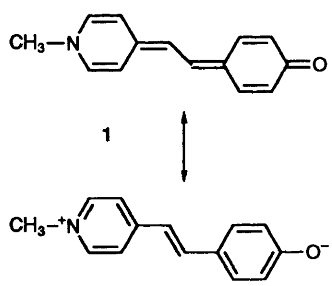
Solvato- and Halo-chromic Behaviour of some 4-[(*N*-Methylpyridiniumyl)methylidineamino]phenolate Dyes

Clodoaldo Machado, Maria de Graça Nascimento and Marcos Caroli Rezende*
Departamento de Química, Universidade Federal de S. Catarina, Florianópolis, SC 88040-970, Brasil

The solvato- and halo-chromic behaviour of the phenolate dyes **4–6** is described and compared with their analogues **1** and **3**. The observed trends are discussed and rationalized in terms of semiempirical molecular orbital calculations.

Merocyanine dyes constitute a class of compounds which have attracted great interest in the past decades, both from the theoretical as well as the practical point of view. Among them, dye **1**, first described nearly 40 years ago,[1] has been the starting point for structural variations that included modifications of the pyridinium and/or phenoxide rings and of the ethenylene bridge.[2–5] Thus, the solvatochromic properties of the isomer **2** were recently described.[5] Buncel *et al.*[3,4] also explored the solvatochromism of dye **3**, among others, and proposed from these studies the new π* azo scale, for measuring the dipolarity/polarizability of solvents.



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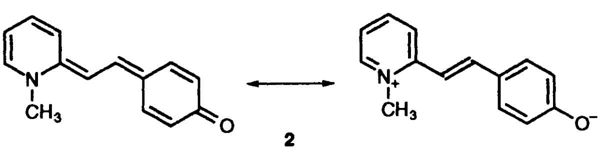

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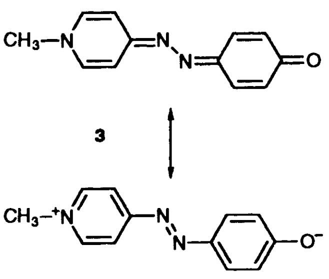

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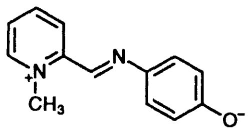
From the theoretical point of view, various papers have dealt with the reverse solvatochromism exhibited by dye **1**.[2,6–10] This 'unusual'[9] or 'surprising'[11] phenomenon consists of a reversal in the solvatochromic behaviour of the dye, changing from a positive (bathochromic shifts of λ_{max} with increasing solvent polarity) to a negative solvatochromism as the medium polarity is increased. It is generally accepted that this is due to the varying contributions of the two extreme canonical formulae shown for dyes **1–3**, a non-polar quinonoid structure which predominates in solvents of low polarity, and a zwitterionic formula, which becomes increasingly stable in polar media.[11]

The direct observation of this solvatochromic reversal, predicted by semiempirical calculations,[7,8] is not straightforward because of the low solubility of dye **1** in pure solvents of low polarity. Authors have resorted to spectroscopic observation of solvent mixtures, deriving values of λ_{max} in the pure non-polar components from experimental curve extrapolations.[9]

In the present paper we report on the solvato- and halochromic properties of the imino dyes **4–6**, represented here by their polar canonical structures. These compounds attracted our interest for several reasons. Firstly, the description of the solvatochromic properties of dyes **4** and **6** complements the existing data concerning compounds **1–3**. It also allows an overall view of this series of dyes, as the unsaturated group joining the two rings is changed from CH=CH to CH=N and N=N. Secondly, we had the hope of arriving at dyes more soluble than **1** in non-polar media, so that we could observe their anticipated reverse solvatochromism directly from spectroscopic measurements in pure solvents. Thirdly, we considered the behaviour of dye **5**, where the enforced zwitterionic structure was expected to reduce or even abolish solvatochromism. On the other hand, we were puzzled by a report on the hyperpolarizability of substituted stilbenes, which described unexpectedly high values of the second-order coefficient β for non-conjugated donor–acceptor groups, as being in a (2,3') or a (4,3') substitution pattern.[12] Since second-order polarizabilities often correlate with the solvatochromic properties of dyes,[13] it seemed interesting to compare compounds **4** and **6** with **5** and investigate how the isomeric substitution of the pyridinium ring might affect the solvatochromic properties of this series of dyes. Finally, we were also interested in extending our observations on the cationic halochromism of **1**[14] to related systems, such as the imino merocyanines **4** and **6**.



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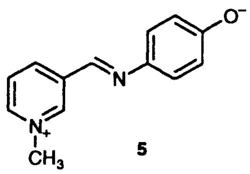

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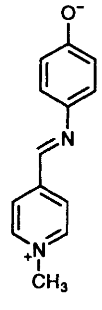

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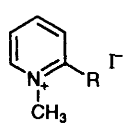
Results and Discussion

Dyes **4–6** were obtained *in situ* from the corresponding pyridinium iodides **7–9** by basic deprotonation in solution.

The variation of the longest wavelength absorption band of

Table 1 Position of the longest wavelength band of dyes **4**–**6** in different solvents

	λ_{max}/nm		
Solvent	**4**	**5**	**6**
Water	466	419	473
Propane-1,2,3-triol	488	—	498
Ethane-1,2-diol	494	—	503
Methanol	504	439	513
Ethanol–Water (80:20)	515	—	523
Ethanol	535	461	543
Butan-1-ol	560	475	570
Propan-2-ol	573	—	588
Acetonitrile	586	—	607
Dimethylsulfoxide	595	530	620
Dimethylformamide	601	529	627
Dichloromethane	617	—	662
Chloroform	626	—	672
2-Methylpyridine	619	—	662
Ethyl acetate	606	—	651
Tetrahydrofuran	616	—	656



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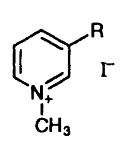

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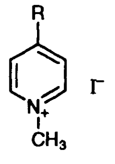

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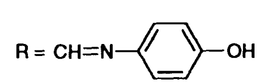

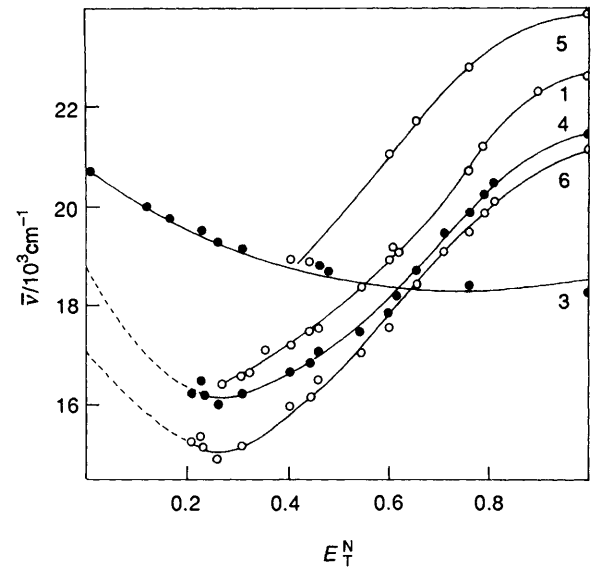

Fig. 1 Variation of the wavenumber $\bar{\nu}$ of the longest wavelength band of dyes **1** and **3**–**6** with the polarity E_T^N of the solvent. Data for compounds **1** and **3** were taken from refs. 9 and 3 respectively. Curves for **1**, **3**, **4** and **6** are third-order polynomials fit to the data by a non-linear least-square procedure. Coefficients for the general equation $\bar{\nu} = a + b(E_T^N) + c(E_T^N)^2 + d(E_T^N)^3$ are, for compound **1**: $a = 17\,820$, $b = -13\,790$, $c = 37\,700$, $d = -18\,990$; compound **3**: $a = 20\,806$, $b = -78\,177$, $c = 75\,639$, $d = -22\,509$; compound **4**: $a = 18\,710$, $b = -20\,660$, $c = 47\,130$, $d = -23\,660$; compound **6**: $a = 17\,040$, $b = -17\,910$, $c = 46\,520$, $d = -24\,490$.

dyes **4**–**6** in various solvents is presented in Table 1. A plot of the corresponding wavenumbers $\bar{\nu}$ for all dyes against the normalized polarity parameter E_T^N in each solvent[15] is shown in Fig. 1. For the sake of comparison, the variation of $\bar{\nu}$ with E_T^N for the merocyanine **1**[9] and the azo merocyanine **3**[3] are also given in the graph.

The reverse solvatochromism of dyes **4** and **6** is discernible in Fig. 1, where minima in the curves occur in media of low polarity like chloroform ($E_T^N = 0.259$). The range of polarity variation is narrower for dye **5**. This is because we could not generate any coloured species from **8** in media of less polarity than dimethylformamide (DMF) ($E_T^N = 0.404$). This seems to be a general limitation for this family of compounds. Jacques[9] could only report experimental values of transition energies for compound **1** in solvents with $E_T^N \geqslant 0.270$, so that only the branch of the curve corresponding to a negative solvatochromic behaviour could be drawn with his data (Fig. 1). The same limitation was encountered by Abdel-Halim,[5] when following the solvatochromism of isomer **2** in solvents of decreasing polarity. Our data therefore represent an improvement over previous reports, as the solvatochromic reversal of these merocyanines is directly observed in pure solvents of low polarity. This is not unprecedented, as one may gather from Buncel's reports[3] on the solvatochromism of azo merocyanines. However, as has been pointed out,[4] compound **3** constitutes a different class of moderately dipolar species, as opposed to the highly dipolar dye **1**. This can be seen from Fig. 1, where the solvatochromic behaviour of **3** is very different from that of dyes **1**, **4** and **6**.

The poor solubility of these latter dyes in non-polar solvents is not the only obstacle to the construction of the positive solvatochromic branch of Fig. 1. The appearance, in low polarity solvents, of other bands in the visible spectrum was noted and discussed previously for **1** and related compounds.[10,16–19] We observed the same phenomenon for dyes **4** and **6**. The longest wavelength band of **6**, recorded, for example, in pure DMF, undergoes a bathochromic shift in DMF–CCl_4 mixtures, as the volume percentage of the less polar co-solvent is augmented. This is accompanied by the appearance of a shoulder at a smaller wavelength and an eventual splitting of the band, so that the unambiguous assignment of the solvatochromic band becomes increasingly difficult in non-polar solvents.

In this report we have considered the longest wavelength band in the visible as the 'true' solvatochromic band. The λ_{max} values in low polarity solvents given in Table 1 correspond to this band.

Various interpretations for the appearance of multiple bands in low polarity solutions of these merocyanines have been proposed.[2,10,16–19] This problem is far from settled and it is not our intention to delve into it here. However, it concerns us, since some interpretations have led the authors to deny any intrinsic reverse solvatochromism of these dyes.[10,17] This raises the question of the reality of a positive solvatochromic branch in the low polarity region for these dyes.

As mentioned before, reasonable objections may be raised against the evidence which has been put forward in favour of this reversal. On the other hand, semiempirical calculations[8] do predict a positive solvatochromism for these dyes in their quinonoid form. Attempts to discard this,[10] based on a presumably inadequate CNDO/S optimization of the molecular geometry of **1**, are not convincing. We have performed calculations starting from geometries optimized with an AM1 program and generating polar forms for dyes **1**, **4** and **6** by a procedure different from that of Botrel *et al.*[8] (see below). Nevertheless, our results agree with their report of a positive solvatochromism for these dyes in low polarity media.

Clearly, these questions await further investigation. We have therefore been cautious when drawing the curves of Fig. 1, distinguishing between the experimentally observable branch in medium-to-high polarity solvents and the extrapolated branch, where a positive solvatochromism should be observed.

Table 2 Wavenumbers corresponding to the $S_0 \rightarrow S_1$ transition for dyes **1**, **3**, **4** and **6** in a non-polar medium ($E_T^N = 0$)

	$\tilde{\nu}/10^3$ cm^{-1}	
Dye	Experimental	Calculated
1	16.89[a]	20.92
3	20.73[b]	21.26
4	18.71[c]	19.63
6	17.04[c]	19.54

[a] Extrapolated value in cyclohexane, see ref 9. [b] Value in hexane, see ref. 3. [c] Extrapolated value from a third-order polynomial fit (see Fig. 1).

MO Calculations.—Table 2 gives the wavenumbers corresponding to the $S_0 \rightarrow S_1$ transition for dyes **1**, **3**, **4** and **6**, obtained from INDO/SCI calculations. These results refer to the non-polar, quinonoid form of each dye, as the optimized bond distances in each case show clearly. The experimental values given in the Table for comparison were obtained either from extrapolations of third-order polynomial fits to the data (see Fig. 1) or from spectroscopic measurements in solvents with E_T^N values as close as possible to zero.

The transition energy obtained for compound **1**, 20.92 × 10^3 cm^{-1} (2.59 eV), compares favourably with the value of 23.79 × 10^3 cm^{-1} (2.95 eV) calculated by Botrel and co-workers,[8] which, in the authors' words, 'is too high by 1 eV'. It is also better than the values obtained by Catalán *et al.*[10] (22.17 × 10^3 cm^{-1}) and by Luzhkov and Warshel[19] (21.87 × 10^3 cm^{-1}).

If we assume that the trends shown in Fig. 1 for the more polar portion of the curves are maintained in the non-polar region, the $S_0 \rightarrow S_1$ transition wavenumbers for the quinonoid forms should increase in the order **6** < **4** < **1** < **3**. This is the order of calculated $\tilde{\nu}$ values listed in Table 2. With the exception of compound **1**, with a reported value obtained by extrapolation of second-order polynomials,[9] this is also the order of the 'experimental' values given in the Table.

It is clear from Fig. 1 that the solvatochromic behaviour of dyes **1** and **4**–**6** is very similar. This is reasonable for dyes **4** and **6**, when compared with **1**, but is less so for dye **5**, where the direct through-conjugation between the oxide donor and the positive nitrogen acceptor is prevented by the *meta*-substitution on the pyridinium ring.

Replacement of a CH by an N atom in **1**, yielding dye **6**, should lead to little qualitative change in the solvatochromism of these substrates.[4] This is confirmed by the curves of Fig. 1. In addition, for a given solvent, it is seen that the imino dyes absorb at longer wavelengths (smaller wavenumbers) than dye **1**, the transition energies increasing in the order **6** < **4** < **1**. The reason for this may be sought in the comparison of the HOMOs and the LUMOs of these dyes.

CI calculations show that, in all cases, the major (92–96%) contribution to the $S_0 \rightarrow S_1$ transition is the configuration arising from a one-electron promotion from MO 40 (HOMO) to 41 (LUMO). It is therefore reasonable to analyse the longest wavelength absorption of these compounds in terms of their HOMOs and LUMOs. Fig. 2 gives the atomic orbital coefficients of the HOMO and LUMO of dye **4**. Their distribution is very similar to the pattern exhibited by merocyanine **1**, described by Botrel and co-workers.[8]

A characteristic feature of this transition is the size inversion of the coefficients of the C=C (and C=N) bridge, as the molecule is excited from MO 40 to MO 41. This inversion should be facilitated for the C=N bridge, compared to the C=C group, because of the greater electronegativity of the nitrogen atom, which can thus accommodate more easily a greater charge density in the LUMO. This results in a greater stabilization of the LUMO of imino dyes **4** and **6** and a consequent decrease of the energy gap for the HOMO–LUMO transition.

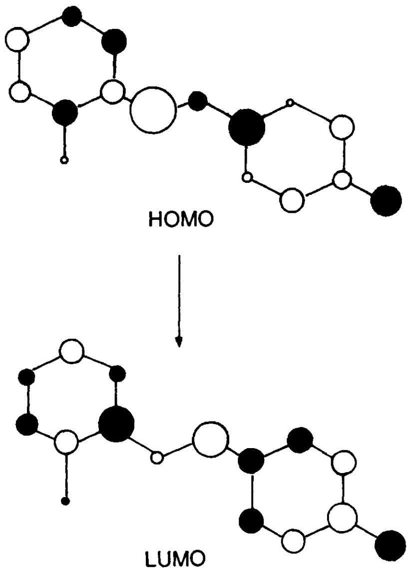

Fig. 2 Atomic orbital coefficients for the HOMO and LUMO of the quinonoid form of dye **4**

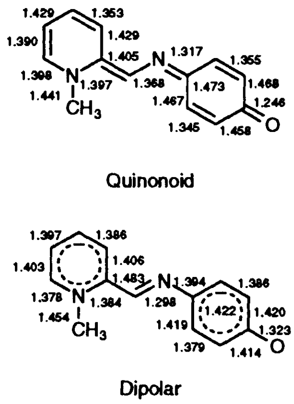

Fig. 3 Calculated bond lengths (pm) for the quinonoid and a dipolar structure of dye **4**

The solvatochromic behaviour of dye **5** could only be recorded in polar solvents. In order to extend our MO analysis to this compound, we must therefore compare the HOMOs and the LUMOs of the zwitterionic form of the imino compounds under study.

Calculations with these dipolar forms may be carried out readily by submitting the molecule to an external electric field. For example, a point charge of +2 close (2 pm) to the oxygen atom of the phenoxide moiety polarizes the whole molecule, shifting its geometry to a structure closer to the pure zwitterionic form,[20] as can be seen from the optimized bond distances thus obtained for compound **4**, shown in Fig. 3.

The HOMO and LUMO charge densities for these dipolar forms of the isomers **4** and **5** are shown in Fig. 4. Inspection of these molecular orbitals reveals a fundamental difference between the polymethine **4**, where a direct through-conjugation between the O^- and the N^+ chain-end heteroatoms occurs, and the isomer **5**, where this conjugation is absent.

Following Dähne's distinction between charge-transfer (CT) and charge-resonance (CR) dyes,[21] we identify compound **5** as an example of the former, while polymethines **4** and **6** constitute examples of dyes where charge resonance predominates.

In fact, the degree of charge transfer in a HOMO–LUMO excitation may be estimated by computing the total charge gained (lost) by the acceptor (donor) moiety of the molecule. This can be seen in Fig. 4, where we represent graphically how the total π-charge-densities in the HOMOs and LUMOs are

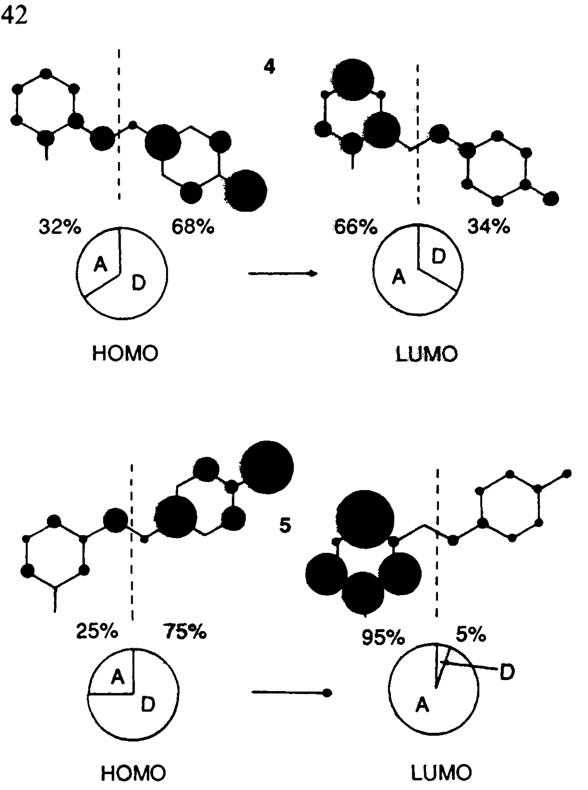

Fig. 4 Estimated charge transfers for the HOMO→LUMO transitions of the dipolar structures of dyes **4** and **5**. Circles of variable size represent π-electron-charge densities on each atom. The percentage charge distributions between the donor D and the acceptor moiety A are shown for all HOMOs and LUMOs.

shared by the donor–acceptor fragments of each molecule. For compound **4** the HOMO distribution yields a distribution where *ca.* 68% of the charge accumulates on the donor, leaving 32% for the acceptor moiety. This situation is reversed in the LUMO, where the donor shares 34% and the acceptor 66% of the total charge. The charge transfer for this transition is thus (68%–34%) = (66%–32%) = 34% of the available charge in the MO.

The same estimate may be carried out for compound **5**, with the result that, in this case, nearly 70% of the available charge is transferred from the donor to the acceptor moiety.

Ideal polymethines with pure CR-character exhibit zero charge transfer on excitation. Conversely, an ideal CT dye is expected to transfer 100% of the total HOMO charge which accumulates on the donor to the acceptor moiety. It is clear that neither **4** nor **5** conform to these ideal behaviours. However, while **5** is very nearly a CT dye, compound **4** approaches the pure CR-character, with some degree of charge transfer.

Halochromic Studies.—Halochromic studies involving dyes **4** and **6** employed sodium iodide, various alkali and alkaline-earth perchlorates, and five different solvents (MeOH, EtOH, 2-PrOH, DMF and MeCN).

The behaviour of the two dyes was very similar. This is illustrated in Fig. 5 where the variations in wavenumber of the longest wavelength band of dyes **4** and **6** are shown in DMF and 2-PrOH, in the presence of increasing concentrations of added electrolytes.

In all cases, $LiClO_4$ induced larger halochromic shifts than either NaI or $NaClO_4$: hypsochromic shifts of 30 (in DMF) and 50 nm (in 2-PrOH), compared with 10 and 35 nm, respectively, for the same concentration (0.05 mol dm^{-3}) of $NaClO_4$. In addition, both NaI and $NaClO_4$ had practically the same effect on both dyes. These observations are in agreement with the anticipated cation-dominated halochromism of this family of imino dyes.[14]

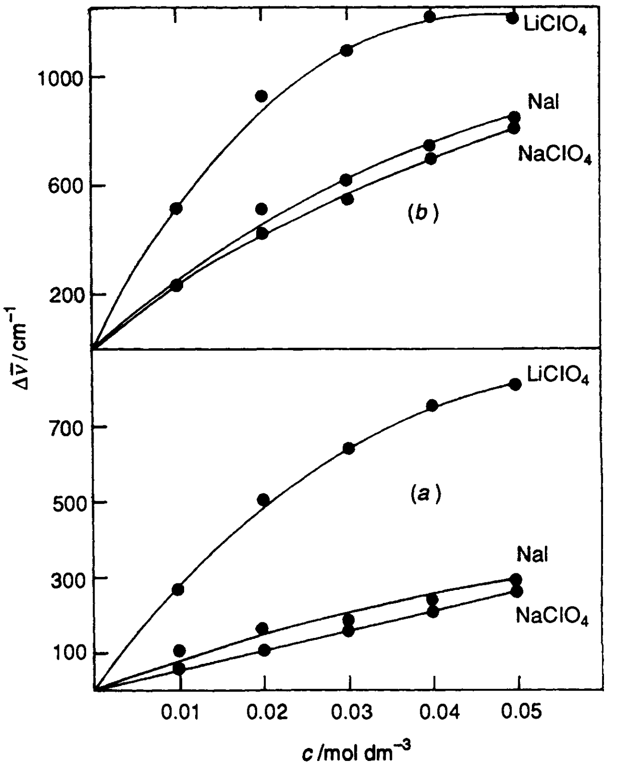

Fig. 5 Wavenumber variation $\Delta\bar{\nu}$ of the longest wavelength band of an iminophenolate dye in the presence of increasing concentrations, *c*, of a lithium or sodium salt; (*a*) halochromic shifts of dye **6** in DMF; (*b*) halochromic shifts of dye **4** in propan-2-ol

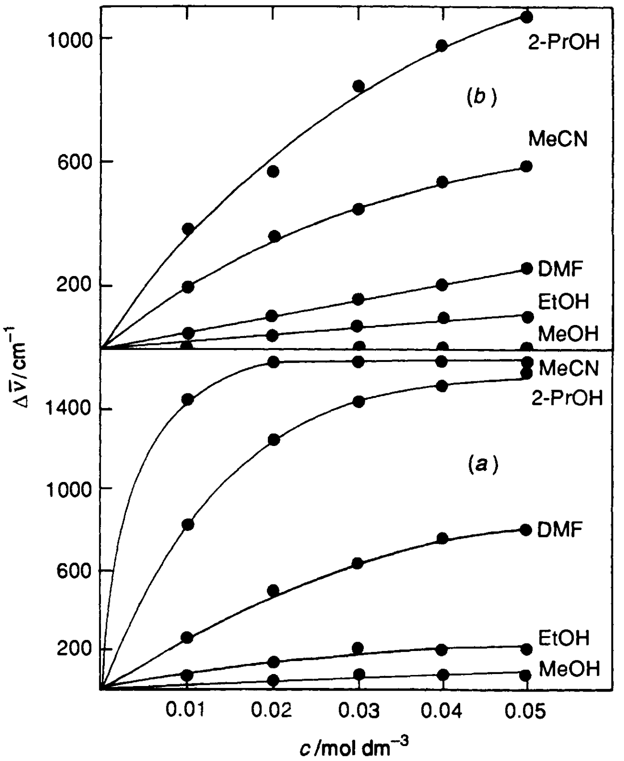

Fig. 6 Wavenumber variation $\Delta\bar{\nu}$ of the longest wavelength band of dye **6** in various solvents, in the presence of increasing concentrations, *c*, of lithium (*a*) or sodium (*b*) perchlorate

Fig. 6 compares the halochromic shifts of dye **6** in various organic solutions of $LiClO_4$ and $NaClO_4$. The sensitivity of the

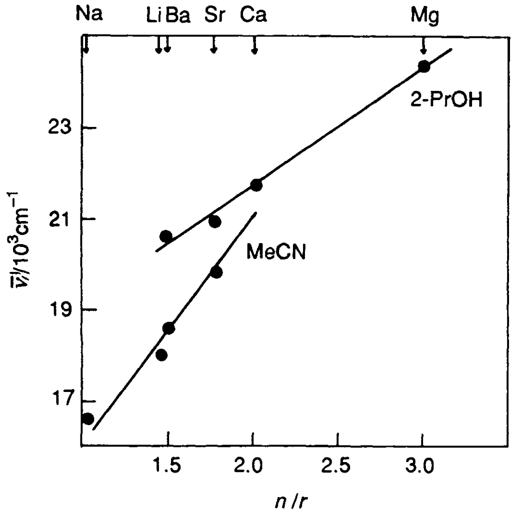

Fig. 7 Solutions of dye **6** (*ca.* 10^{-4} mol dm^{-3}) in propan-2-ol or acetonitrile, in the presence of a fixed concentration ($c = 5 \times 10^{-3}$ mol dm^{-3}) of various alkali and alkaline-earth perchlorates. Variation of the wavenumber of the longest wavelength band of **6** with the effective ionic charge n/r of the added cation. (Ionic radii r were taken from the Handbook of Chemistry and Physics, 1984–1985, 65th ed., CRC Press, Florida, p. F-165.)

dye to Li^+ in these solvents increases in the order MeOH < EtOH < DMF < 2-PrOH < MeCN. For Na^+ this order is slightly changed: MeOH < EtOH < DMF < MeCN < 2-PrOH. As shown previously,[14,22,23] this sensitivity is a measure of the dye–cation association in solution, which is influenced in two ways by the solvent. Firstly, dye–solvent interactions, especially arising from hydrogen bonds, tend to reduce the dye–cation association. This explains the order found for the alcoholic solvents, where the dye is least sensitive to the added cation in the solvent capable of the strongest hydrogen bonds (MeOH). Secondly, good donor solvents tend to solvate the added cation, thus diminishing the dye–cation association. The non-protic DMF and acetonitrile compete with the phenoxide moiety of the dye for the cation. This results in smaller halochromic shifts, the dye being least sensitive in the better donor solvent (DMF).

The curious inversion observed for 2-PrOH and MeCN in Fig. 6, when Li^+ is replaced by Na^+ in solution, may be interpreted as arising from a balance between the effects discussed above. This balance is tilted by the nature of the added cation. The harder Li^+ species is less solvated than Na^+ in MeCN. Being smaller, Li^+ is also better solvated than Na^+ by the hindered propan-2-ol molecules. These effects add to the result that Li^+ association with the dye is relatively much larger in MeCN than in 2-PrOH, as compared with Na^+. For the latter cation, the greater solvation in MeCN, reinforced by the comparatively smaller degree of solvation in 2-PrOH, leads to the inversion that is eventually observed.

We have finally investigated the dependence of the halochromic shifts of dye **6** on the charge density of the added cation.

When various salt solutions of the $E_T(30)$ dye were investigated in acetonitrile, a linear dependence was observed when ΔE, the charge-transfer energy of the substrate, was plotted against the effective ionic charge (n/r, where n is the cation charge and r its ionic radius) of the added metal cation.[24,25] Since the $E_T(30)$ dye, a pyridiniophenolate betaine, also exhibits cationic halochromism,[26] we wondered if the same linear dependence could be obtained for other dyes with a similar behaviour, like **4** and **6**.

Fig. 7 shows plots of $\tilde{\nu}$ against n/r for dye **6** in acetonitrile and propan-2-ol. Reasonable linear plots were obtained in both cases. This suggests that the cationic halochromism of phenoxide dyes follows general patterns, which are valid for different families of compounds. This should not come as a surprise, if we accept the qualitative model which describes this form of halochromism as fundamentally reflecting the associations in solution of the metal cation and the phenoxide group.[14,22,23,26]

In conclusion, we have investigated the solvatochromic and halochromic properties of dyes **4**–**6** in various solvents. Dyes **4** and **6** exhibit reverse solvatochromism, with minima in their plots of $\tilde{\nu}$ *vs.* E_T^N occurring in low polarity media, like chloroform. Spectra of dye **5** could only be obtained in solvents of reasonable polarity. All imino dyes exhibited negative solvatochromism in solvents of medium to high polarity and their behaviour paralleled the solvatochromic shifts reported for merocyanine **1**. INDO-CI calculations on these systems rationalize the observed trends of relative transition energies in non-polar media. In addition, the analysis of the HOMO→LUMO transitions of **4** and **5** provides a means of distinguishing and classifying the imino compounds as predominantly charge-resonance polymethines (**4** and **6**) and charge-transfer dyes (**5**). The spectral analyses of organic solutions of dye **6** in the presence of various salts confirmed its anticipated cation-dominated halochromism. Halochromic shifts of this dye in salt solutions of propan-2-ol and acetonitrile showed a linear dependence on the effective ionic charge of the added cations.

Experimental

M.p.s were obtained with a Koffler hot-stage apparatus and were not corrected. ^1H NMR spectra were recorded on a Varian 60 MHz instrument, employing tetramethylsilane as the internal reference. UV–VIS spectra were obtained with a Beckmann DU-65 spectrometer.

N-*Methyl*-X-(4-*hydroxyphenyliminomethyl*)*pyridinium Iodides*.—A solution of the *N*-methyl-*X*-formylpyridinium iodide (0.5 g, 2 mmol), prepared by reaction of iodomethane and the corresponding pyridinecarboxaldehyde,[27] and 4-hydroxyaniline (0.22 g, 2 mmol) in ethanol (15 cm^3) to which a few drops of glacial acetic acid were added, was heated in a water-bath (80–90 °C) for 15 min. After cooling, the precipitated product was collected and recrystallized in absolute ethanol. In this way, the following *X*-substituted *N*-methylpyridinium iodides were prepared.

Compound **7** (X = 2). 80% Yield, m.p. 209–211 °C (Found: C, 46.0; H, 3.8; N, 8.0. $C_{13}H_{13}IN_2O$ requires C, 45.88; H, 3.82; N, 8.23%); δ_H([$^2H_6$]DMSO) 4.60 (3 H, s, N-Me), 6.85 (2 H, d, *J* 8, arom. CH *ortho* to OH), 7.55 (2 H, d, *J* 8, arom. CH *meta* to OH), 8.1–8.2 (1 H, m, py), 8.6–8.7 (1 H, m, 2 H, py) and 8.9–9.1 (2 H, m, HC=N and CH *ortho* to NMe).

Compound **8** (X = 3). 83% Yield, m.p. 200–202 °C (Found: C, 45.7; H, 3.8; N, 8.0); δ_H([$^2H_6$]DMSO) 4.25 (3 H, s, N-Me), 6.60 (2 H, d, *J* 8, arom. CH *ortho* to OH), 7.15 (2 H, d, *J* 8, arom. CH *meta* to OH), 7.8–8.1 (1 H, m, py), 8.5–8.9 (3 H, m, py) and 9.2 (1 H, s, CH=N).

Compound **9** (X = 4). 85% Yield, m.p. 225–227 °C (Found: C, 45.7; H, 3.8; N, 7.9); δ_H([$^2H_6$]DMSO) 4.35 (3 H, s, N-Me), 6.75 (2 H, d, *J* 8, arom. CH *ortho* to OH), 7.45 (2 H, d, *J* 8, arom. CH *meta* to OH), 8.40 (2 H, d, *J* 7, pyrid. CH *meta* to NMe), 8.90 (1 H, s, CH=N) and 9.1 (2 H, d, *J* 7, pyrid. CH *ortho* to NMe).

Solvato- and Halo-chromic Measurements.—All analytically pure solvents were further redistilled or dried over molecular sieves.

The *N*-methylpyridinium phenoxides **4**–**6** were generated *in* *situ* by the addition of a pellet of KOH to the organic solutions of the corresponding pyridinium iodides **7–9** (5×10^{-4}–10^{-3} mol dm^{-3}) in various solvents. Low polarity media sometimes required sonication for the generation of distinctly coloured solutions of the deprotonated compounds. In water, methanol and ethanol the hydroxide concentration was 10^{-3} mol dm^{-3}. Variation of this concentration in the aqueous or alcoholic solutions of the dyes had no effect on the position of the absorption band in the visible.

All coloured solutions thus prepared had their visible spectra immediately recorded.

For the halochromic measurements, salt solutions of different concentrations were prepared by dilutions of a stock solution of the dye containing the electrolyte. Dilutions were performed with a dye solution of the same concentration, which contained no salt.

Semiempirical calculations were performed on an Apollo *10000* computer, utilizing the MOPAC 6.0 and the SCF/CI ZINDO packages. Geometries were first optimized by means of the AM1 method.[28] The only imposed restriction was the planarity of the two aromatic rings. The optimized geometries were then fed into an INDO/CI program[29] that included a total of 199 configurations, arising from all possible one-electron excitations from the occupied MOs 23–40 into the virtual MOs 41–51. The dipolar structures of the imino dyes **4** and **5** were generated by optimization of the geometry of the dyes in the proximity (2 pm distance from the oxygen atom) of a point charge of +2.

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