PERKIN 2

Solvatochromic and halochromic properties of some phosphonioarylimino- and phosphonioarylazo-phenolate betaine dyes

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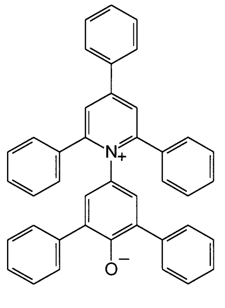
The synthesis and characterisation of two new solvatochromic phosphonium betaine systems is reported. Both 4-*N*-(*o*-triorganophosphoniobenzylidene) aminophenolate and 4-(*o*-triphenylphosphoniophenyl-azo)phenolate betaine dyes exhibit negative solvatochromism, consistent with a transition to a significantly less polar excited state. The solvatochromic properties of these compounds are compared with those of a related series of pyridinium iminophenolate betaines, and also with those of the Reichardt betaine dye. Cation-induced halochromism is also observed on treating acetonitrile solutions of the phosphonium betaine dyes with alkali halides.

Of the many compounds that exhibit some degree of solvatochromism, Reichardt's pyridinium *N*-phenoxide betaine dye (**1**)[1] is noteworthy for its exceptionally large negative solvatochromism effect in solvents of increasing polarity, and for the wide range of solvatochromic shifts exhibited. The longest-wavelength intramolecular charge-transfer absorption band is hypsochromically shifted by 9730 cm^{-1} (357 nm) on going from diphenyl ether ($\lambda_{max} = 810$ nm) to water ($\lambda_{max} = 453$ nm). This and related compounds have attracted much interest as indicators of solvent polarity,[2] and also because they exhibit other interesting effects such as halochromism, piezochromism and chiro-solvatochromism.[3] Compounds exhibiting solvatochromism are also of potential interest as systems which may exhibit non-linear optical properties under appropriate circumstances. In this paper, we report the synthesis and characterisation of two new types of solvatochromic systems, the *N*-(*o*-phosphoniobenzylidene)-4-aminophenolate betaine dyes **2**, and the related azo system **3**, which also exhibit a pronounced negative solvatochromic effect, and also exhibit halochromism. A comparison of the properties of **2** and **3** with those of the related *N*-methylpyridinium betaine dyes **4** is also presented.



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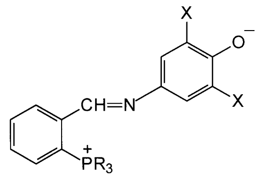

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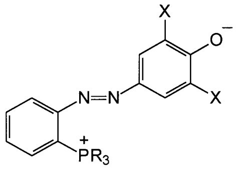

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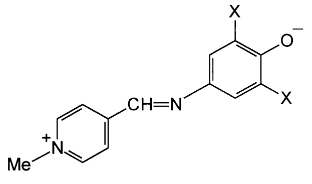

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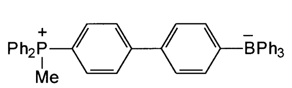
Few solvatochromic phosphonium betaine systems appear to have been described. The dipolar system **5** has been prepared and shown to exhibit a limited degree of solvatochromism.[4] The phosphonium phenolates **6** (R = Me or Ph) have also been characterised, and, although reported to show an intense charge-transfer absorption band in the visible region (λ_{max} 480–500 nm, in dichloromethane), their solvatochromic properties do not appear to have been studied.[5]



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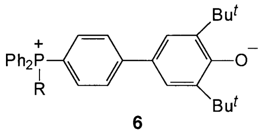

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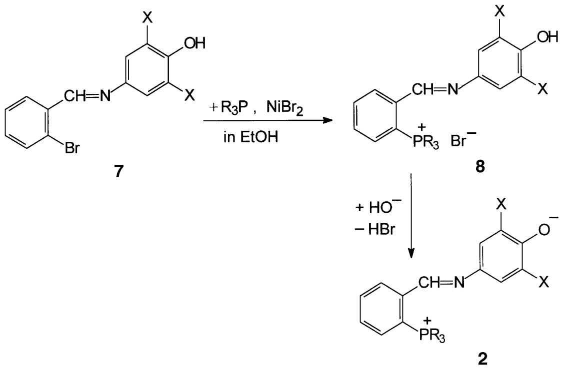
The synthetic route to the above phosphonio-iminophenolate betaine dyes **2** (R = Ph or Bu; X = Cl, Br, Ph or Bu^t) is shown in Scheme 1.



Scheme 1

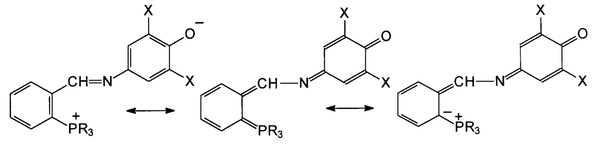
The iminophenol precursors **7** (X = Cl, Br, Ph or Bu^t) were easily accessible by the reactions of the appropriate 2,6-disubstituted 4-aminophenols with 2-bromobenzaldehyde in ethanol. Conversion to the related phosphonium salts **8** was accomplished under mild conditions in refluxing ethanol on treatment of the imines **7** with *either* triphenyl- *or* tributylphosphine in the presence of nickel(II) bromide as catalyst, the *o*-haloarylimine acting as a coordination template for the metal ion, which directs facile replacement of the *o*-halogen by phosphine *via* a kinetic template effect, as previously established for a range of related systems.[6] Treatment of the phosphonium salts **8** (usually yellow–brown solids) with aqueous alkali, followed by solvent extraction into dichloromethane, enabled the isolation of the betaine dyes **2** as a range of deep-red, purple or blue solids. Treatment of the betaine dyes in aqueous ethanol with dilute hydrochloric acid resulted in conversion to the parent phosphonium salts. Consistent with this formulation, the betaines gave a negative halide ion test on treatment with silver nitrate–nitric acid. All of the betaine dyes exhibited in solution negative solvatochromism, the position of the visible absorp-

Table 1 Long-wavelength UV–VIS absorption maxima of the phosphonium-iminophenolate betaine dyes **2** in eight solvents of different polarity

Solvent	λ_{max}/nm					
	R = Ph; X = Ph	R = Ph; X = Bu^t	R = Ph; X = Cl	R = Ph; X = Br	R = Bu; X = Cl	R = Bu; X = Br
Methanol	498	532	446	454	426	424
Ethanol	522	566	472	474	444	438
Acetonitrile	562	598	504	496	470	460
Acetone	604	628	536	534	504	502
Dichloromethane	596	616	532	532	510	508
Ethyl acetate	642	652	564	insol.	insol.	insol.
THF[a]	648	662	578	insol.	insol.	insol.
Toluene	686	insol.	insol.	insol.	insol.	insol.

[a] Tetrahydrofuran.

tion band moving towards shorter wavelength as the solvent polarity increased (Table 1). Thus, for example, the betaine dye **2** (R = Ph, X = Ph) appeared red in methanol (λ_{max} 498 nm), violet in acetonitrile, (λ_{max} 562 nm), purple in dichloromethane (λ_{max} 596 nm), blue in acetone (λ_{max} 604 nm) and green in toluene (λ_{max} 686 nm), giving a maximum frequency range of *ca.* 5500 cm^{-1}, approximately half that of the Reichardt betaine. The observation of negative solvatochromism reflects the stabilisation in the more polar solvents of the ground-state dipolar betaine form **2a**, relative to the less dipolar excited-state forms **2b** and **2c**, in which the dipolar ylidic form **2c** would be expected to be dominant, in view of the minimal d-orbital involvement in the bonding in formally pentacovalent but four-coordinate (λ^5–σ^4) phosphorus compounds.[7] The presence of phenyl substituents at phosphorus clearly shifts the absorption maximum to longer wavelengths, although the effect is not large. More significant is the effect of the groups flanking the oxygen atom bearing the negative charge, the less polar substituents (phenyl and *tert*-butyl) moving the absorption maximum towards longer wavelength by *ca.* 100 nm.



2a **2b** **2c**

For each of these compounds, a plot of the wavenumber relating to the longest wavelength visible absorption band against the normalised solvent polarity parameter E_T^N for the Reichardt betaine dye (Fig. 1) reveals a negative solvatochromic behaviour which correlates reasonably well with that observed for the Reichardt betaine.[2,3]

^{31}P NMR studies reveal that, on conversion of the phosphonium salts **8** to the respective betaines **2**, the phosphorus nucleus becomes shielded by 0.5–1.0 ppm. The ^{1}H NMR spectra also point to significant differences in the electronic environment on conversion to the betaines. In the triphenylphosphonium salts **8** (R = Ph), the protons *meta* to the phenol group appear as a sharp singlet at δ 6.10, as a result of shielding by the phenyl groups of the triphenylphosphonio moiety. [This effect is not observed in the related tributylphosphonio systems **8** (R = Bu), in which the signals of the two protons *meta* to the phenol group merge with those of the other aromatic protons in the range δ 7.0–7.5.] On conversion of the triphenylphosphonio salts to the related betaines, the above signal at δ 6.1 ppm disappears, these H-atoms then appearing as part of the aromatic multiplet between δ 7.0 and 8.8. In the triphenylphosphonio-salts and -betaines, the signal due to the imino CH cannot easily be discerned as a separate entity within the aromatic proton envelope. However, it is easily observed in the case of the tributylphosphonio systems as a singlet at δ 8.7–8.8; on

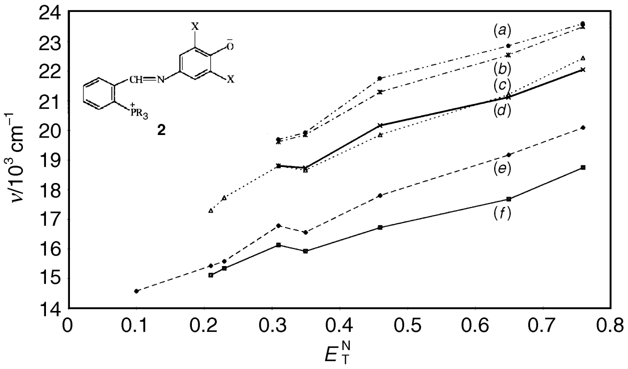
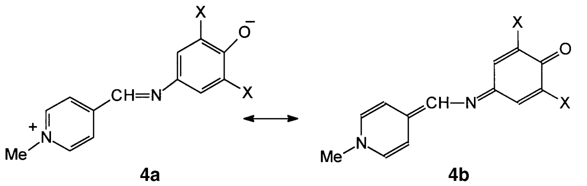


Fig. 1 Plot of wavenumber of longest wavelength visible absorption band of the phosphonium phenolate betaine dyes (**2**) against the normalised polarity parameter E_T^N. Key to compounds: (*a*) R = Bu, X = Br; (*b*) R = Bu, X = Cl; (*c*) R = Ph, X = Cl; (*d*) R = Ph, X = Br; (*e*) R = Ph, X = Ph; (*f*) R = Ph, X = Bu^t.

conversion to the related betaines, the imino proton becomes shielded by *ca.* 0.5 ppm, appearing at δ 8.3.

It was of interest to compare the solvatochromic properties of the above phosphonioiminophenolate betaines **2** with those of the pyridinium iminophenolate betaines **4**, for which the possibility of internal charge-transfer between the dipolar ground state **4a** and the less dipolar excited state **4b** would be expected to be more significant than in the above phosphonio-iminophenolate systems. The parent member of the pyridinium series **4** (X = H) has recently been prepared and shown to exhibit significant negative solvatochromism, in the range λ_{max} 473 nm (in water) to λ_{max} 672 nm (in chloroform), although some evidence was also presented of *reverse* solvatochromism in this compound in pure solvents of low polarity.[8]



4a **4b**

We have now prepared three further examples of this system, namely **4** (X = Cl, Br or Bu^t), in order to extend the comparison with our phosphonio-iminophenolates. These were prepared by the reaction of pyridine-4-carbaldehyde with the appropriate 2,6-disubstituted 4-aminophenol, followed by quaternisation with iodomethane at the pyridine nitrogen, and subsequent deprotonation with aqueous base to give the betaine dyes as blue–black solids. These exhibited negative solvatochromism when dissolved in solvents of increasing polarity (Table 2), although some evidence of irregular behaviour is shown by **4** (X = Bu^t). In the case of **4** (X = Cl or Br), the range of solvents able to be explored was smaller than for the above phosphonio-betaines, owing to the limited solubility of these pyridinium betaines in less polar solvents. Surprisingly, perhaps, the solvatochromic range of the phosphonioiminophenolate betaines is very similar to that of the pyridiniumiminophenolates, in spite of the assumed reduced possibilities for electron transfer in the former. However, the frequency range of these systems is considerably smaller than that exhibited by the Reichardt betaine dye **1**.

A plot of the wavenumber for the longest wavelength absorption band of the pyridinium betaines **4** (X = Cl, Br, H, Bu^t) against the Reichardt E_T^N parameters (Fig. 2) reveals a broadly similar trend for the dihalophenolates as for **4** (X = H). However, the di-*tert*-butylphenolate **4** (X = Bu^t) exhibits only a small negative solvatochromism in the more polar solvents, and then a significant trend to positive solvatochromism in the less polar solvents.

Table 2 Long-wavelength UV–VIS absorption maxima of the *N*-methyl-pyridinium-iminophenolate betaine dyes **4** in nine solvents of different polarity

	λ_{max}/nm			
Solvent	X = Cl	X = Br	X = Bu^t	X = H[8]
Methanol	510	512	616	513
Ethanol	540	540	618	543
Acetonitrile	578	572	634	607
Acetone	590	600	664	—
Dichloromethane	insol.	insol.	634	662
Chloroform	insol.	insol.	630	672
Ethyl acetate	insol.	insol.	626	651
THF	insol.	insol.	620	656
Toluene	insol.	insol.	610	—

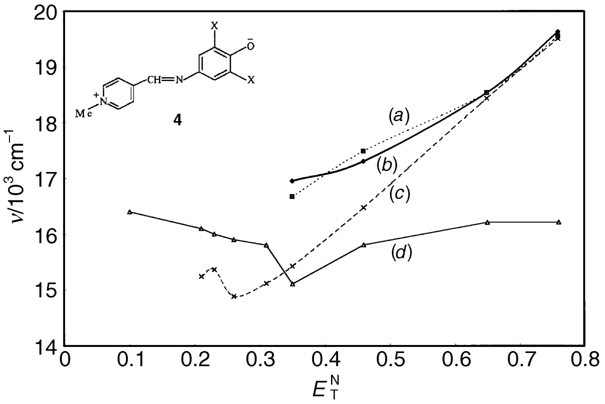
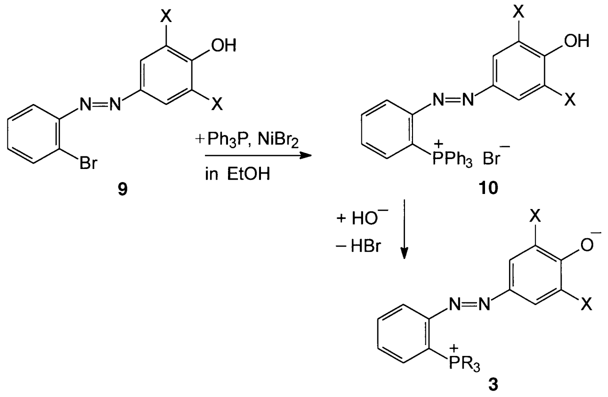


Fig. 2 Plot of wavenumber of longest wavelength visible absorption band of the pyridinium phenolate betaine dyes (**4**) against the normalised polarity parameter E_T^N. Key to compounds: (*a*) X = Br; (*b*) X = Cl; (*c*) X = H; (*d*) X = Bu^t.



Scheme 2

Table 3 Long-wavelength UV–VIS absorption maxima of the *o*-triphenylphosphoniophenylazophenolate betaine dyes **3** in four solvents of different polarity

	λ_{max}/nm		
Solvent	X = F	X = Cl	X = Me
Ethanol	508	514	550
Dichloromethane	548	548	568
Ethyl acetate	552	558	564
Toluene	566	572	570

Table 4 Halochromic properties of phosphonio- and pyridinium-phenolate betaine dyes in acetonitrile solution

Added salt	Concentration/mol dm^{-3}	λ_{max}/nm	$\Delta\lambda$/nm[a]
2 (R = Ph; X = Cl)			
Without salt	—	504	—
LiI	10^{-4}	476	28
LiI	2×10^{-4}	464	40
LiI	1×10^{-2}	458	46
LiI	10^{-1}	438	66
NaI	10^{-2}	478	26
NaI	10^{-1}	460	44
4 (X = Cl)			
Without salt	—	576	—
LiI	10^{-2}	518	58
LiI	10^{-1}	512	64
NaI	10^{-2}	556	20
KI	10^{-2}	572	4
3 (X = Cl)			
Without salt	—	534	—
LiI	10^{-2}	500	34
LiI	10^{-1}	498	36
NaI	10^{-2}	526	8
KI	10^{-2}	534	0

[a] $\Delta\lambda = \lambda_{max}$ (without salt) − λ_{max} (with salt).

Finally, we have also investigated the effect on solvatochromic properties of replacing the imino group in the phosphonioiminophenolates by the azo group, as in the phosphonioarylazophenolate betaines **3**. These were prepared as outlined in Scheme 2, the key step being the reaction of the *o*-bromodiarylazophenols **9** with triphenylphosphine in the presence of nickel(II) bromide in refluxing ethanol, again utilising the established kinetic template effect in systems of this type for the facile replacement of halogen by a trivalent phosphorus reagent,[9] to give the phosphonium salts **10**, which, on treatment with aqueous alkali, gave the betaine dyes **3** (X = F, Cl or Me) as deep red–black solids. On treatment with dilute hydrochloric acid, these were re-converted to the parent phosphonium salts. Consistent with their formulation, the betaines gave a negative halide ion test on treatment with silver nitrate–nitric acid. The phosphonioazophenolate betaines also exhibited negative solvatochromism (Table 3), but, compared to the related phosphonioiminophenolates, the solvatochromic range was not as great. Again, a shielding of the phosphorus nucleus of *ca.* 1 ppm was noted in the ^{31}P spectra of the betaines **3** relative to the parent salts.

All three types of betaine dyes (**2**–**4**) also exhibited halochromism on treatment with the alkali metal cations, Li$^+$, Na$^+$ and K$^+$ (as iodides) in acetonitrile solution. As the concentration of the metal salt increased, the visible absorption band shifted towards shorter wavelength consistent with stabilisation of the dipolar ground state *via* interaction of the phenolate centre with the metal cation (Table 4). As would be expected, the magnitude of the effect decreased in the order Li$^+$ > Na$^+$ > K$^+$, as the polarising power of the cation decreased.

Experimental

^{31}P and ^{1}H NMR studies were carried out using a Bruker AC250 FTNMR Spectrometer. Mass spectra were recorded on a VG Micromass 7070F instrument. Solvents were purified and dried by standard methods.

Preparation of imine intermediates

4-Amino-2,6-di-*tert*-butylphenol[10] and 4-amino-2,6-diphenylphenol[11] were prepared by literature methods. 4-Amino-2,6-dichlorophenol and 4-amino-2,6-dibromophenol were available commercially.

General procedure

The respective aminophenol and *either* 2-bromobenzaldehyde *or* pyridine-4-carbaldehyde (1 equiv.) were heated together in ethanol under nitrogen for 2–3 h. On cooling, the imine usually crystallised out of solution and was isolated by filtration. If no crystals appeared on cooling, the ethanolic solution was evaporated, and the residue triturated with light petroleum, prior to recrystallisation.

The following compounds were isolated.

***N*-(*o*-Bromobenzylidene)-4-amino-2,6-dichlorophenol.** Brown crystals (74%), mp *ca.* 155–156 °C (from dichloromethane–diethyl ether) (Found: C, 45.30; H, 2.45; N, 4.05. $C_{13}H_8ONCl_2$-Br requires C, 45.25; H, 2.35; N, 4.05%), $\delta_H(CDCl_3)$: 5.90 (s, 1H, OH); 7.2 (m, 4H); 7.7 (d, 1H); 8.2 (d, 1H); 8.9 (s, 1H, CH=N).

***N*-(*o*-Bromobenzylidene)-4-amino-2,6-dibromophenol.** Brown crystals (76%), mp *ca.* 116–118 °C (from dichloromethane–diethyl ether) (Found: C, 36.05; H, 1.95; N, 3.20. $C_{13}H_8ONBr_3$ requires C, 36.00; H, 1.85; N, 3.25%), $\delta_H(CDCl_3)$: 6.0 (s, 1H, OH); 7.3 (m, 4H); 7.7 (d, 1H); 8.2 (d, 1H); 8.8 (s, 1H, CH=N).

***N*-(*o*-Bromobenzylidene)-4-amino-2,6-di-*tert*-butylphenol.** Orange crystals (48%), mp *ca.* 109–110 °C (from acetonitrile) (Found: C, 65.00; H, 6.80; N, 3.50. $C_{21}H_{26}ONBr$ requires C, 64.95; H, 26.75; N, 3.60%), $\delta_H(CDCl_3)$: 1.2 (s, 18H); 5.2 (s, 1H, OH); 7.1 (s, 2H); 7.4 (m, 2H); 7.6 (d, 1H); 8.2 (d, 1H); 8.9 (s, 1H, CH=N).

***N*-(*o*-Bromobenzylidene)-4-amino-2,6-diphenylphenol.** White crystals (62%), mp *ca.* 124–126 °C (from ethanol–diethyl ether) (Found: C, 70.15; H, 4.20; N, 3.25. $C_{25}H_{18}ONBr$ requires C, 70.10; H, 4.25; N, 3.25%), $\delta_H(CDCl_3)$: 5.5 (s, 1H, OH); *ca.* 6.5–8.0 (m, 15H); 8.2 (d, 1H); 8.9 (s, 1H, CH=N).

***N*-(4-Pyridylmethylidene)-4-amino-2,6-dichlorophenol.** Brown crystals (93%), mp *ca.* 222–224 °C (from ethanol–diethyl ether) (Found: C, 54.15; H, 3.05; N, 10.45. $C_{12}H_8ON_2Cl_2$ requires C, 53.95; H, 3.00; N, 10.50%), $\delta_H(CD_3OD)$ 7.4 (s, 2H); 7.9 (d, 2H); 8.7 (m, 3H).

***N*-(4-Pyridylmethylidene)-4-amino-2,6-dibromophenol.** Brown–yellow crystals (65%), mp *ca.* 215–217 °C (from ethanol–diethyl ether) (Found: C, 40.40; H, 2.35; N, 7.75. $C_{12}H_8ON_2Br_2$ requires C, 40.50; H, 2.25; N, 7.85%), $\delta_H(CD_3OD)$ 7.6 (s, 2H); 7.9 (d, 2H); 8.5 (d, 1H); 8.7 (t, 2H).

***N*-(4-Pyridylmethylidene)-4-amino-2,6-di-*tert*-butylphenol.** Orange crystals (52%), mp *ca.* 201–203 °C (from acetonitrile) (Found: C, 77.20; H, 8.45; N, 9.05. $C_{20}H_{26}ON_2$ requires C, 77.40; H, 8.45; N, 9.00%), $\delta_H(CD_3OD)$ 1.6 (s, 18H); 7.2 (s, 2H); 7.9 (d, 2H); 8.7 (t, 3H).

Synthesis of *o*-bromophenylazophenols. *o*-Bromoaniline (1.5×10^{-2} mol) was dissolved in aqueous HCl (1 mol dm^{-3}; 45 ml) and then diluted with ice–water (60 ml), and the mixture cooled to *ca.* 0–5 °C. A solution of sodium nitrite (1.5×10^{-2} mol) in water (15 ml) was added dropwise to the cold acid solution over 10 min, with stirring. After the addition of *ca.* 90% of the sodium nitrite, the solution was tested with KI paper for the presence of excess nitrous acid. Sulfamic acid (*ca.* 1 g) was then added until the KI paper test was negative.

Meanwhile, the 2,6-disubstituted phenol (1.5×10^{-2} mol) in sodium hydroxide (1 mol dm^{-3}; 45 ml) was diluted with water (60 ml) and cooled to *ca.* 0–5 °C. The above diazonium solution was added slowly over 15 min, ensuring pH > 9 (*ca.* 30 ml of 2 M sodium hydroxide required). After the mixture had been stirred for 1 h, the pH was adjusted to *ca.* 7 with glacial acetic acid. This caused a brown or orange precipitate to form. This was filtered off and washed with water before drying in the air to give the crude solid, which was usually purified by recrystallisation from diethyl ether–light petroleum.

The following azo-dyes were isolated.

4-(*o*-Bromophenylazo)-2,6-difluorophenol. Brown crystals (81%), mp *ca.* 85–87 °C (from diethyl ether–light petroleum) (Found: C, 46.30; H, 2.30; N, 8.80. $C_{12}H_7ON_2BrF_2$ requires C, 46.05; H, 2.25; N, 8.95%), $\delta_H(CDCl_3)$: 5.6 (s, 1H, OH); *ca.* 7.5–8.5 (m, 6H).

4-(*o*-Bromophenylazo)-2,6-dichlorophenol. Brown crystals (94%), mp *ca.* 134–136 °C (from diethyl ether–light petroleum) (Found: C, 41.70; H, 2.10; N, 8.00. $C_{12}H_7ON_2BrCl_2$ requires C, 41.65; H, 2.05; N, 8.10%), $\delta_H(CDCl_3)$: 6.2 (s, 1H, OH); *ca.* 7.0–8.0 (m, 6H).

4-(*o*-Bromophenylazo)-2,6-dimethylphenol. Orange crystals (91%), mp *ca.* 130–131 °C (from diethyl ether–light petroleum) (Found: C, 55.35; H, 4.35; N, 8.90. $C_{14}H_{13}ON_2Br$ requires C, 55.10; H, 4.30; N, 9.20%), $\delta_H(CDCl_3)$: 2.2 (s, 6H); *ca.* 7.0–8.0 (m, 6H).

Synthesis of phosphonium salts and conversion to the related betaines

The appropriate *o*-bromophenyliminophenol (10^{-3} mol) or *o*-bromophenylazophenol (10^{-3} mol) was heated in ethanol (15 cm^3) with *either* triphenylphosphine *or* tributylphosphine (2×10^{-3} mol) and nickel(II) bromide (0.5×10^{-3} mol), under nitrogen, for 3–4 h. After cooling, the solution was poured into aqueous potassium bromide (10% w/v), and the phosphonium salt extracted into dichloromethane. Evaporation of the dried extract gave the crude salt, which, after repeated tituration with diethyl ether, was purified by recrystallisation or, sometimes, by conversion to the related phosphonium perchlorate by treatment with lithium perchlorate in aqueous methanol. For conversion to the related betaine dyes, the salts were dissolved in dichloromethane, and the solution shaken with dilute aqueous sodium hydroxide solution. After drying, the organic layer was evaporated to give the related phosphonium betaine dye, which was usually purified by recrystallisation. The following compounds were characterised.

2-(4-Hydroxy-2,6-dichlorophenyliminomethyl)phenyl(triphenyl)phosphonium bromide. This was obtained as brown solid, mp *ca.* 249–250 °C (from dichloromethane–diethyl ether). Perchlorate salt: Found: C, 59.51; H, 3.68; N, 2.21. $C_{31}H_{23}O_5NPCl_3$ requires: C, 59.40; H, 3.70; N, 2.23%, $\delta_P(CD_3OD)$ 27.0. $\delta_H(CD_3OD)$: 6.10 (2H, s), *ca.* 7.0–8.4 (19H, m), 8.50 (1H, CH=N, s). *m/z* (FAB) 526 (cation, M^+, ^{35}Cl).

***N*-[*o*-(Triphenylphosphonio)benzylidene]-4-amino-2,6-dichlorophenolate.** This was obtained as a red solid (59%), mp *ca.* 265–266 °C (from dichloromethane–diethyl ether) (Found: C, 68.70; H, 4.19; N, 2.63. $C_{31}H_{22}NPOCl_2{\cdot}H_2O$ requires C, 68.39; H, 4.44; N, 2.57%), $\delta_P(CD_3OD)$ 26.3. $\delta_H(CD_3OD)$ *ca.* 7.0–8.80 (22H, br m). *m/z* (FAB) 526 (cation, M^+).

2-(4-Hydroxy-2,6-dibromophenyliminomethyl)phenyl(triphenyl)phosphonium bromide. This was obtained as brown solid, mp 222–223 °C (from dichloromethane–diethyl ether). Perchlorate salt. Found: C, 52.10; H, 3.24; N, 1.96. $C_{31}H_{23}O_5N$-$PClBr_2$ requires C, 52.02; H, 3.24; N, 1.96%. $\delta_P(CD_3OD)$ 27.0. $\delta_H(CD_3OD)$ 6.30 (2H, s), *ca.* 7.0–8.70 (20H, brm). *m/z* (FAB) 618 (100%, cation, M^+, ^{81}Br).

***N*-[*o*-(Triphenylphosphonio)benzylidene]-4-amino-2,6-dibromophenolate.** This was obtained as a red solid, mp *ca.* 239–241 °C (from dichloromethane–diethyl ether) (Found: C, 58.24; H, 3.69; N, 2.14. $C_{31}H_{22}NPBr_2{\cdot}H_2O$ requires C, 58.79; H, 3.82; N, 2.21%), $\delta_P(CD_3OD)$ 26.3. $\delta_H(CD_3OD)$ *ca.* 7.0–8.60 (22H, br m). *m/z* 618 (100%, cation, M^+, ^{81}Br).

2-(4-Hydroxy-2,6-di-*tert*-butylphenyliminomethyl)phenyl(triphenyl)phosphonium bromide. This was obtained as green–yellow crystals (85%), mp *ca.* 239–241 °C (from dichloromethane–diethyl ether). Perchlorate salt. Found: C, 69.41; H, 6.31; N, 2.08. $C_{39}H_{41}O_5NPCl$ requires C, 69.9; H, 6.17; N, 2.09%, $\delta_P(CD_3OD)$ 26.2. $\delta_H(CDCl_3)$ 1.5 (18H, s), 5.20 (1H, OH, s), 6.10 (2H, s), *ca.* 7.0–8.50 (20H, m). *m/z* (FAB) 570 (100% cation, M^+).

***N*-[*o*-(Triphenylphosphonio)benzylidene]-4-amino-2,6-di-*tert*-butylphenolate.** This was obtained as a blue solid, mp *ca.* 231–232 °C (from dichloromethane–diethyl ether) (Found: C, 80.53; H, 7.02; N, 2.36. $C_{39}H_{40}ONP{\cdot}H_2O$ requires C, 79.7; H, 7.2; N, 2.38%), $\delta_P(CD_3OD)$ 25.4. $\delta_H(CDCl_3)$ 1.5 (18H, m), 6.0 (2H, s), *ca.* 7.0–8.0 (20H, m). *m/z* (FAB) 570 (100%, cation, M^+).

2-(4-Hydroxy-2,6-diphenylphenyliminomethyl)phenyl(triphenyl)phosphonium bromide. This was obtained as yellow crystals (57%), mp *ca.* 270–272 °C (from dichloromethane–diethyl ether) (Found: C, 74.35; H, 4.72; N, 2.02. $C_{43}H_{33}BrNOP$ requires: C, 74.78; H, 4.82; N, 2.03%), $\delta_P(CDCl_3)$ 25.6. $\delta_H(CDCl_3)$ 5.5 (1H, s, OH), *ca.* 7.0–8.2 (31H, m), 8.7 (1H, s, CH=N).

_N_-[_o_-(Triphenylphosphonio)benzylidene]-4-amino-2,6-diphenylphenolate. This was obtained as a blue solid, mp *ca.* 175–178 °C (from dichloromethane–diethyl ether) (Found: C, 80.10; H, 5.23; N, 2.15. $C_{43}H_{32}ONP{\cdot}2H_2O$ requires C, 79.98; H, 5.62; N, 2.17%), $\delta_P(CDCl_3)$ 25.60. $\delta_H(CDCl_3)$ 7.0–8.5 (ArH, m).

2-(4-Hydroxy-2,6-dichlorophenyliminomethyl)phenyl(tributyl)phosphonium bromide. This was obtained as a yellow–brown solid (58%), mp *ca.* 206–208 °C (from dichloromethane–diethyl ether) (Found: C, 55.55; H, 6.50; N, 2.55. $C_{25}H_{35}ONPCl_2Br$ requires C, 54.86; H, 6.45; N, 2.56%), $\delta_P(CD_3OD)$ 33.50. $\delta_H(CD_3OD)$ *ca.* 1.0–3.0 (br m, 27H), *ca.* 7.0–7.5 (6H, m, ArH), 8.7 (1H, CH=N, s). *m/z* (FAB) 467 (100%, cation, M^+, ^{35}Cl).

_N_-[_o_-(Tributylphosphonio)benzylidene]-4-amino-2,6-dichlorophenolate. This was obtained as an orange solid, mp *ca.* 220–221 °C (from dichloromethane–diethyl ether) (Found: C, 64.24; H, 7.45; N, 2.96. $C_{25}H_{34}ONPCl_2$ requires C, 64.38; H, 7.35; N, 3.00%), $\delta_P(CD_3OD)$ 32.2. $\delta_H(CD_3OD)$ *ca.* 1.0–3.0 (27H, br m), *ca.* 7.0–7.5 (6H, m), 8.3 (1H, s). *m/z* (FAB) 467 (100%, cation, M^+, ^{35}Cl).

2-(4-Hydroxy-2,6-dibromophenyliminomethyl)phenyl(tributyl)phosphonium bromide. This was obtained as a brown solid (62%), mp *ca.* 202–203 °C (from dichloromethane–diethyl ether) (Found: C, 47.22; H, 5.60; N, 2.18. $C_{25}H_{35}ONPBr_3$ requires C, 47.47; H, 5.42; N, 2.22%), $\delta_P(CD_3OD)$ 33.6. $\delta_H(CD_3OD)$ *ca.* 1.0–3.0 (br m, 27H), *ca.* 7–7.5 (6H, m), 8.8 (1H, CH=N, s). *m/z* (FAB) 559 (100%, cation, M^+, ^{81}Br).

_N_-[_o_-Tributylphosphonio)benzylidene]amino-2,6-dibromophenolate. This was obtained as a brown solid, mp *ca.* 221–222 °C (from dichloromethane–diethyl ether) (Found: C, 53.90; H, 6.32; N, 2.42. $C_{25}H_{34}ONPBr_2$ requires C, 54.07; H, 6.17; N, 2.52%), $\delta_P(CD_3OD)$ 32.20. $\delta_H(CD_3OD)$ *ca.* 1.0–3.0 (27H, br m), *ca.* 7.0–8.5 (6H, m), 8.3 (1H, s). *m/z* (FAB) 559 (100%, cation, M^+, ^{81}Br).

2-(4-Hydroxy-2,6-difluorophenylazo)phenyl(triphenyl)phosphonium bromide. A red solid, mp 275–277 °C (Found: C, 62.60; H, 4.00; N, 4.60. $C_{30}H_{22}BrF_2ON_2P$ requires C, 62.60; H, 3.85; N, 4.85%), $\delta_P(CDCl_3)$: 23.7. $\delta_H(CDCl_3)$: 5.0 (1H, s, OH); 6.5–8.5 (m, 21ArH).

4-[_o_-(Triphenylphosphonio)phenylazo]-2,6-difluorophenolate. A deep-red solid, mp >300 °C (Found: C, 73.00; H, 4.40; N, 5.45. $C_{30}H_{21}F_2ON_2P$ requires C, 72.85; H, 4.30; N, 5.65%), $\delta_P(CDCl_3)$: 22.0. $\delta_H(CDCl_3)$: 6.2 (s, 2H), 7.5 (m, 19ArH).

4-[_o_-(Triphenylphosphonio)phenylazo]-2,6-dichlorophenolate. A red solid, mp 290–293 °C (Found: C, 68.65; H, 4.10; N, 5.25. $C_{30}H_{21}Cl_2ON_2P$ requires C, 68.3; H, 4.00; N, 5.30%), $\delta_P(CDCl_3)$: 22.6. $\delta_H(CDCl_3)$ 7.0–8.5 (ArH, m).

2-(4-Hydroxy-2,6-dimethylphenylazo)phenyl(triphenyl)phosphonium perchlorate. A red solid, mp 200–203 °C (Found: C, 65.65; H, 4.85; N, 4.65. $C_{32}H_{28}O_5N_2PCl$ requires C, 65.50; H, 4.80; N, 4.75%), $\delta_P(CD_3OD)$: 2.42. $\delta_H(CD_3OD)$: 6.7 (s, 2ArH); 7.5–8.2 (m, 19ArH).

4-[_o_-(Triphenylphosphonio)phenylazo]-2,6-dimethylphenolate. A black solid, mp 253–255 °C (Found: C, 78.75; H, 5.70; N, 5.65. $C_{32}H_{27}ON_2P$ requires C, 79.00; H, 5.60; N, 5.75%), $\delta_P(CD_3OD)$ 23.4. $\delta_H(CD_3OD)$: 2.0 (s, 6H, CH_3), 6.5–8.0 (m, 21ArH).

Preparation of 4-(4-hydroxyphenyliminomethyl)-_N_-methylpyridinium salts and related betaine dyes

The respective 4-pyridyl imino phenol (4×10^{-3} mol) and iodomethane (4.4×10^{-3} mol) in ethanol were heated under reflux under nitrogen for *ca.* 4–5 h. After cooling, the precipitated product was collected and recrystallised from ethanol (or dichloromethane)–diethyl ether. In some cases, if the salt was still impure after recrystallisation, it was necessary to convert the salt to the corresponding perchlorate by treatment of an aqueous methanolic solution of the salt with aqueous lithium perchlorate.

The purified salt was dissolved in dichloromethane and shaken with several portions of dilute sodium hydroxide solution. After drying, the organic layer was evaporated to give the corresponding betaine dyes, which were usually purified by recrystallisation. If the salt was insoluble in dichloromethane, it was dissolved in acetonitrile (warming if necessary) and heated with 1 equiv. of DBU. The solution was stirred for 0.5 h and then filtered to isolate the corresponding betaine dyes.

The following compounds were characterised.

4-(4-Hydroxy-2,6-dichlorophenyliminomethyl)-_N_-methylpyridinium iodide. Brown solid (71%), mp 269–270 °C (from ethanol–diethyl ether) (Found: C, 38.00; H, 2.70; N, 6.75. $C_{13}H_{11}ON_2Cl_2I$ requires C, 38.15; H, 2.70; N, 6.85%), $\delta_H(CD_3OD)$ 4.5 (d, 3H); 7.6 (s, 1H); 8.2 (d, 2H); 8.5 (d, 1H); 9.0 (m, 3H).

4-(4-Hydroxy-2,6-dibromophenyliminomethyl)-_N_-methylpyridinium iodide. Brown solid (70%), mp 204–206 °C (from ethanol–diethyl ether) (Found: C, 31.55; H, 2.25; N, 5.55. $C_{13}H_{11}ON_2Br_2I$ requires C, 31.35; H, 2.25; N, 5.60%), $\delta_H(CD_3OD)$ 4.5 (d, 3H); 7.8 (s, 1H); 8.2 (d, 2H); 8.5 (d, 1H); 8.8 (t, 2H); 9.0 (d, 1H).

4-(4-Hydroxy-2,6-di-_tert_-butylphenyliminomethyl)-_N_-methylpyridinium perchlorate. Brown solid (61%), mp *ca.* 232–234 °C (from dichloromethane–diethyl ether) (Found: C, 57.80; H, 6.60; N, 6.20; $C_{21}H_{29}O_5N_2Cl{\cdot}H_2O$ requires C, 56.95; H, 7.05; N, 6.30%), $\delta_H(CD_3OD)$ 1.4 (m, 18H); 4.5 (s, 3H); 7.4 (s, 2H); 8.5 (d, 2H); 8.9 (t, 3H).

4-(_N_-Methylpyridinium-4-ylmethylideneamino)-2,6-dichlorophenolate. Black solid, mp *ca.* 224–226 °C (from ethanol–diethyl ether) (Found: C, 54.70; H, 3.75; N, 10.00. $C_{13}H_{10}ON_2Cl_2$ requires C, 55.55; H, 3.60; N, 9.95%), $\delta_H(CD_3OD)$ 4.2 (s, 3H); 7.6 (m, 3H); 8.6 (m, 4H).

4-(_N_-Methylpyridinium-4-ylmethylideneamino)-2,6-dibromophenolate. Black solid, mp *ca.* 214–216 °C (from ethanol–diethyl ether) (Found: C, 42.30; H, 3.00; N, 7.85. $C_{13}H_{10}ON_2Br_2$ requires C, 42.20; H, 2.70; N, 7.50%), $\delta_H(CD_3OD)$ 3.5 (m, 3H); 7.6 (s, 2H); 7.8 (d, 2H); 8.6 (t, 3H).

4-(_N_-Methylpyridinium-4-ylmethylideneamino)-2,6-di-_tert_-butylphenolate. Blue solid, mp *ca.* 199–202 °C (from dichloromethane–diethyl ether) (Found: C, 74.10; H, 8.40; N, 8.05. $C_{21}H_{28}ON_2{\cdot}H_2O$ requires C, 73.65; H, 8.85; N, 8.20%), $\delta_H(CD_3OD)$ 1.4 (m, 18H); 4.0 (m, 3H); 7.4 (s, 2H); 7.7 (d, 2H); 8.0 (t, 3H).

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