Linear Free Energy Relationships. IV.[1] Synthesis and Spectral Characterization of Some New Solvatochromics. *N*-(*p*-Substituted)benzyl-2′-hydroxy-4-stilbazolium Betaines

HARRY W. GIBSON AND F. C. BAILEY
Webster Research Center, Xerox Corporation, Webster, N.Y. 14580

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The spectral data for the present series of compounds indicate that the long wavelength $\pi \rightarrow \pi^*$ transition in each case involves transfer of negative charge from the phenol–quinone moiety to the pyridyl ring. Two separate features bear on this point: the transition energy dependence on (*i*) substituent and (*ii*) solvent. The plots of transition energy *vs.* Hammett substituent constant for the salts and the betaines have negative slopes as expected for such a transition. The plots of transition energy for the betaines *vs.* the solvent polarity parameter have large positive slopes, which are evidence for a large decrease in dipole moment upon excitation, consistent with such a transition. Through study of the p*H* dependence of the spectrum, the pK_a of the parent compound was found to be 8.37 at 22°. From this pK_a the apparent σ_{ortho} for the *N*-benzylstilbazolium substituent was estimated to be 0.75.

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Les données spectrales concernant la nouvelle série de composés indiquent que dans chaque cas la transition $\pi \rightarrow \pi^*$ observée à grande longueur d'onde implique un transfert d'une charge négative de la position phénol–quinone vers le cycle pyridyl. Il y a deux caractéristiques principales qui suggèrent cette conclusion: la dépendance de l'énergie de transition sur (*i*) les substituants et (*ii*) le solvant. Les courbes montrant l'énergie de transition en fonction des constantes de Hammett pour des substituants sous formes de sels ou de bétaines possèdent des pentes négatives telles que l'on pourrait les prédire pour de telles transitions. Les courbes de l'énergie de transition pour les bétaines en fonction du paramètre pour la polarité du solvant montrent de fortes pentes positives; ceci indique qu'il y a un fort abaissement du moment dipolaire lors de l'excitation et ceci est en accord avec une telle transition. A l'aide d'études sur l'influence du p*H* sur le spectre, on a pu évaluer que le pK_a du composé de base est 8.37 à 22°. En se basant sur ce pK_a, on a pu estimer que la valeur apparente du σ_{ortho} pour le substituant *N*-benzylstilbazolium est de 0.75. [Traduit par le journal]

Introduction

Solvatochromic compounds undergo changes in 'color' with changes in solvent (1). In valence bond terminology this is ascribed to the variation in relative contribution of two resonance forms to the hybridized structure and molecular orbital calculations support this picture (2). Compounds which show the largest solvatochromic effects are those possessing extreme resonance forms: a polarized or zwitterionic one and a delocalized or quinoidal one. Increasing polarity of the solvating medium thus shifts the electron distribution of the ground state continuously toward the polar resonance from while the structure of the excited state is affected negligibly (Franck–Condon principle); this results in a change in energy difference and absorption wavelength (3). Such compounds have, therefore, served as empirical solvent polarity indicators (1, 3, 4).

Our interest in solvatochromics arises from our work relating molecular orbital energy levels and structure by means of linear free energy relationships (5–7). In a previous report (6) the synthesis and absorption spectra of solvatochromic compounds **1** were described. In this series the energy of the longest wavelength band is linearly related to the substituent constant in all five solvents examined (6). This is in contrast to the generally limited success of such correlations in substituted benzenes (8). Part of this latter difficulty may arise from crossover of energy levels as substituents are changed and the resultant problem of proper assignment of transitions. However, such linear correlations of *hν* and substituent constant are observed in dyes (9–12),

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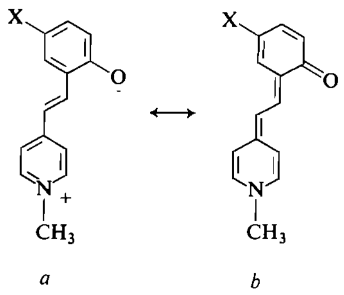
[1] For parts I–III, see refs. 5–7. For part V, see ref. 34.

where the identity of the absorption is readily assigned to a given transition for the entire series due to its isolation in the visible portion of the spectrum, and in donor–acceptor complexes of both inter-(13–15) and intramolecular (14) types. In intermolecular charge transfer transitions, it also is known that to a good approximation $h\nu = I - A + C$ (16), where I is the ionization potential of the donor, A is the electron affinity of the acceptor, *i.e.*, the energy levels of the orbitals involved, and C is a constant containing solvation, polarization, and nonbonding terms. Thus, a linear relationship between I and σ, and A and σ may be inferred.

Although not generally thought of in these terms, intramolecular charge transfer transitions can be similarly considered. Thus, attachment of a substituent at a particular site causes a larger perturbation of the energy levels in that moiety than in the other portion of the charge transfer couple. Thus, the primary effect is to vary the highest occupied orbital (ionization potential) of the donor moiety or the lowest unoccupied orbital (electron affinity) of the acceptor portion. In series **1**, as X becomes more electron withdrawing, the long wavelength transition energy increases. On the basis of these substituent and solvent effects on the absorption spectra, it was concluded that the long wavelength absorption transition involves transfer of electron density from the phenol–quinone moiety to the pyridyl ring, *i.e.*, excitation involves conversion of a ground state resembling **1***a* to an excited state more like **1***b*. Thus, the effect of substituent is primarily to alter the energy of the highest occupied molecular orbital associated with the phenolate–quinone moiety. The fact that this energy is lowered (ionization potential raised) by electron withdrawing groups is consistent with substituent effects on ionization potentials in other aromatic systems (5, 7).[2]



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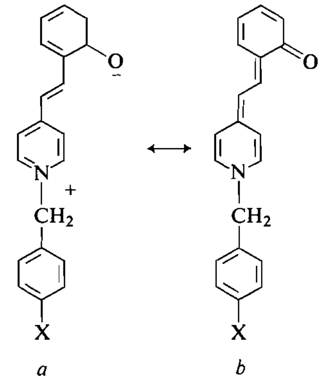
To corroborate this picture of the long wavelength transition of these compounds, we chose to examine *N*-(*p*-substituted)benzyl-2′-hydroxy-4-stilbazolium betaines (**2**). In this series of compounds, the substituent is attached to the pyridyl portion of the molecule. Since this is the acceptor portion of the molecule in the model deduced previously, the primary effect of the substituent is expected to be a result of alteration of the lowest unoccupied molecular orbital. By study of series **1** and **2**, substituent effects on the donor and acceptor portions can be discerned to some extent independently, in addition to the effects of solvent on the resultant electronic transitions.



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Discussion

Synthesis

The synthesis of this new solvatochromic series is analogous to our previous work (6). 4-Picoline (**3**) and the *p*-substituted-benzyl bromides (**4**) react in tetrahydrofuran(THF) to yield the quaternary salts (**5**) in ~90% yields. The yields, melting points, and elemental analyses are given in Table 1.

Condensation of the quaternary salts **5** with salicylaldehyde (**6**) in the presence of piperidine led to the (*p*-substituted)benzyl-2′-hydroxy-4-stilbazolium bromides (**7**) in variable yields. The synthesis and characterization data are summarized in Table 2. As expected all of these com-

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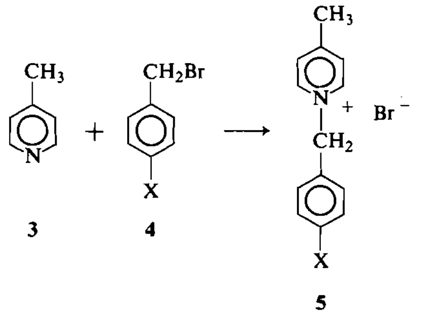
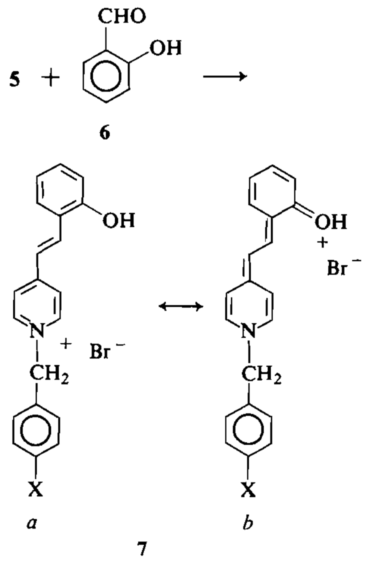
[2] For example the first four ionization potentials of substituted pyridine-*N*-oxides (data of Maier and Muller (33)) are linearly correlated (correlation coefficients r = 0.994, 0.995, 0.945, 0.935, respectively) with positive slopes by sums of σ^{+}_{para} substituent constants.



pounds are more soluble in organic solvents than the corresponding methiodides of series **1**. Significantly, none of the 1 : 1 complexes of **2** and **7** was observed; these compounds differ in this respect from series **1**, which form such complexes with the corresponding hydriodide salts.



In addition to the compounds listed in Table 2, the syntheses of **7**, X = CN, NO_2, were also pursued. Though these compounds were believed to have been prepared, they could not be isolated in pure form even by column chromatography.

Similarly attempts to isolate and purify the solvatochromic series **2** after their generation by base treatment of **7** were unsuccessful. Attempted recrystallization led to formation of intractable gums. These may be polymers arising from intermolecular electron transfer reactions. This proclivity for gum formation was also observed in the previously studied **1**, X = OCH_3.

Spectral Characterization

The ultraviolet–visible spectrum of the salt **7**, X = H, in water is shown in Fig. 1. Compounds **2** were generated *in situ* by addition of NaOH to solutions of the salts **7**. The spectra were then recorded within a few minutes time. The spectrum of **2**, X = H, in water is shown in Fig. 2. As can be seen by comparison of Figs. 1 and 2, the major spectral change is a shift of the long wavelength band from 372 to 458 nm. The spectra of other salts **7** and solvatochromics **2** were recorded in a

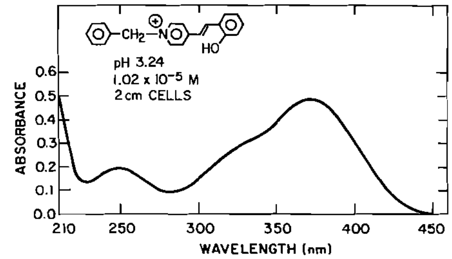


FIG. 1. Ultraviolet–visible absorption spectrum of *N*-benzyl-2′-hydroxy-4-stilbazolium bromide (**1**, X = H) in H_2O (borate, phosphate, acetate buffer (24), p*H* 3.243).

TABLE 1. (*p*-Substituted)benzyl-4-picolinium bromides (**5**)

			Analyses (%)							
			Calculated				Found			
X	Yield (%)	Melting point[a] (°C)	C	H	N	Br	C	H	N	Br
OCH_3	86	155.5–156.0	57.15	5.48	4.76	27.17	57.19	5.48	4.75	27.22
CH_3	89	159.0–160.5	60.44	5.80	5.04	28.73	60.36	5.71	5.05	28.79
H	90	158.5–159.5	59.10	5.34	5.30	30.25	59.60	5.26	5.08	30.18
Br	89	168.5–169.0	45.51	3.82	4.08	46.59	45.58	3.77	4.12	46.64
CN	87	217.0–218.5	58.14	4.53	9.69	27.64	57.90	4.78	9.65	27.64
NO_2	94	184.5–186.0[b]	49.28[c]	5.02	8.21	23.42	48.88	4.44	8.37	24.07

[a] Recrystallized from ethanol–benzene unless noted otherwise.
[b] Recrystallized from methanol–benzene.
[c] Calculated for methanolate.

TABLE 2. *N*-(*p*-Substituted)benzyl-2′-hydroxy-4-stilbazolium bromides (7)

			Analyses (%)							
			Calculated				Found			
X	Yield (%)	Melting point[a] (°C)	C	H	N	Br	C	H	N	Br
OCH_3	80	221.5–222.5	63.32	5.06	3.52	20.07	63.26	5.07	3.55	20.12
CH_3	39	99–101	65.98	5.27	3.66	20.90	65.64	5.55	3.69	20.94
H	56	211–213	65.23	4.93	3.80	21.70	64.88	5.28	3.76	21.76
Br	44	167–171	53.72	3.83	3.13	35.74	53.55	4.01	3.03	35.60

[a] Recrystallized from methanol.

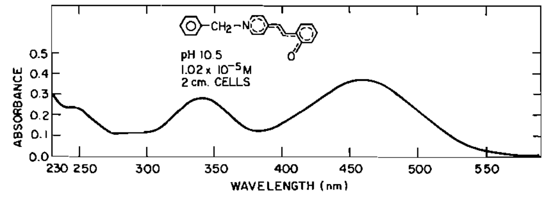


FIG. 2. Ultraviolet–visible absorption spectrum of *N*-benzyl-2′-hydroxy-4-stilbazolium betaine (2, X = H) in H_2O (borate, phosphate, acetate buffer (24), p*H* 10.484).

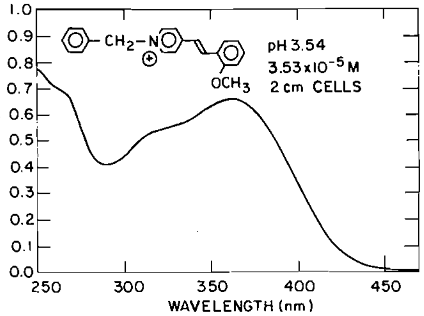


FIG. 3. Ultraviolet–visible absorption spectrum of *N*-benzyl-2′-methoxy-4-stilbazolium bromide (9) in H_2O (citric acid, sodium citrate buffer (31), p*H* 3.544).

variety of other solvents as well and similar changes occur.

To demonstrate unequivocally that the solvatochromic species do have structure **2** and not that of the ylid **8** (and associated resonance forms) resulting from removal of a benzylic proton from **7**, the *O*-methyl derivative (**9**) of **2**, X = H, was synthesized and examined. The m.p., n.m.r. spectrum, and solution properties of **9** are very similar to those of **2**, X = H. The u.v.–visible spectrum of **9** in aqueous acid is shown in Fig. 3; its λ_{max}(362 nm) and ε (9.55 × 10^3) are very similar to those of **2**, X = H (Fig. 1; 372; 9.55 × 10^3). The spectrum is unchanged in solutions of p*H* up to 10.5 (Fig. 4). Thus, the benzylic protons of **9** are not sufficiently acidic to be removed at this p*H*. It is, therefore, concluded that the structure of the solvatochromic compounds under discussion is indeed **2**.

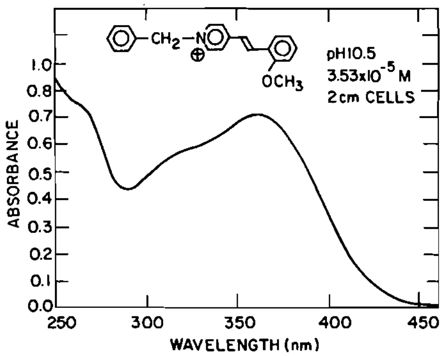
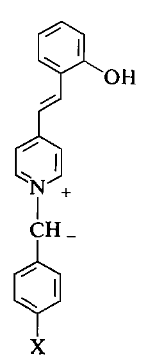


FIG. 4. Ultraviolet–visible spectrum of *N*-benzyl-2′-methoxy-4-stilbazolium bromide (9) in H_2O (sodium hydroxide, sodium bicarbonate buffer (32), p*H* 10.484).

The long wavelength transition energies of salts **7** and the solvatochromics **2** are displayed as a function of substituent constant, σ_X, in Figs. 5 and 6, respectively. It is significant that



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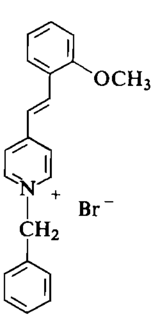

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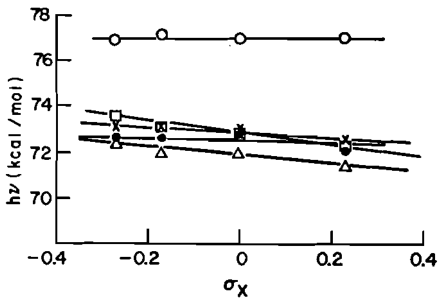


FIG. 5. Energy of longest wavelength transition *vs.* Hammett substituent constant for *N*-(*p*-substituted)-benzyl-2′-hydroxy-4-stilbazolium bromides (7): ○ H_2O: $h\nu = -0.164\sigma_X + 76.9$ ($r = 0.358$); □ 95% EtOH: $h\nu = -2.64\sigma_X + 72.8$ ($r = 0.986$); △ *i*-PrOH: $h\nu = -1.94\sigma_X + 71.8$ ($r = 0.942$); × *t*-BuOH: $h\nu = -1.33\sigma_X + 72.8$ ($r = 0.943$); ● $CHCl_3$: $h\nu = -0.955\sigma_X + 72.4$ ($r = 0.614$).

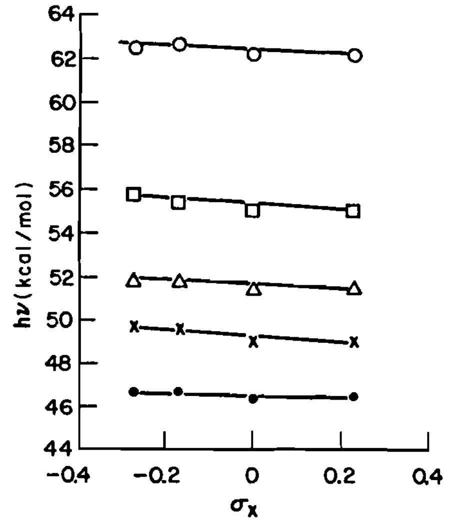


FIG. 6. Energy of longest wavelength transition *vs.* Hammett substituent constant for *N*-(*p*-substituted)-benzyl-2′-hydroxy-4-stilbazolium betaines (2): ○ H_2O: $h\nu = -0.708\sigma_X + 62.4$ ($r = 0.907$); □ 95% EtOH: $h\nu = -1.28\sigma_X + 55.3$ ($r = 0.968$); △ *i*-PrOH: $h\nu = -1.02\sigma_X + 51.6$ ($r = 0.938$); × *t*-BuOH: $h\nu = -1.40\sigma_X + 49.3$ ($r = 0.993$); ● $CHCl_3$: $h\nu = -0.466\sigma_X + 46.5$ ($r = 0.884$).

straight lines result and that the slopes are all negative, in contrast to the highly positive slopes for the series **1** and the corresponding hydriodide salts (6). Results for series **1** are shown in Fig. 7 for direct comparison.

As pointed out above the substituents in **2** and **7** are attached to the acceptor portion of the molecule and their effect is primarily a consequence of changes in the lowest unoccupied orbital. It has been demonstrated both by 'charge transfer' spectroscopy (13–15, 17) and electrochemistry (15, 18–20) that the electron affinity increases with σ_X in aromatic compounds; that is, the energy of the lowest unoccupied orbital level decreases. On this basis for both of the present series **2** and **7** then, increasing the electron withdrawing power should cause a decrease in transition energy. This is what is observed (Figs. 3 and 4).

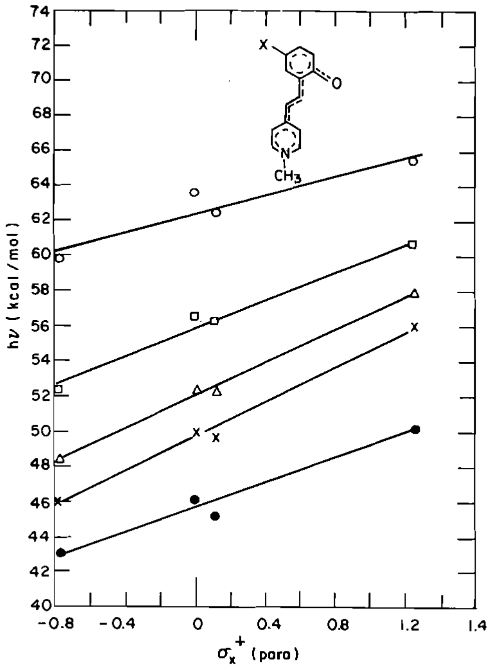


FIG. 7. Energy of longest wavelength transition *vs.* electrophilic substituent constant for *N*-methyl-5′-substituted-2′-hydroxy-4-stilbazolium betaines (**1**): ○ H_2O: $h\nu = +2.66\sigma^+ + 62.4$ ($r = 0.949$); □ 95% EtOH: $h\nu = +3.98\sigma^+ + 55.8$ ($r = 0.990$); △ *i*-PrOH: $h\nu = +4.70\sigma^+ + 52.0$ ($r = 0.998$); × *t*-BuOH: $h\nu = +4.96\sigma^+ + 49.7$ ($r = 0.995$); ● $CHCl_3$: $h\nu = +3.47\sigma^+ + 45.6$ ($r = 0.983$).

A further point is that while the results for series **1** were fit better by σ^+ (the electrophilic substituent constant) than by σ (the normal Hammett substituent constant), with the present compounds σ fits better than σ^+ as judged on the basis of the correlation coefficient, *r* (*e.g.*, **2** in H_2O, 0.907 *vs.* 0.696; **2** in 95% EtOH, 0.968 *vs.* 0.959; **2** in *i*-PrOH, 0.938 *vs.* 0.736). Again, this is consistent with the nature of the transition. In series **1** and the corresponding salts, σ^+ fits better since the substituent X is on the phenolate–

quinone moiety which becomes positively (or less negatively) charged; in series **2** and **7** the substituent is nearer the pyridyl ring which becomes negatively (or less positively charged) and hence σ would be expected to describe the energetics better than σ^+.

A word should be said regarding the relative magnitudes of the slopes of $h\nu$ *vs.* σ for series **1** and **2**. For series **1** slopes using σ (not σ^+ as reported (6)) range from $+1.7$ to $+8.7$, whereas in the present case (**2**) the range is -0.5 to -1.4, as shown in Fig. 6. The larger slopes in **1** are due to the fact that the substituents are directly attached to the chromophore, whereas in **2** they are not in conjugation with the chromophore because of the presence of the insulating methylene group.

Thus, the negative slopes of Figs. 5 and 6 and the better fit by σ support the previous conclusion regarding the nature of the electronic transitions in compounds **1** and **2** and the corresponding salts. The transition involves conversion from a ground state structure resembling **2***a* (and **7***a*) to an excited state structure more like **2***b* (and **7***b*). The transitions are most certainly of $\pi \rightarrow \pi^*$ type on the basis of recent molecular orbital calculations for compound **10** (2, 23) and the large extinction coefficients ($\sim 10^4$).

In Fig. 8 the transition energy of **7** is plotted as a function of the solvent polarity parameter, E_T (21). These plots are all nonlinear but the degree of solvatochromism is relatively small ($\Delta h\nu \sim 5$ kcal/mol). For comparison, nitrobenzene's ^1L_a band suffers a 2.5 kcal/mol decrease in energy when the solvent is changed from water to ethanol (22). The magnitudes are similar to those observed previously as are the shapes of the curves (6). The nonlinearity of these plots indicates that on a molecular level these salts are not solvated in the same manner as the reference compound used to evaluate E_T. This could be due to variations in the extent of ion pairing or degree of solvation because of the steric effect of the counter ion.

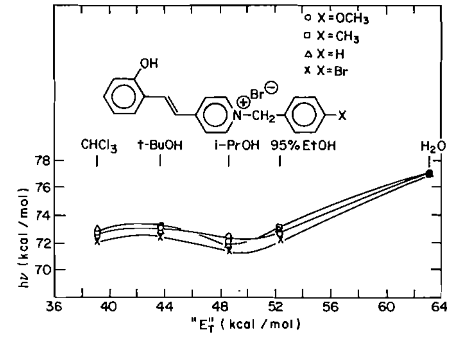


FIG. 8. Energy of longest wavelength transition *vs.* solvent polarity parameter for *N*-(*p*-substituted)benzyl-2′-hydroxy-4-stilbazolium bromides (**7**).

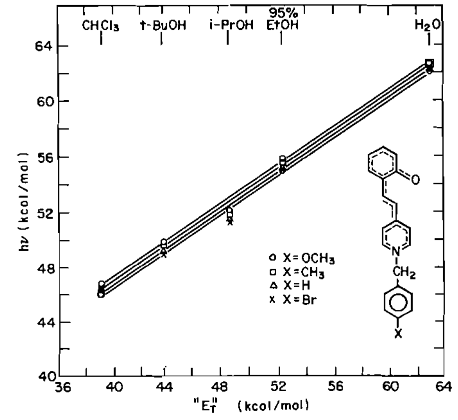


FIG. 9. Energy of longest wavelength transition *vs.* solvent polarity parameter for *N*-(*p*-substituted)benzyl-2′-hydroxy-4-stilbazolium betaines (**2**): X = OCH$_3$: $h\nu = 0.699E_T + 20.2\,(r = 0.996)$; X = CH$_3$: $h\nu = 0.687E_T + 19.2$ ($r = 0.998$); X = H: $h\nu = 0.673E_T + 19.8$ ($r = 0.997$); X = Br: $h\nu = 0.670E_T + 19.7$ ($r = 0.996$).

Figure 9 is a plot of the transition energy of **2** as a function of the solvent polarity parameter, E_T. As with **1**, large positive slopes are observed. The slopes of the lines are very similar to each other (0.67–0.69) and to those of **1**, X = OCH$_3$, H, Cl (0.71–0.73) (6). The range of solvatochromism ($\Delta h\nu$) in the present compounds **2** is about the same as observed in compounds **1** (6). Like the situation with **1**, the large positive slope of Fig. 9 is indicative of a large decrease in dipole moment (charge distribution) with excitation (1). This result corroborates the conclusion that light absorption converts a ground state resembling **1***a* or **2***a* to an excited state which resembles **1***b* or **2***b* to a greater extent.

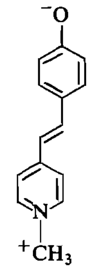
Acidity

It was deemed of interest to ascertain the acidity of the stilbazolium salts **7** as a measure of the relative electron distribution in **7** and the corresponding 'anion' **2**. In view of the small spectral changes encountered in both of these series, the acidity of **7**, X = H, alone was determined in the belief that changes in acidity would also be small across the series.

A series of aqueous buffer solutions comprised of sodium hydroxide, boric, phosphoric, and acetic acids covering a p*H* range from 3.2 to 10.5 was prepared (24). Solutions of **7**, X = H, at 10^{-5} *M* were prepared using these buffer solutions, so as to eliminate the possibility of associative phenomena. By comparison of the ratio of the long wavelength peak due to **2**, X = H, at 458 nm (see Fig. 2) to that at 372 nm due to **7**, X = H, (see Fig. 1) and taking into account the extinction coefficients measured at the extreme high and low p*H*'s ,the pK_a of **7**, X = H, at 22° was determined to be 8.37 (±0.01 standard deviation, three different buffer solutions).

Recently, the pK_a of the conjugate acid of **10** (as the hydriodide salt) was similarly evaluated by spectroscopic means and found to be 8.57 at room temperature (23). Thus **7**, X = H, is somewhat more acidic than the salt of **10**. The increase in acidity must be due to the substitution of an *N*-benzyl group for an *N*-methyl group inasmuch as the conjugate acid of **10** and its 2′-hydroxyl analog (**1**, X = H) (6) have identical pK_a's within experimental error (25). The *N*-benzyl group is expected to be more electron withdrawing than the *N*-methyl substituent on the basis of the Hammett substituent constants of $CH_2C_6H_5$ and CH_3 (−0.09 and −0.16, respectively) as well as those of C_6H_5 and H (0.02 and 0.00, respectively) (26). Thus the benzyl group would cause a larger net positive charge on the pyridinium ring and the rest of the conjugated system and in this way enhance the acidity.

Furthermore, it is interesting to note that the pK_a of salicylaldehyde (**6**) is reported to be 8.37 (27) and 8.34 (28) at 25°, virtually identical to that of **7**, X = H. Salicylaldehyde is significantly less acidic than the isomeric *p*-hydroxybenzaldehyde (pK_a 7.62 (27, 28)); this difference is attributed to hydrogen bonding in the former in concert with the mesomeric effect in the latter (28). Nonetheless, the identity of the acidities of **6** and **7**, X = H, is very striking. The net effects of the *N*-benzylstilbazolium and formyl substituents on the acidity of *ortho* substituted phenol are identical. Thus, one can assign to the *N*-benzylstilbazolium substituent a value of +0.75 for the apparent *ortho* substituent constant (σ_{ortho}) based on that of the CHO group (29). In view of the known complexity in treatment of the effects of *ortho* substituents (30), detailed discussion of the observed results seems unwarranted at this time.



10

In conclusion, the spectral examination of a new series of *N*-(*p*-substituted)benzyl-2′-hydroxy-4-stilbazolium betaines (**2**) substantiates our previous conclusion based on the related *N*-methyl-5′-substituted-2′-hydroxy-4-stilbazolium betaines (**1**) (6). The conclusion was that the long wavelength transition in **1**, **2**, and their salts involves the π → π* excitation of a predominantly zwitterionic ground state to a more delocalized or quinoidal excited state, *i.e.*, **1***a* → **1***b*, **2***a* → **2***b*, and **7***a* → **7***b* in valence bond terms. The experimental evidence in support of this is the dependence of the transition energy on (*i*) substituent and (*ii*) the polarity of the solvent. The first point bears on the effect of substituents on molecular orbital energy levels; in the present series the energy of the lowest unoccupied orbital was effectively varied while in the former that of the highest occupied orbital was effectively varied, both by substituent changes. The second point relates to the large changes in dipole moments (or electron distributions) upon excitation, which are negative in both systems. The solvatochromism of this new series **2** is similar in magnitude to that of the previous series (**1**), while the dependence of the transition energy on substituent is much less striking in the present series.

The pK_a of the parent salt **7**, X = H, at 22° is 8.37. This compound is slightly more acidic than the conjugate acid of **10** whose pK_a is 8.57 (23). This increase in acidity is attributed to the electron withdrawing effect of the *N*-benzyl group relative to the *N*-methyl group. From the pK_a a value for the apparent σ_{ortho} of the *N*-benzylstilbazolium substituent in phenols is found to be 0.75.

Experimental

General

Melting points are corrected. Analyses are by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

(p-Substituted)benzyl-4-picolinium Bromides (5)

To a solution of 18.6 g (0.200 mol) of 4-picoline (**3**) in 150 ml THF was added 0.205 mol of the *p*-substituted benzyl bromide (**4**). The mixture was refluxed for 2.5 h and filtered. The solid was washed with *n*-hexane and recrystallized from ethanol–benzene. The results are summarized in Table 1.

(p-Substituted)benzyl-2′-hydroxy-4-stilbazolium Bromides (7)

To a solution of 0.100 mol of the quaternary salt **5** in a minimum amount of methanol (50–100 ml) was added 15.3 g (0.125 mol) of salicylaldehyde (**6**) and 2.5 ml piperidine. After 3.5 h reflux the solution was concentrated, cooled, and filtered. The solid was recrystallized from methanol. Table 2 summarizes the results. The n.m.r. spectrum of **7**, X = H, in CD_3SOCD_3 was typical: δ 3.38 (s, 1H, O*H*), 5.78 (s, 2H, CH_2), 6.6–8.0 (m, 11H, aromatic *H*), 8.20 (d, 2H, H_3, H_5, J = 6 Hz), 9.05 (d, 2H, H_2, H_6, J = 6 Hz).

N-Benzyl-2′-methoxy-4-stilbazolium Bromide (9)

This was prepared by the above procedure using *o*-anisaldehyde and **5**, X = H. The desired product, isolated in about 30% yield by elution from acidic alumina with chloroform, was recrystallized three times from isopropanol: yellow plates, m.p. 187.0–187.5°.

Anal. Calcd. for $C_{21}H_{20}NBrO$: C, 65.97; H, 5.27; N, 3.66; Br, 20.90. Found: C, 65.11; H, 5.10; N, 3.72; Br, 21.44.

Its u.v.–visible spectra in aqueous acid and base are shown in Figs. 3 and 4: λ_{max} 362, ε 9.55 × 10^3 in base and 9.25 × 10^3 in acid; n.m.r. (CD_3SOCD_3): δ 3.88 (s, 3H, OCH_3), 5.84 (s, 2H, CH_2), 6.8–8.0 (m, 11H, aromatic), 8.21 (d, 2H, H_3, H_5, J = 6 Hz), 9.11 (d, 2H, H_2, H_6, J = 6 Hz). **9** was also prepared in 79% yield by reaction of benzyl bromide and 2′-methoxy-4-stilbazole, which was synthesized by condensation of 4-picoline and σ-anisaldehyde. 2′-Methoxy-4-stilbazole has b.p. 163°/0.5 mm; n.m.r. ($CDCl_3$) δ 3.71 (s, 3H, OCH_3), 6.7–7.8 (m, 4H, H_3, H_4, H_5, H_6), 7.29 (d of d, 2H, H_3, H_5, J = 2, 6 Hz), 8.51 (d of d, 2H, H_2, H_6, J = 2, 6 Hz).

Anal. Calcd. for $C_{14}H_{13}NO$: C, 79.59; H, 6.20; N, 6.63. Found: C, 79.00; H, 6.61; N, 6.39.

Ultraviolet–Visible Spectra

These were recorded on a Cary 15 instrument in quartz cells using matched reference cells containing solvent. Triply distilled water, commercial 95% ethanol (U.S. Industrial Chemicals), spectrophotometric grade 2-propanol (Baker), chloroform (Baker), and reagent grade *t*-butyl alcohol (Baker) were used.

The spectra of the salts **7** were determined first. Then a drop of 10% aqueous sodium hydroxide was added to 5 ml of the solution to generate the solvatochromic **2**. These stoppered solutions were stirred for a few minutes prior to spectral determination. Concentrations were 10^{-4}–10^{-5} *M*.

Determination of pK_a of 7, X = H

Buffer solutions were prepared from sodium hydroxide, boric acid, phosphoric acid, and acetic acid (24); these were not of constant ionic strength. The p*H* values were determined at 22° on a Beckman Research p*H* meter calibrated using standard buffer solutions. An aqueous 1.02 × 10^{-4} *M* solution of **7**, X = H, was then diluted to 1.02 × 10^{-5} *M* with each of the following buffer solutions: p*H* 3.243, 8.293, 8.629, 8.866, and 10.484. Spectra were determined at 22° as before in 2-cm cells using the appropriate buffer as reference. From the lowest p*H* solution the extinction coefficient of the 372 nm peak due to **7**, X = H, was found to be 9.55 × 10^3 while that of the 458 nm peak of **2**, X = H from the highest p*H* solution was 7.42 × 10^3. Due to the fact that there was absorption at 372 nm in **2**, X = H, the absorption at this wavelength at the intermediate p*H*'s was corrected in direct proportion to the 458 absorption. The pK_a of **7**, X = H, was then determined for these solutions by the equation:

$$\mathrm{p}K_a = \mathrm{p}H - \log\left[\frac{A_{458}\varepsilon_{372}}{A_{372}\varepsilon_{458}}\right]$$

which is derived from

$$K_a = \frac{[\mathrm{H}^+][\mathbf{2}, \mathrm{X = H}]}{[\mathbf{7}, \mathrm{X = H}]}$$

The average pK_a value of the three intermediate buffer solutions was 8.37 with a standard deviation of 0.01.

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