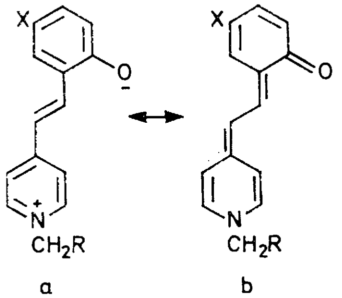
Linear Free Energy Relationships. Part VII.[1] Synthesis and Properties of a Novel ' Double-barrelled ' Solvatochromic Compound

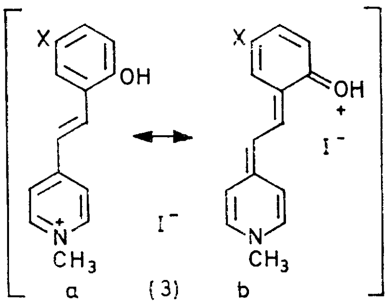
By **Harry W. Gibson** * and **Fowtrey C. Bailey**, Webster Research Center, Xerox Corporation, Webster, New York 14580, U.S.A.

The synthesis of bis-[2-(2-hydroxyphenyl)-1-(*N*-methyl-4-pyridinio)vinyl]methane di-iodide from 1,3-bis-(4-pyridyl)propane was accomplished in 7% yield. This compound was of interest for the study of possible intramolecular interactions as a model for some analogous intermolecular complexes discovered and described earlier. The u.v.–visible absorption spectra of this diprotonated species, and its mono- and un-protonated (solvatochromic) conjugate bases have been examined, as well as their acid–base behaviour. A linear plot of absorption energy *versus* the solvent polarity parameter is consistent with the results of analogous species previously studied. The decreased acidity of the double-barrelled species is unexpected in view of its double positive charge and suggests an interaction (probably hydrogen-bonding) between the two halves. The lack of fluorescence of the double-barrelled solvatochromic species also suggests an intramolecular excited state complex (exciplex). Low solubility precluded detailed analysis by i.r. and n.m.r. spectroscopy.

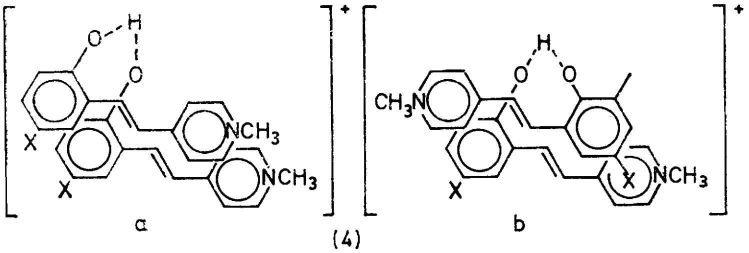
SOLVATOCHROMIC compounds,[2,3] those whose absorption spectra (usually in the visible region) change with solvent, have been of interest to us in probing the effects of structure on molecular orbital energy levels.[4,5] In previous reports the synthesis and spectral properties of series (1) and (2) were described.[6,7] Another report[1] describes the ground state acidity of these compounds in relation to electron distribution. In the synthesis of series (1) a 1 : 1 complex (4) of (1) and the corresponding salt (3) was isolated in each case except X = H.[6] Two possible



(1) R = H
(2) R = C_6H_4Y-*p*



(3)



(4)

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[1] Part VI, H. W. Gibson and F. C. Bailey, *J.C.S. Perkin II*, 1976, 196.

[2] W. Liptay, *Angew. Chem. Internat. Edn.*, 1969, **8**, 177.

[3] C. Reichardt, *Angew. Chem. Internat. Edn.*, 1965, **4**, 29.

[4] H. W. Gibson, *Canad. J. Chem.*, 1973, **51**, 3065.

[5] J. E. Kuder, H. W. Gibson, and D. Wychick, *J. Org. Chem.*, 1975, **40**, 875.

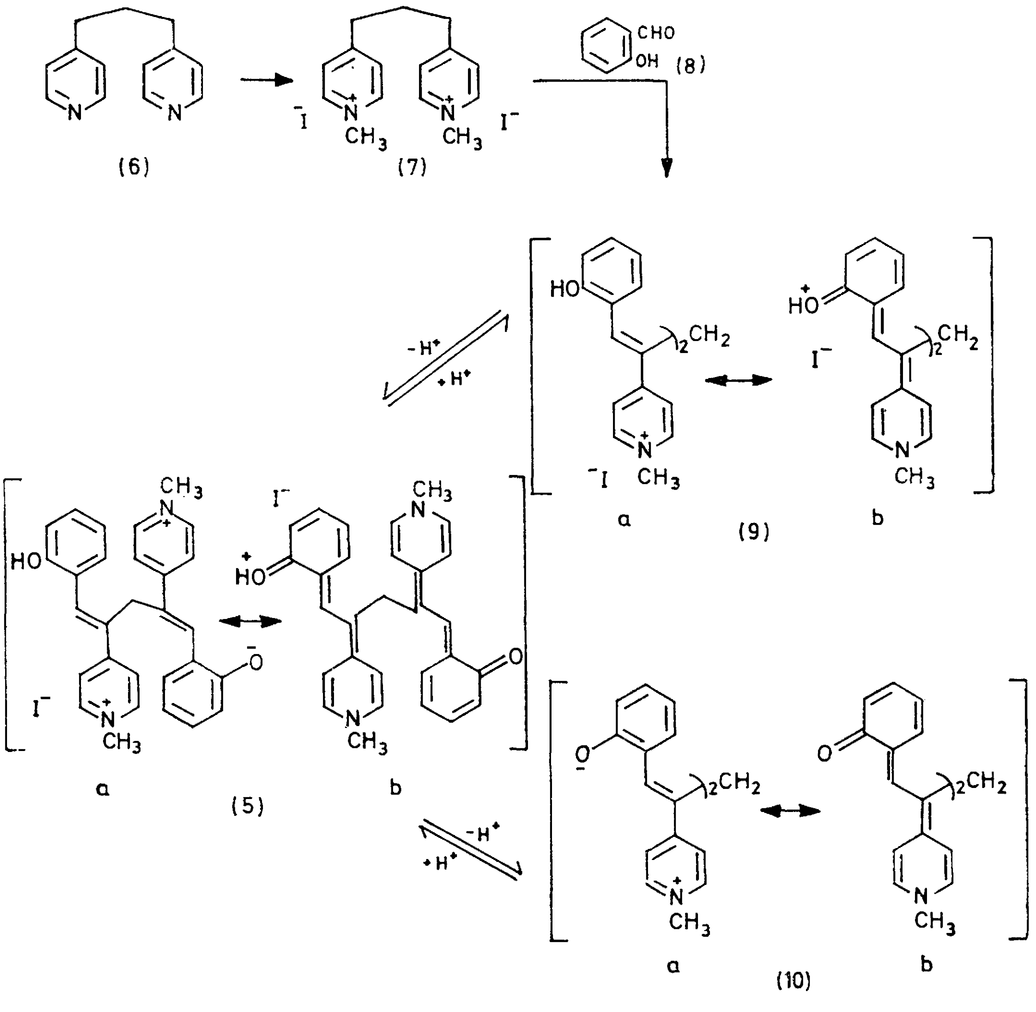
[6] H. W. Gibson and F. C. Bailey, *Tetrahedron*, 1974, **30**, 2043.

[7] H. W. Gibson and F. C. Bailey, *Canad. J. Chem.*, 1975, **53**, 2162.

structures (4a and b) were proposed for the complexes. Structure (4a) involves a parallel alignment similar to the structure of the 1 : 1 phenol–benzoquinone complex.[8] In structure (4b) an antiparallel arrangement exists. The present report describes the synthesis of a covalently bound model of complexes (4) and the study of its properties.

DISCUSSION

(A) *Synthesis*.—Based on the proposed structures for the 1 : 1 complexes (4), the synthesis of the covalently bonded analogue dimer (5) was undertaken. 1,3-Bis-(4-pyridyl)-propane (6) was reacted with methyl iodide in tetrahydrofuran to afford in 97% yield the salt (7). This was reacted with salicylaldehyde (8) in methanol using piperidine as the base; the desired salt (9) was isolated in 7% yield.



(B) *Acidity*.—The acidity of (9) was determined by potentiometric titration of an aqueous solution at room temperature. The data were analysed to take into account the ionization of (5) as it forms[9] to (6). The results are: pK_{a1} 9.20 ($\pm$0.04) and pK_{a2} 10.24 ($\pm$0.04). The pK_a of (3; X = H) by the potentiometric method is 8.36 ($\pm$0.07) and spectrophotometrically[1] in buffer solutions 8.49 ($\pm$0.03). Thus the first ionization constant of (9) is 0.8 pK units higher than that of (3; X = H), and the second is 1.8 higher. This is a surprising result on electrostatic grounds. If there were no through space interaction between the two halves of (9), one would expect, since it is a doubly charged species, that it would be *more* acidic than (3; X = H), which bears only a single positive charge. The experimental results seem to demand a stabilizing interaction between the two halves of (9) relative to (3; X = H). Similarly, the high pK_a of (5) implies a stabilizing effect between the halves of (5).

(C) *Spectral Characterization*.—The u.v.–visible spectrum of (9) in aqueous solution is shown in Figure 1a. This spectrum may be compared to that of the iodide (3; X = H) which is shown in Figure 1b. For the short wavelength absorption at *ca.* 227 nm the extinction coefficient for (9) is about twice that for (3; X = H) as

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[8] T. T. Harding and S. C. Wallwork, *Acta Cryst.*, 1953, **6**, 791; H. Matsudo, K. Osaki, and I. Nitta, *Bull. Chem. Soc. Japan*, 1958, **31**, 611.

[9] A. Albert and E. P. Serjeant, ' Ionization Constants of Acids and Bases,' Wiley, New York, 1962, pp. 51—55.

expected on the basis of the presence of two 2-phenyl-1-pyridiniovinyl chromophores per molecule of (9). The fluorescence spectra for (9) and (3) (Figures 1a and b) are very similar and are mirror images of the absorption spectra. The fluorescence excitation spectra of (9) and (3; X = H) in dilute (10^{-5}M) solutions indicate that the absorptions leading to fluorescence at *ca.* 540 nm are very nearly identical for the two compounds and occur at *ca.* 320 and *ca.* 400 nm. This means that the differences in the absorption spectra are quantitative rather than qualitative.

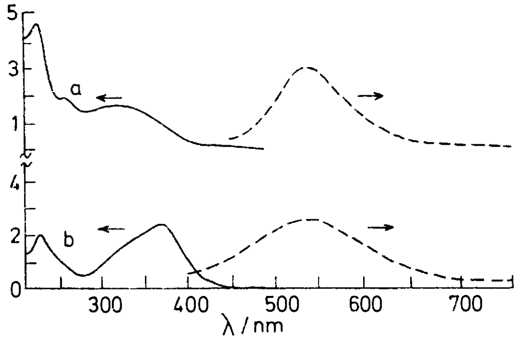

FIGURE 1 a, U.v.-visible spectrum of (9) in aqueous acid (pH 3.24, 1.03 × 10^{-5}M), solid line; fluorescence spectrum in aqueous HCl (pH 2.08, 2.50 × 10^{-5}M), dashed line; b, u.v.-visible spectrum of (3; X = H) in aqueous acid (pH 3.24, 1.06 × 10^{-5}M), solid line; fluorescence spectrum in aqueous HCl (pH 2.08, 2.05 × 10^{-5}M), dashed line

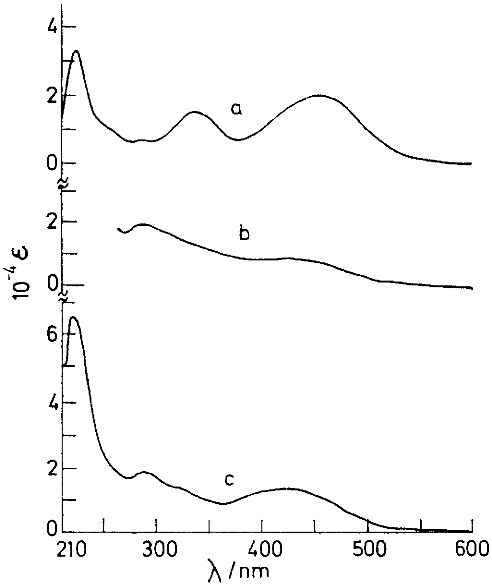

FIGURE 2 a, U.v.-visible spectrum of (1; X = H) in aqueous base (pH 10.5, 1.06 × 10^{-5}M); b, u.v.-visible spectrum of (5) in aqueous base (pH 9.67) obtained by subtraction of contributions of (9) and (10); c, u.v.-visible spectrum of (10) in aqueous NaOH (pH 12.8, 1.03 × 10^{-5}M)

The u.v.-visible absorption spectrum of (1; X = H) is given in Figure 2a. The spectrum for a solution of (10) is depicted in Figure 2c. In both cases, the long wavelength peak results from a shift of the long wavelength absorption of the corresponding salts (3; X = H) and (9). With the exception of the longest wavelength peaks, (1; X = H) and (10) have very similar $\lambda_{max.}$. The extinction coefficients of the transitions at *ca.* 220 and 287 nm are nearly twice as large for (10) as for (1; X = H), as expected. For the *ca.* 320 nm and longest wavelength transitions the extinction coefficients of (10) are lower than those of (1; X = H). The fluorescence spectrum of (1; X = H) bears a mirror image relationship to the absorption spectrum. The 635 nm fluorescence excitation spectrum of (1; X = H) shows bands at 470 and *ca.* 420 nm. Under similar conditions fluorescence of (10) could not be detected.

In previous reports we deduced that the longest wavelength transition in both (1) and (3) involved a charge transfer promotion of a π electron from the phenol–quinone ring to the pyridyl–pyridinium ring.[6,7] Thus the excited states contain a greater contribution from resonance forms (1b) and (3b) than the ground states. This conclusion was based on two sets of empirical information: (a) the dependence of the wavelength on substituents X [as X becomes more electron releasing in (1) and (3), $\lambda_{max.}$ increases;[6] as Y becomes more electron releasing in (2) and corresponding salts, $\lambda_{max.}$ decreases[7]] and (b) the dependence of the wavelengths on solvent [as solvent polarity increases, $\lambda_{max.}$ of (1) and (2) decrease, implying that the transition involves a decrease in dipole moment as anticipated for transitions like (1a) $\longrightarrow$ (1b) and (2a) $\longrightarrow$ (2b)].[7]

The dependence of the energy ($h\nu$) of the long wavelength absorption maximum of (10) on solvent polarity, E_T, is described by the equation $h\nu = 0.625\ E_T + 30.7$ (correlation coefficient r 0.984; standard deviation 0.8 kcal mol^{-1}). The plot is similar to that of (1; X = H) except for having higher energies.[6,*] As noted above the fluorescence excitation spectrum of (1; X = H) indicates that the long wavelength band is comprised of two separate transitions (*ca.* 420 and *ca.* 470 nm), the shorter of which corresponds to the absorption maximum of (10). The tail of (10) does extend out as far as that of (1) which suggests that the 470 nm peak is present but is weaker in (10). If one were able to resolve the long wavelength absorption of (10), the energies would presumably be similar to those of (1; X = H). Thus we conclude that the longest wavelength transitions in both new compounds (10) and (9) are of the same type as in (1) and (3), namely (10a) $\longrightarrow$ (10b) and (9a) $\longrightarrow$ (9b).

The spectrum of (9) at pH 3 was recorded and stored in the computer, followed by that of (10) at pH 13. The spectrum of the mixture of species (9), (5), and (10) at pH 9.67 was similarly stored. Then the spectra of (9) and (10) appropriately scaled in accord with calculated concentrations were sequentially subtracted, yielding

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[*] Interestingly (1; X = NO_2) displays a curved plot. We had overlooked ref. 10 previously and ascribed the curvature to specific interactions.[6] It appears that this conclusion was in error and curvature is theoretically anticipated[10] if the solubility of the compound allows spectral examination in low polarity media.

[10] H. G. Benson and J. N. Murrell, *J.C.S. Faraday II*, 1972, 137.

the absorption spectrum of (5) (Figure 2b). The spectrum of (5) is very similar to that of (10) (Figure 2c) in both wavelength and ε. In fact these two spectra bear the same relationship to one another as those of (1) and (4).[6]

(D) *Rationalization of Results*.—The pK_a results demand a stabilizing feature in (9) and (5) relative to monomeric (3) or a destabilizing effect in (5) and (10) relative to (1). There are two such possible interactions in (5) and (9). The first is the effect of the methylene bridge, comprised of electronic and steric interactions. Neither effect would be expected to cause an order of magnitude difference in the acidity of (9) and (5). The second and more likely possibility is that hydrogen bonding of OH to OH in (9) and OH to O^- in (5) decreases the acidity. Examination of molecular models shows that coplanarity about the double bonds is best maintained in conformations in which the two halves are nearly perpendicular to one another. In one of these conformations the two hydroxy-groups of (9) are essentially in contact; π-hydrogen bonding is also possible. Unfortunately it is not possible to study this point by i.r. or n.m.r. spectroscopy due to the lack of solubility of (9) in non-polar media such as chloroform and carbon tetrachloride.

We conclude that the short wavelength bands of (1; X = H), (3; X = H), (9), and (10) are due to electronic transitions within the individual aromatic rings, primarily because their positions and intensities are little effected by conversion of (3) to (1) or (9) to (10). The lower intensities of the charge transfer long wavelength bands in ' dimeric ' forms (9) and (10) relative to (3) and (1), respectively, may reflect a lower degree of coplanarity of the two aromatic rings in the phenylpyridiniovinyl systems of the more sterically crowded (9) and (10). The fact that the energies of these transitions for (1; X = H) and (10), and (3; X = H) and (9) are the same seems to rule out the possibility of a *cis*-configuration in the ground states of (9) and (10).

The lack (or greatly reduced intensity) of fluorescence excitation by the long wavelength absorption bands of (10) in contrast to the situation for (1) is indicative of other pathways for de-excitation. The simplest explanation is that radiationless decay is more efficient for (10) than (1). However, this is not the case for salt (9), seemingly indicating that the dimeric structure does not promote radiationless decay relative to the monomeric structure. An excited state intramolecular complex (exciplex) appears to be a possibility, especially in view of the existence of ground state complexes of type (4). It is possible that electrostatic repulsion in the double salt (9) prevents such complexing. Another possibility is that photochemical reaction intervenes with (10) and not with (1) as a consequence of the proximity of the conjugated systems of (10) or increased energy content of the excited state of (10) because of steric factors.

The conclusions drawn from this work are (a) the relationship between the spectra of (5) and (1) relative to that between (1) and (4) indicates that (5) is a good model for (4), (b) the pK_a values of (5) and (9) indicate hydrogen-bonding in the ground state and suggest the same for (4), and (c) the lack of fluorescence in (10) and presumably (5) suggest that an exciplex may exist with these compounds and (4) as well.

EXPERIMENTAL

General.—M.p.s are corrected. Elemental analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Michigan. U.v.–visible spectra were recorded on a Cary model 15 instrument using matched cells. Fluorescence spectra were recorded on an Aminco–Bowman spectrofluorimeter with freshly prepared nitrogen purged solutions and are uncorrected.

1,3-*Bis*-(N-*methyl-4-pyridinio*)*propane Di-iodide* (7).—A solution of 1,3-bis-(4-pyridyl)propane (40.0 g, 0.202 mol) (Aldrich), iodomethane (62.5 g, 0.440 mol), and tetrahydrofuran (THF) (260 ml) was refluxed for 5 h, then filtered to give the crude product (92.8 g, 97%). One recrystallization from ethanol–benzene and two from ethanol yielded pale yellow *crystals*, m.p. 141.0—144.0° (Found: C, 37.25; H, 4.15; N, 5.8; I, 52.6. $C_{15}H_{20}I_2N_2$ requires C, 37.35; H, 4.2; N, 5.8; I, 52.65%).

Bis-[2-(2-*hydroxyphenyl*)-1-(N-*methyl-4-pyridinio*)*vinyl*]-*methane Di-iodide* (9).—A solution of (7) (57.8 g, 0.120 mol), salicylaldehyde (8) (38.0 g, 0.310 mol), piperidine (6 ml) and methanol (140 ml) was refluxed for 3.5 h and taken to dryness, leaving a dark gum. Extraction with a boiling mixture of benzene (150 ml) and methanol (50 ml) gave a dark solid (6 g, 7%). Five recrystallizations from methanol gave orange *crystals*, m.p. 255.0—257.5°. The u.v.–visible and fluorescence spectra of (9) are shown in Figure 1 (Found: C, 49.75; H, 4.15; N, 4.15; I, 36.95. $C_{29}H_{28}N_2I_2O_2$ requires C, 50.45; H, 4.1; N, 4.05; I, 36.75%).

Determination of pK_a *Values of* (9).—Potentiometric titrations of 2×10^{-4}M aqueous solutions of (9) with 6.5×10^{-4}M-potassium hydroxide solution were carried out using a Beckman research model pH meter calibrated with standard buffer solutions. Analysis of the data taking the ionization of the ' monoanion ' (5) to the ' dianion ' (10) into account [9] led to pK_{a1} 9.20 (±0.04) and pK_{a2} 10.24 (±0.04). As a check on the method, the pK_a of (3; X = H) was determined by the same method to be 8.36 (±0.07) at 22.5°; spectrophotometric analysis gave 8.49 (±0.03) at 23° in buffer solutions.[1]

Buffer Solution.—The spectrum of (5) was extracted from the spectrum of the equilibrium mixture resulting from dissolution of (9) at a level of 2.70×10^{-5}M in a sodium carbonate–sodium hydrogen carbonate buffer [11] of pH 9.67.

[6/097 *Received*, 15th *January*, 1976]

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[11] ' Handbook of Chemistry and Physics,' Chemical Rubber Co., Cleveland, 1973, pp. J-195—198