On the Solvatochromic Reversal of Merocyanine Dyes. Part 1. The UV–VIS Spectroscopic Behaviour of Vinylogous γ-Pyridones

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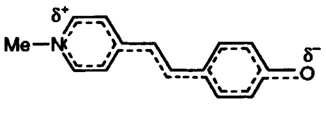
A theoretical approach is described to rationalize and predict the solvatochromic behaviour of vinylogous γ-pyridones. The theoretical curves obtained are shown to reproduce the experimental UV–VIS spectroscopic behaviour of dyes **1**, **2**, **3** and **5**. The model reconciles previous conflicting reports on the solvatochromism of these and related dyes.

Solvatochromic dyes generally exhibit steady bathochromic (positive solvatochromism) or hypsochromic shifts (negative solvatochromism) in solution, as polarity of the medium is increased. Some dyes may change their behaviour in solution with a change of solvent, and revert the sign of their solvatochromic shifts at a given polarity. Compound **1** is generally regarded as a classical example of this. It displays negative solvatochromism in polar solvents and positive solvatochromism in media less polar than chloroform.



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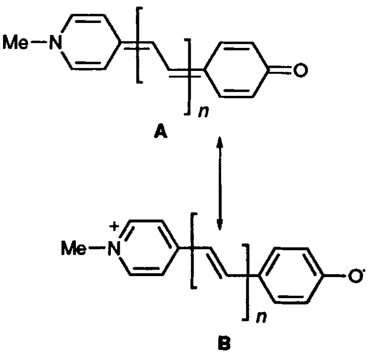
This intriguing behaviour has attracted the attention of many researchers, since the dye was originally described by Brooker *et al.* nearly 40 years ago.[1] However, in spite of four decades of active investigation, theoretical questions continue to be asked regarding the spectroscopic behaviour of this and related compounds. A review of the recent literature brings to light several points of controversy in the interpretation of their spectral properties. For example, the solvatochromic reversal of **1** was rationalized by semiempirical molecular orbital calculations[2,3] and confirmed by spectroscopic measurements in mixed solvents.[4] Later, Luzhkov and Warshel, following a different theoretical approach, calculated the transition energies of dye **1** in a polar and a non-polar medium and found λ_{max} values of 389 and 477 nm respectively, which implies a negative solvatochromism for this compound.[5] More recently, employing AM1 optimized structures and a CNDOVS method, Morley[6] arrived at λ_{max} values of 587 and 470 nm for the same dye in a polar and a non-polar medium respectively. These results, which imply a positive solvatochromism of dye **1**, are, in the words of the author, 'diametrically opposed to previous calculations'.

There is also little agreement on a related phenomenon, namely, the appearance of multiple bands in the visible spectra of these dyes in non-polar solvents. Hünig *et al.*[7] interpreted this as arising from hydrogen-bonded species in solution, in equilibrium with the free dye. Tsukada *et al.*[8] proposed that these bands reflected equilibria between *cis–trans* isomers of **1**. This was rejected by Catalán *et al.*,[9] who also denied any reverse solvatochromism of these dyes, criticizing the proposal by Botrel *et al.*[3] and by Jacques.[4] The explanation of Catalán and co-workers,[9] that these bands are due to splittings of electronic levels by vibrational states, is at variance with the interpretation of Niedbalska and Gruda[10] who, while denying the reverse solvatochromism of these compounds, ascribed it to aggregation phenomena in solution.

We recently described the solvato- and halo-chromic properties of three isomeric iminophenolate dyes related to **1**.[11] We obtained experimental evidence of a reversal in the solvatochromic behaviour of these dyes in chloroform and dichloromethane, but could not go much beyond these non-polar solvents, because of their low solubility in media of reduced polarity. Following the generally accepted view that these compounds undergo structural changes as the medium polarity is changed, we envisaged for the new dyes resonance contributions from two extreme canonical forms, a non-polar, quinonoid structure and a dipolar, zwitterionic form. Similar non-polar (**A**) and dipolar (**B**) structures are shown for the general case of an *N*-methylpyridiniophenolate dye, where the donor and acceptor groups are joined by an unsaturated bridge of variable length (–CH=CH–)$_n$.

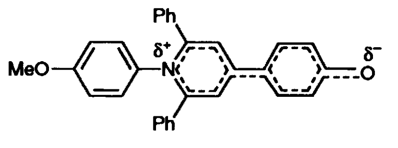


Compound **1** is a particular case of the above structures, for $n = 1$.

Since resonance between the two canonical forms should in principle exist for all compounds of this series, it seems reasonable that the resulting reverse solvatochromism should also occur for other members with *n* not equal to 1. In fact, the reverse solvatochromism of **1** is generally explained in terms of variations of the hybrid structure of the canonical forms **A** and **B**, as the medium polarity is changed. All merocyanines capable of such structural variations with the solvent polarity should, in principle, exhibit reverse solvatochromism.

The simplest member of this series is the biaryl dye, where $n = 0$. Reichardt *et al.*[12] described the solvatochromic properties of the related compound **2**, a γ-vinylogous pyridone.

This compound exhibits negative solvatochromism only, in



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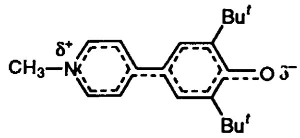
apparent contradiction with the hypothesis formulated above that *all* vinylogous amides of this series should display reverse solvatochromism.

In the present paper we shall be concerned with the generality of the phenomenon of reverse solvatochromism of pyridiniophenolate dyes. In order to do so, compound 3, synthesized by



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Thiébault *et al.*,[13] was employed for solvatochromic measurements in a variety of solvents.

This interesting dye incorporates two *tert*-butyl substituents, which render it more lipophilic than Reichardt's dye 2, thus allowing spectroscopic measurements in solvents of low polarity. In addition, by eliminating the unsaturated bridge between the two aryl groups, we rule out the possibility of *cis–trans* isomerism in solutions of this symmetrical compound. We may thus put to test the interpretation of Tsukada *et al.*[8] of the appearance of multiple bands in the visible spectra of such dyes in non-polar media. In addition, by comparing dyes 3 and 1, we may gain further insight into the phenomenon of reverse solvatochromism, and try to answer the question of how general it is. Finally, our analysis may provide a general picture that reconciles the conflicting interpretations that are found in the literature.

Results and Discussion

We tackled the question on the generality of the reverse solvatochromism of vinylogous γ-pyridones by developing a model which might account for the variations of the longest-wavelength-band transition energy of these dyes with the polarity of the medium. With a few exceptions,[3] authors have usually estimated these transition energies E_T in only one or two dye 'environments', so that an overall picture of the E_T variation with the medium polarity has never been obtained. This has led to contradictory statements, when particular points in a theoretical curve are taken for the whole solvatochromic behaviour of the dye.

We started from the assumption that the $S_0 \longrightarrow S_1$ transition energy of these dyes was, to a first approximation, equal to their HOMO–LUMO energy gap. Previous calculations involving configuration interactions have shown that the HOMO–LUMO transition in these systems is the major contributor (>94%) for this absorption.[3,6,9,11] We thus calculated the HOMO–LUMO energy gap for the pyridiniophenolate molecule as it acquires an increasing dipolar character because of environmental changes. This continuous structural variation could be accomplished by positioning point charges in the vicinity of the molecular structure. We had recently employed this approach in the study of pyridinioiminophenolate dyes,[11] unaware of the publication by Morley,[6] who employed essentially the same methodology for theoretical studies of dye 1 and related compounds. Morley's conclusion that the zwitterionic form of compound 1 gives rise to a smaller transition energy than the quinonoid form, 'in apparent contradiction with previous theories', is an example of an incomplete view of the problem. Since only a few dipolar structures were considered, comparing two extreme situations, the non-polar quinonoid and the polar zwitterionic forms of dye 1, does not tell us about what happens in between them, or whether a reversal in the solvatochromic behaviour of the compound is theoretically expected. In order to gain a complete view of this phenomenon, we must scan the various dipolar structures of the dye, that should correspond to different polar environments, by continuously varying the distance between the molecule and the point charges. We found that this could be conveniently achieved, following the AM1 method, by bringing a 'sparkle' of charge +2 gradually closer to the phenoxide oxygen of structure 1, along the C–O bond axis.

Since we wanted to relate our calculations to experimental observations, we had to find in addition some kind of correspondence between the theoretical structural variations of the dyes in solution and the experimental variations in the polarity of the solvent. We thus devised a 'polarity' scale based on the elongation of the C–O bond of these dyes, as the medium polarity is increased. In the absence of any point charges, geometry optimization of dye 1 by the AM1 method led to a nearly quinonoid structure, with a C–O bond distance of 1.247 pm. This value was taken as the non-polar extreme of our 'polarity' scale for dye 1. The other extreme should be the C–O bond distance of a dipolar structure of 1 in a protic, polar solvent, like water. Since this value was not accessible experimentally, we arbitrarily assumed it to be equal to the C–O bond length of a structure polarized by a +2 sparkle at a distance of 2 pm from the phenoxide oxygen. For dye 1, this value was close to 1.32 pm. We felt that this might be an acceptable estimate for the C–O bond length of a pyridiniophenolate dye in water for the following reasons. Allmann reported a value of 1.291 pm for the C–O distance of a pyridiniophenolate crystallized with one molecule of ethanol.[14] In water, a stronger hydrogen-bond donor solvent, this distance should be larger, but not so large as in a fully protonated phenoxide with an electron-withdrawing substituent, such as *p*-nitrophenol. The C–O bond distance in this compound is 1.352 pm.[15] An intermediate value of 1.32 pm was thus taken as a reasonable guess for the C–O bond distance of dye 1 in water.

With these extreme values fixed, we built a normalized scale, that might parallel the empirical E_T^N polarity scale[16] and thus allow comparison of our theoretical predictions with experimental observations. Our 'polarity' scale P was thus defined, for any pyridiniophenolate dye, as $P = (d_{C-O} - d_{C-O^o})/(d_{C-O^p} - d_{C-O^o})$, where P was the 'polarity' of a medium where the C–O bond distance of the dye equalled d_{C-O}. The values d_{C-O^o} and d_{C-O^p} corresponded to the C–O bond length in the absence and in the vicinity (2 pm) of the doubly positive sparkle, respectively.

We next proceeded to calculate the HOMO–LUMO energy gap E_T for structures 1 and 4 as the medium 'polarity' P was changed by the approaching sparkle, placed at a variable distance d from the phenoxide oxygen of those systems.

Initial geometry optimizations of structures 1 and 4 by the AM1 method yielded essentially planar molecules. This planarity was neither altered by the approaching sparkles, nor by the addition of two *tert*-butyl substituents adjacent to the phenoxide oxygen, as in 3. In the case of system 4, however, we decided to consider, besides the coplanar structure, other conformations which deviated from the full coplanarity of the aryl rings. This was motivated by the known structural variability of biphenyl systems, where the dihedral angle between the two rings may assume different values, depending on the nature of the ring substituents or the physical state of the

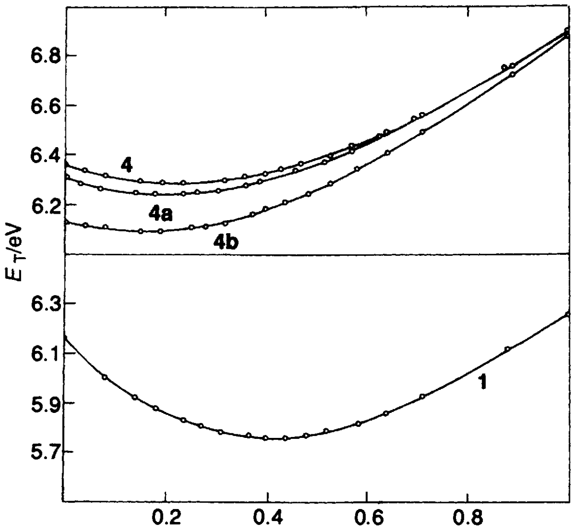
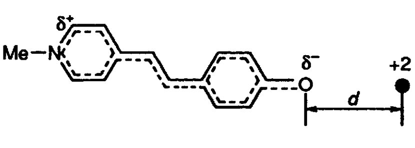


Fig. 1 Variation of the HOMO–LUMO energy gap E_T of systems **1**, **4**, **4a** and **4b** with the normalized 'polarity' value P



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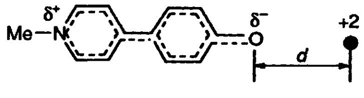

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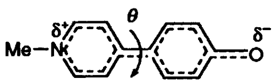
compounds.[17] Thus, we also calculated and drew plots of the variation of E_T with P for systems **4a** and **4b**, with dihedral angles θ of 15 and 30° respectively.



4 $\theta = 0°$
4a $\theta = 15°$
4b $\theta = 30°$

Inspection of Fig. 1 shows that all systems are expected to exhibit solvatochromic reversal somewhere along the 'polarity' scale. Whether this reversal may actually be observed depends on how close our arbitrary 'polarity' scale mimics other empirical scales, like Reichardt's E_T^N, for example. Of course, we cannot expect them to be superimposable. Our scale emphasizes the non-polar region, because of the assumption of setting $P = 0$ for a C–O bond distance of the free molecule in the gas phase. In addition, unlike the E_T^N scale, it also ignores hydrogen-bond effects, which are very important in protic, polar solvents, with the result that, again, the non-polar region is exaggerated in our normalized scale. Nevertheless, the trends observed in Fig. 1 should be confirmed experimentally. For example, the point of solvatochromic reversal of dye **1** is shifted to smaller polarity values, when the unsaturated bridge between the two rings is eliminated. Distortion from planarity leads to further shifts towards the non-polar region, so that, in the case of compound **4**, only the branch of negative solvatochromism may become eventually accessible experimentally.

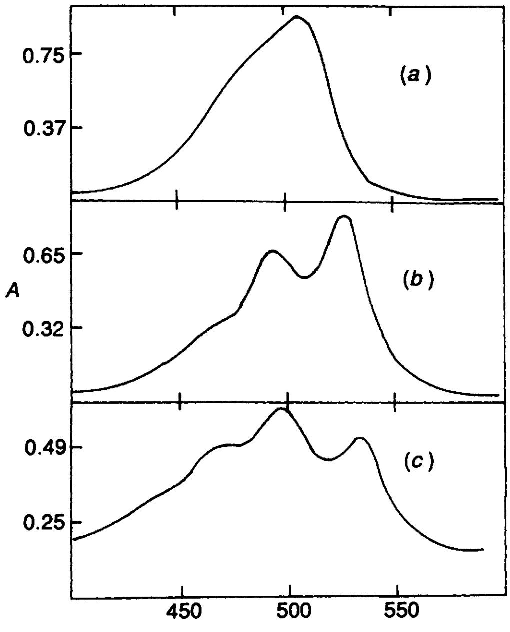


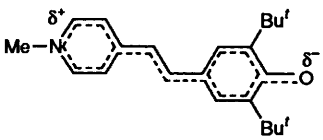
Fig. 2 UV–VIS absorption spectra of dye **3** (concentration *ca.* 10^{-4} dm^3 mol^{-1}) in: (*a*) acetonitrile, (*b*) chloroform and (*c*) carbon tetrachloride

Table 1 Variation of the λ_{max} values of the longest wavelength absorption band in the visible spectrum of dye **3** with the solvent polarity

Solvent	E_T^N value	λ_{max}/nm
Water	1.000	447
Methanol	0.762	481
Ethanol	0.654	502
Acetonitrile	0.460	504
Dimethyl sulfoxide	0.444	505
N,*N*-Dimethylformamide	0.404	507
Dichloromethane	0.309	521
Chloroform	0.259	526
Ethyl acetate	0.228	519
Diethyl ether	0.117	525
Tetrachloromethane	0.052	533

Table 1 lists the λ_{max} values of the longest wavelength band in the visible spectrum of dye **3**, in solvents of decreasing polarity. It is seen that dye **3** exhibits negative solvatochromism throughout the investigated polarity range. The same solvatochromic behaviour was reported for the vinylogous γ-pyridone **2**. These observations are thus in agreement with the trends observed in Fig. 1, since compounds **2** and **3** are structurally related to system **4**.

As for dye **1**, Jacques[4] provided evidence for a reversal of its solvatochromic behaviour in solvents of low polarity ($E_T^N < 0.2$). This view was recently contested by Catalán *et al.*[9] who studied the more lipophilic dye **5**.



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The spectra of this compound in most solvents consisted of multiple bands in the visible region, a trend which is also found, to a variable degree, in other vinylogous γ-pyridones, like **3** (see Fig. 2). By deconvolution of the main absorption bands in various solvents, the Spanish group concluded that no

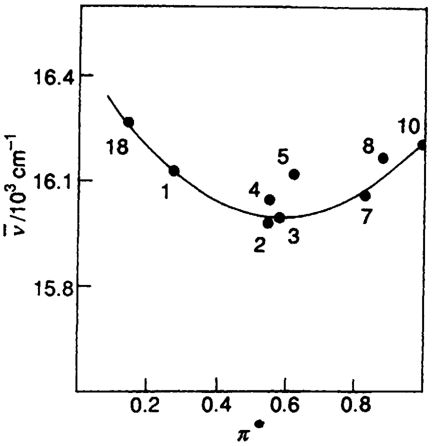

Fig. 3 Variation of the wavenumber $\bar{\nu}$ of the first band ($S_0 \longrightarrow S_1$) of compound **5** with Taft's polarizability parameter π^* of the medium. Data were taken from ref. 9 and the original solvent numbering was retained: 1, diethyl ether; 2, dioxane; 3, tetrahydrofurane; 4, ethyl acetate; 5, methyl formate; 7, tetramethylurea; 8, *N*,*N*-dimethylformamide; 10, dimethyl sulfoxide; 18, triethylamine.

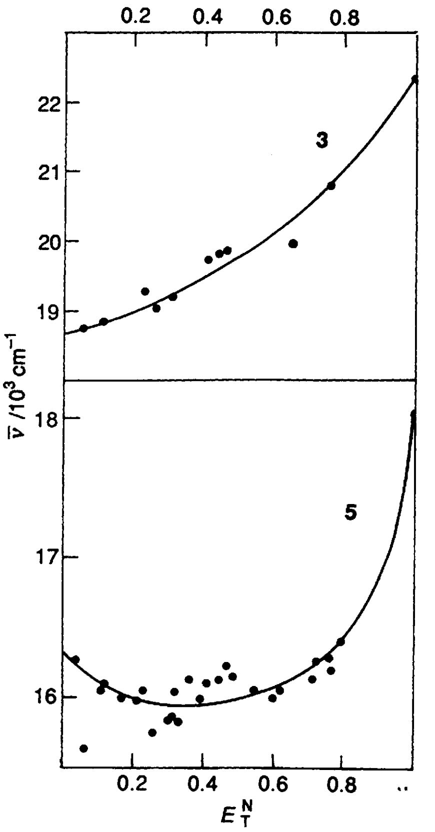

Fig. 4 Variation of the wavenumber $\bar{\nu}$ corresponding to the $S_0 \longrightarrow S_1$ transition of dyes **3** and **5** with the polarity $E_T{}^N$ of the medium. Data for compound **5** were taken from ref. 9.

Table 2 Calculated charge densities on the N and O atoms, and position of the calculated solvatochromic reversal along the *P* coordinate, for systems **1**, **4**, **4a** and **4b**

System	Charge density on N	Charge density on O	*P* value[a]
1	−0.195	−0.329	0.40
4	−0.184	−0.343	0.24
4a	−0.183	−0.345	0.21
4b	−0.177	−0.350	0.15

[a] 'Polarity' value *P* where the minimum of the curve of Fig. 1 occurs.

solvatochromic reversal was observed for the $S_0 \longrightarrow S_1$ transition band of **5**.

Jacques' contention is weakened by the fact that the positive solvatochromic branch of his curve for compound **1** could only be drawn with extrapolated values,[4] because of the scarce solubility of this dye in non-polar media. The presence of two *tert*-butyl substituents in **5** renders this dye more soluble in non-polar solvents. It also reduces its sensitivity to hydrogen-bond interactions with protic solvents. Accordingly, the solvatochromism of compound **5** is much less pronounced than that of compound **1**, especially in protic solvents. However, in the absence of hydrogen-bond interactions with the solvent, as in non-polar media, the two dyes should behave similarly. In fact, solvatochromic shifts for both dyes in non-polar solvents are rather small, and an unequivocal detection of a solvatochromic reversal is not an easy task.

Jacques' proposal relied upon a plot of $\bar{\nu}$ *vs.* π^*, which clearly showed the 'two branches solvatochromism' of **1** (see Fig. 3 of ref. 4). A similar plot with the data for compound **5** [see Fig. 7(*a*) of ref. 9] led the Spanish group to conclude that 'a reversal of solvatochromism . . . is not observed in the zone of low polarity'.[9]

This apparent inconsistency may be solved by noticing that Catalán *et al.* included in their plot data points from protic solvents. This was explicitly avoided by Jacques and it is easy to see why: hydrogen-bond-donating solvents, like alcohols, for instance, would mask and distort any eventual correlation between $\bar{\nu}$ and π^*, as in fact happened in the plot of the Spanish group. If the same data are plotted with Jacques' precaution of omitting data points from solvents with Taft's α values different from zero, Fig. 3 is obtained, which shows a shallow, but discernibly concave curve, indicative of a solvatochromic reversal of **5** in the zone of low polarity. This is reinforced by the graphs of Fig. 4, where we compare the data for compound **3**, reported in the present work, with the transition energies of the first band of compound **5**, published by Catalán *et al.*[9] A shallow concavity is again discernible in the curve of $\bar{\nu}$ *vs.* $E_T{}^N$ of compound **5**,[18] but not of dye **3**. These plots should be compared with the theoretical curves and systems of Fig. 1. It is easy to see that the observed trends match the theoretical predictions.

We are now in a position to tackle the question posed in the introduction: why do systems like **1** or **5** exhibit a solvatochromic reversal, while the vinylogous γ-pyridones **2** and **3** do not?

We have shown that, in fact, all of these systems are expected to show minima in their plots of E_T *vs.* the 'polarity' of the medium *P*. What determines the actual observation of this reversal is the position of these minima along the 'polarity' coordinate. Shifting this minimum to either extreme of the scale may result in a 'virtual' reversal, not actually observed, which lies beyond the range of experimental polarities.

We should then be concerned with the structural factors which govern the position of the point of solvatochromic reversal along coordinate P. They have to do with the relative contributions of the two extreme canonical forms, the non-polar quinonoid **A** and the zwitterionic aromatic **B**, to the hybrid structure of the vinylogous γ-pyridone.

Calculations on the systems **1**, **4**, **4a** and **4b** show that, in all cases, in the gas phase the major canonical contributor to the hybrid structure is the non-polar quinonoid form A. In each case, the relative contribution of the quinonoid form may be inferred from the calculated charge densities on the N and the O atoms. As the dipolar character of the hybrid increases, the N atom should become less negatively charged, as it transfers more of its charge to the oxygen atom. This is shown in Table 2, where it is seen that the charge transfer from N to O increases in the order **1** < **4** < **4a** < **4b**, which is also the order of relative stability of the dipolar, zwitterionic contributor **B** to the hybrid. Table 2 also gives the positions, along the polarity coordinate *P*, of the theoretical solvatochromic reversal for these systems.

We see that this reversal takes place at progressively smaller polarity values (less polar media) as the relative contribution of the dipolar form **B** to the hybrid increases. In other words, for a given family of vinylogous γ-pyridones, stabilization of the zwitterionic contributor, relative to the quinonoid form, tends to shift the point of reversal to less polar media, until it eventually becomes 'virtual', that is, not actually observable.

For example, in the series **4**, **4a** and **4b**, increasing the torsional angle θ between the two rings favours the zwitterionic form **B**, and shifts the minima of Fig. 1 to a less polar region. If we compare systems **1** and **4**, the same argument applies. In both systems the aryl rings are coplanar. However, in **4**, the greater proximity of the two rings causes a steric repulsion between the *ortho*-hydrogens. As a result, the C–C bond between the two rings in **4** is stretched, an effect which decreases the stability of the quinonoid form **A** and favours the zwitterionic contributor **B**. As can be seen in Figs. 1 and 3, this has the effect of shifting the point of solvatochromic reversal of system **1** (or of dye **5**), which is actually observed, to a less polar, 'virtual' region for system **4** (or dye **3**), where it is no longer detected.

We should now comment on the various interpretations of the multiple bands which are observed in the visible spectra of many of these dyes. Clearly, our observation that these bands are also present in the spectra of compound **3** (see Fig. 3) rules out the interpretation of Tsukada *et al.*[8] that they originate from equilibria between *cis–trans* isomers. Dye aggregation seems a more plausible explanation for the appearance of these bands. Evidences have been presented of deviations from Lambert–Beer's law for γ-vinylogous pyridones[10] related to **1**. The isolation of other merocycanine aggregates which show two absorptions in cyclohexane, assigned to monomeric and dimeric forms, lends credence to this interpretation.[19] However, we should bear in mind that dye aggregation *per se* does not rule out the occurrence of a solvatochromic reversal in solution. We may always focus our attention on the fate of the band which corresponds to the monomeric species and follow its λ_{max} shifts in various solvents. We have shown in the present paper that, either by direct reading of the spectra of solutions of a dye, as we have done with compound **3**, or by deconvolution of the multiple bands, as has been done for compound **5**,[9] general trends of solvatochromic shifts emerge, in agreement with theoretical predictions.

It is noteworthy that not all pyridiniophenolate dyes form aggregates. Solutions of the $E_T(30)$ dye ($c = 10^{-4}$–10^{-3} mol dm^{-3}) have been carefully investigated and found not to violate Lambert–Beer's law. The same careful measurements have not been carried out with compound **2**, but the normal behaviour of its long-wavelength-absorption bands and the good linear correlation of its E_T with $E_T(30)$ values in various solvents may be taken as an indication that it does not form aggregates.[20] These observations pose difficulties to the alternative interpretation that the multiple bands of these dyes arise from the splitting of electronic levels by vibrational states, through interactions of the solvent with the phenoxide oxygen.[9] It is difficult to see why this splitting should occur for compound **5**, but not for compound **2**, since in both cases the same interactions of the solvent with the phenoxide oxygen are bound to take place.

In conclusion, our theoretical model allows a qualitative prediction of the solvatochromic behaviour of vinylogous γ-pyridones. In principle, all such compounds are expected to exhibit solvatochromic reversal at some point along our theoretical 'polarity' coordinate *P*. The actual observation of this point of reversal depends on its position along that coordinate. In regions of extreme polarity values we may encounter a 'virtual' solvatochromic reversal, that lies beyond the reach of experimental observations. This simply happens because our theoretical scale *P* cannot be expected to correlate with other empirical polarity scales which incorporate specific solvent effects such as, for example, hydrogen-bond interactions with the dye. Nevertheless, our model reproduces observed trends and explains the different behaviour of dyes **1** and **5**, which do exhibit a solvatochromic reversal, and dyes **2** and **3**, which do not. It also reconciles previous conflicting reports, which are shown to originate from incomplete views of the phenomenon. The present approach remains to be tested with other merocyanines, for which changes of the solvatochromic behaviour have been reported without a general theoretical interpretation. This test, and the extension of our conclusions to other systems, will be the subject of a future report.

Experimental

The preparation of dye **3** has been described.[13]

Semiempirical MO calculations were performed with an Apollo 10 000 computer, employing the AM1 method of the MOPAC 6.0 package.[21] All molecular structures were geometrically optimized with the only constraint of planarity of the aromatic rings. HOMO–LUMO energy gaps were then determined for each structure perturbed by the proximity of a 'sparkle' of charge + 2, positioned at a variable distance *d* from the phenoxide oxygen of the dye, along the C–O bond axis. The resulting curves of E_T *vs.* *P* were drawn with data points obtained by varying this distance in the range of 2–15 pm.

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