# LINEAR FREE ENERGY RELATIONSHIPS—II[a]
## SYNTHESIS AND SPECTRAL CHARACTERIZATION OF SOME NEW SOLVATOCHROMICS: 5'-SUBSTITUTED-2'-HYDROXY-4-STILBAZOLE DERIVATIVES

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**Abstract**—A series of 5'-substituted-2'-hydroxy-4-stilbazolium methiodides was prepared by reaction of 5-substituted salicylaldehydes and 4-picoline methiodide. Reaction of these with base leads to the corresponding betaines, which are highly solvatochromic. In addition, 1:1 complexes of the methiodide salts and the betaines were isolated from the initial reaction.

The energies of the long wavelength transitions of the salts, the betaines and the 1:1 complexes of these are directly proportional to the electrophilic substituent constants ($\sigma^+$) and the slopes are positive. Hence, the transitions appear to involve electron transfer from the salicyl ring to the pyridyl moiety.

The solvatochromisms of the betaines and the complexes are directly proportional to the solvent polarity parameter, $E_T$. The slopes are positive, meaning the dipole moments decrease upon excitation, again consistent with the charge transfer transition mentioned above. The relative slopes are rationalized on the basis of substituent effects.

## INTRODUCTION

Solvatochromic compounds undergo 'color' changes, i.e., shifts in absorption wavelength, when the solvent is changed. To some extent, all compounds are solvatochromic inasmuch as spectral shifts occur in passing through the gas, liquid, solid and solution phases.[1a] These spectral shifts arise because of variable intermolecular interactions between solutes and 'solvents' in the condensed phases.

The solvatochromic compounds that undergo large shifts may generally be described in terms of two extreme resonance contributors: one of these is quinoidal or delocalized; the other is a nonquinoidal or polarized form. The change in absorption wavelength with solvent does not arise from

coexistence of two tautomers, but rather from variation in the contribution of these extreme resonance forms to the resonance hybrid.[2] Thus, as solvent polarity is varied in a mixture of solvents, the absorption maximum moves continuously; there is no isosbestic point. A striking example of solvatochromism is provided by compound **1** which has $\lambda_{max}$ 453 nm (yellow) in water and $\lambda_{max}$ 810 nm (blue–green) in diphenyl ether.[3]

Quite a number of solvatochromatic compounds which undergo substantial color changes have been reported. The most extensive work seems to be that of Brooker and colleagues.[4] Their work dealt with merocyanines prepared by condensation reactions of active methyl substituted heterocycles. An examples of this type is compound **2**.

The main interest in solvatochromics has been their use as empirical solvent polarity indicators.[5,6]

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*Ref. 7 is considered Paper I of this series.



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2
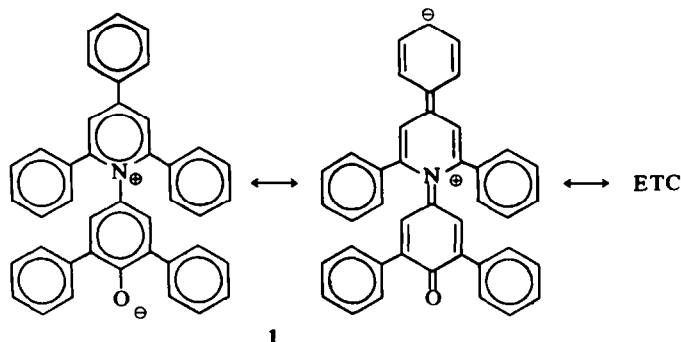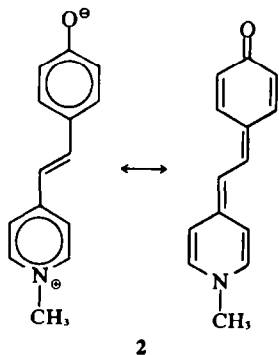
Such a parameter is relevant to correlation of solvent effects on the rates and pathways of chemical reactions. We wished to prepare a series of substituted compounds so that the sensitivity of molecular orbital energy levels to substituent effects could be further pursued.[7] The requisite pyridine compounds with a range of substituents of varying electronic character are not readily available. Compounds of type 3 and 4 are undesirable because, in addition to the electronic effect of the substituent, steric factors would influence the degree of solvatochromism.



3          4
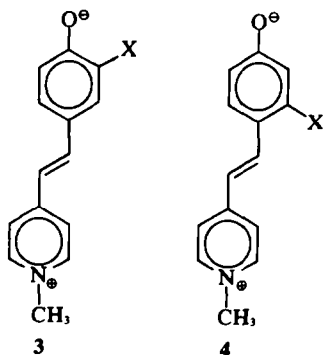
Therefore, we chose to synthesize and examine stilbazole type compounds 5. In these compounds, the variable substituent X is *para* to the hydroxyl–quinone moiety and *meta* to the stilbazole bond; thus steric effects of X are minimal and electronic effects can be compared.



a          b
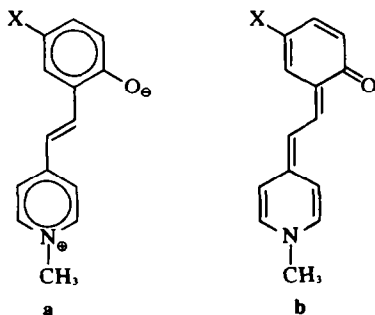
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## DISCUSSION

(a) *Synthesis and structure determination.* With the exception of the parent compound, X=H, compounds 5 have not been reported. The synthesis of these compounds is analogous to synthesis of 2.[4] Treatment of 4-picoline methiodide (6) with weak base and substituted salicylaldehyde 7 affords 5'-X-2'-hydroxy-4-stilbazolium methiodide (8). The yields, m.ps and analyses are given in Table 1.



6          7          8
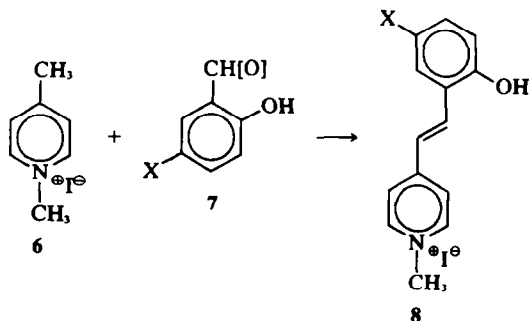
The intermediates 8 themselves are interesting. The only previously reported example, 8, X=H purportedly exists in two forms, a *trans* form 8 and a *cis* form 9.[8] The compound with the longer wavelength absorption (383 nm ethanol), m.p. 235–6°, was assigned the *trans* structure 8 on that basis, while the compound with $\lambda_{max}$ 325 nm, m.p. 224–225°, was assigned structure 9. These compounds were prepared by another route, namely, treatment of isomeric stilbazoles 10 and 11 with methyl iodide. Only 8 reportedly resulted from condensation of 6 and 7, X=H. Inspection of the literature, however, reveals that two different m.p. for this product have been reported: 218–219°[9,10] and 240°,[11] all for material recrystallized from methanol. It thus appeared that condensation of 6 and 7, X=H does lead to both 8 and 9 or two crystal forms of one of these.

Recrystallization from methanol gave samples of m.ps 236·5–237·5° (yellow–orange) and 219·0–220·0° (somewhat less orange)(Table 1). The UV and NMR spectra of these samples were identical. The infrared spectra in potassium bromide displayed only subtle differences. Therefore, we have concluded that these are two interconvertible crystal forms of the same compound, that to which Horowitz assigned structure 8, X=H.[8] This assignment was based only on the facts that the compound was derived from the *trans* stilbazole 10 and had the higher $\lambda_{max}$. Generally speaking, the *trans* form has the higher $\lambda_{max}$ for styrenes because in the *cis* form steric interference prevents coplanarity and the attendant increase in conjugation. In the present system, however, examination of molecular models indicates fairly good overlap of the two aromatic moieties in the *cis* form 9. In this configuration, a charge transfer interaction of the
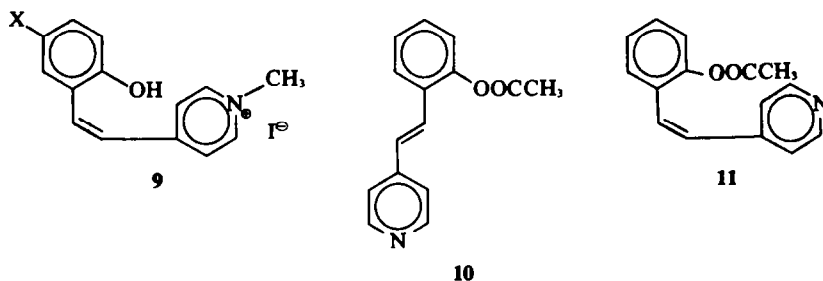
**9**  **11**  **10**

Table 1. Products of reaction of 5-substituted salicylaldehydes (7) and 4-picoline methiodide (6)

| | | | | Calcd. | | | | Found | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | **8**[a] | | | | |
| X | % Yield | M.P. °C | %C | %H | %N | %I | | %C | %H | %N | %I |
| H | 91 | 219·0–220·0[b] | 49·58 | 4·16 | 4·13 | 37·42 | | 49·35 | 4·31 | 4·09 | 37·34 |
| | | 219·0–220·0[c] | | | | | | 49·55 | 4·12 | 4·17 | 37·29 |
| | | 236·0–238·0[d] | | $C_{14}H_{14}NOI$ | | | | 49·33 | 4·33 | 4·08 | 37·31 |
| NO₂ | 0 | 292·0–293·0[i] | 43·77 | 3·41 | 7·29 | 33·04 | | 43·45 | 3·32 | 7·38 | 32·92 |
| | | | | $C_{14}H_{13}N_2O_3I$ | | | | | | | |
| Cl | 40 | 248·0–250·0[g] | 45·01 | 3·51 | 3·75 | 33·97 | | 44·81 | 3·44 | 3·58 | 34·03 |
| | | | | $C_{14}H_{13}NClOI$ | | | | | | | |
| OMe | 54 | 270·0–272·0[i] | 48·80 | 4·37 | 3·79 | 34·37 | | 48·81 | 4·17 | 3·82 | — |
| | | 267·0–271·0[j] | | $C_{16}H_{16}NO_2I$ | | | | 48·71 | 4·23 | 3·80 | 34·42 |

| | | | | Calcd. | | | | Found | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | **12**[a] | | | | |
| X | % Yield | M.P. °C | %C | %H | %N | %I | | %C | %H | %N | %I |
| H | 0 | — | — | — | — | — | | — | — | — | — |
| NO₂ | 99 | 268·0–269·5[e] | 52·51 | 3·94 | 8·75 | 19·82 | | 52·49 | 4·02 | 8·82 | 19·85 |
| | | 273·0–275·0[f] | | $C_{28}H_{25}N_4O_6I$ | | | | 52·47 | 3·93 | 8·80 | 19·85 |
| Cl | 48 | 227·5–229·0[h] | | $C_{28}H_{23}N_2Cl_2O_2I$ | | | | | | | |
| | | | 54·30 | 4·07 | 4·52 | 20·49 | | 54·33 | 4·04 | 4·76 | 20·96 |
| OMe | 44 | 208·5–209·0[k] | | $C_{30}H_{31}N_2O_4I \cdot H_2O$ | | | | | | | |
| | | | 57·33 | 5·29 | 4·46 | 20·19 | | 57·46 | 4·74 | 4·46 | 20·26 |

[a] Recrystallized from methanol and dried in vacuo at 25° unless otherwise noted.
[b] Yellow stout needles.
[c] Yellow stout needles dried *in vacuo* at 110°C.
[d] Yellow–orange rhombic crystals.
[e] Red needles.
[f] Burgundy rhombic crystals.
[g] Yellow–orange rhombic crystals. Calcd. %Cl 9·49, found 9·37.
[h] Plum colored fine needles. Calcd. %Cl 11·45, found 11·68.
[i] Yellow microcrystals or plates.
[j] Violet rhombic crystals.
[k] Fine green–violet needles.
[l] Prepared from 12, X=NO₂ by treatment with HI; recrystallized from methanol containing HI; dried in vacuo > 100° 3–4 hrs just prior to analysis.

electron-poor pyridinium moiety and the electron-rich phenol portion could give rise to a long wavelength transition. In KBr the compounds do not have the band at 1675 cm⁻¹ expected for a *trans* configuration.[12] However, the fact that these compound are salts may alter the C=C stretching frequency. The CH out-of-plane vibration occurs at 965 cm⁻¹, as required for the *trans* configurations; there is no absorption in the *cis* CH vibration region, 675–730 cm⁻¹. Due to the complexity of the spectrum, it is not possible to make rigorous NMR assignments without detailed analysis or study of deuterated analogs. On the basis of the IR data and the fact that the longer wavelength isomer was

prepared from the *trans* stilbene,[8] the *trans* assignment **8** is very likely correct.

Like **8**, X=H the compound from **7**, X=OMe exists in two forms; one is yellow–orange microcrystals or plates and the other is green rhombic crystals. The IR spectra of the two in potassium bromide are virtually·indistinguishable; the visible-UV absorption maxima are also identical.

In addition to the expected product **8**, in every case except X=H, complex **12** was isolated. In fact, with X=NO₂ this was the sole product. The yields, melting points and analyses of these complexes are also given in Table 1.

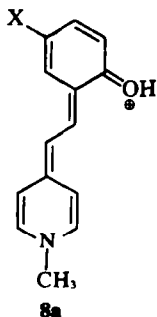possibility that some of the complexes are of type **12a** and other of type **12b**, however.

It is noteworthy that **12**, X=H was not isolated. This is surprising since **8**, X=H should be more acidic than **8**, X=OMe due to the electron releasing character of the OMe group. It may be that complex formation depends on a balance of electron richness and deficiency in the phenol-quinone moieties of **5** and **8** and that with X=H the proper balance is not present.

Treatment of an aqueous solution of the salt **8** with sodium hydroxide led to the formation of the desired **5**. The product yields, melting points and
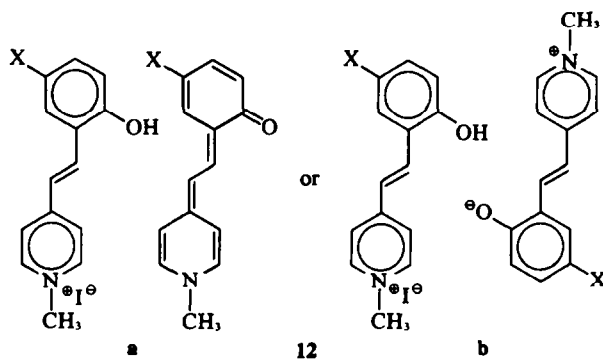


These complexes apparently arise by initial formation of **5** by loss of a proton from **8**, either in the reaction itself under the influence of piperidine or during recrystallization. Interaction of **5** and **8** leads to the charge transfer complex **12**. Covalently bonded combinations of **5** and **8** can be excluded on the basis of spectral properties and chemical transformations (see below). These complexes are less soluble that the salts **8**.



The complexes **12** could exist in two geometries, one where the pyridine rings are juxtaposed and the phenol-quinone moieties overlap (**12a**) and a second where the pyridine moieties overlap with the phenol-quinone moieties (**12b**). The H-bond possible between the phenol and quinone moieties in **12a** is similar to that in phenol-benzoquinone molecular complexes.[13] In no case was more than one form of **12** isolated. This does not exclude the

analyses are shown in Table 2. In all cases except X=H, the product **5** when recrystallized from water had water of crystallization. The compounds also seem to be somewhat hygroscopic. In the case of **8**, X=H, both the high and low melting forms gave rise to the same product, further corroboration of the fact that they are dimorphic modifications. **5**, X=OMe was prepared from a mixture of **8**, X=OMe and **12**, X=OMe. This indicates that **12** is not covalently bonded product of **5** and **8**.

(b) *Spectral characterization.* Initially, compounds **5** and **8**, X=H, were examined at several concentrations in 95% ethanol-water as a prelude to determination of the equilibrium constants for formation of **12** from **5** and **8**. The spectra did not obey Beer's law, i.e., the extinction coefficient for various absorptions varied with concentration. The position of the absorption bands was not sensitive to concentration, though in some cases broadening occurred. This behavior is apparently analogous to that found for compound **2**;[14] it could be due to association[15] or acid-base equilibrium.[14] For this reason, only the $\lambda_{max}$ values will be reported here.

In order to obtain the spectrum of **8**, X=NO₂ in solution it was necessary to add a drop of hydrochloric acid; if this was not done, the long wavelength band observed corresponded to **5**, X=NO₂. This is an indication of the acidity of this phenol; water, 95% ethanol and isopropanol are not generally considered to be very strong bases ·toward protons! While this was not such a major problem with the other members of series **8**, it was

Table 2. Synthesis of solvatochromic betaines **5** by base treatment of 5'-substituted-2'-hydroxy-4-stilbazolium methiodides (8)

| X | Yield % | M.p. °C | Calcd. %C | %H | %N | Found %C | %H | %N |
|---|---|---|---|---|---|---|---|---|
| H | 91 | 212·0–214·0[b] | 79·59 | 6·20 | 6·63 | 78·78 | 6·07 | 6·85 |
| NO₂ | 90 | 276·0–277·0[c] | 64·49 | 4·83 | 10·74 | 64·57 | 5·00 | 10·77 |
| Cl | 74 | 103·0–106·0[d] | 66·01[f] | 5·14 | 5·50 | 65·63[e] | 5·30 | 5·45 |
|  |  | 206·0–208·0[e] |  |  |  | 66·11[h] | 5·11 | 5·51 |
| OMe | 68 | 100·5–102·5[i] | 69·48[k] | 6·61 | 5·40 | 67·45[l] | 6·06 | 5·25 |
|  |  | 192·0–193·0[j] |  |  |  | 69·55[m] | 6·71 | 5·49 |

[a] Recrystallized from water unless otherwise specified.

[b] The same product was obtained from the two dimorphic forms of 8, X = H, m.ps 219·0–220·0°, 236·5–237·5. Green crystalline plates, dried *in vacuo at* 110°. Analysis calcd. for C₁₄H₁₃NO. Sample was not dried just prior to analysis.

[c] Prepared by base treatment of 12, X = NO₂; Recrystallized from methanol, dried *in vacuo* > 100° 3–4 hr just prior to analysis. Analysis calcd. for C₁₄H₁₂N₂O₃ · ¹/⁴H₂O.

[d] After vacuum drying at 25° for 16 hr, deep red fine needles.

[e] After drying *in vacuo* at 25° for 65 hr or at 110° for 4 hr, green fine needles.

[f] Analysis calcd. for C₁₄H₁₂ClNO · ¹/²H₂O.

[g] Sample m.p. 206·0–208·0 not dried just prior to analysis.

[h] Sample m.p. 206·0–208·0 dried *in vacuo* > 100° 4 hours just prior to analysis; % Cl: calcd., 13·92; found, 13·92.

[i] Dried *in vacuo* at 25° for 5 hr, green plates.

[j] Dried *in vacuo* at 82° for 16 hr, green plates.

[k] Analysis calcd. for C₁₅H₁₅NO₂ · H₂O.

[l] Sample m.p. 192·0–193·0 not dried just prior to analysis.

[m] Sample m.p. 192·0–193·0 dried *in vacuo* > 100° 4 hr just prior to analysis.

found that some broadening and shifting did occur in the absence of added acid.

The energy of the long wavelength transition of 8 is a linear function of the para electrophilic substituent constant, $\sigma^+$ (*para*), as is shown in Fig 1. The use of the 'normal' substituent constant gave lower correlation coefficients in every solvent, e.g., in water $\sigma^+$ gives r = 0·989, $\sigma$ gives r = 0·950. The electrophilic substituent constants were developed for reactions in which the aromatic nucleus itself becomes positively charged; as previously shown, $\sigma^+$ generally correlates ionization potentials better than $\sigma$.[7] Their validity here may be attributed to generation of a positive (or partial positive) charge on the aromatic ring bearing the substituent. In other words, the electronic transition in question could be one involving charge (electron) transfer between the phenol and pyridyl moieties, i.e., a transition involving a ground state like 8 to an excited state more like 8a. This proposal draws support from the fact that the slope of the h, · $\sigma^+$ plots are positive; as X becomes more electron withdrawing, it becomes more difficult to transfer an electronic charge from the phenol ring to the pyridyl ring and the transition energy increases.

The observed dependence of transition energy on substituent is not consistent with a transition involving transfer of an electron from the iodide ion to the pyridyl ring; such a transition would be lowered in energy by electron-withdrawing substituents by inductively increasing the extent of positive charge on the pyridine ring, thereby in-
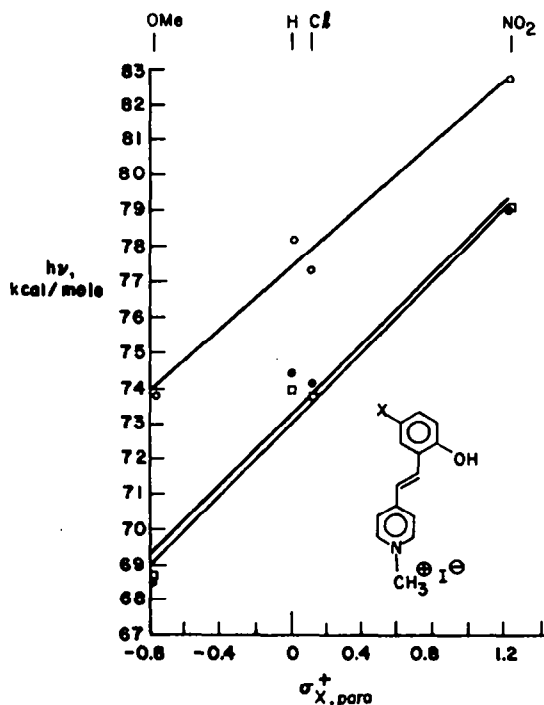


Fig 1. Transition energy of long wavelength band of 5'-substituted-2'-hydroxy-4-stilbazolium methiodides (8) versus electrophilic substituent constants $\sigma^+$. ○ H₂O (HCl), h$\nu$ = 4·35 $\sigma^+$ + 77·4, r = 0·989 □ 95% EtOH (HCl), h$\nu$ = 5·05 $\sigma^+$ + 73·1, r = 0·990 ● 2-PrOH (HCl), h$\nu$ = 5·05 $\sigma^+$ + 73·3, r = 0·977.

creasing its electron affinity. A direct dependence of transition energy on the normal $\sigma$ has been reported for such a transition.[16]

The solvatochromism of the salts **8** is quantitatively compared to the solvent polarity parameter, $E_T$, which is the transition energy of solvatochromic **1** in the same solvents[3] expressed in kcal/mole, in Fig 2. As can be seen, as $E_T$ decreases from 63·1 ($H_2O$) the transition energy initially decreases but then levels off and increases again slightly. None of these compounds exhibits notable solvatochromism; nitrobenzene's $^1L_a$ band undergoes a 2·5 kcal/mole transition energy decrease when the solvent is changed from water to ethanol.[1b] The leveling off (and slight increase) of $h\nu$ as $E_T$ decreases in the present case does appear to be somewhat unusual.
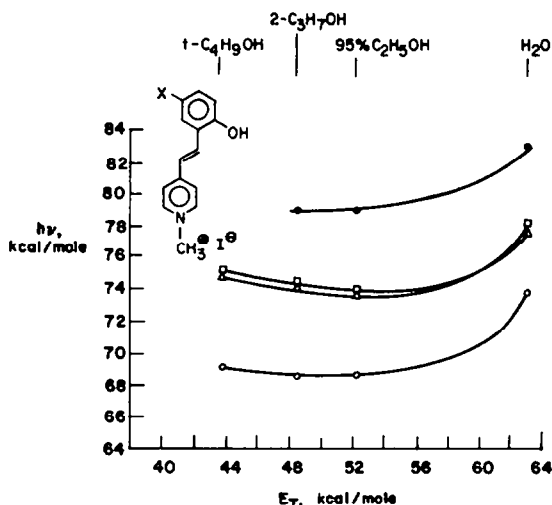


Fig 2. Transition energy of long wavelength band of 5'-substituted-2'-hydroxy-4-stilbazolium methiodides (8) versus solvent polarity parameter $E_T$. ○ X = OMe □ X = H △ X = Cl ● X = NO₂.

The energy of the long wavelength transition in series **5** was also examined in several solvents. The substituent effects are constant from solvent to solvent, as shown in Fig 3. As can be seen in each solvent the transition energy is a linear function of $\sigma_x^+$ (*para*). The transition energies are not linearly related to the normal *meta* or *para* substituent constants. The correlation with $\sigma^+$ may indicate, as with **8**, the importance of structures in which the quinoidal portion takes on a positive charge or equivalently a less negative charge via an intramolecular charge transfer transition. This is consistent with a transition for which the ground state is zwitterionic, while the excited state is more quinoidal; i.e., the ground state resembles **5a** and the excited state is more like **5b**.

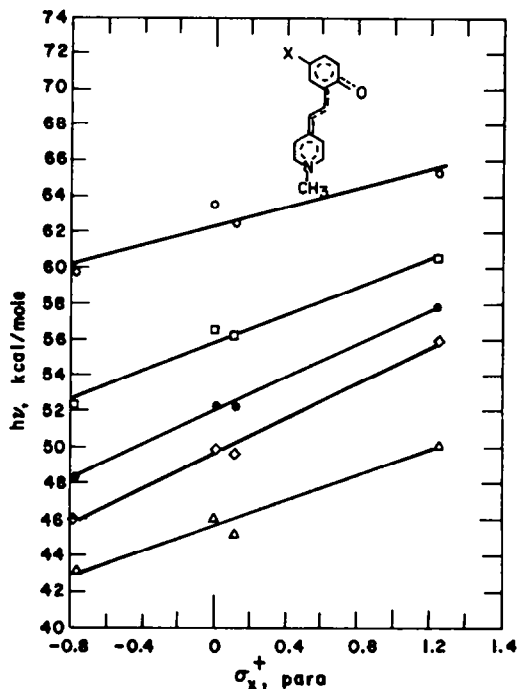The complexes **12**, X=NO₂, OMe absorb at



Fig 3. Energy of longest wavelength transition versus electrophilic substituent constant for 5'-substituted-2'-hydroxy-4-stilbazolium methiodide betaines (**5**). ○ $H_2O$, $h\nu = 2·66\ \sigma_x^+ + 62·4$, r = 0·949 □ 95% EtOH, $h\nu = 3·98\ \sigma^+ + 55·8$, r = 0·990 ● 2-PrOH, $h\nu = 4·70\ \sigma^+ + 52·0$, r = 0·998 ◇ t-BuOH, $h\nu = 4·96\ \sigma^+ + 49·7$, r = 0·995 △CHCl₃, $h\nu = 3·47\ \sigma^+ + 45·6$, r = 0·983.

0–6 nm shorter wavelength while **12**, X=Cl absorbs at 1–2 nm longer wavelength than the neutral species **5**. This similarity is undoubtedly due to substantial dissociation of the complexes into components **5** and **8** in solution. The complexes are of low solubility ($< 10^{-4}$M). The fact that slightly different wavelength transitions occur for the complexes may be due to peak broadening by low concentrations of the complexes themselves. As mentioned above, evaluation of the dissociation constant for the complexes is complicated by the apparent association equilibrium of components **5** and **8** individually.

These results are shown for the various solvents in Fig 4 as a function of the $\sigma^+$ *para* substituent constant. Again, very good straightline correlations of transition energy and the electrophilic substituent constant result.

To evaluate this series of solvatochromics as indicators of solvent polarity, we compared our results to those of a standard solvatochromic, namely, **1**. In Fig 5, the transition energies of compounds **5** are plotted versus those of **1**[3] in a series of solvents. As can be seen, each substituted solvatochromic **5** gives an excellent linear correlation (r = 0·995 to 0·996). For the nitro derivative,
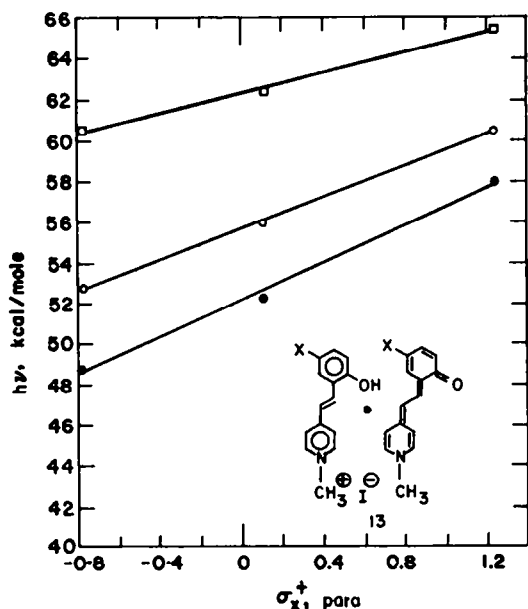
Fig 4. Energy of longest wavelength transition vs electrophilic substituent constant for 1:1 complexes 12 of 5'-substituted-2'-hydroxy-4-stilbazolium methiodides (8) and the corresponding betaines (5) □ H₂O, h$\nu$ = 2·44 $\sigma_x^+$ + 62·4, r = 0·998 ○ 95% EtOH, h$\nu$ = 3·87 $\sigma_x^+$ + 55·6, r = 0·999 ● 2-PrOH, h$\nu$ = 4·58 $\sigma_x^+$ + 52·2, r = 0·994.

however, there is some anomalous behavior. The transition energies for chloroform and dichloroethane fall below the straight line described by the more polar solvents ($E_T > 42$ kcal/mole). The result in acetone falls on the line. To see if there was some specific interaction with the chloro compounds, ethyl acetate was used as solvent; it too falls below the line, but not as much below as the chloro compounds. The point for dimethoxyethane is above the line. We are not, at this time, able to rationalize these results beyond saying that some specific interaction[6b] of these solvents takes place with the nitro compound, either with the nitro group itself or as a result of its presence.

Comparison of the slopes of the correlation lines of Fig 5 is enlightening. The smallest slope is that of the nitro compound 5, X=NO₂, while the largest is that of 5, X=H. The nitro compound, therefore, is the least sensitive to solvent effects and has the largest transition energy. The long wavelength band probably involves charge transfer from the phenolquinone moiety to the pyridyl ring,[18] e.g., 5a → 5b, in view of the fact that as the solvent polarity ($E_T$) increases, so does h$\nu$, implying a decrease in dipole moment upon excitation.[5] Thus, as the solvent becomes less polar, the ground state becomes more like 5b and the transition energy to a state resembling 5b is lowered. In 5, X=NO₂ the electron-
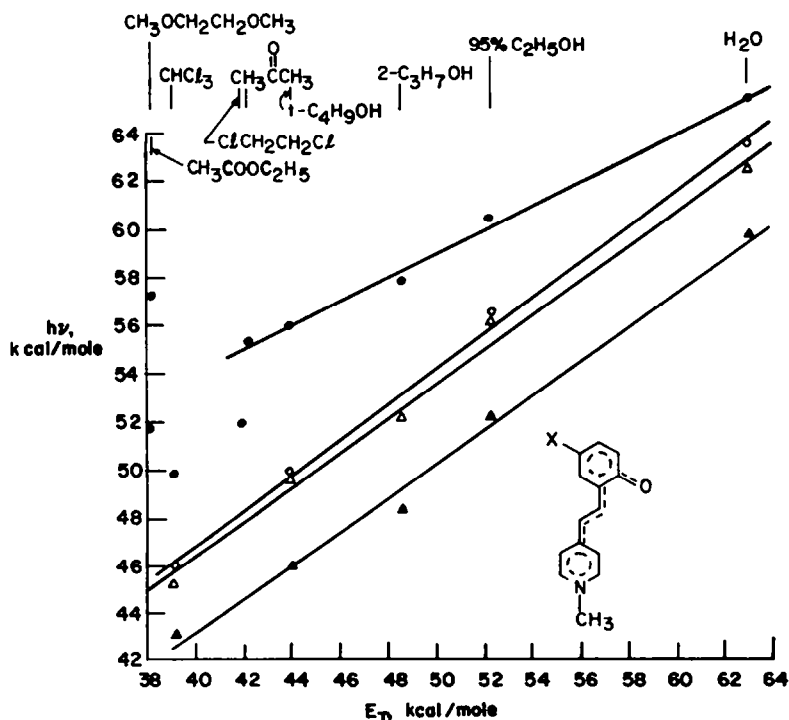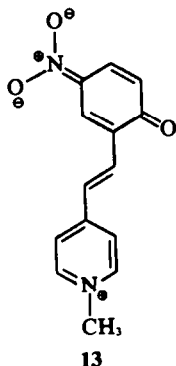


Fig 5. Energy of longest wavelength transition of 5'-substituted-2'-hydroxy-4-stilbazolium methiodide betaines (5) vs solvent polarity parameter $E_T$. ○ X = H, h$\nu$ = 0·732 $E_T$ + 17·5, r = 0·996 △ X = Cl, h$\nu$ = 0·718 $E_T$ = 17·7, r = 0·995 ▲ X = OMe, h$\nu$ = 0·706 $E_T$ + 15·0, r = 0·996 ● X = NO₂, h$\nu$ = 0·491 $E_T$ + 34·5, r = 0·998 for $E_T > 42$.

withdrawing effect of the substituent opposes this solvent effect due to contributions of type 13, tending to maintain a zwitterionic form, even in non-polar solvents. In contrast, 5, X=OMe is expected to have lower transition energies due to the increased electron richness of the phenol-quinone moiety, and indeed it does. The slope of the $h\nu$ vs $E_T$ line (Fig 5) for 5, X=OMe is not much different from 5, X=H and 5, X=Cl, however.



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The total ranges of transition energies for compounds 5 are less in each case than for compound 1 but are comparable to 2. Similarly, from the data for complexes 12, plots of transition energies in various solvents as a function of $E_T$ were constructed (Fig. 6). The results are comparable to
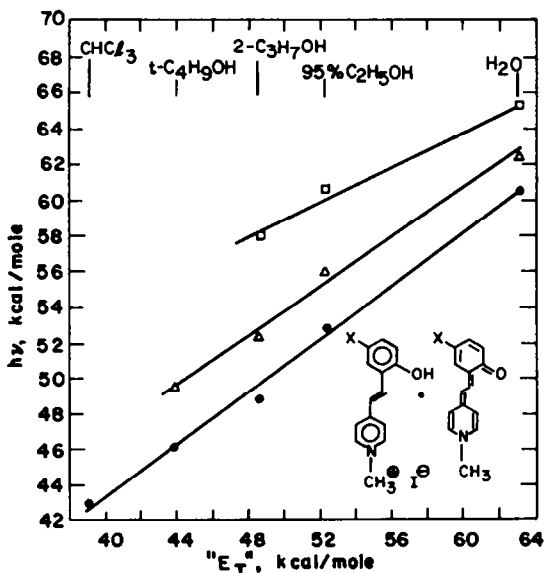


Fig 6. Energy of longest wavelength transition of 1:1 complexes 12 of 5'-substituted-2'-hydroxy-4-stilbazolium methiodides (8) and the corresponding betaines (5) vs solvent polarity indicator $E_T$. □ X = NO₂, $h\nu = 0.503$ $E_T + 33.9$, r = 0.995 △ X = Cl, $h\nu = 0.685$ $E_T + 19.5$, r = 0.996 ● X = OMe, $h\nu = 0.744 E_T + 13.5$, r = 0.997.

those for 5; here, however, the slopes do increase significantly as $\sigma^+$ decreases, as expected on the basis of the above arguments.

The fact that the spectral shifts of compounds 5 and complexes 12 are directly proportional to those observed with 1, 2 and other solvatochromics means that these compounds all respond to solvents in the same manner; thus, compounds 5 and complexes 12 do not interact in any anomalous specific way with any of the solvents tested (except, of course, 5, X=NO₂ with solvents of $E_T < 42$). However, it has been concluded that for all solvatochromics capable of hydrogen bonding, this is the major factor involved in the spectral changes.[18]

The correlation and rationalization of the present results in terms of substituent constants are further evidence of the utility of linear free-energy relationships in understanding physical properties on a molecular basis. Examination of homologous series so that these principles can be applied, therefore, substantially increases the understanding of the process in equation. The application of these principles to other properties of these compounds will be reported at a later date.

EXPERIMENTAL

General. M ps are corrected. IR spectra were recorded on a Perkin Elmer Model 267, NMR spectra on a Joelco C-60H and UV-visible spectra on a Cary Model 15. Elemental analyses were performed by Spang Laboratories, Ann Arbor, Michigan.

4-Picoline methiodide (6). To a soln of 4-picoline (100 g, 1.00 mole) and 800 ml ether was added slowly and cautiously MeI (168 g; 1.19 mole). An immediate exothermic reaction occurred and a ppt formed. After 1 hr reflux, the cream-colored solid was filtered off, washed with ether and dried in vacuo; it weighed 187 g (74%) and had m.p. 147.0°–151.5°, reported m.p. 138°–140°.[11]

5'-Substituted-2'-hydroxy-4-stilbazolium methiodides (8) and the 1:1 complexes 12 of 8 and betaines 5. To a stirred mixture of 6 (0.144 mole), 7, (0.180 mole) and 300 ml MeOH was added 5 ml piperidine. The solids then dissolved and the soln darkened within a few seconds. After 3½ hr reflux, the mixture was cooled and filtered. In all cases but X=H, this material was mainly comprised of complex 12. Concentration of the filtrate led to the isolation of more product, this being mainly the salt 8. Separate fractional recrystallizations from MeOH afforded the pure compounds 8 and 12. In the case of X=NO₂ only 1:1 complex 12, X=NO₂ was isolated. The salt 8, X=NO₂ was prepared by adding 2.00 ml of 48% HI to a soln of 2.00 g of 12, X=NO₂ in 25 ml water and 400 ml MeOH, concentrating, filtering to afford 2.3 g (93%) of yellow–orange solid and recrystallizing from MeOH containing a small amount of HI. These results are summarized in Table 1.

N-Methyl-5'substituted-2'-hydroxy-4-stilbazolium betaines (5). A warm soln of the salt 8 in the minimum amount of an aqueous methanolic soln (X=H: 5 g in 40 ml

25% MeOH; X=Cl: 9g in 95 ml 21% MeOH; X=OMe: 15 g in 425 ml 59% MeOH) was treated with 0·2 ml of 50% NaOH aq per gram of 8. In the cases of X=Cl, OMe the products precipitated upon cooling and were filtered; for X=H concentration of the solution was necessary. Similar treatment of the complexes 12 yielded 5; in the case of 12, X=NO₂ 3 g were dissolved in 800 ml 95% MeOH, treated with 3 ml of 50% NaOH aq, and the soln was concentrated. These results are given in Table 2.

*UV/visible spectra* were recorded in quartz cells using matched reference cells containing solvent: triply distilled water, commercial 95% ethanol (U.S. Industrial Chemicals), spectrophotometric grade 2-PrOH (Baker) and CHCl₃ (Baker), reagent grade (solid) t-BuOH (Baker), reagent grade actone (Baker), reagent grade EtOAC (Baker), purified 1,2-dichoroethane (Baker) and distilled (spinning band) dimethoxyethane. The spectra of betaines 5 and complexes 12 were recorded without any additives to the soln. In the case of salts 8 a drop of HCl was added to each 20 ml soln to preclude ionization to 5. This proved necessary for X=NO₂ and was done as a precaution for X=Cl, H, OMe. HI can also be used, but the spectra must be measured immediately or oxidative changes (darkening) will alter the spectra. The concentrations were not always measured, but were in the range $10^{-4}$ to $10^{-3}$ M, generally. In some cases spectra could not be obtained due to insolubility.

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