with those reported for the conjugate acid of 4-aminoazobenzene<sup>25</sup> suggest that hydrolysis of the azomethine linkage had occurred before the spectra were obtained. The identity of the measured first and second acid dissociation constants attributed to benzyldene- $p'$ -phenylazoaniline and 1-methyl-4-carboxystyrylcarboxaldehyde- $p'$ -phenylazoanil by

(25) G. Cilento, E. C. Miller and J. A. Miller, *J. Am. Chem. Soc.*, **78**, 1718 (1956).

these workers also suggests that the constants apply to a common product.

The basicities of several aromatic and heteroaromatic amines have been related to  $\pi$ -electronic energies and electron densities.<sup>26-28</sup> For a series of closely related amines, linear correlations have been obtained between measured  $pK_a$ 's and the calculated electron densities at the position of the basic center in the isoconjugate hydrocarbons. Such correlations require that the ratio of partition functions,  $f_B/f_{BH^+}$ , remain reasonably constant throughout the series. Under these circumstances,  $\Delta E_p$ , the change in potential energy, becomes a measure of (but is not equal to)  $\Delta F$ .

We were interested in finding to what extent  $\Delta E_p$  would predict the position of protonation in  $p$ - and  $p'$ -dimethylamino Schiff bases, *i.e.*, at amino or azomethine nitrogen. Since the valence state of these two nitrogens is different, one would expect that  $f_{IB}/f_{IIB} \neq f_{Ib}/f_{IIIa}$  and  $f_{Ic}/f_{IIIc} \neq f_{Ic}/f_{IIIb}$  and that therefore  $\Delta E_p$  might not predict the position of protonation in the mono-acid cation.

The difference in  $\pi$ -energy between IIb and IIIa and between IIc and IIIb may be estimated by perturbation theory with the use of eq. 7,<sup>17</sup> where  $q_r$  is the electron density on the  $r$ th atom. Denoting by  $y$  the dif-

$$dE \cong \sum_r q_r d\alpha_r \quad (7)$$

ference in Coulomb integral between  $\text{>N}$  and  $-\text{CH}_2^{\ominus}$

and by  $q$  the electron density on a bridge carbon atom in stilbene (unity), it is readily shown that

$$E_{IIb} - E_{IIIa} \cong 0.787\beta + q_1y + q_7z - qx \quad (8)$$

$$E_{IIc} - E_{IIIb} \cong 0.787\beta + q_1y + q_6z - qx \quad (9)$$

in which  $0.787\beta$  is the difference in  $\pi$ -electronic energy between the alternant hydrocarbon ion V and stilbene. In estimating the energies of IIIa and IIIb, the inductive effect of the ammonium group has been neglected. Since  $(q_7z - qx) < (q_6z - qx) < 0$  and  $y$  and  $\beta$  are negative terms, it is clear that  $E_{IIb} - E_{IIIa} < 0$  and  $E_{IIc} - E_{IIIb} < 0$  and therefore protonation at azomethine nitrogen (at  $0^\circ\text{K}$ . in the gas phase) should be favored in both cases. In solution at  $25^\circ$ , however, Ic is protonated predominantly at the dimethylamino nitrogen, and thus other factors such as solvation energies must be considered to explain this reversal.

Molecular orbital calculations show that, in general, protonation of an N-heteroaromatic amine at the heterocyclic nitrogen results in a decrease in  $\pi$ -electronic energy, whereas protonation of the exocyclic nitrogen results in an increase in this energy.<sup>26-28</sup> These differences may be of the order of 20-80 kcal./mole, depending upon the value assigned to the resonance integral. In solution, however, differences in *free energy* ( $\Delta F$ ) for protonation at heterocyclic *vs.* amino nitrogen are rarely as high as 10 kcal./mole. In the case of aminopyridines and aminoquinolines<sup>26</sup> protonation in solution is still favored at heterocyclic nitrogen by  $\sim 1-7$  kcal./mole, whereas in the  $p'$ -amino Schiff bases the  $\Delta F$ 's for protonation at azomethine and amino nitrogen are quite similar.

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(27) N. S. Hush, *J. Chem. Soc.*, 684 (1953).

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