

# Electronic Structure of Solvent-Polarity Indicators

## Solvatochromism and Tautomeric Equilibria of Styryl-Merocyanines

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Solvatochromic and halochromic behaviour of two unsymmetrical merocyanine-type dyes, namely 2-[2'- and 4'-hydroxystyryl]-pyridinium methiodide, are studied.

In alcoholic and hydrogen-bond-acceptor (HBA) solvents their visible absorption spectra exhibit an additional long-wavelength band suggesting the existence of tautomeric equilibria in their solutions. The tautomeric equilibrium constants in triethanolamine-acetone mixed solvents are determined.

Quantum mechanical MO method PPP- $\pi$ -SCF-CI is used to calculate the electronic spectra and the underlying keto-enol-tautomeric stability. Deprotonation of the OH group is shown to provide destabilization in binding energy in excess of 5 eV in agreement with the experimental results indicating that these indicators exist mainly as protonated species (enol form) in their solutions.

Furthermore, solvent-induced changes in the ground-state electronic structures are examined by means of  $^1\text{H}$ -NMR spectroscopy and the PPP calculations.

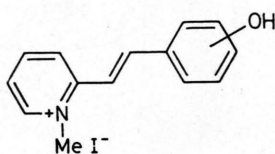
### 1. Introduction

During the course of our investigations on the solvatochromic behaviour of some solvent-polarity indicators of the hydroxy styryl-types I and II we have observed in amphiprotic (hydrogen-bond-acceptor-donor, HBA-D) and hydrogen-bond-acceptor (HBA) solvents an extreme long-wavelength band beside the visible short-wavelength band which was found alone in non-hydrogen-bond (NHB) solvents. This prompted us to further look for the possible existence of keto-enol tautomerism in such solutions.

Similar observations in case of hydroxy azo dyes have been reported in the literature [1–4]. The study of hydroxy azo dyes has been of great value for the theoretical understanding of the phenomenon of tautomerism which is very important in colour chemistry. The azo-hydrazone tautomeric equilibrium has been investigated by many workers using almost every available spectroscopic method [1–6]. Various MO methods have been applied to support the existence of such an equilibrium [1, 3, 7].

The present paper deals with the above mentioned phenomenon in case of the hydroxy aza-free merocyanine-type dyes I and II.

Their solvatochromism, halochromism and  $^1\text{H}$ -NMR spectra will be discussed in terms of calculated



I: para-OH II: ortho-OH

parameters of interest applying the SCF-CI-MO method within the PPP approximation [8].

### 2. Experimental and Computation

Dyes I and II were the courtesy of Prof. Dr. Z. H. Khalil and were used without further purifications. Spectroscopically pure solvents were used (BDH). Buffer solutions were prepared as recommended by Britton and Robinson [9]. Triethanolamine (p. a. Merck) was used.

The UV-VIS absorption spectra were recorded at constant temperature (30 °C) on a Pye Unicam SP 1800 spectrophotometer.  $^1\text{H}$ -NMR spectra were measured in  $d_6$ -DMSO and  $\text{D}_2\text{O}$  solvents using a Varian T 60 spectrometer.

Table 1. SCF-Parameters [10].

Atom	$I_\mu(\text{eV})$	$\gamma_{\mu\mu}(\text{eV})$	$Z_\mu$	$\beta_{C-\mu}(\text{eV})$ [11]
C	11.16	11.13	1	– 2.39
$\dot{\text{N}}$	17.96	12.45	1	– 2.576
$\ddot{\text{N}}$	28.72	16.72	2	– 2.30
$\ddot{\text{O}}$	17.70	15.23	1	– 3.07
$\ddot{\text{O}}$	32.90	21.53	2	– 2.27
O–	25.30	18.48	2	– 2.27

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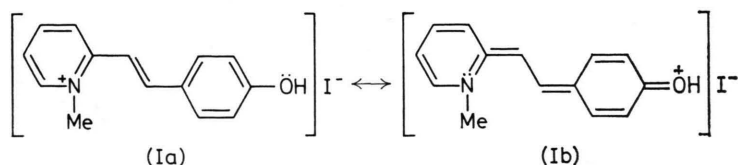
The parameters used for the PPP calculations are summarized in Table 1 [10, 11], assuming equal bond lengths ( $=1.40 \text{ \AA}$ ) and equal bond angles ( $=120^\circ$ ). In the configuration interactions the highest occupied five MO's and the lowest unoccupied five MO's were considered. The two centre-electron repulsion integrals were calculated using the Mataga-Nishimoto relation [12]. The computations were performed in the Computation Centre of Ain Shams University.

### 3. Results and Discussion

#### 3.1. Solvatochromism

The spectral data of dyestuffs I and II as measured in HBA-D, HBA and NHB solvents are sum-

marized in Table 2. The absorption spectra of I and II in NHB solvents exhibit a charge-transfer (CT) transition from the donor part of the molecule containing the OH group to the acceptor cationic heterocyclic ring through the olefinic  $\text{CH}=\text{CH}$  bridge similar to that found in similar molecules [13, 14]. Negative solvatochromism is observed and could be explained on the basis of the polymethine concept of Dähne [15–17]: As the solvent polarity increases (measured by its  $E_T$ - [18] or  $\pi$ -value [19, 20]), the ground state electronic structure of the dyes changes from the polymethine-like state (structure of equal contributions from the Ia and Ib canonical structures) towards the more polar structure Ib.



The data of Table 2 show that the CT transition shows a more pronounced hypsochromic shift in the amphiprotic solvents as their polarity increases. Bayliss and McRae [21] have shown that the underlying change in the electronic structure of

similar indicators is mainly due to the hydrogen bonding capability of the solvent rather than its bulk polarity. Thus, we attribute this remarkable negative solvatochromism of indicators I and II in HBA-D solvents to the formation of type-A hydrogen

Table 2. The visible absorption spectral data for the MH and M forms of the indicators I and II in different solvents<sup>a</sup>.

Solvent	$\alpha$	$\beta$	$\pi$	$E_T^b$	I				II			
					MH		M		MH		M	
					$\lambda^c$	$\epsilon^d$	$\lambda^c$	$\epsilon^d$	$\lambda^c$	$\epsilon^d$	$\lambda^c$	$\epsilon^d$
<i>HBA-D</i>												
H <sub>2</sub> O	1.017	0.14	1.090	63.1	365	22.1	...	...	358	21.2	...	...
MeOH	0.990	0.62	0.586	55.5	382	24.1	474	2.0	374	22.7	480	2.1
EtOH	0.850	0.77	0.540	51.9	388	31.2	500	2.8	376	31.1	506	2.9
2-PrOH	0.687	0.92	0.505	48.6	391	32.1	512	3.0	380	31.9	514	2.9
<i>HBA</i>												
DMSO	—	0.752	1.000	45.0	386	28.9	530	2.9	374	29.0	534	2.9
DMF	—	0.710	0.875	43.8	385	28.9	530	2.8	374	28.9	534	2.9
Acetone	—	0.499	0.683	42.2	378	28.9	530	1.2	370	29.0	534	1.2
Ethyl-acetate	—	0.481	0.545	38.1	374	26.0	530	2.3	366	26.3	533	2.6
Dioxan	—	0.386	0.553	36.0	358	22.0	446	2.1	350	24.0	450	2.2
<i>NHB<sup>e</sup></i>												
CH <sub>2</sub> Cl <sub>2</sub>	—	—	0.802	41.1	398	31.2	...	...	385	32.0	...	...
CHCl <sub>3</sub>	—	—	0.760	39.1	396	30.8	...	...	382	31.0	...	...
CCl <sub>4</sub>	—	—	0.294	32.5	406	...	...	...	390	...	...	...
Cyclohexane	—	—	0.000	31.2	410	...	...	...	394	...	...	...

<sup>a</sup> See scheme 1. <sup>b</sup> in kcal mole<sup>-1</sup>. <sup>c</sup> in nm. <sup>d</sup> in l mole<sup>-1</sup> cm<sup>-1</sup> · 10<sup>-3</sup>.

<sup>e</sup> the indicators are partially soluble in these solvents; the  $\epsilon$  value is not certain.

bonding [22, 23] by the HBD capability of the solvent (its acidity  $\alpha$ -value) to the indicator's oxygen atom of the OH group.

It is of interest to note that  $\lambda_{CT}$  of I and II shows positive solvatochromism in HBA solvents, see Table 2. This is probably due to a solvent induced electronic structure change from an unpolar structure resembling (Ia) towards a highly symmetrical ideal polymethine-like structure.

Interestingly the visible absorption spectra of I and II in amphiprotic and HBA solvents exhibit a second weak band in the region of 530 nm. This band imparts a purple component to the green-yellow colour of the dyes I and II solutions. This is due to proton transfer from the hydroxyl group of the indicators to the solvent molecules, leading to the formation of the structures  $Ma \longleftrightarrow Mb$  according to Scheme 1.

The data in Table 2 indicate that  $\lambda_{CT}^M$  shows negative solvatochromism as the acidity of the solvent, its  $\alpha$ -value, increases.  $H_2O$  acts mainly as a powerful HBD solvent toward the dyes as their spectra in water solutions exhibit only one band due to the absorption of the protonated species MH. In HBA solvents,  $\lambda_{CT}^M$  is practically invariant with the solvent basicity parameter  $\beta$ - or the  $\pi$ -value of the polarity of the solvent indicating that the ground state electronic structure of the deprotonated forms of these indicators is highly symmetrical, i.e. mainly polymethine-like. However, in dioxan  $\lambda_{CT}^M$  is hypsochromically shifted probably due to solvent structural effects [24].

The above mentioned negative solvatochromism of IMH, IM, IIMH and IIM in HBA-D and NHB solvents due to structure variation towards structure (Ib) is supported by PPP-quantum chemical calculations and  $^1H$ -NMR measurements as previously reported [14, 17, 25]. The effect of increasing solvent polarity on the calculated ground state  $\pi$ -electron density distribution is simulated by making the oxygen atom of the OH group more electronegative (the valence state ionisation energy of oxygen ( $I_O$ ) is changed from 32.90 eV, see Table 1, to 34.90 eV). The results are represented in Figure 1. Inspection of Fig. 1 shows that the calculated  $\pi$ -electron density alternation decreases with increasing solvent polarity. Moreover, the calculated measure of the symmetry deviation from the ideal polymethine state, the  $\Sigma$  parameter [15] (defined in this work as the sum of the  $\pi$ -charge density on one half of the mole-

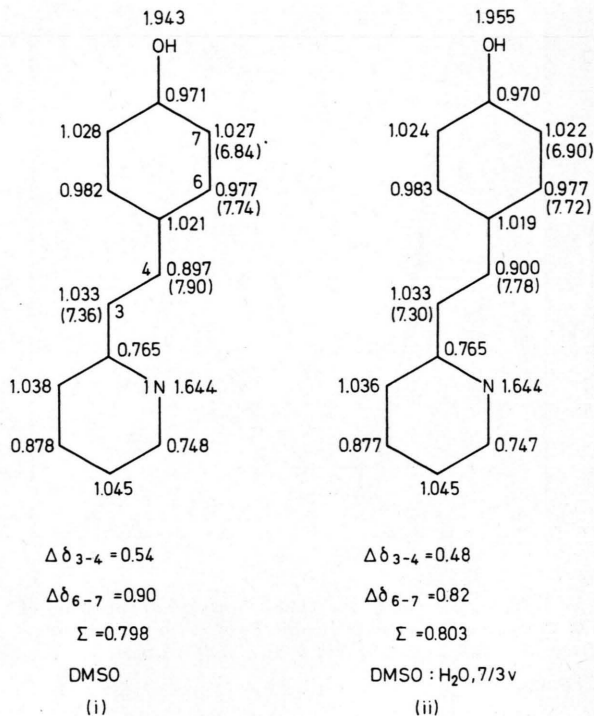


Fig. 1. Effect of the increasing solvent polarity from (i) to (ii) on the calculated  $\pi$ -electron density and on the  $^1H$ -NMR chemical shift ( $\delta$  value in ppm, between parentheses), see text.

cule minus that sum of the other half of the molecule), increases in going from nonpolar to polar solvent and therefore confirms the above results, see Figure 1.

In order to study the ground state electronic structure of I and II more closely, their  $^1H$ -NMR spectra are recorded. The  $^1H$ -NMR spectrum of dye I shows quartet signals corresponding to an AA'BB' system of the  $p$ - $C_6H_4$ -group ( $J=8.8$  Hz) and an AB system of the trans olefinic bridge ( $J=16.0$  Hz). The chemical shifts ( $\delta$ ) are given in Figure 1. Unfortunately, the spectrum of dye II is complex. The spectrum of dye I confirms the idea of partitioning the whole conjugated system of the dye molecules into three building blocks: the heterocyclic ring, the trans-CH=CH bridge and the benzenoid moiety [1, 2, 26]. Solvent induced changes in the ground state electronic structure of I are examined by studying the variation in its  $^1H$ -NMR spectrum. However, due to insufficient solubility of dye I (for NMR measurements) in most solvents, the present study is limited to two solvents only. Fortunately, a



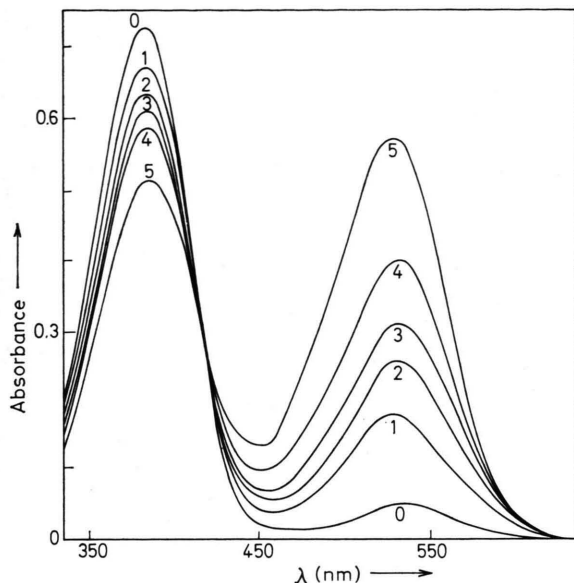


Fig. 2. The variation of the visible absorption spectrum of the acetone solution of indicator I (0), with TEA concentration: 1) 0.3, 2) 0.6, 3) 0.9, 4) 1.5, and 5) 1.8 M.

noticeable change in the  $\delta$  values is observed, as indicated in Figure 1. It is found that as the polarity of the solvent increases,  $\Delta\delta$  (the experimental measure of electron density alternation [17]) decreases. Thus, the ground state electronic structure of I and II becomes less symmetrical, i.e. becomes more (Ib)-like, in more polar solvents, confirming the above result.

### 3.2. Tautomeric Equilibrium and Halochromism

The presence of a prototropic tautomeric equilibrium can be demonstrated by the solvent dependence of the solution spectra. Deprotonation of the OH group of I and II is more pronounced when the

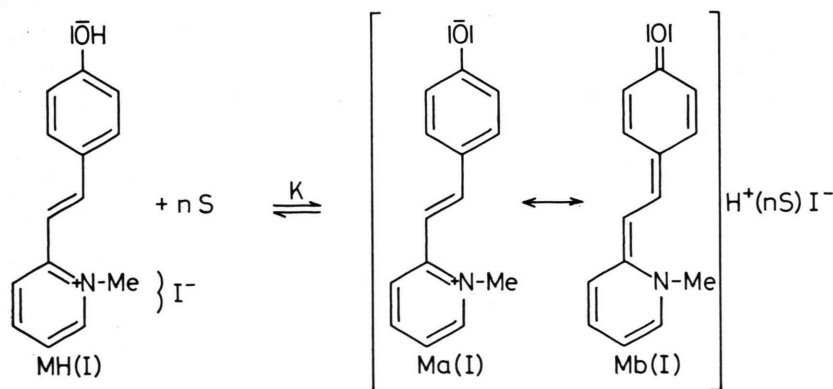
more basic solvent triethanolamine (TEA) is used. The spectral curves obtained in different triethanolamine (TEA)-acetone mixtures are shown for dye I in Figure 2. Similar behaviour is noticed for dye II. The intensity of  $\lambda_{CT}^{MH}$  decreases as the concentration of TEA in the solvent mixture increases, while the long-wavelength CT-band of the M form is intensified. A sharp isosbestic point occurs indicating the presence of two absorbing species ( $MH \rightleftharpoons M$ ) at equilibrium, see Scheme 1.

The tautomeric equilibrium constant  $K$  for dyes I and II was determined by measuring the absorbancy  $A_{obs}$  at  $\lambda_{CT}^M$  as a function of TEA concentration at 30 °C (see Figure 2). The following equation was employed [27]:

$$\frac{[D]}{A_{obs}} = \frac{1}{K\epsilon} \cdot \frac{1}{[TEA]} + \frac{1}{\epsilon},$$

where  $[D]$  is the dye concentration ( $=2.52 \times 10^{-5}$  M, for I and II) and  $\epsilon$  is the molar absorptivity of the tautomer M ( $[TEA]$  is varied from 0.30 to 1.80 M). The plot of  $[D]/A_{obs}$  against  $1/[TEA]$  is linear. The values of  $K$  and  $\epsilon$  were calculated from the slope and intercept of the line. The determined values are:  $K(I) = 1.1$ ,  $K(II) = 1.3$  l mole $^{-1}$  and  $\epsilon(I) = 45400$ ,  $\epsilon(II) = 46000$  l·mole $^{-1}$  cm $^{-1}$ . Although these values of  $K$  are small, the very intense M form (mainly Mb form) substantially influences the visible spectra of I and II.

The PPP-SCF-CI MO technique was used to calculate the tautomer electronic spectra and their  $\pi$ -binding energies, bond orders and charge densities. The molecular diagrams of I and II are represented in Figure 3. The resulting properties of interest are tabulated in Table 3. Deprotonation in each case leads to a lowering of the transition



Scheme 1: nS is any number of solvent molecules (HBA or HBA-D solvents)

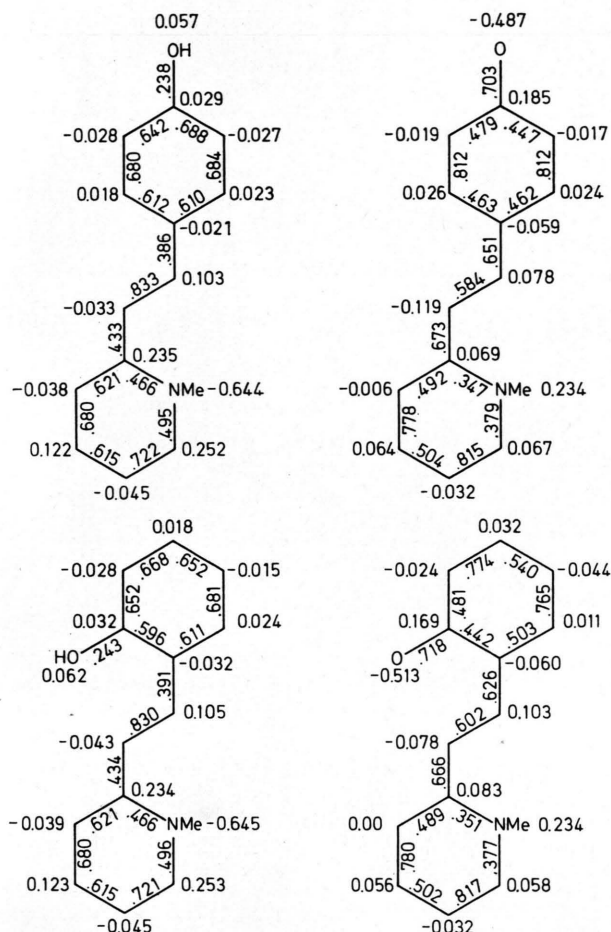


Fig. 3. Net  $\pi$ -charge densities and  $\pi$ -bond orders of the tautomeric forms of molecules I and II.

Table 3. Band maxima, intensities, SCF binding energies ( $E$ ), transition energies and oscillator strengths of different forms of indicators I and II.

Molecular form	$\lambda_{\max}^a$ nm	$\epsilon_{\max}$ l. mole $^{-1}$ cm $^{-1}$	$-E$ (eV)	$\Delta E$ (eV)		$f$ calc.
				calc.	obs.	
I MH	386	28.900	397.5	3.312	3.211	1.150
I Ma <sup>b</sup>	452	30.000	388.0	2.869	2.742	1.277
I Mb	530	2.900	392.4	2.355	2.339	1.748
II MH	374	29.000	407.0	3.300	3.314	0.982
II Ma <sup>b</sup>	450	26.300	400.0	2.640	2.750	0.210
II Mb	534	2.900	401.8	2.273	2.321	0.790

<sup>a</sup> in DMSO.

<sup>b</sup> in aqueous medium of pH = 10.2; it is the least stable form as its  $E$  value suggests.

energies which is in satisfactory agreement with the observed results.

Regarding the relative tautomer stabilities, the data in Table 3 show that deprotonation of the hydroxyl group provides a destabilization in binding energy amounting to 5.1 eV and 5.2 eV for I and II, respectively. This result supports the conclusion drawn from the  $K$  values that these dyes exist mainly as protonated MH-forms in their solutions.

It is of interest to investigate the halochromic behaviour of the dyes under investigation. Their visible absorption spectra in aqueous solutions of different pH (Fig. 4) show an isosbestic point as would be expected for a simple protolytic equilibrium between MH and M species (mainly of structure Ma) given in Scheme 1. The calculated transition energies for the enolate species (Ma) are in good agreement with those experimentally observed (see Table 2). From the recorded spectra, the determined pK values at 30 °C are 8.36 and 8.31  $\pm$  0.02 for I and II, respectively. The ortho isomer is slightly more acidic than the para one. This is due to the reduced electron density on the o-OH group; see Figure 3.

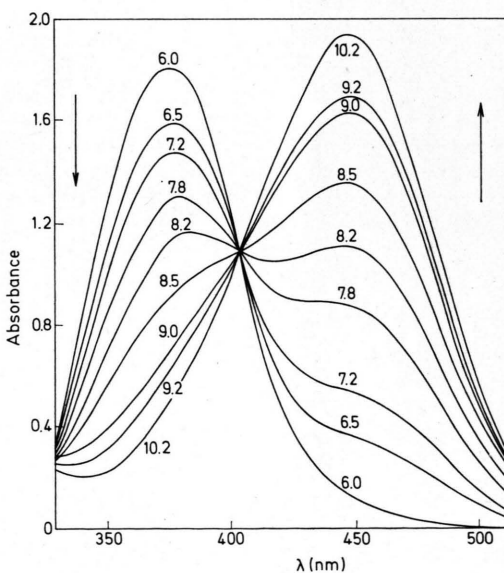


Fig. 4. Variation of the visible absorption spectrum of aqueous solutions of indicator I with the pH of the medium.

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