New solvatochromic and halochromic phosphonium betaine dyes.

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New Solvatochromic and Halochromic Phosphonium Betaine Dyes

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ABSTRACT

This thesis is concerned with the synthesis and characterisation of three new types of solvatochromic systems, the 4-N-(o-phosphoniobenzylidene)aminophenolate betaines, the 4-(o-triphenylphosphoniophenylazo) phenolate betaines, and a comparison with the related 4-methyl(or hexadecyl)pyridinium-4-methylidene iminophenolate betaines. The coordination template effect in the nickel-catalysed formation of arylphosphonium salts has been reviewed and applied in the synthesis of the phosphonium betaine dyes. The structural confirmation of these betaine dyes was carried out by NMR and mass spectral analyses, together with the results of microanalysis.

The solvatochromic behaviour of these dyes was investigated in detail by dissolution in a range of organic solvents and measurement of their longest-wavelength absorption bands using UV/Visible spectroscopy, which revealed that the phosphoniophenolate betaines have the possibility of two structures, e.g., the dipolar betaine form and a less polar form. The effects of substituents on their solvatochromic properties have also been discussed. Most of the betaines studied display highly negative solvatochromism as the solvent polarity increases, and their absorption maxima are linearly related with the standard E_T^N values for the Reichardt betaine, which suggests a possible application of these betaines prepared as indicators of solvent polarity. However a few of the N-alkyl pyridinium betaines exhibited an unusual reverse solvatochromism effect.

The negative halochromic behaviour of selected betaines has also been studied, a hypsochromic shift of the long-wavelength CT absorption band being observed on addition of salts.

The ability of representative members of a family of N-hexdecylpyridinium imino- phenolate betaines prepared in this study to form Langmuir-Blodgett films has been explored by Prof.G.Ashwell (Cranfield Univ.). Non-linear optical properties of such films have been observed, together with other properties that may form the basis of sensor techniques.

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1.1 . Solvent Polarity

It is well known that solvents have a strong influence on reaction rates and chemical equilibria as well as on the position of spectral absorption maxima[1]. Usually, chemists have tried to understand solvent effects in terms of the so-called solvent polarity, which is not easy to define precisely or to express quantitatively. The simplicity of idealised electrostatic solvation models has led to the use of parameters such as the dielectric constant ($\in_r$), permanent dipole moment (μ), refractive index (n), or functions thereof. However, this procedure is often inadequate because the intermolecular interactions are much more complicated. In addition to non-specific interactions such as electrostatic forces arising from coulombic effects between charged ions and dipolar molecules (i.e.ion-ion, ion-dipole, dipole-dipole interactions) and polarization forces arising from dipole moments induced in molecules by nearby ions or dipolar molecules (i.e.ion-nonpolar molecule, dipolar-nondipolar molecule, two nonpolar molecules), there exist also specific interactions such as hydrogen bonding, and electron-pair donor(EPD)/electron-pair acceptor (EPA) forces [2].

Therefore, from a more practical point of view, Reichardt defined solvent polarity as "the overall solvation capability (or solvent power) of a solvent"[3], which in turn depends on the action of all possible non-specific and specific, intermolecular interactions between solute ions or molecules and solvent molecules, excluding those interactions leading to definite chemical alterations of the solute molecules[2].

1.2. Solvatochromism and solvatochromic compounds[1]

The inadequacy of defining solvent polarity in terms of simple physical parameters has led to the establishment of so-called empirical scales of solvent polarity by means of UV/Visible spectroscopic measurements in solution[1, 4]. A common approach is to assume that some particular equilibrium, reaction rate, or spectral absorption is a suitable model for other solvent-dependent processes. Various empirical solvent polarity scales have been developed in this way. In order to establish empirical scales of solvent polarity, chemists have investigated compounds that exhibit different colours in different solvents, resulting in a change in the position of a UV-Visible absorption band by the medium. This efffect called solvatochromism.

The term solvatochromism refers to the shift of an electronic absorption band of a solute when the polarity of the solvent is varied. It is caused by differential solvation of the ground and first excited state of the light-absorbing molecule.

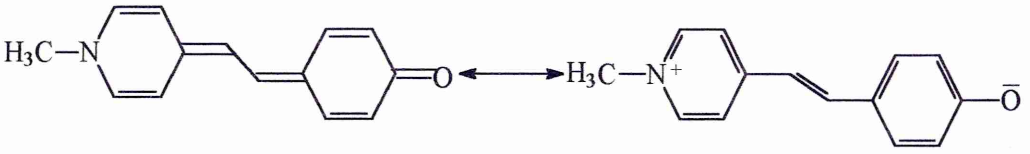
If, with increasing solvent polarity, the ground-state molecule is better stabilised by solvation than the molecule in the first excited state, negative solvatochromism will result. Or vice versa, better stabilisation of the molecule in the first exited state relative to that in the ground state, with increasing solvent polarity, will lead to positive solvatochromism. The " first excited state" means the so-called Frank-

Condon excited state[5] with the same solvation pattern as the corresponding ground state, whereas the ground state corresponds to an equilibrium ground state.

Negative solvatochromism involves the longest-wavelength absorption band shifting towards the blue region of the spectrum with increasing solvent polarity. It is also described as a hypsochromic shift. Positive solvatochromism involves the longest-wavelength absorption band shifting towards the red region. This is also termed a bathochromic shift.

The solvatochromism observed depends on the chemical structure and physical properties of chromophore and the solvent molecules. In general, dye molecules with a large change in their permanent dipole moment upon excitation exhibit a strong solvatochromism. If the solute dipole moment increases during the electronic transition ($\mu_g < \mu_e$), positive solvatochromism normally results. In the case of a decrease of the solute dipole moment upon excitation ($\mu g > \mu e$), negative solvatochromism is usually observed. Solutes with this solvatochromic behaviour can be commonly found among so-called meropolymethine dyes (particularly among merocyanine dyes) and among compounds with inter- or intramolecular charge transfer (CT) absorption[1].

Solvatochromic dyes generally have steady positive or negative solvatochromism. However, the existence of reverse solvatochromism has been proposed in various papers[6]. For example, the merocyanine dye 4-[2-methyl-4-pyridinio) ethenyl] phenolate (1) shows a particularly interesting reverse solvatochromism. As the solvent polarity increases, it first exhibits a bathochromic shift of +762cm^{-1} (28nm) from cyclohexane (592nm) to chloroform (620nm) and then a hypsochromic shift of -5733cm^{-1} (178nm) from chloroform (620nm) to water (442nm)[6a].



(A) (B)

(1)

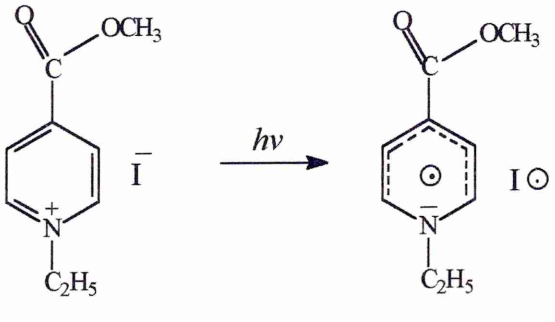
This surprising reversed solvatochromism indicates clearly that the ground-state electronic structure of this dye changes, with increasing solvent polarity, from the quinonoid structure (A) to the benzenoid structure (B), i.e., in solvents of low polarity, the nonpolar form (A) will predominate and the dipolar form (B) becomes stable in polar media. In agreement with this reverted solvatochromism for the $\pi \rightarrow \pi^*$ transition, the dipole moments of the ground and excited states are in the following order: $\mu_g < \mu_e$ in nonpolar solvents and $\mu_g > \mu_e$ in polar solvents.

Because of the simplicity of UV/Vis/near-IR spectroscopic measurements, empirical parameters of solvent polarity have been preferably determined by means of solvatochromic compounds. The first suggestion that solvatochromic dyes should be used as indicators of solvent polarity was made by Brooker *et al*, who defined the

χ_R and χ_B scales[7]. However, Kosower was the first to set up an empirical solvent scale, the Z-scale[8]. Other scales which have been described include: the π* scale of Kamlet et al.[9], the PRM scale of Dahne *et al.*[10], the π*azo scale of Buncel *et al.*[11], the Ps scale of Middleton *et al.*[12], the $E_T(30)$ scale of Dimroth and Reichardt[13], the E_k scale of Walther[14], the ϕscale of Dubois *et al.*[15], the S scale of Zelinskii *et al.*[16] and the E_B scale of Wrona *et al.*[17].

Of the many types of compounds studied, four have been proved to be particularly good models for the empirical determination of solvent parameters because of their pronounced solvatochromic properties:

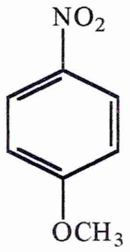
a)The Z scale of Kosower was obtained from the intermolecular charge-transfer (CT) transitions absorption using the negatively solvatochromic 1-ethyl-4-methoxycarbonyl pyridinium iodide (2) as a reference substance. The longest wavelength band of the ground-state ion-pair complex of this compound corresponds to an intramolecular transfer of an electron from the iodide to the pyridinium ion .



(2)

In methanol , this dye has a maximum at 342nm (29230cm^{-1}) and in pyridine, it has a maximum at 430nm (23270cm^{-1}), a shift of -5960cm^{-1}(88nm).

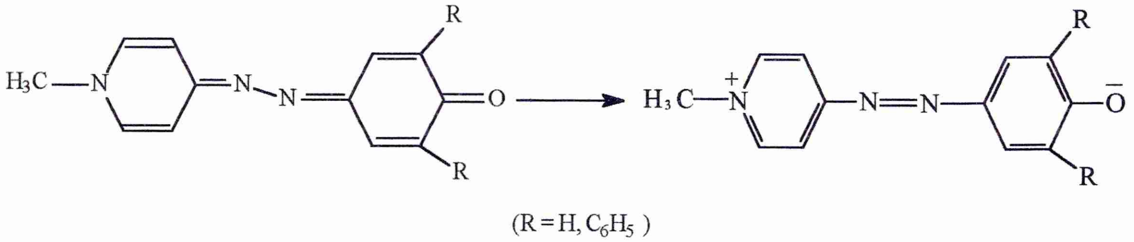
b) The π* scale of Kamlet was based on solvent-induced shifts of the long-wavelength π → π* absorption bands of seven nitroaromatic indicators such as 4-methoxynitrobenzene (3) , 4-(diethylamino)-nitrobenzene etc. This electronic transition is connected with an intermolecular charge transfer from the electron-donor part (OMe, NR_2, alkyl) to the acceptor part (NO_2, COC_6H_5) through the aromatic system.



(3)

For compound (3), its longest-wavelength intermolecular absorption band is shifted by +2400cm^{-1}(22nm) on going from cyclohexane (293nm, 34120cm^{-1}) to dimethyl sulfoxide (315nm, 31720cm^{-1}). Hence, the first exited state is more dipolar than the ground state, with the observed positive solvatochromism as a consequence.

c). The new π^*_{azo} scale of Buncel was based on six positively-solvatochromic azo merocyanine dyes such as the 4-(1-methylpyridiniumazo)-2,6-disubstituted phenolate (4) as primary indicators.

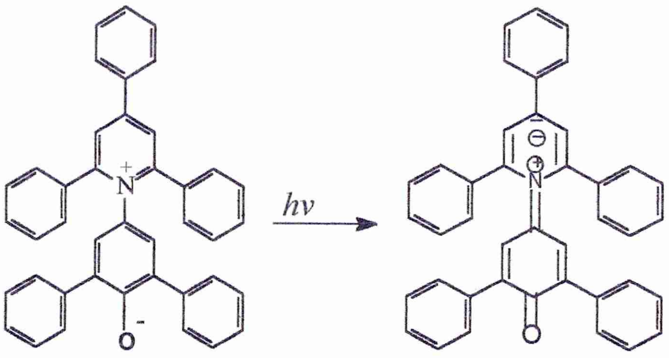


(4)

A comparison of the π^* scale of Kamlet with the π^*_{azo} scale of Buncel shows that π^* and π^*_{azo} are not equal, but satisfactorily linearly correlate with each other.

d). The E_T (30) scale of Reichardt was obtained from the longest wavelength UV/Vis absorption of the pyridinium N-phenoxide betaine (5). It is the basis of the more successful approaches to solvent polarity and is widely used.

The negatively solvatochromic pyridinium N-phenoxide betaine dye (Reichardt dye) exhibits one of the largest solvatochromic effects ever observed; Its long-wavelength intermolecular charge-transfer (CT) absorption band is shifted by $-9730 cm^{-1}$ (357nm) on going from water (λ=453nm) to diphenyl ether (λ=810nm). Solutions of the Reichardt dye are red coloured in methanol, violet in ethanol, blue in isoamyl alcohol, green in acetone, and yellow in anisole, thus comprising the whole visible region and allowing even a visual estimation of the solvent polarity.



(A: μg =15D) >> (B: μe=6D)

(5)

This outstanding negative solvatochromism stems from the unequal, differential solvation of its highly dipolar zwitterionic ground state (A) relative to its less dipolar first exited state (B), in agreement with a considerable charge transfer from the phenolate to the pyridinium part of the molecule.

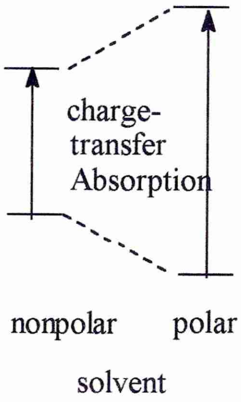
This extraordinary large solvent-induced shift of the visible $\pi \rightarrow \pi^*$ absorption band of intermolecular charge-transfer character has been used to introduce an empirical parameter of solvent polarity, called the E_T (30) value. The E_T (30) values are simply defined as the molar electronic transition energies of the Reichardt dye (see scheme 1), dissolved in the solvent and measured in kcal/mol at room temperature (25°C) and normal pressure(bar), according to eq(1) [13]:

$$E_T(30)(\text{kcalmol}^{-1}) = hc\nu_{max} N_A = (2.8591\times10^{-3})\nu_{max}(\text{cm}^{-1})$$

$$= 28591/\lambda_{max}(\text{nm}) \qquad (1)$$

where h is Planck's constant, c is the speed of light in a vacuum, N is Avogadro's number, and v_{max} and λ_{max} are, respectively, the frequency and wavelength of the intermolecular charge-transfer $\pi \rightarrow \pi^*$ absorption band of Reichardt's dye. The molar transition energy E_T will be used in the present work to compare various indicator-solvent media interactions.

Scheme 1-1



$ET(30) = h\,c\,v\,NA$

= molar Transition Energy

The $E_T(30)$ ranges from 63.1kcal/mol for water , as the most polar solvent , to 30.7kal/mol for tetramethylsilane(TMS), as least polar solvent. A high $E_T(30)$ value corresponds to high solvent polarity.

In order to avoid recalculation of $E_T(30)$ values from kcal/mol into kJ/mol, a normalised and dimensionless E_T^N value was introduced and defined according to eq(2)[18], using water and tetramethylsilane(TMS) as extreme polar and nonpolar solvents, respectively.

$$E_T^N = \frac{E_T(\text{solvent}) - E_T(\text{TMS})}{E_T(\text{water}) - E_T(\text{TMS})} = \frac{E_T(\text{solvent}) - 30.7}{32.4} \qquad (2)$$

The E_T^N scale ranges from 0.00 for TMS to 1.00 for water. The higher the E_T^N value, the more polar the solvent.

The $E_T(30)$ value as well as the E_T^N value can be equally used. The $E_T(30)$ value gives an immediate insight of the solvent polarity. However, E_T^N values are easier to handle, particularly in multiparameter correlation equations.

According to the $E_T(30)$ and E_T^N values, organic solvents can be roughly divided into three groups:[1]

a). HBD(H-bonding donor)or"protic"solvents: $E_T(30)$:47~63kcal/mol; E_T^N :0.5~1.0. For example, $E_T(30)$ of ethanol is 51.9 kcal/mol and E_T^N is 0.710.

b). Dipolar non-HBD or "aprotic"solvents: $E_T(30)$: 40~47 kcal/mol; E_T^N : 0.3~0.5. For example, $E_T(30)$ of acetone is 42.2kcal/mol and E_T^N is 0.355.

c). Apolar non-HBD solvents: $E_T(30)$: 30~40kcal/mol; E_T^N : 0.0~0.3. For example, $E_T(30)$ of ethyl acetate is 38.1 kcal/mol and E_T^N is 0.228.

Because of their solvatochromic properties, many betaine dyes have been proposed and used as solvent polarity indicators.

For example, the empirical parameter $E_T(30)$ based on the Reichardt dye has found manifold applications in the study of solvent effects, not only for pure solvents[19], but also for numerous binary solvent mixtures[1, 20], for aqueous and non-aqueous electrolyte solutions[21], for microheterogeneous solutions such as micelles, vesicles, phospholipid bilayers, surfactants, tensides[22], and for the characterisation of the polarity of polymers[23] and of chromatographic materials[24].

Recently, betaine dyes such as the Reichardt dye have been proposed as sensitive materials in chemical sensors for solvent vapour detection[25].

The combined use of optical fibres and chemical indicators has led to a new class of optical sensors called solvatochromic-based fibre optic chemical sensors(FOCS)[26]. In these devices , a solvatochromic dye such as the Reichardt dye is immobilised on the tip of an optical fibre or used as its cladding. When a FOCS is introduced into a liquid or gaseous medium to be analysed, the chemical solvatochromic agent undergoes a reaction and generates an optically detectable modification which is characteristic of the chemical composition of the analyte.

A solvatochromic dye-doped polymer can also be used as an indicator in an analytical system. For example, a method for the *in situ* detection of polar additives such as methanol in hydrocarbon blends has been developed by Hubert *et al*[27]by using the well known solvatochromic effect. In this technique, a dye-doped polymer film in which the Reichardt dye was selected as the solvatochromic chemical detector and poly (methyl methacrylate) (PMMA)as the matrix was prepared by spin-coating onto glass slides. It has a high solvatochromic sensitivity towards polar additives in hydrocarbon blends. These polymer films also have the required properties to design a fibre optical chemical sensor(FOCS) based on the solvatochromic effect.

The solvatochromic approach was also extended to characterise solid polymers as solvent phases by preparing thin films of the polymers with dissolved dyes and measuring the UV-visible absorption spectra of the films[28]. The resulting solvatochromic measures of dipolarity/ polarizability, hydrogen-bond acidity and hydrogen bond basicity show great potential for determining the solubility and sorption properties of polymers with gaseous, liquid, and solid solutes, as well as with bulk liquid solvents.

It should be noticed that while there are many solvatochronic compounds, only a few of them have been proposed as solvent polarity indicators. It is not easy to draw a distinct line between solvatochromic compounds in general and those which have been occasionally proposed as potential solvent polarity indicators. According to Reichardt[29], a solvatochromic compounds used to establish solvent polarity scales should meet the following requirements:

a) It should be easily available.

b) It should be a crystalline compound of definite chemical structure.

c) It should possesses sufficient solubility in most of solvents.

d) No chemical reactions should occur with the solvent.

e) The longest wavelength UV/Vis absorption band should be shifted bathochromically or hypsochromically with increasing solvent polarity to as great an extent as possible.

f) The molar decadic extinction coefficient of the solvatochromic absorption band should be sufficiently large.

g) The solvatochromic absorption band should be preferably located within the visible region.

h) The chemical structure of the indicator compound should be of the kind for which all important nonspecific and specific probe/solvent interactions should be possible.

The number of different solvent polarity scales can be reduced by finding that some of these scales are interrelated with each other. Many of the empirical parameters of solvent polarity derived from similar probe molecules are linearly correlated to each other. A useful solvent scale should at least include representative examples of all different solvent classes.

1.3 Thermochromism, Piezochromism, Halochromism[1, 30].

In principle, all solvatochromic compounds should also exhibit the phenomena of thermo-solvatochromism, piezo-solvatochromism, halochromism and chiro-solvatochromism i.e. the position of the long -wavelength CT absorption band of the dissolved compound depends not only on the polarity of solvent, but also on the temperature of the solution[31], the external pressure applied to the solution[32], the nature and concentration of added salts[33], and possibly, in the case of chiral betaine dyes, on the configuration of enantiomerically pure , homochiral solvents[34].

Thermochromism (usually negative) is caused by the increased differential stabilisation of the dipolar electronic ground state, relative to the less dipolar excited state with decreasing solution temperature. The lower the solution temperature, the higher the corresponding $E_T(30)$ values and the better the solvation capability of the solvent.

The piezochromic effect is also caused by the differential solvent-mediated stabilisation of the betaine ground state, relative to its less dipolar excited state, with increasing external pressure. The higher the external pressure, the higher the $E_T(30)$ value of the solvent.

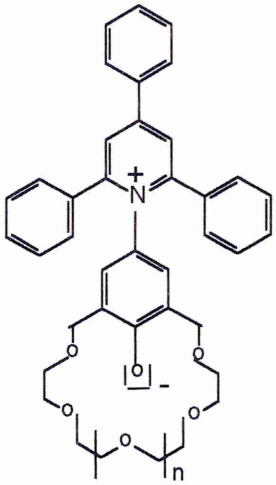
The addition of salts [e. g. KI, NaI, LiI, BaI_2, and $Mg(ClO4)_2$ etc] to a solution of a betaine can cause a hypsochromic shift of its solvatochromic CT-absorption band that is called halochromism. The term halochromism was first introduced by Baeyer and Villiger[35] and has been used until now to describe the colour change of a dissolved compound on addition of acid or base [e.g.$(C_6H_5)_3C\text{-}OH$ (colourless) $+H_3O^{\oplus} \rightarrow (C_6H_5)_3C^{\oplus}$ (yellow) + $2H_2O$]. In contrast to this trivial halochromism (each chemical reaction leads to products with UV/Vis spectra which are different from that of the starting compounds), the salt-induced band shifts of betaine dyes constitute a new type of true or genuine halochromism ,which is not companied by a chemical alteration of the chromophore[36].

Reichardt suggested the term "negative (positive) halochromism" for a hypsochromic (bathchromic) shift of the UV/Vis absorption band of a dissolved substance on increasing electrolyte concentration.

The shift of its long-wavelength CT absorption band depends on the nature and concentration of salt added[1, 37]. The shift increases with the electrolyte order, that is with the increasing effective cation charge (e.g. Ionic charge/ionic radius [38, 33b]) . In contrast, the anions seem to have little or no influence on this type of halochromism[35]. There exists even an almost linear correlation between the salt-induced negative halochromic shift of the Reichardt dye and the charge-to-size ratio(effective charge) of the cations of the added alkali and alkaline earth salts.

The position of CT absorption bands depends on the ionisation energy of the electron donor and on the electron affinity of the electron acceptor. Thus, the cations of the salts added increase the ionisation energy of electron-donor part because of the electrostatic $O^{\ominus}$ /M $^{\oplus}$ interaction. This corresponds to an increase in CT excitation energy and results in a salt-induced hypsochromic shift, similar to the effect of protonation[37b] (e.g. the salt ions in the media act like Lewis acids toward indicators). If an electron-withdrawing substituent is introduced into the acceptor part causing an increase in its electron affinity, it will cause a bathochromic shift of the CT absorption band. Generally, the halochromism results from change in the microenviroment of the dye, caused by the addition of the salt.

In order to enhance and make the dye more cation-selective , the crown ether ring (6) was introduced into the phenolate moiety of Reichardt dye[31].



(6, n=0~2)

The crown-ether substituted betaines constitute a very sensitive, new class of so-called chromoionophoric dyes , possibly useful as cation indicators.

1.4. Solvatochromic compounds with non-linear optical properties.

In addition to their applications in the study of solvent polarity, betaine dyes have also been researched for non-linear optical (NLO) properties such as second-harmonic generation (SHG), e.g., frequency doubling of laser radiation[39].

The field of non-linear optics is involved with the discovery of lasers. Franken *et al*[40] demonstrated that when a beam of red light from a ruby laser is illuminated in a quartz crystal, the frequency of the emerging ultraviolet component was doubled compared with incoming red light. This double-frequency phenomenon is termed the 'second harmonic'.

In the early stages of the study of non-linear optics, NLO studies were focused mainly on inorganic materials. A few typical examples of inorganic NLO materials are: $LiNbO_3$, $KTiOPO_4$(KTP), $Ba_2NaNb_5O_{15}$, $NH_4H_2PO_4$(ADP), HIO_3, LiB_2O_5, CdSe, $AgGaSe_2$, Te and SiO_2 etc. Recently, research activities have been directed towards developing new organic molecular and polymeric NLO systems because of their large SHG coefficients.

In the presence of the high electromagnetic field of a laser beam, the induced polarisation P in a macroscopic medium can be written as a power series of the applied field E:

$$P = \chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \ldots \quad (3)$$

where $\chi^{(1)}$, $\chi^{(2)}$ and $\chi^{(3)}$ are the first-order, second-order, and higher susceptibilities of the molecule; $\chi^{(1)}$is a tensor which follows the symmetry properties of the crystal[41]. This is termed linear optics. The tensor $\chi^{(2)}$ gives rise to second-harmonic generation(SHG) whereas $\chi^{(3)}$ causes third-harmonic generation (THG). It is these second-order and third-order terms, or" non-linear" terms, that give rise to a number of interesting optical effects in the field of " non-linear optics". Since $\chi^{(n)}$ are tensor quantities, the orientations of the molecule in a crystal lattice are important factors. If the molecular assembly has a centre of symmetry, $\chi^{(2)}$ is zero, and non-linear effects are not observed.

Second-order and third-order non-linear optical effects are correlated with the quadratic hyperpolarizability β and cubic hyperpolarizability γ respectively.

When a molecule is placed in an external electric field, a redistribution of electron density results, changing its dipole moment. The polarisation P induced in a molecule by an external electric field E can be written, analogously to Eq(3), by the following relationship:

$$P = \alpha E + \beta E^{2} + \gamma E^{3} + \ldots (4)$$

Hence, β is a measure of the second-order NLO effect. In general, the situation is not one-dimensional, in that an electric field applied in one direction can induce a dipole moment in a different direction. In this case equation (4) becomes censorial :

$$P = \alpha_{ij} E_j + \beta_{ijk} E_j E_k + \ldots \quad (5)$$

* α_{ij} is first-rank tensor, β_{ijk} is a second-rank tensor, etc.

To be of interest for SHG, a compound must posses a reasonably large second-order molecular polarizability (β). On the basis of both theoretical considerations and experimental results, the types of molecular structures that can have large β and could display strong SHG are structures with electron-donating groups and electron-accepting groups linked through some conjugated π-electron system. Molecules with these structure are often highly solvatochromic[1]. There is a connection between solvatochromism and SHG.

Those structural features that give rise to large β usually also give rise to strong solvatochromism. On this basis, a promising class of compounds for SHG are the

Reichardt-type pyridinium-N-phenolate betaine dyes due to their strong solvatochromism and highly delocalized π-electron systems.

There are number of experimental techniques which have been used for measurements of $\chi^{(2)}$ effects or β. Only some of the important ones are mentioned here. Kurtz and Perry [42] developed a convenient and fast experimental technique for diagnosing SHG of powdered samples, i.e., a classical powder technique. In this method, a laser is directed onto a powdered sample and the magnitude of SH intensity I^{2W} yielded from a powder is compared with the SH intensity of powdered standard materials such as quartz, urea, etc. The method of Maker fringes[43] is one of the most versatile techniques for determining SHG tensor elements (*d* coefficients). SHG coefficients are evaluated relative to those of standard materials e.g. quartz, KH_2PO_4 etc. The other common technique for measuring the molecular second-order polarizabilities β is electric field induced second-harmonic generation (EFISH)[44]. In this method, an electric field is applied to a solution of the compound to be tested, and a laser beam is passed through the solution. The induced second-order nonlonearity can produce a signal at 2υ, from which β can be detected.

Recently, a simple experimental method based on solvatochromism for estimating β of small organic molecules has been developed by Paley and Harris[45].

First, the solvatochromic equation (6) is used to obtain the exited-state dipole moment of the dye:

$$\nu_S - \nu = A\left[\frac{n^2 - 1}{2n^2 + 1}\right] + B\left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2}\right] \qquad (6)$$

where $B = [\,2/4\pi\varepsilon_0 h a^3\,]\,\mu_g\,(\mu_g - \mu_e)$

ν_S, ν — the laser frequency of transition in a solvent and in vacuum, respectively.

ε — the static dielectric constant of the solvent

n — the refractive index of the solvent

A, B — constants

μ_g , μ_e —the ground- and excited-state dipole moments of the solute, respectively.

ε_0 — the permittivity of vacuum

h — Plank's constant

a — the radius of the spherical cavity that the solute molecule occupies in the solvent

Second, if the x direction is chosen as that of the electric and laser field, the excited state dipole moment is then used in the two-level model and the setting of i, j, and k equal to x results in a relatively simple expression for second-order polarizability:

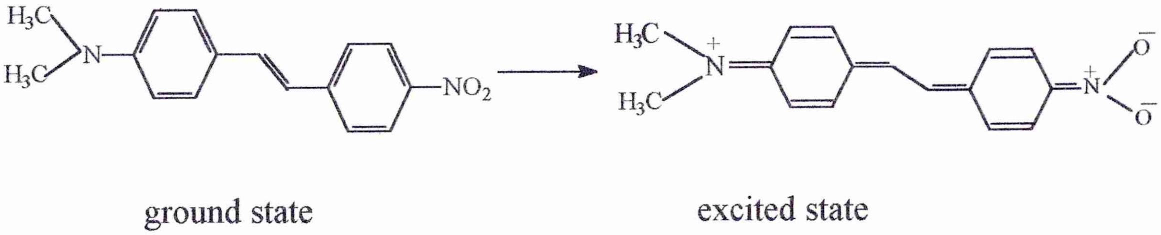
$$\beta_{xxx}(2\nu) = 2/3h^2 \times \mu_{eg}{}^2\,(\mu_e - \mu_g) \times 2/(\,\nu_{eg}{}^2 - \nu^2)\,(\,\nu_{eg}{}^2 - 4\nu^2) \qquad (7)$$

where:

ν_{eg} — the laser frequency of transition from ground to first excited state and

μ_{eg} — the transition dipole moment between ground and excited state.

Therefore, in order to optimise β, both μ_{eg} and ν_{eg} should be quite large. This objective can be accomplished by enhancing the electron-donating and electron-withdrawing activities of the donor and acceptor subsituents separated by a conjugated π-electron system. For example, consider dimethylamino-4'-nitrostilbene (see scheme 1-2).[46]



Scheme 1-2

The dimethylamino (electron-donating group) and nitro (electron-withdrawing group) are at the opposite ends of the molecule which increases intramolecular charge transfer, resulting in a very high β value (260×10^{-30} esu). In most of these molecules which have such donor and acceptor groups, the charge transfer takes place primarily along the axis of the permanent ground state dipole moment of the molecule (i.e., the x axis). If the applied field is pointed in the direction of x axis, the molecule is most easily polarized in the x direction. As a consequence the dominant component of the tensor β_{ijk} is β_{xxx}, often referred to in the literature as β_{CT} (charge transfer).

However, simply because a compound has a large β does not ensure that it will be useful for SHG. The quantity β is a molecular property. It indicates that a single isolated molecule of some compound is capable of SHG. It does not, however, guarantee that the compound will exhibit SHG in bulk form. If the molecular second-order coefficients are to be observable as a bulk property ($\chi^{(2)}$) of the material , the molecules should be arranged in a noncentrosymmtric fashion[39].

For example, although Reichardt'dye has a large β_{xxx} value (34×10^{-30} esu), which indicates this compound should indeed be capable of efficient SHG, it has a centre of symmetry, and hence second-order nonlinearity vanishes. However, the β studies provide at least first-hand primary information that assists in designing new organic molecules with large NLO properties.

Broadly speaking, the majority of organic molecules crystallise in centro- symmetric space groups and therefore fail to exhibit SHG activity. Several strategies for forming acentric crystals have been proposed including : chirality[47, 45], steric hindrance [48], the Langmuir-Blodgett (LB) technique[49], guest-host systems[50], and electrical poling[51] methods. These methods have been found useful for ensuring a dipolar alignment favourable for exhibiting SHG activity.

In general, SHG studies on organic materials have been performed on single crystals, L-B films, NLO dye-functionalized polymer films, liquid crystals, gust-host systems and polymers.

Quite a few organic single crystals with considerable optical non-linear effects have been found such as urea and 2-methyl-4-nitro-aniline. However, because many compounds like the Reichardt dye, having a large polarizability β value, crystallise in centrosymmtric space group, this makes them of no use for SHG.

Hence the number of organic crystals which have useful NLO properties are limited. However, the potential of the NLO material for SHG in poled polymer films is high. The large dipole moment in the ground state can enhance alignment of the betaine molecules located within a polymer system with the poling field, which increases the efficiency of poled polymer films for SHG. For example, in the *p*-nitroaniline (p-NA)-poly (oxyethylene) (POE) system[52], where *p*-nitroaniline is the non-linear optical doping molecule as the guest and POE is the matrix material as the host, above the glass transition temperature(T_g), the guest molecules of the films rotate freely and are aligned inside the polymer with the help of a low intensity electric field. The system is cooled to room temperature while still being polarised. Finally the field is removed, leaving crystallised films (p-NA-POE inclusion complexes) which have acentric structures due to the alignment of p-NA molecules along their polar axis and these are found to exhibit intense and long-term SHG activity.

Another potential film technique for SHG is the formation of Langmuir-Blodgett (L-B) films. The technology of L-B films has become a very active area of research recently. The method is especially important as a means of imposing a noncentrosymmetric structure onto a material and provides a means of controlling precisely the film thickness as well as aligning polar molecules which are capable of displaying SHG activity.

Although the L-B technique was originally developed using materials such as fatty acids , which have very low NLO coefficients, the technique has been extended to aromatic organic molecules.

In this technique, amphiphilic organic molecules (having both a hydrophilic and hydrophobic portions) are dissolved in a suitable volatile solvent. The deposition process is carried out by initially spreading a monolayer of the organic molecule onto the surface of a purified liquid (the subphase is normally water) in a so-called Langmuir trough, compressing the monolayer into a two-dimensional solid under constant surface pressure, and then repeatedly dipping the substrate to be coated into and out of the subphase.

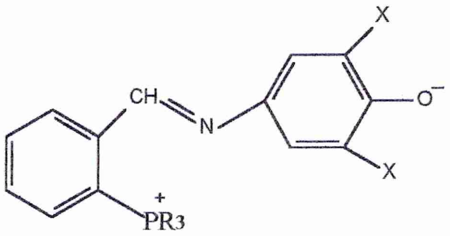
There are several kinds of non-centrosymmtric L-B films. According to their types of deposition, they are classified as X-, Z- and Y-types. If deposition only occurs when the substrate is being withdrawn from the subphase, i,e. the molecules stack in a head-to-tail manner, and this deposition mode is called Z type. The deposition mode in which the molecules stack in a tail-to-head is X type. The most common deposition is Y type where the molecules stack in a head to head and tail to tail configuration.

Conventional Y type films are symmetrical in character and are therefore unlikely to yield non-linear effects. An alternative approach to producing noncentrosymmetric structures is to use alternate layers of two different materials where the contributions of adjacent molecules do not cancel[53].

1.5. Aim of the present work

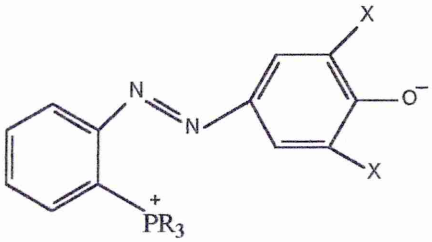
In this thesis, the synthesis and characterisation of three new types of solvatochromic systems that could be used as potential solvent polarity indicators is described:

a).4- N(*o*-phosphoniobenzylidene)- amino-2,6-disubstituted phenolate betaines



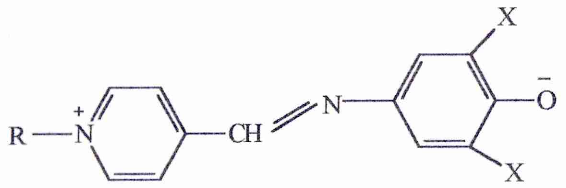
R=Ph or Bu; X=Cl, Br, Ph, Bu, or H

b). 4-N(*o*-phosphoniophenylazo)-2,6- disubstituted phenolate betaines



R=Ph; X=F, Cl, or CH_3

c). 4-(N-methyl or hexadecyl-pyridinium-4-methylidene)-2,6-disubstituted amino phenolate betaines.



R=CH_3 or $C_{16}H_{33}$; X=Cl, Br, or Bu

Synthetic routes to a range of structures of each of type have been explored and developed. The substituent groups at both positive and negative centres have been varied.

The solvatochromic properties of each betaine have been investigated in a range of organic solvents, with measurement of their respective longest-wavelength absorption bands using UV/Vis spectroscopy. The effect of variation in structure on the solvatochromic properties has been evaluated.

The halochromic properties of some betaines has also been demonstrated by addition appropriate salts into solutions of the betaines.

Some other potential applications of such solvatochromic compounds such as NLO have been also investigated.

References

(1). C. Reichardt. *Solvents and solvent Effects in Organic Chemistry,* 2nd ed.; VCH Publishers: Weinheim, 1988.

(2). P.L . Huyskens; W. A.P Luck. *Chem.Rev.,* 1988, *88,* 963.

(3). C. Reichardt. *Angew. Chem.,* 1965, *77,* 30.

(4).a. T. W . Buntley; G . Liewellyn.*Prog. Phys.Org.Chem. 1990, 17, 121;* b. W.R.Fawcett,. *J. Phys.chem.*, 1993, *97,* 9540.

(5). a. J . Frank. *Trans.Faraday Soc.* 1926, *21,* 536; b. C.U. Condon. *Phys.Rev.*, 1928, *32,* 858.

(6). a. P. Jacques, *J. Phyls. Chem.*, 1986, *90,* 5535.

b. Bijay K.Mishra. *Bull. Chem. Soc. Jpn.*, 1996, *69,* 2581

(7). L.G.S. Brooker; A.C. Craig. *J.Am. Chem. Soc.*, 1965, *87,* 2443.

(8). E.M. Kosower. *J. Am. Chem. Soc.*, 1958, *80,* 3253..

(9). M. J. Kamlet; J. -L. M. Abboud. *J. Am. Chem. Soc.*, 1977, *99,* 6027

(10). S . Dahne; F . Shob. *Ukr.Khim.2h.*1975, *41,* 1170 *; Chem. Abstr.*,1976, *84,* 43086j.

(11). E . Buncel; S . Rajagopal. *J. Org. Chem.*, 1989, *54,* 798.

(12). B. K . Freed; J. *J* . Biesecker. *Fluorine Chem.*, 1990, *48,* 63.

(13). C . Reichardt; K . Dimroth. *Liebigs Ann. Chem.*, 1963, *1,* 661..

(14). D. *J* . Walther. *Prakt. Chem.*, 1974, *316,* 604.

(15). J.-E . Dubois,. *Tetrahedron Lett.*, 1966, *20,* 1815.

(16). I. A . Zhmyreva; V. V. Zelinskii, *Dokl.Akad. Nauk SSSR, Ser. Khim.*, 1959, *129*, 1089.

(17). A . Janowski; I . Turowska-Tyrk; P. K. Wrona. *J.Chem. Soc., Perkin Trans.2,* 1985, 821.

(18). C. Reichardt. *Liebigs Ann. Chem.*, 1983, 721.

(19).C. Reichardt, *Pure Appl. Chem.*, 1982, *54,* 1867.

(20). a. K. Dimroth and C.Reichardt. *Z.Analyt. Chem.*, 1966, *215,* 344.

b. J. G. Dawber, J. Ward. *J. Chem. Soc., Faraday Trans. 1,* 1988, *84*, 713.

(21). C . Reichardt; G . Schafer; *Collect. Czech. Chem. Commun,* 1990, *55,* 97.

(22). a. M. B. Lay. C. J. Drumord, *J. Colloid Interface Sci.*, 1989, *128,* 602.

b. P. Plieninger and H. Baumgartel. *Ber. Bunsges. Phys. Chem.*, 1982, *86,* 161.

c. R. A . Hobson; F . Grieser. *J.Phys. Chem.*, 1994, *98,* 274.

(23). a. S . Spange; D . Keutel; F . Simon. *J. Chim. Phys.*, 1992, *89,* 1615.

b. R. A . McGill; M. S . Paley. *J. M. Polym. Prepr.*, 1990, *31,* 578.

(24). a. B.P . Johnson; B . Gabrielsen. *Anal. Lett.*, 1986, *19,* 939

b. J.J . Micheis; J. G. Dorsey. *Langmuir,* 1990, 414

(25). F. L . Dickert; A. Haunschild. *Adv.Mater.*, 1993, *5,* 887

(26). A. Harmer and A. Scheggi in'Optical Fiber Sensors: Systems and Application' Artech House, Norwood, 1989, Vol, 2, Ch.16, 599.

(27). H . Christine; F. Denis. *Polymer, 36, 13,* 1995, 2663

(28). M.S Paley; R.A. McGill. *Macromolecules,* 1990, *23,* 4557

(29). C. Reichardt. *Chem.Rev.*, 1994, *94,* 2314.

(30). C. Reicgardt. *Chem. Soc. Rev.*, 1992, 147.

(31). R. I. Zalewski, C. Reichardt, C. *J. Chem. Res., (S)* 1990, 280.

(32).W.S. Hammack, D. N. Hendrickson, *J. Phys, Chem.*, 1989, *93*, 3483.

(33). a C. Reichardt, G. Schafer, *Collect. Czech. Chem.Commun,* 1990, *55,* 97.

b. G. Hollmann, F. Vogtle, *Chem.Ber.*, 1984, *117,* 1355.

(34). C. Reichardt, M. wilk, *Liebigs Ann. Chem.*, 1990

(35). A. Bayer, V. Villiger, *Ber. Dtsch. Chem. Gas,* 1902, *35,* 1189.

(36). C. Reichardt, S. Asharin. Fard. *Angew. Chem.*, 1991, *103*, 614; *ibid. Int. Ed,* 1991, *30,* 558.

(37). a. C. Reichardt, E. Harbusch-Cornert, *Liebigs Ann. Chem.*, 1988, 839.

b. Y. Pocker and J. C. Ciulla, *J. Am. Chem. Soc.*, 1989, *111,* 4728.

(38*)*. H. Bock and H. -F. Herrmann, *Helv. Chim. Acta,* 1989, *72,* 1171.

(39). *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D.S., Zyss, J., Eds.; Acadmic press: Orlando, FL, 1987; Vol.1.

(40). P. A. Franken; A.E. Hill. *Phys.Rev.Lett.*, 1961, *7,* 118

(41). D. J. Williiams. *Angew. Chem., Int. Ed. Engl.,* 1984, *23,* 690.

(42). S.K. Kurtz,; T.T. Perry. *J.Appl. Phys.,* 1968, *39,* 3798

(43). P.D. Maker; P.W. Terhune. *Phys. Rev. Lett.,* 1962, *8,* 21

(44). C.C. Teng; A.F. Garito. *Phys.Rev.,* 1983, *28,* 6766.

(45). M. S . Paley; J. M. Harris. *J. Org. chem.,* 1991, *56,* 568; 1989, *54, 3774*

(46). Hari Singh Nalwa . *Applied Oganometallic Chemistry. 1991, 5, 349*

(47). J . Zyss; J. F. *J* . Nicoud. *Chem. Phys.,* 1984, *81,* 4160

(48). B.F . Levine; C.G . Bethea. *J, Appl. Phys.,* 1979, *50,* 2523

(49) a. O.A. Aktispetrov, N.N. Akhmediev. *Sov.Tech. Phys., 11* (1985) 249

b. P. Stroeve; E . Franses. *Thin Solid Films.* 1987, *152,* 405

(50). a.K.D. Singer, J. E. Soha. *Appl. Phys. Lett., 49* (1986) 248.

. b. S.D. Cox; T.E. Gier*; J, Am, Chem. Soc.,* 1989, *110,* 2986

(51). J.E . Sohn; K. Singer. *Polym. Mater. Sci. Eng.,* 1986, *55,* 532.

(52). Toshiyuki Watanabe; kazuo Yosshinaga. *J. Chem. Soc., Chem. Commun.,* 1988, 250.

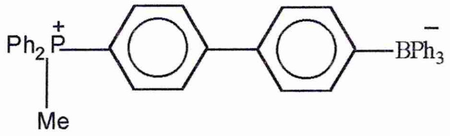
(53). B. Holcroft; M.C. Petty; G.G, Roberts. *Thin Solid Films,* 1985, *134,* 83.

Chapter 2

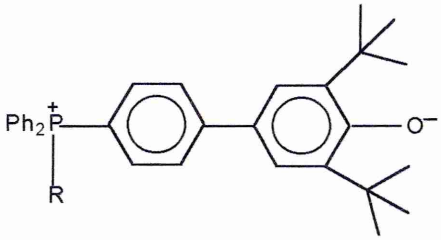
The Synthesis and Characterisation of Phosphonium Salts and Related Betaines

2.1. Introduction

Only a few solvatochromic phosphonium betaine systems appear to have been described. For example, the dipolar system (1) has been prepared and shown to exhibit a limited degree of solvatochromism[1]. The phosphonium phenolates (2, R = Me or Ph) have also been characterised, and reported to show charge-transfer visible absorption band in the region 480-500nm, in dichloromethane, but their solvatochromic properties do not appear to have been studied[2].

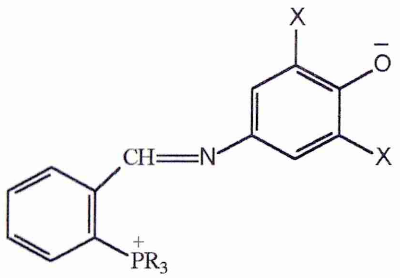


(1)

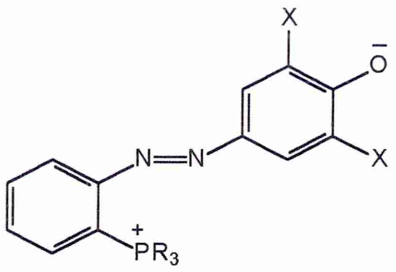


(2)

This chapter describes the synthesis and characterisation of two new types of solvatochromic systems, the N-(o- phosphoniobenzylidene) aminophenolate betaines (3), and the related azo system (4), making use of the established coordination template effect[3] in the metal ion-catalysed synthesis of arylphosphonium salts which bear suitable donor groups in the position *ortho* to phosphorus.



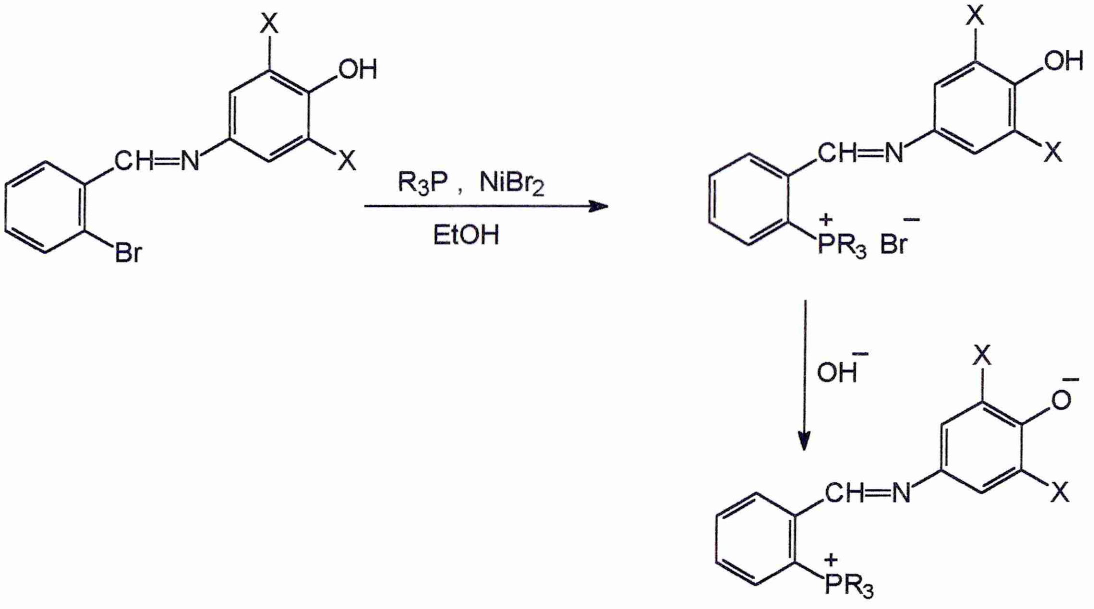
(3)



(4)

2.2 Synthesis of phosphonio-iminophenolate betaines

The synthetic route to the above phosphonio-iminophenolate betaines is shown in scheme 1:



Scheme 1

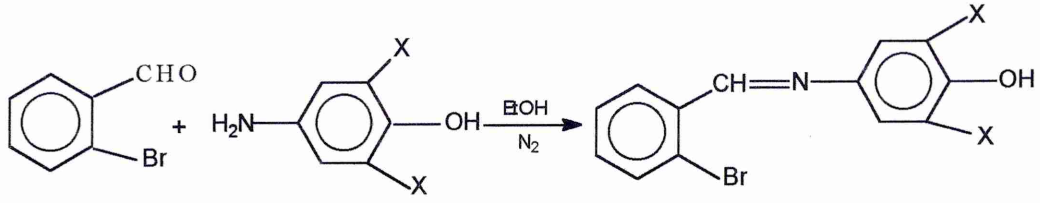
In these betaines, the positively-charged centre is either a triphenylphosphonio- or tributylphosphonio- group. The negative charge is generated from the disubstituted phenol unit by treatment with base.

The two X groups *ortho* to the phenoxide unit have been varied in order to modify the solvatochromic properties of the betaine. In the present work, compounds with X=Br, Cl, Ph, Bu^t, or H were prepared.

This synthetic route includes three main steps that are described as below:

2.2.1. Preparation of the imines used for synthesis of phosphonium salts

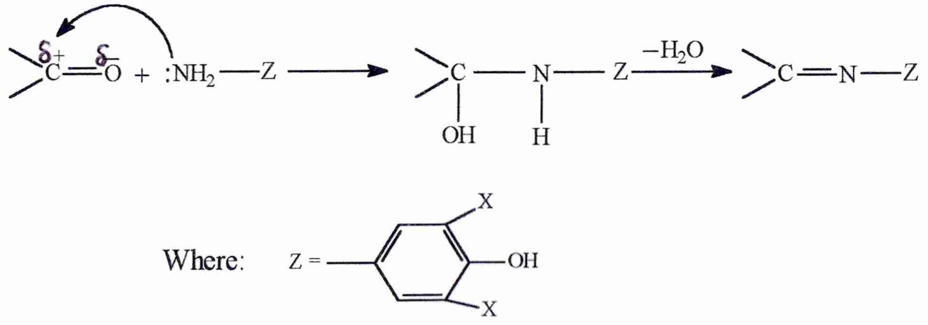
The route for the synthesis of the iminophenol intermediates is shown in scheme 2:



Scheme 2

The iminophenol precursors (X = Cl, Br, Ph or Bu^t) were easily accessible by the reactions of the appropriate 3, 5-disubstituted aminophenols with 2-bromo-benzaldehyde in ethanol.

This reaction is an addition-elimination reaction. The mechanism is shown in scheme 3:



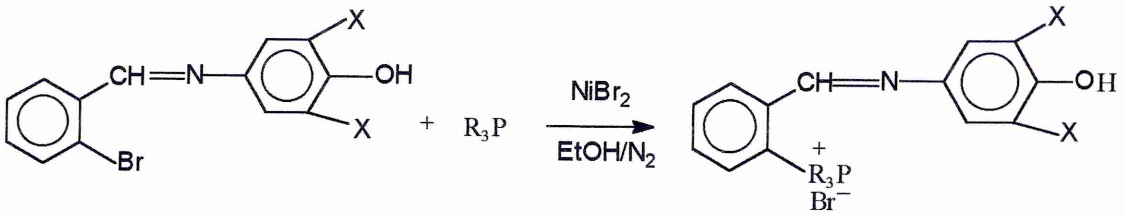
X= H, Cl, Br, Bu^t, or Ph

Scheme 3

The amine nucleophile, which possesses an unshared electron pair at nitrogen, first attacks the carbonyl group to give an intermediate aminal, which then loses water to form the stable imine product.

2.2.2. Preparation of phosphonium salts

The synthetic route is shown in scheme 4:

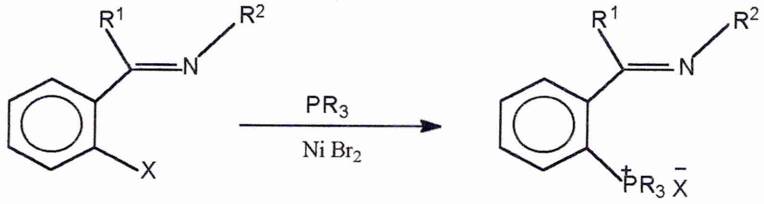


scheme 4

Conversion to the related phosphonium salts was accomplished under mild conditions in refluxing ethanol on treatment of the imines with either triphenyl- or tri-t-butyl- phosphine in the presence of nickel 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. According to the literature, the reactions of tertiary phosphines with most aryl halides to form phosphonium salts normally only proceed at high temperature (150 ~ 200 C) in the presence of a transition-metal salt catalyst, e.g. $CoBr_2$, Ni Br_2 or $CuBr_2$. These reactions are usually carried out in the absence of a solvent, although it is possible to carry out the reaction in refluxing benzonitrile (b.p190°C)[4].

However, under appropriate conditions, with aryl halides bearing appropriate donor substituents in the *ortho* position and in the presence of transition metal salt catalyst, the formation of phosphonium salts from the reaction of tertiary phosphines with aryl halides can occur under mild conditions in refluxing ethanol (80°C).

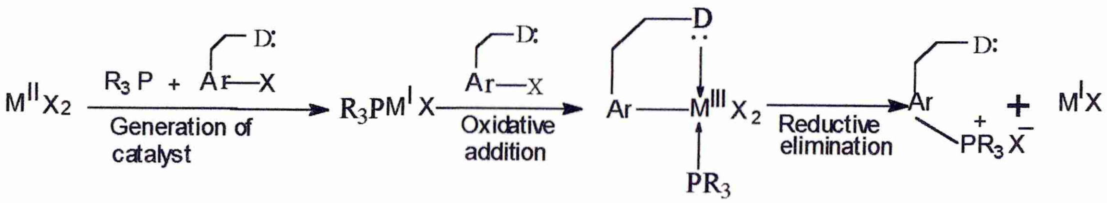
For example, in the nickel (II) bromide-catalyst reactions of the o-haloaryl-imines (5) with tertiary phosphine, the three reagents were heated together under reflux in ethanol to yield the related phosphonium salts (6)[3]. The o-haloaryimine acts as a coordination template for the metal ion. The halogen in the *ortho* position to the nitrogen-containing donor group was replaced by tertiary phosphine *via* a kinetic template effect.



(R^1 = H or Me; R^2 = Aryl; R^3 = Ph or Bu; X=Cl, Br, I)

(5)　　　　　　　　(6)

A possible mechanism for this reaction is shown in scheme 6:



(A)

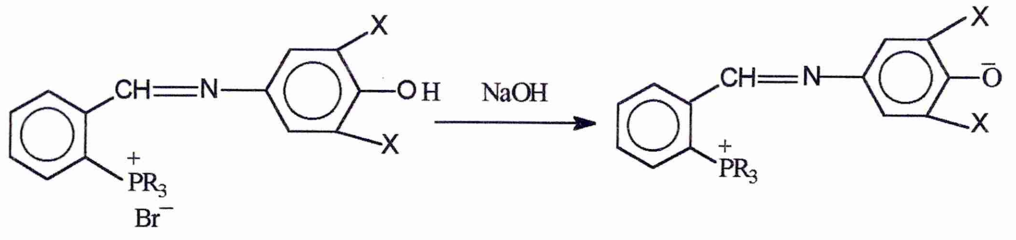
Scheme 6

The metal salt is initially reduced in the presence of the phosphine and o-halo-arylimine template to a lower oxidation state e.g. M (I) (the active catalytic species), which then undergoes a coordination template-assisted oxidative insertion into the carbon-halogen bond to form the intermediate (A), involving a M (III) atom. Reductive-elimination then follows, with the formation of the phosphorus-carbon bond and the regeneration of the catalyst M (I).

In the present work , the reaction of the iminophenols with a triaryl- or tri-n-butyl- phosphine in the presence of $Ni^{II}Br_2$ under reflux in ethanol shows the same coordination template effect as in scheme 6, forming the arylphosphonium salts in good yield. The phosphonioiminophenol salts were usually yellow-brown solids that could be recrystallised from dichloromethane and ether.

2.2.3. Preparation of the related phosphonium betaines

This reaction is shown as scheme 7:



(A) (B)

Scheme 7

The phosphonium salts were dissolved in dichloromethane, and the solution was shaken with aqueous alkali. The organic layer was then separated, dried ($MgSO_4$), and evaporated to give the corresponding betaines which sometimes appeared as a solid or as an oil. The residue was triturated with diethyl ether to give a solid product, as a range of deep red, purple, or blue solids which were purified by recrystallization. Treatment of the betaines in aqueous ethanol with dilute hydrochloric acid resulted in conversion to the parent phosphonium salts and the colour changed into yellow due to protonation at the phenolic oxygen atom. Under basic conditions, the colour of the betaine returned. Consistent with their formulation, the betaines gave a negative halide ion test on treatment with silver nitrate-nitric acid.

2.3. NMR studies which provide evidence of structure.

^{31}P and ^{1}H nmr spectra were recorded on a Bruker AC 250 Fourier-transform (FTNMR) spectrometer. ^{1}H chemical shifts were measured relative to TMS as standard at δ =0.0 ppm. ^{31}P chemical shifts were measured relative to 85% orthophosphoric acid as internal standard (δ = 0.0ppm). Spectra were recorded in $CDCl_3$ or CD_3OD.

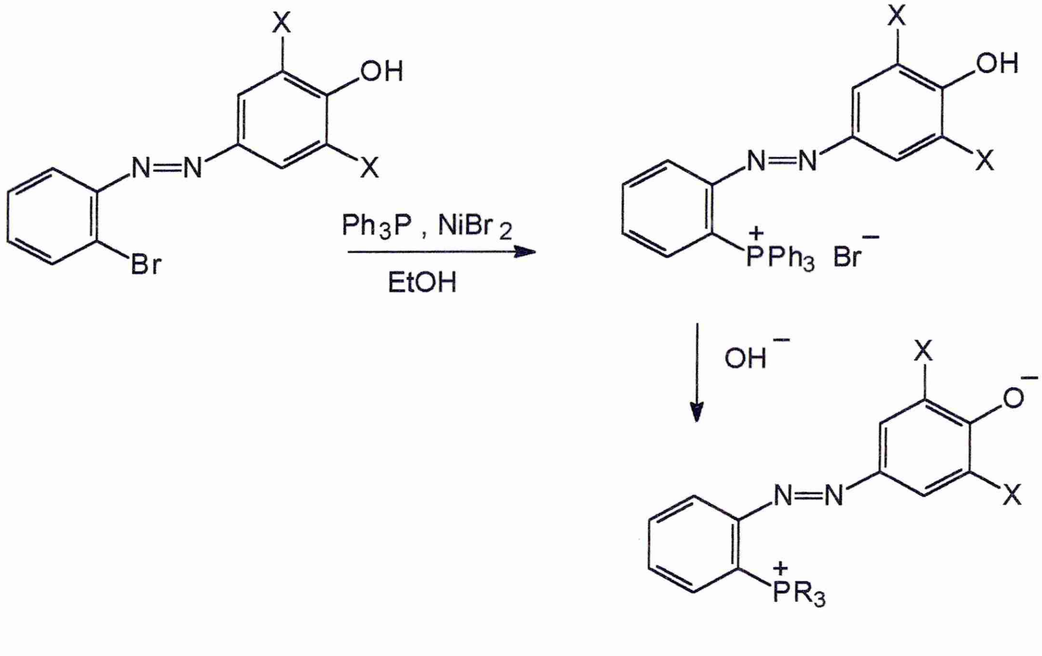
For the iminophenols, ^{1}H nmr ($CDCl_3$) clearly showed the imino CH = N being present as a singlet at δ = ~ 8.8 ppm (X = Cl, Br, Bu^{t}, Ph). The phenolic -OH was observed as a broad singlet at δ = ~5.9 ppm for the dichloro and dibromo phenols (X = Cl, Br), at δ = 5.2 ppm for the di-t-butylphenol (X = Bu^{t}) and δ = 5.5 ppm for the diphenylphenol (X = Ph), due to shielding effects of the butyl and phenyl groups.

^{31}P nmr spectroscopy confirmed the presence of phosphorus in the phosphonium salts and betaines, showing a single sharp resonance signal and revealed that, on conversion of the phosphonium salts to the respective betaines, the phosphorus nucleus becomes shielded by 0.5 ~ 1.0 ppm. Thus, e.g., for the parent di-t-butyl imino phosphonium salt (scheme 7,A, R = Ph, X = Bu^t), the phosphorus signal appears as a singlet at $\delta = 26.2$ppm being shifted slightly to $\delta = 25.4$ ppm for the related betaine (scheme 7, B, R = Ph, X = Bu^t).

The ^1H nmr spectra also pointed to significant differences in the electronic environment on conversion to the betaines. In the triphenylphosphonium salts (scheme 7, A, R = Ph, X = Cl, Br, Bu^t), the protons *meta* to the phenol group appear as a sharp singlet at $\delta = 6.10 \sim 6.3$ ppm (except X = Ph), as a result of shielding by the phenyl groups of the triphenylphosphonio moiety. (This effect is not observed in the related tributylphosphonio systems (R = Bu^t), in which the signals of the two protons *meta* to the phenol group merge with those of the other aromatic protons in the range $\delta = 7.0 - 7.5$ ppm. On conversion of the triphenylphosphonio salts to the related betaines, the above signal at $\delta = 6.1$ ppm disappears, these protons then appearing as part of the aromatic multiplet between $\delta = 7.0 - 8.8$ ppm. In the triphenylphosphonio- salts and betaines, the signal due to the imino CH = N 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 $\delta = 8.7 - 8.8$ ppm; on conversion to the related betaines, the imino proton becomes shielded by ca 0.5 ppm, appearing at $\delta = 8.3$ ppm.

2.4. Preparation of azo phosphonium betaines

The effect on solvatochromic properties of replacing the imino group in the phosphonioiminophenolates by azo, as in the phosphonioarylazophenolate betaines (4) has also been studied. These compounds were prepared as outlined in scheme 8:



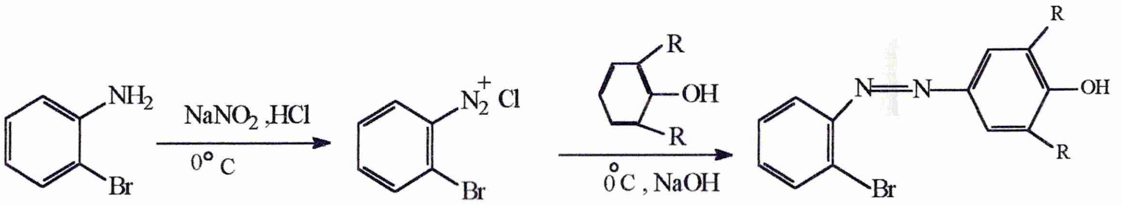
(4)

Scheme 8

This synthesis route includes two main steps that are described as below:

2.4.1. Preparation of o-bromophenylazophenols used for synthesis of phosphonium salt

Azo dyes are made almost exclusively by the diazotization of a primary aromatic amine to give a diazonium salt. The diazo compound is then coupled with a second substance, usually a phenol or an aromatic amine. The reaction products retain the nitrogen atoms of the diazonium ion as an -N=N- bridge between the aromatic rings. In present work, the synthesis of azodyes involves the generation of an - N_2^+ electrophilic diazonium ion followed by a coupling reaction with a phenol under cold alkaline conditions. The reaction route is shown in scheme 9a:

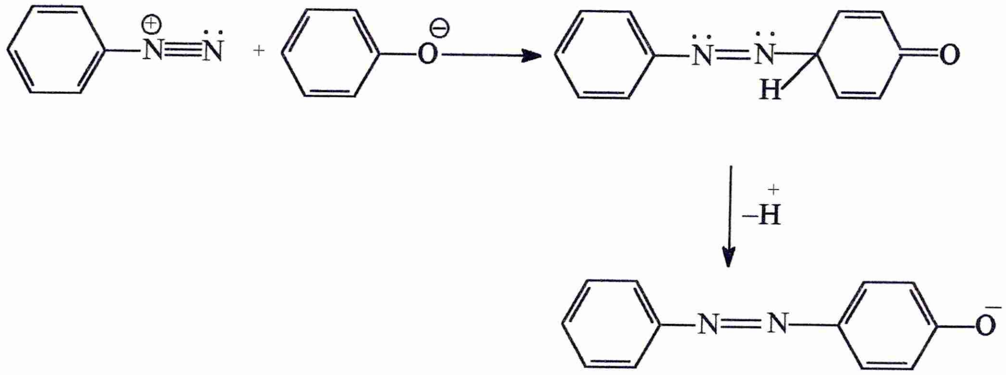


scheme 9a

The diazonium ion Ar-N_2^+ is produced by reaction of the *ortho*-bromoaniline with nitrous acid (generated *in situ* from the sodium nitrite and hydrochloric acid). The cold acid condition slows down the decomposition of the unstable diazonium ion.

Sulphamic acid is added to the mixture to quench excess nitrous acid that may interfere with further reactions.

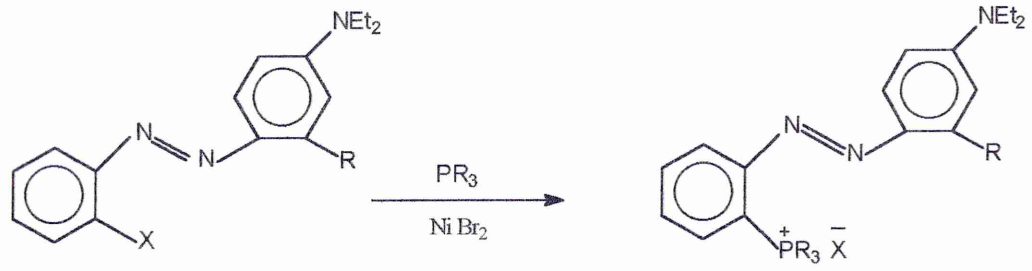
The diazonium ion formed is a weak electrophile. It is able to attack a strongly activated aromatic ring. This electrophilic substitution reaction usually takes place in weak alkaline solution, such as dilute aqueous sodium hydroxide. Under these conditions, the 2, 6-disubstituted phenol exists in equilibrium with the related phenoxide ion which contains a more strongly activating group (electron-releasing, -O$^-$ group), than -OH group of the phenol. Attack at the *para-* or *orth-* carbon atom is favoured. The mechanism of the coupling reaction may be represented as scheme 9b:



scheme 9b

2.4.2. Preparation of azo phosphonium salts and related betaines

These reactions were carried out as outlined in scheme 8, the key step being the reaction of the o-bromodiarylazophenols 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 (triphenylphosphine), to give the phosphonium salt. Thus, it has been shown that the nickel (II) bromide- or copper (II) acetate- catalysed reactions of the o-haloarylazo dyestuffs (7) with tertiary phosphines under reflux in ethanol yields the related phosphonium salts (8)[6]:



(7) (8)

The likely mechanism of these reactions is also shown above in scheme 6. The o-haloarylazo dyestuff acts as a coordination template for the metal ion . The halogen *ortho* to the azo group is replaced by tertiary phosphine *via* the kinetic template effect.

The phosphonium salts were then treated with aqueous alkali (NaOH) to give the betaines (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 and nitric acid.

2.5. NMR studies of azo compounds

In the ^{1}H nmr ($CDCl_3$) spectra of the azodyes, the -OH group appeared as singlet at $\delta = 5.6$ ppm (X = F) or $\delta = 6.2$ ppm (X = Cl), while the -OH group of compound ($X = CH_3$) moved to higher field and coincided partly with the methyl singlet at $\delta = 2.2$ ppm, due to the shielding effect of the methyl groups. The broad multiplet in the aromatic region δ = 7.0 ~ 8.5 ppm integrated for 6H. In all cases, the -OH signal disappeared on shaking with D_2O.

For the azophosphonium salts and betaines, the presence of phosphorus was confirmed by ^{31}P nmr. On conversion of the salt to the respective betaine, the phosphorus nucleus becomes shielded by 0.5 ~ 2ppm. The multiplets in the aromatic region of the ^1H nmr spectra (δ = 6.5 ~ 8.5) represented the 21 aromatic hydrogen atoms.

For the dimethyl azophenol salt and betaine (4, X = CH_3), the methyl (CH_3) group appeared as a singlet at δ = 2.0 (6H), presumably due to shielding effect of the electron clouds of the phenyl groups attached to phosphorus.

2.6. Experimental

^{31}P nmr, and ^1H nmr. studies were carried out using a Brüker AC250 FTNMR Spectrometer. Mass Spectra were recorded on a VG Micromass 7070F instrument using the FAB technique in which the compounds were usually dissolved in 3-nitro-benzyl alcohol (NBA) (in a few cases, the compounds were dissolved in glycerol).

2.6.1. Preparation of imine intermediates

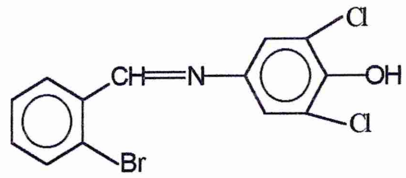
The general procedure for the synthesis of imines was as follows :

A solution of 2-bromobenzaldehyde (6×10^{-3} mol) with the respective 4-amino-2,6-disubstituted phenol (6×10^{-3} mol) in ethanol (15~20cm^3) was heated under reflux under nitrogen for 1~2 hours. Following standing overnight, the solution was suction filtered to isolate the solid imine. If no solid appeared overnight, the mixture was evaporated and the residue triturated in diethyl ether. The imines were usually purified by recrystallization .

The following compounds were isolated:

a. 4-N(o-bromobenzylidene)amino-2,6-dichlorophenol

The expected structure of this compound is shown as (9):



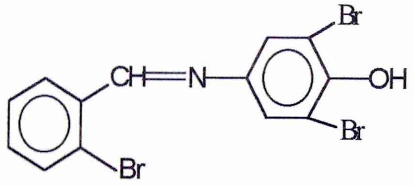
(9)

According to the above procedure, 2-bromobenzaldehyde(1.11g ,6x10^{-3} mol) and 4-amino-2,6-dichlorophenol(1.6g ,6x10^{-3} mol) in ethanol (20cm^3) were heated under reflux under nitrogen for 2 hours. After cooling to room temperature, the precipitate formed was filtered off and recrystallized from dichloromethane and petrol to give the product as a pale brown solid (1.4g, 74%), m.p 155~156°C. δ ^{1}H nmr(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) ppm.

Found: C, 45.30; H, 2.45; N, 4.05% $C_{13}H_8ONCl_2Br$ requires: C, 45.25; H, 2.35; N, 4.05%

b. 4-N(o -bromobenzylidene)amino-2,6-dibromophenol

The structure of this compound is shown as (10):



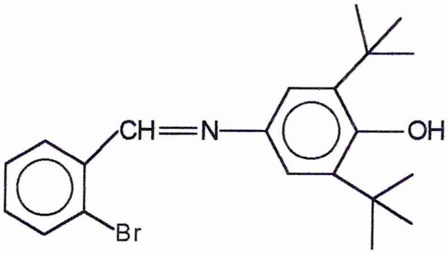
(10)

Analogous to the procedure described for compound (9), this was synthesised by heating 2-bromobenzaldehyde (1.11g, 6mmol) and 4-amino-2,6-dibromophenol (1.6g, 6mmol) in ethanol under reflux under nitrogen for 2 hours. Isolated as a brown solid (1.99g, 76%), m.p 116~118°C (from dichloromethane and diethyl ether). δ ^{1}H nmr ($CDCl_3$): 6.0(s,1H,OH), 7.3(m, 4H), 7.7(d, 1H), 8.2(d, 1H), 8.8(s, 1H,CH=N) ppm.

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%.

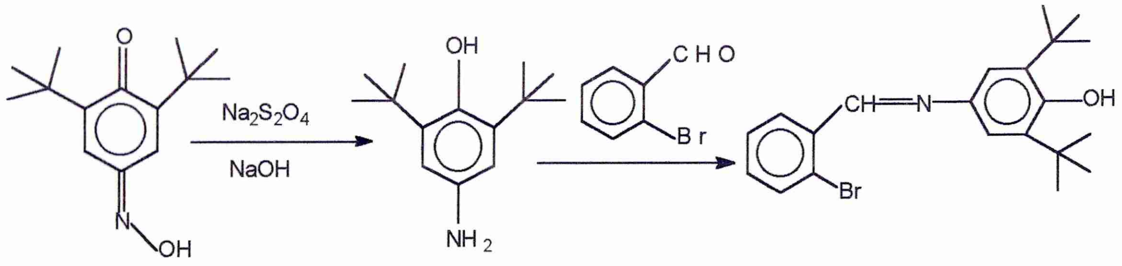
c. ***4-N(o -bromobenzylidene)amino-2,6-di-t-butylphenol***

The structure of this compound is shown as (11):



(11)

The basic route for the synthesis of this compound is shown in scheme (10):



scheme 10

The preparation of this compound includes two steps :

4-amino-2,6-di-t-butylphenol

This synthesis was carried out according to the procedure described in the literature [7]:

2, 6-Di-t-butyl-p-benzoquinone-4-oxime (5.0g, 21.2mmol) was dissolved in the THF (50cm^3). Sodium hydroxide (1.27g, 31.4mmol) in water (50cm^3) was added to the THF solution with stirring. The mixture was then heated to 45°C and sodium hydrosulfite (5.5g, 31.8mmol) added to the solution slowly. After completion of the addition, the mixture was stirred for another 1 hour, during which time its colour changed from deep red to pale yellow/colourless .The stirring must be efficient, otherwise the solution will form two layers. The mixture was poured into a large volume of water. The precipitate formed was filtered off and washed with water to give a white /yellowish product, which was used quickly without further purification in the following step.

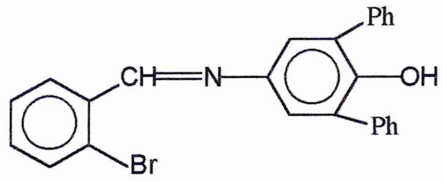
4-N(o -bromobenzylidene)amino-2,6-di-t-butylphenol

According to the procedure given above for compound (9), the 2-bromobenzaldehyde (3.92g, 21.2mmol) with 4-amino-2,6-di-t-butylphenol prepared *in situ* was heated in ethanol (20cm^3) under reflux under nitrogen for 2 hours. After cooling, the precipited solid was filtered to give orange crystals (3.3g, 48%), m.p 109~110°C (from acetonitrile). δ^1H ($CDCl_3$): 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) ppm.

Found: C, 65.00; H, 6.80; N, 3.50% $C_{21}H_{26}ONBr$ requires:C, 64.95; H, 6.75; N, 3.60%.

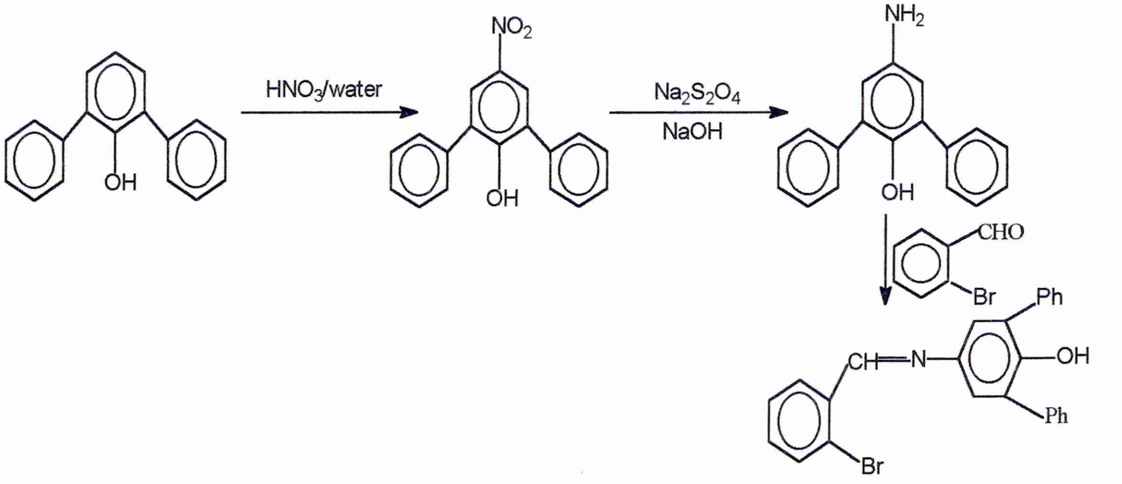
d. *4-N(o -bromobenzylidene)amino-2,6-di-phenylphenol*

The structure of this compound is shown as (12):



(12)

The synthetic route includes three steps which are shown as scheme 11:



scheme 11

The first two steps for the preparation of the 4-amino-2,6-diphenylphenol were carried out according to the procedures described in the literature [8]:

4-nitro-2,6-diphenylphenol

2.6-Diphenylphenol (2.5g, 10.15mmol) was slowly added at room temperature to a well stirred mixture containing nitric acid (65%, 7.5cm^3) and distilled water (7.5cm^3). After a few minutes, the suspension becomes yellowish. The suspension was stirred overnight , finally becoming orange in colour. The crude product was filtered off and carefully washed with distilled water. The solid was dissolved in hot ethanol, treated with a small amount of charcoal and filtered. Recrystallization from ethanol gave large yellow crystals.

4-Amino-2,6-diphenylphenol

4-Nitro-2,6-diphenylphenol (1.5g, 5mmol) was dissolved in boiling aqueous sodium hydroxide solution (5%w/v, 62cm^3). The deep red solution was well stirred, and solid sodium hydrosulfite added in small portions, until the colour changed to pale yellow. After addition of a small excess of sodium hydrosulfite , the solution was kept at boiling temperature for another 15 min. Then the hot mixture was adjusted to pH = 5 with glacial acetic acid, whereupon a precipitate formed. The solution was allowed to cool, and the product filtered off and washed with ice-cold water to give a colourless solid, which acquires a tan colour upon standing for several days.

4-N(o -bromobenzylidene)amino-2,6-diphenylphenol

Analogous to the procedure described for compound (9), a solution of 4-amino-2,6-diphenylphenol (1.3g, 5mmol) in ethanol (20cm^3) and 2-bromo-benzadehyde (0.93g, 5mmol) was heated under reflux under nitrogen for 3 hours. After cooling, a small amount of diethyl ether and some ethanol was added into mixture so that the solid appeared, to give a white product (1.32g, 62%), m.p 124~126°C (from ethanol and diethyl ether). δ^1H ($CDCl_3$): 5.5(s,1H,OH), 6.5~8.0(m, 15H), 8.2(d, 1H), 8.9(s, 1H,CH = N) ppm.

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%.

2.6.2. The preparation of imino phosphonium salts and their conversion to the related betaines.

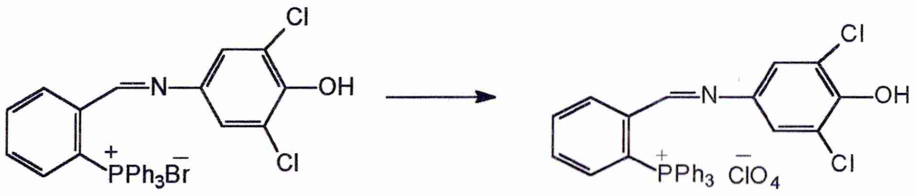
The general procedure was as follows :

The appropriate o-bromoaryliminophenol (2x10^{-3} mol), was heated in ethanol (10~15cm^3) with the tertiary phosphine (4x10^{-3} mol), and nickel (II) bromide (1x10^{-3} mol) under reflux under nitrogen for 4-6 hours. After cooling , the solution was poured into aqueous potassium bromide (10% w/v) and extracted with dichloromethane (3x10cm^3). The dried ($MgSO_4$) organic extract was evaporated and the oily residue triturated several times with portions of dry diethyl ether to give the phosphonium salts, which were usually purified by recrystallization from dichloromethane and diethyl ether. In some cases, in order to achieve satisfactory micro-analytical data, it was necessary to convert the salts to the corresponding perchlorate by treatment with lithium perchlorate in aqueous methanol. For conversion to the related betaines, 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, which was usually purified by recrystallisation.

The following compounds were isolated:

a. ***4-[-(o-triphenylphosphoniobenzylidene)-amino]-2,6-dichlorophenol bromide and perchlorate***

The structure of this compound is shown as (14)



(14)

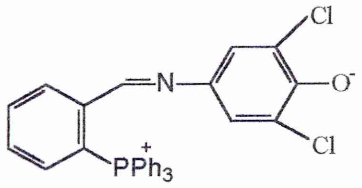
According to the above procedure, 4-N(o-bromobenzylidene)amino-2,6-dichlorophenol (1.4g, 4mmol), triphenylphosphine (2.2g, 8mmol) and nickel bromide (87mg, 0.4mmol) were heated in ethanol (15cm^3) under reflux under nitrogen for 6 hours. After cooling to room temperature, the reaction mixture was poured into aqueous potassium bromide (50cm^3 water containing 1g KBr) in a separating funnel and extracted three times with dichloromethane (15cm^3 x 3). The combined extracts were dried. After filtration, the solvent was removed on a rotary evaporator.

The residue was triturated with diethyl ether affording a brown powder. After recrystallization from dichloromethane and diethyl ether, traces of impurities were still evident on a TLC plate. For characterisation, the salt was converted into the related perchlorate by treating with lithium perchlorate solution to give a pure product, as brown crystals (1.23g, 61.5%), m.p. 249~250°C (from dichloromethane and diether ether) . δ^{31}P nmr (CD_3OD) 27.0ppm. δ^{1}H nmr (CD_3OD) : 6.10 (2H, s), 7.0~8.4 (19H, m), 8.50 (1H, CH = N,s) ppm. M/z(fab) 526 (CationM$^+$, ^{35}Cl).

Found: C, 59.51; H, 3.68; N, 2.21% $C_{31}H_{23}O_5NPCl_3$ (Perchlorate salt) requires: C, 59.40; H, 3.70; N, 2.23%.

b.4-N(o-Triphenylphosphoniobenzylidene)amino-2,6-dichlorophenolate

The structure of this betaine is shown as (15):



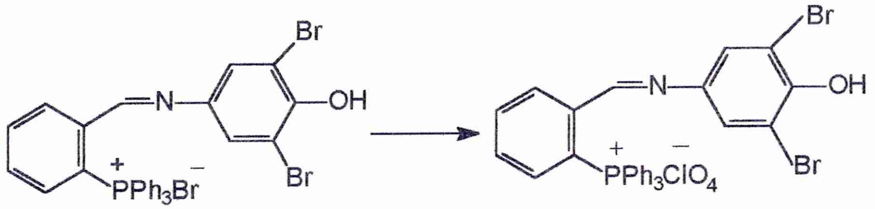
(15)

According to the above procedure, the parent salt was dissolved in dichloromethane, and the solution shaken with diluted aqueous sodium hydroxide solution. After drying, the organic layer was evaporated and triturated with diethyl ether to give the related betaine as a red solid , m.p. 265 ~ 266°C (from dichloromethane and diethyl ether). δ^{31} P nmr (CD_3OD) 26.3ppm. δ^{1} H nmr (CD_3OD) 7.0 ~ 8.80 (22H, brm). M/z (fab) 526(cation, M$^+$).

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%.

c.*4-N(o-Triphenylphosphoniobenzylidene)amino-2,6-dibromophenol Bromide (and Perchlorate)*

The structure of the compound is shown as (16):



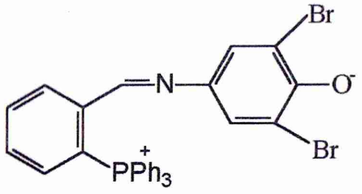
(16)

Analogous to the procedure described for compound (14), 4-N(o-bromo-benzylidene) amino-2,6-dibromophenol (1.09g, 3mmol), triphenylphosphine (1.31g, 6mmol) and nickel bromide (55mg) were heated in ethanol (15cm^3) under reflux under nitrogen for 6 hours and worked up to obtain the product as a brown solid (1.48g, 89%) and then converted it into the related perchlorate for microanalysis, m.p 222 ~ 223°C (from dichloromethane and diethyl ether). $\delta^{31}P$ nmr (CD_3OD) 27.0ppm. δ^1H nmr (CD_3OD) 6.30(2H, s), 7.0~8.70 (20H, brm)ppm. M/z(fab) 618 (100%, cation, M^+, ^{81}Br).

Found: C,52.10; H,3.24; N,1.96% $C_{31}H_{23}O_5NPClBr_2$ (Perchlorate salt) requires: C, 52.02; H, 3.24; N,1.96%.

d. *4-N(o-Triphenylphosphoniobenzylidene)amino-2,6-dibromophenolate*

The structure of this betaine is shown as (17):



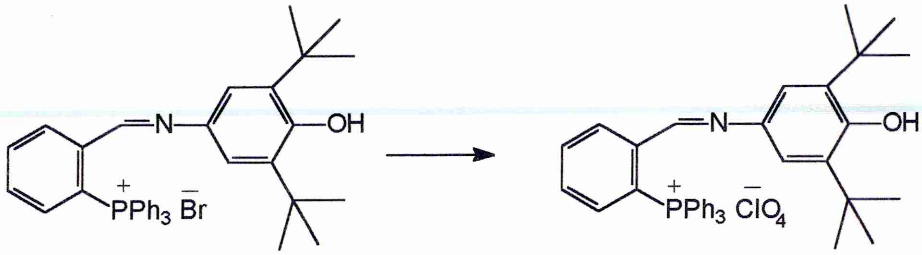
(17)

Analogous to the procedure described for compound (15), this was obtained as a red solid, m.p. 239~241° C (from dichloromethane and diethyl ether). δ^{31}P nmr (CD_3OD) 26.3ppm. δ^1H nmr(CD_3OD) 7.0 ~ 8.60 (22H, brm). M/z 618 (100%, cation, M^+, ^{81}Br).

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% .

e. *4-N(o-Triphenylphosphoniobenzylidene)amino-2,6-di-t-butylphenol Bromide (and Perchlorate)*

The expected product is shown as (18):



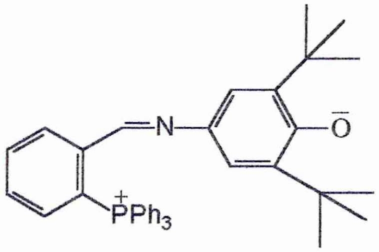
(18)

According to the procedure given above for compound (14), 4-N(o-bromobenzylidene) amino-2,6-di-t-butylphenol (1.58g, 4 mmol), triphenyl-phosphine (2.1g, 8mmol) and nickel bromide (87mg) were heated in ethanol ($10cm^3$) under reflux under nitrogen for 6 hours and worked up to obtain the product as green-yellow crystals (2.21g, 85%) and converted it into perchlorate, m.p.239~241° C (from dichloromethane and diethyl ether). $\delta^{31}P$ (CD_3OD) 26.2ppm. $\delta^{1}H$ nmr ($CDCl_3$) 1.5 (18H, s), 5.20 (1H, OH, s), 6.10 (2H, s), 7.0~8.50 (20H, m) ppm. M/z (fab) 570(100% cation, M^+).

Found: C, 69.41; H, 6.31; N, 2.08% $C_{39}H_{41}O_5NPCl$ (Perchlorate salt) requires: C, 69.9; H, 6.17; N,2.09% .

f.*4-N(o-Triphenylphosphoniobenzylidene)amino-2,6-di-t-butylphenolate*

The structure of this betaine is shown as (19):



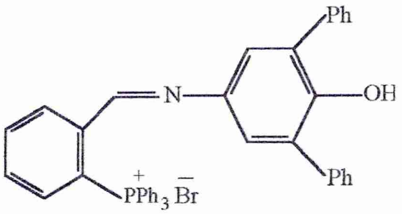
(19)

According to the method given above for compound (15), this was obtained as a blue solid, m.p. 231~232° C (from dichloromethane and diethyl ether). $\delta^{31}P$ (CD_3OD) 25.4ppm. $\delta^{1}H$ nmr ($CDCl_3$) 1.5(18H, m), 6.0(2H, s) 7.0~8.0 (20H, m). M/z (fab) 570(100%, cation, M^+).

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%.

g. *4-N(o-Triphenylphosphoniobenzylidene)amino-2,6-diphenylphenol Bromide*

The expected product is shown as (20):



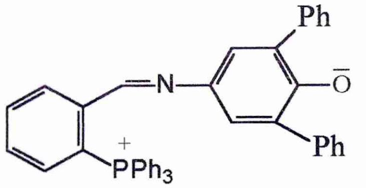
(20)

According to the procedure given above for compound (14), 4-N(o-bromobenzylidene) amino-2,6-diphenylphenol (0.86g, 2 mmol), triphenylphosphine (1.05g, 4mmol) and nickel bromide (87mg) were heated in ethanol ($10cm^3$) under reflux under nitrogen for 6 hours and worked up by usual way and triturated with ether several times to obtain the product as yellow crystals (0.72g, 57%), m.p. 270~272° C (from dichloromethane and diethyl ether). $\delta^{31}P$ nmr ($CDCl_3$) 25.6ppm.$\delta^{1}H$ nmr ($CDCl_3$) 5.5(1H,s,OH), 7.0~8.2 (31H, m), 8.7(1H,s,CH=N)ppm.

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%.

h. *4-N(o-Triphenylphosphoniobenzylidene)amino-2,6-diphenylphenolate*

The structure of this betaine is shown as (21):



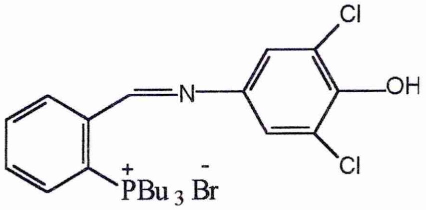
(21)

Analogous to the procedure described for compound (15), this was obtained as a blue solid, m.p. 175~178° C (from dichloromethane and diethyl ether). $\delta^{31}P$ nmr $(CDCl_3)$25.60ppm. $\delta^{1}H$ nmr $(CDCl_3)$ 7.0-8.5(ArH,m) ppm.

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%

i.*4-N(o-Tributylphosphoniobenzylidene)amino-2,6-dichlorophenol Bromide*

The expected product is shown as (22):



(22)

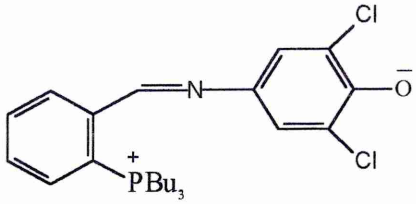
Analogous to the procedure described for (14), 4-N(o-bromobenzylidene)amino - 2,6-dichlorophenol (1.03g, 3 mmol), tributylphosphine(1.21g, 6mmol) and nickel bromide (65mg, 0.3mmol) were heated in ethanol ($15cm^3$) under reflux under nitrogen for 6 hours and worked up to obtain the product (0.96g) as a yellow-brown solid (58%), m.p. 206~208°C (from dichloromethane and diethyl ether).

$\delta^{31}P$ nmr(CD_3OD)33.50ppm. δ^1H nmr(CD_3OD) δ1.0~3.0 (brm, 27H),7.0~7.5 (6H, m, ArH), 8.7(1H,CH=N,s) ppm. M/z(fab) 467 (100%, cation, M^{+} ^{35}Cl)

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%.

j. *4-N(o-Tributylphosphoniobenzylidene)amino-2,6-dichlorophenolate*

The stucture of this betaine is shown as (23):



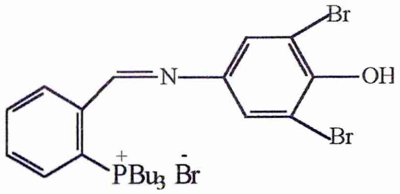
(23)

Analogous to the procedure described for compound (15), this was obtained as an orange solid, m.p. 220~221° C (from dichloromethane and diethyl ether). $\delta^{31}P$ nmr (CD_3OD) 32.2ppm. δ^1H nmr (CD3OD) 1.0~3.0 (27H, brm), 7.0~7.5 (6H, m), 8.3(1H,s) . M/z(fab) 467(100%, cation, M^{+} ^{35}Cl).

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%.

k.*4-N(o-Tributylphosphoniobenzylidene)amino-2,6-dibromophenol Bromide*

The expected product is shown as (24):



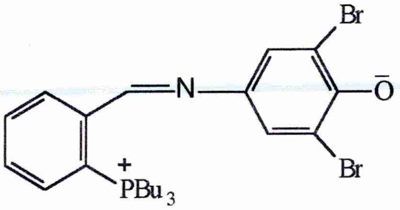
(24)

Analogous to the procedure described for compound (14), 4-N(o-bromo benzylidene)amino-2,6-dibromophenol (1.09g, 2.5 mmol), tributylphosphine (1.01g, 5mmol) and nickel bromide(55mg, 0.3mmol) were heated in ethanol (15cm^3) under reflux under nitrogen for 6 hours and worked up to obtain the product (0.99g) as a brown solid (62%), m.p. 202~203° C (from dichloromethane and diethyl ether). δ^{31}P nmr (CD_3OD) 33.6ppm. δ^{1}H nmr (CD_3OD) 1.0~3.0 (brm, 27H), 7~7.5 (6H, m), 8.8 (1H, CH = N, s). M/z (fab)559 (100% , cation, M^+, ^{81}Br).

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%.

I. ***4-N(o-Tributylphosphoniobenzylidene)amino-2,6-dibromophenolate***

The structure of this betaine is as (25):



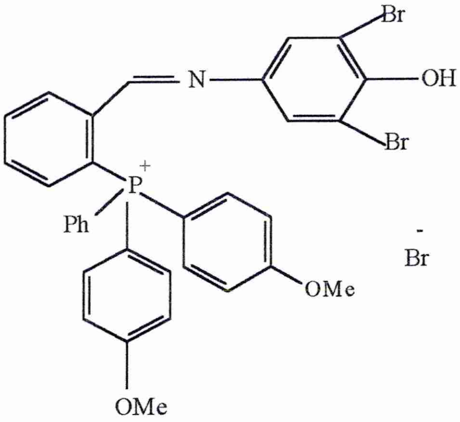
(25)

Analogous to the procedure described for compound (15), this was obtained as a brown solid, m.p. 221~222° C (from dichloromethane and diethyl ether). δ^{31}P nmr (CD_3OD) 32.20ppm. δ^1H nmr(CD_3OD) 1.0~3.0 (27H, brm), 7.0~8.5 (6H, m), 8.3(1H, s) ppm. M/z (fab) 559(100%, cation, M^+, ^{81}Br).

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%.

m.4-N[o-di(p-methoxyphenyl)phenylphosphoniobenzylidene)amino-2,6-dibromophenol bromide

The expected product is shown as (26):



(26)

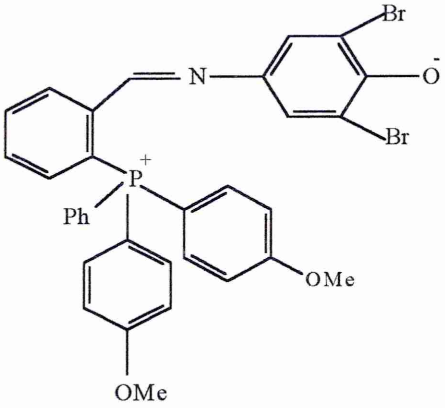
For comparision purposes, the compound in which the triphenylphosphonio group in replaced by di(*p*-methoxyphenyl)phenylphosphonio was also synthesised using 4-N(o-bromobenzylidene)amino-2,6-dibromophenol (0.87, 2mmol) and di(*p*-methoxyphenyl)phenylphosphine (1.3g, 4mmol) . This reaction was carried out in the same way as for the compound (14) to give an orange solid (1.35g, 89%), m.p.180~183°C (from dichloromethane and diethyl ether).

$\delta^{31}P$ nmr ($CDCl_3$) 25.00 ppm. $\delta^{1}H$ nmr ($CDCl_3$) 1.8 (br s, OH), 3.9(6H, s), 6.3(s, 2H), 7.0~8.0(15H, m), 8.1(t, 1H), 8.6(2H, m) ppm.

Found: C, 51.74; H, 3.96 ; N, 1.76% $C_{33}H_{27}O_3NPBr_3 \cdot H_2O$ requires: C, 51.19; H, 3.78; N, 1.81%.

n. *4-N[o-di(p-methoxyphenyl)phenylphosphoniobenzylidene)amino-2,6-dibromophenolate*

The expected product is shown as (27):



(27)

Analogous to the procedure described for compound (15), this was obtained as a red solid, m.p. 202~204° C (from dichloromethane and diethyl ether). $\delta^{31}P$ nmr ($CDCl_3$) 24.20 ppm. $\delta^{1}H$ nmr ($CDCl_3$) 3.9 (6H, s), 6.3(2H, s), 7.0~8.0(18H, br m) ppm.

Found: C, 58.39; H, 4.20 ; N, 1.89% $C_{33}H_{26}O_3NPBr_2$ requires: C,58.69; H, 3.88; N, 2.07%.

2.6.3. *Synthesis of o-bromophenylazophenols*

The general procedure was as followed :

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

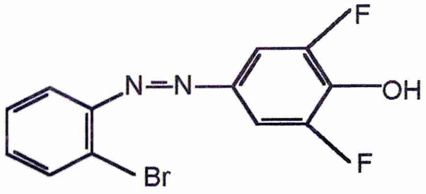
Meanwhile, the 2,6-disubstituted phenol(1.5×10^{-2}mol) in sodium hydroxide (1M, 45cm^3) was diluted with water (60cm^3) and cooled to 0~5°C. The above diazonium solution was added slowly over 15 minutes, ensuring pH>9 (~30cm^3 of 2M sodium hydroxide required). After the mixture was stirred for 1 hour, the pH was adjusted to ~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 recrystallization from diethyl ether and petroleum ether.

The following azodyes were isolated:

a. ***4-(o-bromophenylazo)2,6-difluorophenol*** **.**

The structure of this compound is shown as (28):



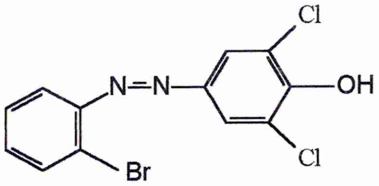
(28)

According the procedure described above, o-bromoaniline (2.5g, 15mmol), aqueous HCl (1M, 45cm^3) and solution of sodium nitrite (1.04g, 15mmol) in water (15cm^3) mixed to produce the diazonium solution which was treated with 2, 6-difluorophenol (1.95g) in sodium hydroxide (1mol, 45cm^3) to give brown crystals (3.80g, 81%), m.p 85~87°C (from diethyl ether and petrol) . δ^1H nmr (CDCl$_3$): 5.6 (s, 1H,OH), 7.5~8.5(m, 6H)ppm.

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%.

b.*4-(o- bromophenylazo)2,6-dichlorophenol*

The structure of this compound is shown as (29):



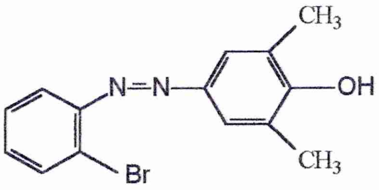
(29)

This compound was prepared by the same way as the above fluorophenol, replacing 2, 6-difluorophenol by 2, 6-dichlorophenol (2.45g, 15mmol) to give brown crystals (4.9g, 94%), m.p 134~136°C(from diethyl ether and petrol). δ^1H nmr(CDCl$_3$): 6.2(s,1H,OH), 7.0~8.0(m, 6H)ppm.

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%.

c.*4-(o̲ -bromophenylazo)2,6-dimethylphenol*

The structure of this compound is shown as (30):



(30)

Analogous to the synthetic method for compound (28) , using 2, 6-dimethylphenol (0.915g, 7.5mmol) to give orange crystals (2.1g, 91%), m.p 130~131°C (from diethyl ether and petrol).δ ^1H nmr(CD_3OD):2.2(s,6H), 7.0~8.0(m, 6H)ppm. 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%.

2.6.4.Synthesis of azophosphonium salts and conversion to the related betaines

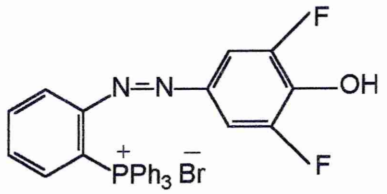
The general procedure was as follows:

The respective o̲-bromophenylazophenol (10^{-3} mole), was heated in ethanol (15 cm^3) with triphenylphosphine (2 x 10^{-3} mole) and nickel (II) bromide (0.5 x 10^{-3} mole), under nitrogen, for 3-4 hours. 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 trituration with diethyl ether, was purified by recrystallisation. For conversion to the related betaines, 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, which was usually purified by recrystallisation.

The following compounds were characterised:

a.*4-(o-Triphenylphosphoniophenylazo)-2,6-difluorophenol Bromide*

The structure of this compound is shown as (31):



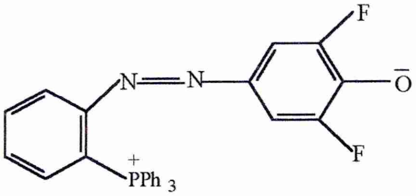
(31)

According the general procedure described above, 4-(o-bromophenylazo)2,6-difluorophenol (1.02g, 3mmol), triphenylphosphine (1.68g, 6mmol) and nickel bromide (66mg) were heated in ethanol (15cm^3) under reflux under nitrogen for 4 hours. After cooling to room temperature, the reaction mixture was poured into aqueous potassium bromide (10% w/v) in a separating funnel and extracted three times with dichloromethane (15cm^3 x3), and the combined extracts were dried with $MgSO_4$. After filtration, the solvent was removed in vacuum in a rotary evaporator to give a red solid (1.79g, 97%), m.p. 275-277°C (from dichloromethane and diethyl ether). $\delta^{31}P$ nmr ($CDCl_3$): 23.7ppm. $\delta^{1}H$ nmr ($CDCl_3$): 5.0 (1H, s, OH), 6.5-8.5 (m, 21ArH) ppm.

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%.

b.4-(o-Triphenylphosphoniophenylazo)-2,6-difluorophenolate

The structure of this compound is shown as (32):



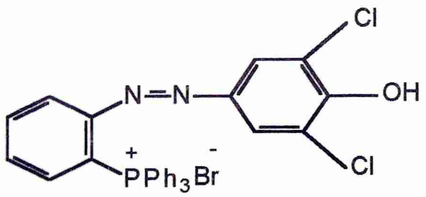
(32)

According the general procedure described above, the related pure salt was shaken with dilute aqueous sodium hydroxide solution to give deep red solid, m.p. >300°C (from dichloromethane and diethyl ether). $\delta^{31}P$ nmr ($CDCl_3$): 22.0 ppm. $\delta^{1}H$ nmr ($CDCl_3$): 6.2(s, 2H), 7.5(m, 19 ArH) ppm.

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%.

c.*4-(o-Triphenylphosphoniophenylazo)-2,6-dichlorophenol Bromid*

The structure of this compound is shown as (33):



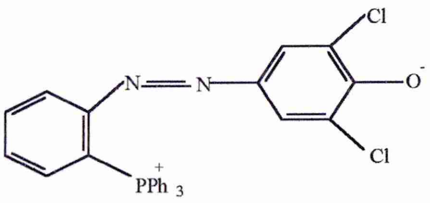
(33)

Analogous to the synthetic method for compound (31), 4-(o-bromo-phenylazo)2,6-dichlorophenol (1.00g, 2.9mmol), triphenylphosphine(1.52g, 5.8mmol) and nickel bromide (63mg) were heated in ethanol (15cm^3) under reflux under nitrogen for 4 hours and worked up in the usual way , triturated with diethyl ether several times, yielding a red solid (0.92g, 52%), m.p 294~296°C (from dichloromethane and diethyl ether). δ^{31}P nmr ($CDCl_3$) 22.72ppm. δ^{1}H nmr ($CDCl_3$) 4.8 (1H,s), 7.0-8.0 (ArH,m) ppm.

Found:C, 67.45; H, 4.04; N, 5.13% $C_{30}H_{22}N_2POCl_2Br$ requires.:C, 59.24; H, 3.65; N, 4.61%. The betaine $C_{30}H_{21}ON_2PCl_2$ requires.:C, 68.32; H, 4.01; N, 5.31%. It would seem to be the betaine rather than the salt (there was very little precipitate in the silver nitrate test).

d.*4-(o-Triphenylphosphoniophenylazo)-2,6-dichlorophenolate*

The structure of this compound is shown as (34):



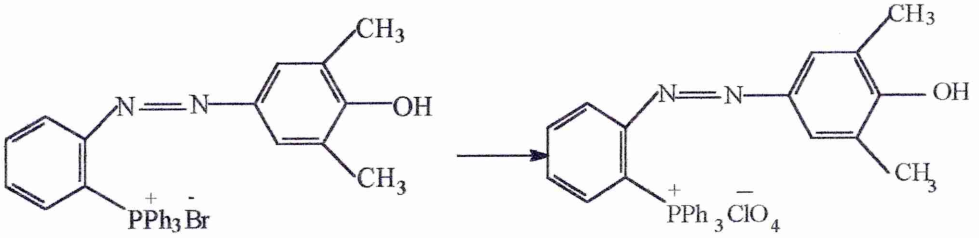
(34)

This was obtained as a red solid, m.p. 290-293°C (from dichloromethane and diethyl ether). δ^{31}P nmr ($CDCl_3$): 22.6 ppm. δ^{1}H nmr ($CDCl_3$) 7.0-8.5 (ArH, m) ppm.

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%.

e.*4-(o̲-Triphenylphosphoniophenylazo)-2,6-dimethylphenol Perchlorate*

The structure of this compound is shown as (35):



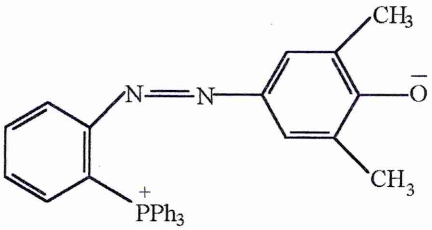
(35)

Analogous to the synthetic method for compound (31) , 4-(o̲-bromophenylazo)2,6-dimethylphenol (0.98g, 3.2mmol), triphenylphosphine (1.68g, 6.4mmol) and nickel bromide (66mg) were heated in ethanol (15cm^3) under reflux under nitrogen for four hours. After recrystallization from dichloromethane and diethyl ether, TLC indicated the presence of impurities. It was therefore converted into the related perchlorate by treating with lithium perchlorate solution to give the pure product as a red solid (1.35g, 86%), m.p. 200-203°C (from dichloromethane and diethyl ether). δ^{31}P nmr CD_3OD): 24.2 ppm. δ^{1}H nmr (CD_3OD): 2.0(s, 6H), 6.7(s, 2ArH), 7.5-8.2(m, 19ArH) ppm.

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%.

f.4-(o-Triphenylphosphoniophenylazo)-2,6-dimethylphenolate

The structure of this compound is shown as (36):



(36)

The pure salt was shaken with dilute aqueous sodium hydroxide solution to give a black solid, m.p. 253-255°C (from dichloromethane and diethyl ether). $\delta^{31}P$ nmr (CD_3OD) 23.4 ppm. δ^1H nmr (CD_3OD): 2.0(s, 6H, CH3), 6.5-8.0 (m, 21 ArH) ppm.

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%.

References

(1). K C Ching, M Lequan, R-M Lequan, A Grisard and D Markovitsi, *J. Chem. Soc., Faraday Trans.*, 1991, *87*, 2225.

(2). C Combellas, H Marzouk, C Suba and A Thiebault, *Synthesis*, 1993, 788.

(3). D W Allen, P E Cropper, P G Smithurst, P R Ashton and B F Taylor, *J. Chem. Soc., Perkin Trans. 1*, 1986, 1989; D W Allen and P E Cropper, *Polyhedron*, 1990, *9*, 129; D W Allen and P E Cropper, *J. Organomet. Chem.*, 1992, *435,* 203.

(4). L. Horner and U.M.Duda, *Tetrahedron Letters,* 5177(1970)

(5). R.T. Morrison, R. N. Boyd, *Organic Chemistry*, 6th Ed, Prentice-Hall, 1992, 873.

(6). D W Allen, I W Nowell, L A March and B F Taylor, *J. Chem. Soc., Perkin Trans. 1*, 1984, 2523.

(7). A M Kjaer and J Ulstrup, *J. Am. Chem. Soc.,* 1987, *109,* 1934.

(8). M A Kessler and O S Wolfbeis, *Synthesis*, 1988, 635 (see also B R Osterby and R D McElvey, *J. Chem. Educ.,* 1996, *73,* 260, 737).

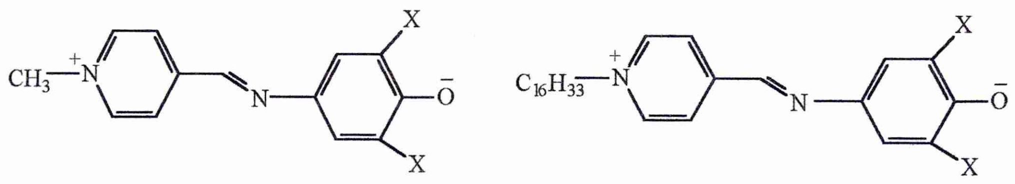
Chapter 3

The Synthesis and Characterisation of N-alkyl Pyridinium Salts and Related Betaines

3.1. Introduction

Pyridinium N-phenoxide betaine dyes have been well studied by Reichardt and widely used as solvent polarity indicators due to their significant solvatochromic properties[1].

In this chapter, the synthesis and characterisation of a series of new solvatochromic systems, the N-methylpyridinium betaines (a) is described. For Langmuir-Blodgett (L-B) film[2] formation and possible non-linear optical property[3] studies, the related N-hexadecylpyridinium betaines (b) have also been prepared which not only display a wider range of the solvatochromic properties, but also exhibit non-linear optical (NLO) properties in the L-B film situation.



(X = Cl, Br or Bu^t)

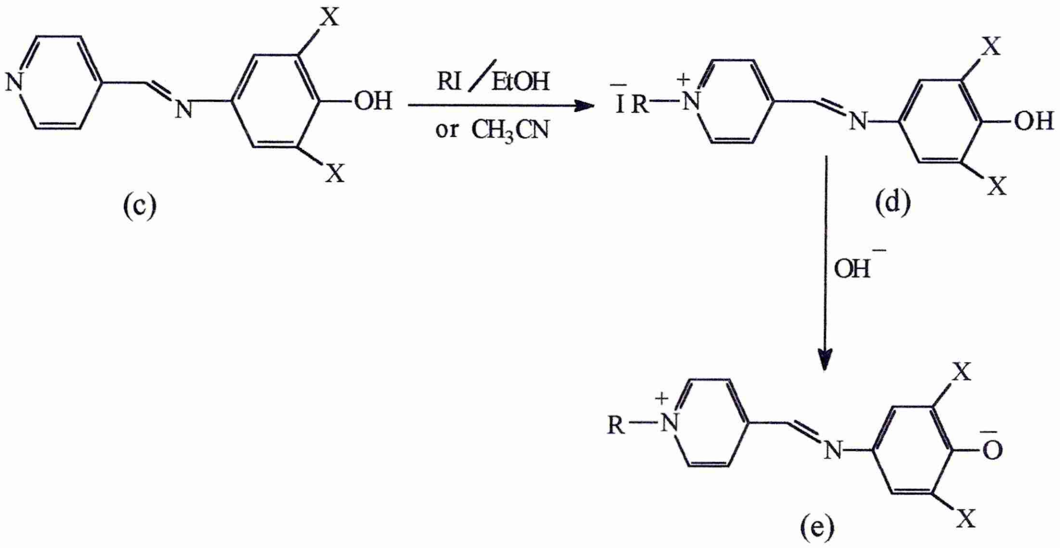
(a) (b)

In the L-B technique, amphiphilic molecules which are suitable for producing L-B films usually possess both hydrophobic and hydrophilic end groups. The hydrophobic end groups are often a long alkyl chain, and in the present work, the long alkyl chain $C_{16}H_{33}$- was attached to the compounds.

3.2. The synthesis of the pyridinium betaines

The parent compound (a, X = H) is described in the literature[4]. Three further examples of both systems, namely (X = Cl, Br or Bu^t) have been prepared in order to extend the comparison with the phosphonio-iminophenolates.

The synthetic route to these betaines is shown in Scheme 1:



(R=CH_3- or $C_{16}H_{33}$-; X=Cl, Br, or Bu^t)

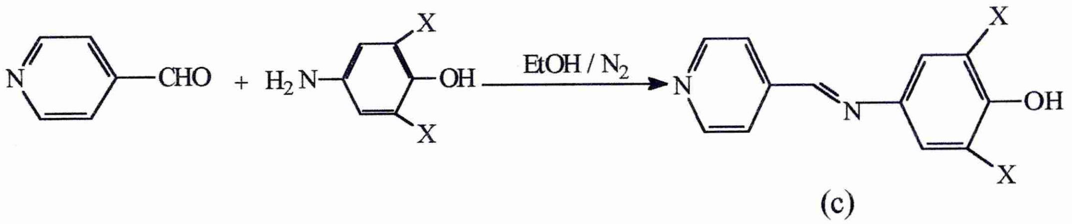
Scheme 1

From the structure of these betaines, it would be predicted that they would exhibit a large permanent dipole moment, in which the phenolate moiety possesses the negative charge (basic electron-pair donor) centre and the pyridinium moiety is the positive (electron-pair acceptor) centre.

This synthesis of these betaines was achieved in two main steps which are described below:

3.2.1. Preparation of imino intermediates used for synthesis of pyridinium salts:

The route for the synthesis of the imines is shown in scheme (2):



(c)

Scheme 2

This reaction was carried out by heating pyridine-4-carboxaldehyde with the appropriate 4-amino-2,6-disubstituted phenol in ethanol under reflux. This reaction is based on the same mechanism of formation of imines which was described earlier in the synthesis of the phosphonioiminophenolates (chapter 2).

3.2.2. Preparation of pyridinium salts and related betaines

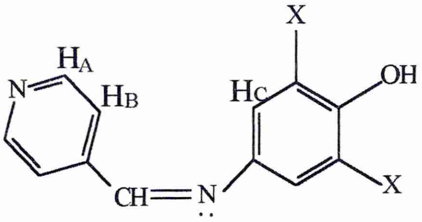
Conversion to the pyridinium salts was accomplished in ethanol or acetonitrile solution under reflux on treatment of the imines with either iodomethane or iodohexadecane. The nitrogen of the pyridine system has a pair of electrons available to form a new covalent bond with carbon atom of the alkyl halide, and hence it acts as a nucleophile. Like a typical tertiary amine, it can react with an alkyl halide to form the related quaternary salt.

Finally, the betaines were obtained as blue-black solids by deprotonation of the pure salts with aqueous base.

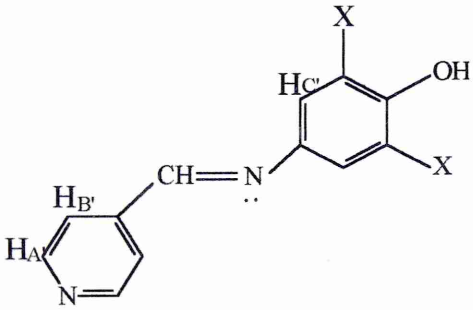
3.3 The ^{1}Hnmr study

All spectra were recorded in either CD_3OD or $CDCl_3$.

For the imine intermediates , the ^{1}H (CD_3OD) nmr spectra showed two sets of signals for compounds (c, X = Cl, Br), of approximately equal intensity, probably due to the isolation of approximately equal amounts of the isomers shown below:



(1c)



(2c)

Thus, the related hydrogens in the two isomers were not in magnetically equivalent environment so that there are two signals for each of H_A, H_B and H_C. However the ^{1}H (CD_3OD) spectra showed that compound (c, X = Bu^t) was isolated largely as one isomer. The signal for the imino CH = N appeared as a part of the aromatic hydrogen multiplet, coinciding with signals from the pyridine ring at $\delta \approx 8.7$ ppm.

For the 4-methyl pyridinium salts, the ^1H nmr (CD_3OD) spectra showed that the signal from the methyl group appeared at $\delta \approx 4.5$ppm. The signal due to methyl group of the dibutyl-substituted system (d, R = CH_3, X = Bu^t) showed only one signal; however, two signals for the methyl and other aromatic hydrogens were evident in the spectra of the related dichloro and dibromo systems , which indicated that two isomers existed in these salts. The imino CH = N signal was observed at about $\delta = 9.0$ppm. On conversion to the betaines, most of signals moved to lower chemical shift by 0.2 ~ 1.0ppm. Two isomers were still present in the betaine (e, R = CH_3, X = Cl), whereas the related bromo and butyl betaines looked consisted largely of one isomer.

For the 4-hexadecylpyridinium salt (d, R = $C_{16}H_{33}$, X = Cl, Br, Bu^t), the ^1Hnmr (CD_3OD) spectrum showed twenty nine hydrogens of hexadecyl group existed as a multiplet at approximately $\delta = 1 \sim 1.5$ ppm. Two hydrogens of hexadecyl group appeared as a multiplet at $\delta = 2.2$ ppm and two hydrogens close to the nitrogen (N^+-CH_2) appeared as a triplet at $\delta = 4.6$ ppm. The ^1H nmr spectrum clearly showed that the bromo salt (d, R = $C_{16}H_{33}$, X = Br) was present as two isomers whereas the related chloro and butyl salt consisted largely of one isomer. All of the imino CH = N signals appeared as a singlet at $\delta \approx 8.9$ ppm. On conversion to the betaines, all of the betaines consisted largely of one isomer and the imino hydrogen appeared at about $\delta = 8.5$ ppm , slightly shielded by ~ 0.4ppm.

In the solvent CD_3OD, all of the signals due to the phenolic -OH disappeared.

3.4. Experimental

3.4.1. Preparation of Imine intermediates used for synthesis of 4-methyl (or hexadecyl) pyridinium salts

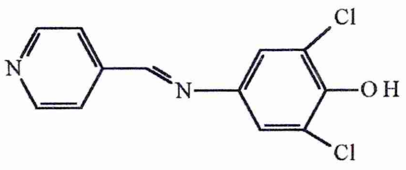
General procedure:-

The respective aminophenol and pyridine-4-aldehyde (1 mol. equiv.) were heated together in ethanol under nitrogen for 2-3 hours. On cooling, the imine usually crystallised out of solution and was isolated by filtration. If no crystals appeared, the ethanolic solution was then evaporated, and the residue triturated with petrol, prior to recrystallisation.

The following compounds were isolated:

a.*4-(4-Pyridylmethylidene)amino-2,6-dichlorophenol.*

The structure of this compound is shown as (1):



(1)

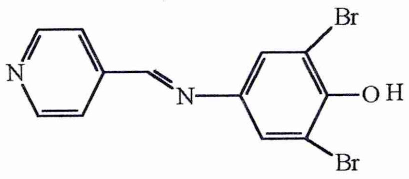
According to the above procedure, it was synthesised by heating pyridine-4-aldehyde (0.86g, 8mmol) and 4-amino-2,6-dichlorophenol (1.32g, 8mmol) in ethanol under reflux under nitrogen for 3 hours. On cooling, the precipitate formed was filtered off and recrystallized from ethanol and diethyl ether to give the product as brown crystals (2.00g, 93%), m.p.222~224°C. δ^1H (CD_3OD)

two isomers: 6.8, 7.4(s, 2H_C environments); two H_AH_B systems centred at 8.20 and 8.05ppm; 8.7(s,1H, CH=N)ppm.

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%.

b.4-(4-Pyridylmethylidene)amino-2,6-dibromophenol.

The structure of this compound is shown as (2):



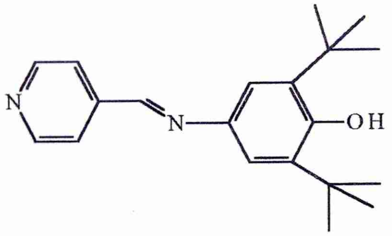
(2)

Preparation of this compound was carried out in the same way as that of compound (2). pyridine-4-aldehyde (0.86g ,8x10^{-3} mol) and 4-amino-2,6-dibromophenol (2.13g ,8x10^{-3} mol) in ethanol (20cm^3) were heated under reflux under nitrogen for 3 hours to give the product as brown -yellow crystals (1.75g, 65%), m.p.215~217°C (from ethanol and diethyl ether). $\delta^1H(CD_3OD)$ two isomers: 6.8, 7.6(s, 2H_C environments); two H_AH_B systems centred at 8.10 and 8.25ppm; 8.7(s,1H, CH=N)ppm.

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%.

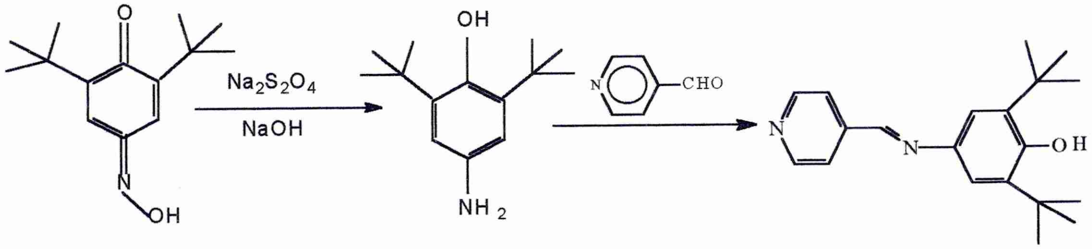
c.4-(4-Pyridylmethylidene)amino-2,6-di-t-butylphenol.

The structure of this compound is shown as (3):



(3)

The basic route for the synthesis of this compound is shown in scheme (3):



scheme 3

The synthesis of 4-amino-2,6-di-t-butylphenol was carried out as described in chapter 2, i.e., 2, 6 di-t-butyl-p-benzoquinone-4-oxime (2.5g, 10.6mmol) was heated with sodium hydrosulfite (5.25g, 30.2mmol) with stirring to give 4-amino-2,6-di-t-butylphenol which was used quickly without further purification in the following step.

Then, according to the procedure given above for compound (1), pyridine-4-aldehyde (1.13g, 10.6mmol) with 4-amino-2,6-di-t-butylphenol prepared *in situ* was heated in ethanol ($20cm^3$) under reflux under nitrogen for 3 hours. After standing overnight, the product appeared as orange crystals which were filtered off (1.58g, 52%), m.p. 201~203°C (from ethanol). $\delta^1H(CD_3OD)$ one isomer: 1.6(s, 18H); 7.25(s, 2H); 7.95(d, 2H); 8.7(t, 3H)ppm.

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%).

3.4.2. Preparation of 4-(1-Methylpyridinium-4-methylidene)aminophenol Salts and related Betaines

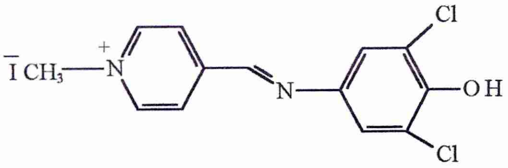
The respective 4-pyridine iminophenol (4×10^{-3} mol) and iodomethane(4.4×10^{-3} mol) in ethanol were heated under reflux under nitrogen for 4~5 hours. After cooling, the precipitated product was collected and recrystallized from ethanol (or dichloromethane) and diethyl ether. In some cases, if the salt was still impure after recrystallization, 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 betaines, which were usually purified by recrystallization. If the salt was insoluble in dichloromethane, it was dissolved in acetonitrile (warming if necessary) and heated with one equivalent of DBU . The solution was stirred for 0.5 hour and then filtered off to isolate the corresponding betaines.

The following compounds were characterised:

a. 4-(1-Methylpyridinium-4-methylidene)amino-2,6-dichlorophenol iodide.

The structure of this compound is shown as (4):



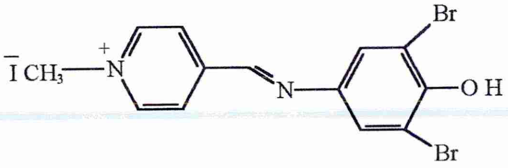
(4)

According to the above procedure, 4-(4-pyridylmethylidene)amino-2,6-dichlorophenol(1.07g, 4mmol) was heated with iodomethane(0.625g, 4.4mmol) in ethanol under reflux under nitrogen for 5 hours. After cooling, the precipitated product was filtered off to give a brown solid (1.09g, 71%), m.p.269~270°C (from ethanol and diethyl ether) . $\delta^1H(CD_3OD)$ two isomers: 4.35, 4.45(s, 2CH3 environments); 6.75, 7.60(s, $2H_C$ environments); two H_AH_B systems centred at 8.3 and 8.95ppm; 8.9(s,1H, CH=N)ppm.

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%.

b. 4-(1-Methylpyridinium-4-methylidene)amino-2,6-dibromophenol iodide.

The structure of this compound is shown as (5):



(5)

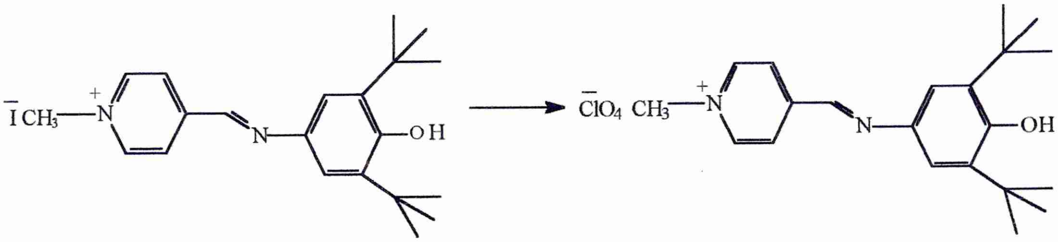
This was prepared as described for compound (4), 4-(4-Pyridylmethylidene) amino-2,6-dibromophenol (1.4g, $4x10^{-3}$ mol) and iodomethane (0.625g, $4.4x10^{-3}$

mol) in ethanol (15cm^3) were heated together under reflux under nitrogen for 5 hours. The product was finally obtained as a brown solid (1.39, 70%), m.p.204~206°C (from ethanol and diethyl ether). δ^1H (CD_3OD) two isomers: 4.4, 4.5(s, 2CH_3 environments); 7.0, 7.7(s, 2H_C environments); two H_AH_B systems centred at 8.55 and 8.7ppm; 8.9(s,1H, CH=N)ppm.

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%.

c.4-(1-Methypyridinium-4-methylidene)amino-2,6-di-t-butylphenol perchlorate.

The expected structure of this compound is shown as (6):



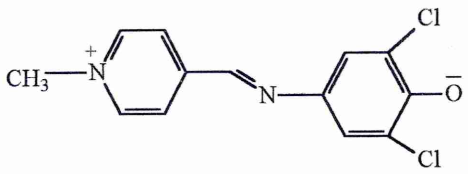
(6)

According to the procedure given above for (6), 4-(4-pyridylmethylidene) amino-2,6-di-t-butylphenol (0.6g, 2x10^{-3} mol) and iodomethane(0.315g, 2.2x10^{-3} mol) in ethanol (15cm^3) were heated together under reflux under nitrogen for 5 hours to give a brown solid (0.52g, 61%) and then converted to the perchlorate for elemental analysis, m.p.232~234°C (from dichloromethane and diethyl ether). δ^1H(CD_3OD) one isomer:1.4(s, 18H); 4.4(s, 3H); 7.4(s,2H); 8.5(d, 2H); 8.9(t, 3H)ppm.

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%.

d. 4-(1-Methypyridinium-4-methylidene)amino-2,6-dichlorophenolate.

The structure of this compound is shown as (7):



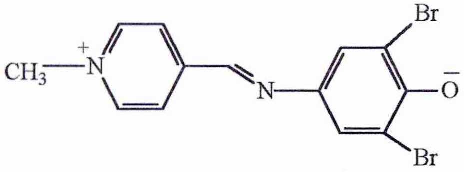
(7)

This betaine was not very soluble in dichloromethane. According to the deprotonation method given above (3.4.2), the related purified salt was dissolved in acetonitrile and stirred with one equivalent of DBU for about 30 min. The mixture was filtered off to give a black solid, m.p.224~226°C (from ethanol and diethyl ether). $\delta^1H(CD_3OD)$ two isomers: 4.25, 4.35(s, $2CH_3$ environments); 7.35, 7.50(s, $2H_C$ environments); two H_AH_B systems centred at 8.3 and 8.55ppm; 8.7(s,1H, CH=N)ppm.

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%.

e. 4-(1-Methylpyridinium-4-methylidene)amino-2,6-dibromophenolate.

The expected structure of this compound is shown as (8):



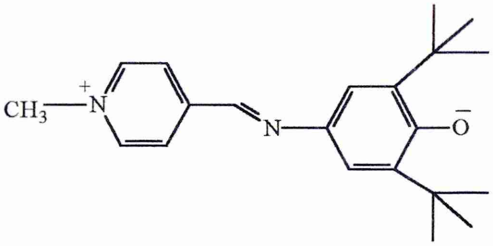
(8)

The deprotonation reaction was carried out using the procedure used for (7); this betaine was isolated as a black solid, m.p.214~216°C (from ethanol and diethyl ether). $\delta^1H(CD_3OD)$ one isomer: 3.5(m, 3H); 7.6(s, 2H); 7.8(d, 2H); 8.5(s, 1H, CH = N); 8.6(d, 2H) ppm.

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%.

f. 4-(1-Methylpyridinium-4-methylidene)amino-2,6-di-t-butylphenolate.

The structure of this compound is shown as (9):



(9)

According to the procedure given above, the related purified salt was shaken with several portions of dilute sodium hydroxide solution to give the product as a blue solid, m.p.199~202°C (from dichloromethane and diethyl ether). $\delta^1H(CD_3OD)$ one isomer: 1.4(s, 18H); 4.0(s, 3H); 7.35(s, 2H); 7.7(d, 2H); 8.05(t, 3H) ppm.

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%.

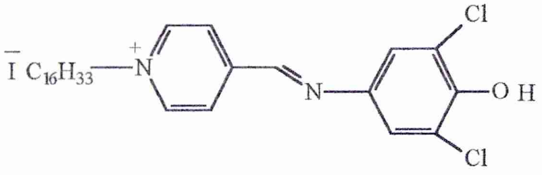
3.4.3.Preparation of 4-(1-n-hexadecylpyridinium-4-methylidene) amino-phenol salts and related betaines

The respective 4-pyridine imino phenol (4×10^{-3} mol) and iodohexadecane (4.4×10^{-3} mol) in acetonitrile (20ml) were heated under reflux under nitrogen for 5~7 hours. After cooling, the solid product was filtered off and purified by recrystallization from dichloromethane and diethyl ether(or petrol). If no solid appeared after standing overnight, the mixture was evaporated and triturated with petroleum. In some cases, it was necessary to convert the salts to the corresponding perchlorate in order to get good microanalytical data.

The purified salt was dissolved in dichloromethane (or acetonitrile) and shaken with several portions of dilute sodium hydroxide solution or stirred with potassium carbonate to give the corresponding betaines, which were usually purified by recrystallization.

The following salts were isolated:

a. 4-(1-n-hexadecylpyridium-4-methylidene)amino-2,6-dichlorophenol iodide.
The structure of this compound is shown as (10):



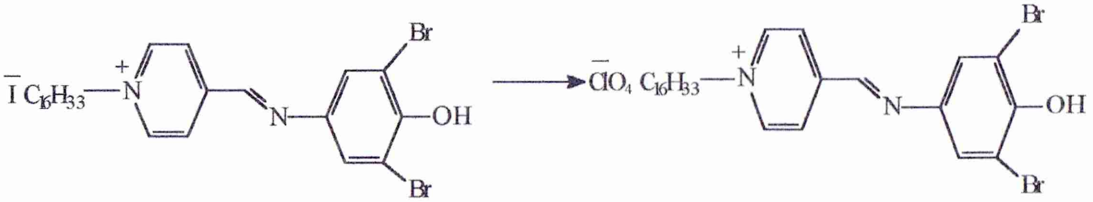
(10)

According to the above procedure, 4-(4-pyridylmethylidene) amino-2,6-dichlorophenol (0.53g, 2mmol) was heated with iodohexadecane (0.77g, 2.2mmol) in acetonitrile (20cm^3) under reflux under nitrogen for 5 hours (there was no reaction in ethanol). After cooling, the precipitated product was filtered off to give a orange-brown solid (0.9g, 73%) which was recrystallized from dichloromethane and diethyl ether to give the pure salt for microanalysis (but in low yield), m.p. 123~125°C. δ^1H(CD$_3$OD) one isomer:1.5(m, 29H); 2.2(m, 2H); 4.6(t, 2H); 7.6(s, 2H); 8.5(d, 2H); 8.9(s, CH = N); 9.05(d, 2H)ppm.

Found C; 54.40; H, 6.70; N, 4.50; $C_{28}H_{41}ON_2Cl_2I$ requires C, 54.30; H, 6.65; N, 4.50%.

b.4-(1-n-hexadecylpyridium-4-methylidene)amino-2,6-dibromophenol perchlorate

The structure of this compound is shown as (11):



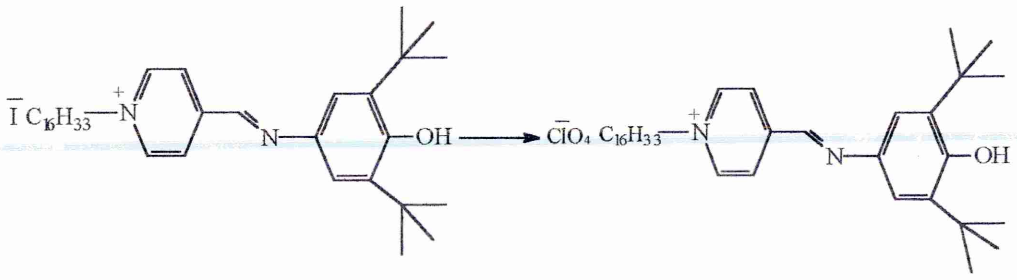
(11)

According to the above procedure for compound (4), 4-(4-pyridylmethylidene)amino-2,6-dibromophenol (1.4g, 4mmol) was heated with iodohexadecane (1.4g, 4.4mmol) in acetonitrile ($20cm^3$) under reflux under nitrogen for 5 hours. After cooling, the product appeared as a oil and was left to crystallise for a few days and then filtered off to give an orange-brown solid (1.34g, 49%). In order to obtain the pure salt for microanalysis, it was converted into the perchlorate salt, m.p. 109~110°C (from dichloromethane and diethyl ether). $\delta^1H(CD_3OD)$ two isomers: 1~1.5(m, 29H); 2.1(m, 2H); 4.6(t, 2H); 6.95, 7.75(s, $2H_C$ environments); two H_AH_B systems centred at 8.6 and 8.75ppm; 8.85(s,1H, CH=N)ppm.

Found C; 49.30; H, 6.35; N, 3.75; $C_{28}H_{41}O_5N_2Br_2Cl$ requires C, 49.40; H, 6.05; N, 4.10%.

c.4-(1-n-hexadecylpyridnium-4-methylidene)amino-2,6-di-t-butylphenol perchlorate.

The structure of this compound is shown as (12):



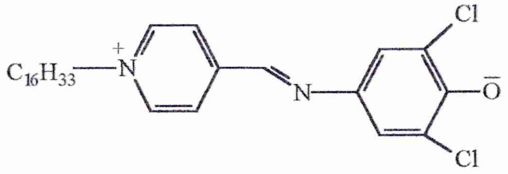
(12)

According to the above procedure for compound (4), 4-(4-pyridylmethylidene)amino-2,6-di-t-butylphenol (0.9g, 3mmol) was heated with iodohexadecane (1.05g, 3.3mmol) in acetonitrile (20cm^3) under reflux under nitrogen for 5 hours. After standing overnight, there was no solid, and hence the solution was evaporated and the residue triturated with petrol (it was too soluble in diethyl ether) to give the product as a yellow-orange solid (0.78, 41%), while was then converted into the perchlorate salt which was recrystallized from dichloromethane and petrol to give the pure salt, m.p. 114~115°C. δ^1H (CD_3OD) one isomer: 1.2 ~ 1.4(m, 29H); 2.1(m, 2H); 4.6(t, 2H); 1.4 ~ 1.5(s, 18H); 7.4(s, 2H); 8.5(d, 2H); 8.85(s, 1H, CH = N); 9.0(d, 2H) ppm.

Found C; 67.95; H, 9.45; N, 4.35; $C_{36}H_{59}O_5N_2Cl$ requires C, 68.05; H, 9.35; N, 4.40%.

d. 4-(1-n-hexadecylpyridinium-4-methylidene)amino-2,6-dichlorophenolate.

The structure of this compound is shown as (13):



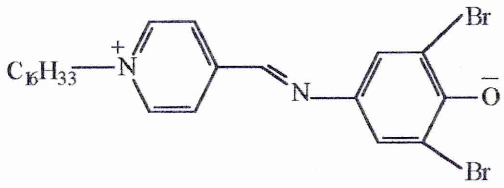
(13)

The purified salt was dissolved in dichloromethane and stirred with one equivalent of potassium carbonate for about one hour at room temperature. Then mixture was then filtered and the filtrate evaporated and triturated with a little petrol to give a purple-black solid, m.p. 114~116°C (from dichloromethane and diethyl ether). $\delta^1H(CD_3OD)$ one isomer: 1.4(m, 29H); 2.0(m, 2H); 4.5(t, 2H); 7.45(s, 2H); 8.2(d, 2H); 8.55(s, 1H, CH = N); 9.3(d, 2H) ppm.

Found C; 60.10; H, 7.20; N, 5.00; $C_{28}H_{40}ON_2Cl_2 \cdot 4H_2O$ requires C, 59.65; H, 8.30; N, 4.95%.

e. 4-(1-n-hexadecylpyridinium-4-methylidene)amino-2,6-dibromophenolate.

The structure of this compound is shown as (14):



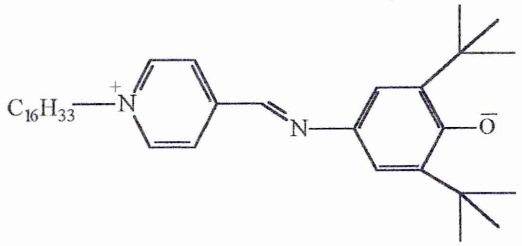
(14)

This betaine was obtained in the normal way, i.e., the parent salt dissolved in dichloromethane was shaken with several portions of dilute sodium hydroxide and after separation and drying, the dichromethane was evaporated to give a purple-black solid m.p 116~118°C (from dichloromethane and diethyl ether). $\delta^1H(CD_3OD)$ one isomer: 1.5(m, 29H); 2.0(m, 2H); 4.5(t, 2H); 7.7(s, 2H); 8.25(d, 2H); 8.5(s, CH=N); 8.8(d, 2H) ppm.

Found C; 56.05; H, 6.90; N, 4.50; $C_{28}H_{40}ON_2Br \cdot H_2O$ requires C, 56.20; H, 7.05; N, 4.70%.

f. 4-(1-n-hexadecylpyridinium-4-methylidene)amino-2,6-di-t-butylphenolate.

The structure of this compound is shown as (15):



(15)

This betaine was obtained in the same way with (14). The product was isolated as a sticky blue solid which was found difficult to purify. Subsequently, it was recrystallized from dichloromethane and petrol to give the pure betaine for microanalysis , which revealed that the betaine contained two water molecules, m.p. 118~120°C. δ^1H ($CDCl_3$) one isomer: 1.0 ~ 2.0 (m, 47H); 2.2(m, 2H); 4.6(t, 2H); 7.3(s, 2H); 7.8(d, 2H); 8.5 (s, 1H, CH = N); 8.8(d, 2H)ppm.

Found C; 75.85; H, 10.35; N, 2.200; $C_{36}H_{58}ON_2 \cdot 2H_2O$ requires C, 75.75; H, 10.95; N, 4.90%

References

1. a). K . Dimroth; C. Reichardt, *Liebigs Ann. Chem.* 1963, *661,* 1-37.

b). C. Reichardt, *Chem. Rev.* 1994, *94,* 2319.

2. O.A. Aktispetrov, N.N. Akhmediev. *Sov.Tech. Phys., 11*(1985)249

3. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D.S., Zyss, J., Eds.; Acadmic press: Orlando, FL, 1987; Vol.1.

4. M . Clodoaldo, *J. Chem.Soc. Perkin Trans. 2* , 1994 , 2539.

Chapter 4

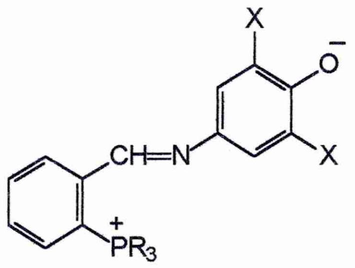
Solvato- and Halo- chromic Properties of Phosphonio- and Pyridinium- Phenolate Betaines

4.1. Introduction

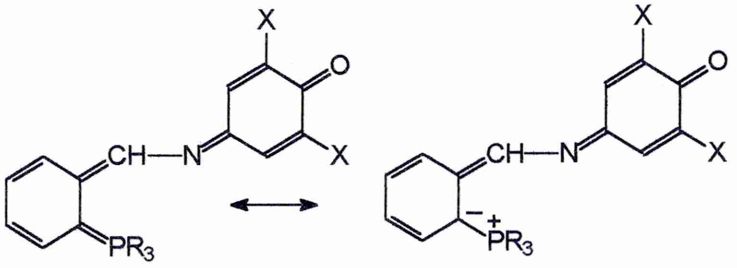
As discussed in chapter 1, the term solvatochromism refers to the shift of an electronic absorption band of a solute when the polarity of the solvent is varied and the term halochromism refers to the shift of the solvatochromic CT-absorption band of a solute when a salt is added to a solution. Most of betaines which have been synthesised (chapters 2 and 3) exhibited not only a pronounced negative solvatochromism, i.e., polar solvents shift its UV/Visible absorption to shorter wavelengths and nonpolar solvents shift it to longer wavelengths, but also showed negative halochromism. In this chapter, the solvatochromic characters of these betaines were investigated by dissolution in a range of organic solvents and measurement of their respective longest-wavelength absorption bands λ_{max} using UV/Visible spectroscopy and the halochromic properties of some of betaines were demonstrated by addition of appropriate salts into solutions of the betaines. A Langmuir-Blodgett (L-B) film of 4-(1-n-hexadecylpyridinium-4-methylidene) amino-2, 6-dichlorophenolate was investigated by Prof. G. Ashwell.

4.2. The solvatochromism of N-(o-phosphoniobenzylidene) amino- phenolate betaines.

All of these betaines exhibited negative solvatochromism, the position of the visible absorption band moving towards shorter wavelength as the solvent polarity increased. For example, the betaine (1, 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 -5,500 cm^{-1}, approximately half that of the Reichardt betaine. The observation of negative solvatochromism reflects the stabilisation in the more polar solvents of the dipolar betaine form (ground state, 1A), relative to the less polar forms (excited state, 1B).



(1A)



(1B)

Hence, all the phosphonio imino betaines possess charge separation in the ground state and the excited state presents a quinonoidal structure.

4.2.1. UV/Visible absorption characteristics of N-(o-phosphonio- benzylidene) aminophenolate betaines.

The longest-wavelength intramolecular CT absorption bands λ_{max} and the corresponding extinction coefficient ε_{max} of these betaines are listed as below. The molar extinction coefficient was calculated according to the equation.: $A = \varepsilon.c.l.$ ($c \approx 1x\ 10^{-4}$ M).

a. 4-N(o-Triphenylphosphoniobenzylidene)amino-2,6-dichlorophenolate

Table 4-1

solvent	**colour**	**wavelength λmax, nm**	**$\varepsilon_{max} \times 10^4 (M^{-1} cm^{-1})$**
methanol	**yellow**	**446**	**0.745**
ethanol	**orange**	**472**	**0.993**
acetonitrile	**red**	**504**	**0.916**
acetone	**red**	**536**	**1.960**
dichloromethane	**red**	**532**	**2.669**
ethyl acetate	**purple**	**564**	**0.720**
THF	**violet**	**578**	**1.638**

This dye exhibits highly negative solvatochromism. Its intramolecular CT absorption band undergoes a hypsochromic shift of about -5120cm^{-1}(132nm) on going from THF (λ_{max} = 578nm) to methanol (λ_{max} = 446nm).

b. 4-N(o-Triphenylphosphoniobenzylidene)amino-2,6-dibromophenolate

Table 4-2

solvent	**colour**	**wavelength λmax, nm**	**$\varepsilon_{max} \times 10^4 (M^{-1} cm^{-1})$**
methanol	**yellow**	**454**	**1.386**
ethanol	**orange**	**474**	**1.128**
acetonitrile	**orange-red**	**496**	**1.556**
acetone	**red**	**534**	**1.780**
dichloromethane	**red**	**532**	**1.838**

The number of solvents which could be used was limited by insufficient solubility in nonpolar solvents. The hypsochromic shift of -3230cm^{-1} (78nm) from 532nm in dichloromethane to 454nm in methanol, was observed which was smaller than for the dichloro betaine compound (a).

c. *4-N(o-Triphenylphosphoniobenzylidene)amino-2,6-di-t-butylphenolate*

Table 4-3

solvent	**colour**	**wavelength λmax, nm**	**$\varepsilon_{max} \times 10^4$ (M^{-1} cm^{-1})**
methanol	**red**	**532**	**2.077**
ethanol	**purple**	**566**	**1.857**
acetonitrile	**blue**	**598**	**2.605**
acetone	**blue-green**	**628**	**2.334**
dichloromethane	**blue-green**	**616**	**2.643**
ethyl acetate	**green**	**652**	**1.180**
THF	**green**	**662**	**3.686**

This betaine showed a very large hypsochromic shift as the solvent polarity increased, i.e., a shift of -3690cm^{-1} (130nm) from 532nm in methanol to 662nm in THF. Its solvatochromism extended over the whole visible region, hence, colour changed from red in methanol to green in THF. However, the colour in the polar solvents, such as methanol and ethanol, faded after several hours due to their weak light fastness property on exposure to light .

d. *4-N(o-Triphenylphosphoniobenzylidene)amino-2,6-diphenylphenolate*

Table 4-4

solvent	**colour**	**wavelength λmax, nm**	$\varepsilon_{max} \times 10^{4} (M^{-1} cm^{-1})$
methanol	**red**	**498**	**1.516**
ethanol	**red**	**522**	**1.826**
acetonitrile	**violet**	**562**	**1.499**
acetone	**blue**	**604**	**1.947**
dichloromethane	**purple**	**596**	**1.626**
ethyl acetate	**green**	**642**	**1.584**
THF	**green**	**648**	**2.205**
Toluene	**green**	**686**	**1.666**

This betaine was readily soluble in all organic solvents and displayed the largest solvatochromic shift of the betaines, which extended over almost the whole visible range , from λ_{max}= 686nm in toluene to λ_{max}= 498nm in methanol, giving a maximum frequency range of -5500cm^{-1} (188nm). The pronounced colour changed from red to green, covering the whole visible region.

e. *4-N(o-Tributylphosphoniobenzylidene)amino-2,6-dichlorophenolate*

Table 4-5

solvent	**colour**	**wavelength λmax, nm**	$\varepsilon_{max} \times 10^{4} (M^{-1} cm^{-1})$
methanol	**yellow**	**426**	**1.800**
ethanol	**yellow**	**444**	**1.888**
acetonitrile	**orange**	**470**	**2.659**
acetone	**red**	**504**	**2.610**
dichloromethane	**red**	**510**	**2.396**

The betaine showed a shorter colour range than the realted triphenylphosphonio betaine with a maximum band shift of -3860cm^{-1} (84nm), from 510nm in dichloromethane to 426nm in methanol.

f. *4-N(o-Tributylphosphoniobenzylidene)amino-2,6-dibromophenolate*

Table 4-6

solvent	**colour**	**wavelength λmax, nm**	**$\varepsilon_{max} \times 10^4$ (M^{-1} cm^{-1})**
methanol	**yellow**	**424**	**1.080**
ethanol	**yellow**	**438**	**1.622**
acetonitrile	**yellow**	**460**	**1.683**
acetone	**orange**	**502**	**1.301**
dichloromethane	**red**	**508**	**2.188**

This betaine also showed a similar solvatochromic property to the above compound e; its absorption band undergoes a hypsochromic shift of about -3890 cm^{-1} (84nm), from 508nm (dichloromethane) to 424nm (methanol).

g. *4-N[o-di(p-methoxyphenyl)phenylphosphoniobenzylidene)amino-2,6-dibromo phenolate*

The solvatochromism of this betaine was also investigated in order to assess the effect of the introduction of electron-donating *p*-methoxy substituents at phosphorus on the solvatochromic properties.

Table 4-7

solvent	colour	wavelength λmax, nm	$\varepsilon_{max} \times 10^4$ (M^{-1} cm^{-1})
methanol	yellow	446	0.804
ethanol	yellow-orange	460	1.794
acetonitrile	orange	496	1.644
acetone	red	520	1.411
dichloromethane	red	520	1.888
ethyl acetate	purple	546	0.642
THF	purple	568	0.960

Like the other iminophosphonio betaines, this betaine also showed a negative solvatochromism. From 568nm in THF to 446nm in methanol, it showed a large hypsochromic shift of -4816cm^{-1} (122nm). However, comparison with compound (b) shows that the effects of introducing the *p*-methoxy substituents is not great, causing a small hypsochromic shift in most solvents, and increasing the solubility range marginally. Presumably, the electron-donating property of the *p*-methoxyphenyl substituent stabilises the dipolar ground state.

4.2.2. Discussion

The molar transition energy E_T has been employed as a measure of the interaction of betaine molecules with solvent systems. The molar transition energy will be used in the present discussion to compare various betaine-solvent media interactions. It can be calculated from equation (1) in chapter 1.

The solvatochromism of each betaine was found to be comparable to that of Reichardt's pyridinium N-phenoxide betaine. The normalized empirical solvent polarity parameters E_T^N of the Reichardt dye[1], the longest-wavenumber intramolecular CT absorption ν_{max} (=1/ λmax) x $10^3 cm^{-1}$ of betaines above, and their corresponding transition energies, E_T kcal/mol, are shown in Table 4-7.

Table4-7

Solvent	$E_T(30)$	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		betaine (g)	
	E_T^N	ν_{max}	E_T	ν_{max}	E_T	ν_{max}	E_T	ν_{max}	E_T	ν_{max}	E_T	ν_{max}	E_T	ν_{max}	E_T
Methanol	0.76	20.1	57.4	18.7	53.5	22.4	64.1	22.0	63.0	23.5	67.1	23.6	67.4	22.4	64.1
Ethanol	0.65	19.2	54.8	17.7	50.5	21.2	60.6	21.0	60.3	22.5	64.4	22.8	65.3	21.7	62.2
Acetonitrile	0.46	17.8	50.9	16.7	47.8	19.8	56.7	20.2	57.6	21.3	60.8	21.7	62.2	20.2	57.6
Acetone	0.35	16.6	47.3	15.9	45.5	18.7	53.3	18.7	53.5	19.8	56.7	19.9	56.9	19.2	55.0
Dichloromethane	0.31	16.8	48.0	16.2	46.4	18.8	53.7	18.8	53.7	19.6	56.1	19.7	56.3	19.2	55.0
Ethyl acetate	0.23	15.6	44.5	15.5	43.9	17.7	50.7							18.3	52.4
T.H.F	0.21	15.4	44.1	15.1	43.2	17.3	49.5							17.6	50.3
Toluene	0.10	14.6	41.7												
$\Delta\nu_{max}$ 1) ΔE_T		- 5.50	- 15.7	- 3.69	- 10.4	- 5.12	- 14.7	- 3.23	- 9.20	- 3.86	- 11.1	- 3.89	- 11.2	- 4.82	- 13.8

1). $\Delta\nu_{max} = \nu_{nonpolar} - \nu_{polar}$; $\Delta E_T = E_{T\ nonpolar} - E_{T\ polar}$

For each of the above compounds, a plot of wavenumber ν of the longest wavelength visible absorption band of the phosphonium betaine against the normalised solvent polarity parameter E_T^N for the Reichardt betaine is shown as fig.1:

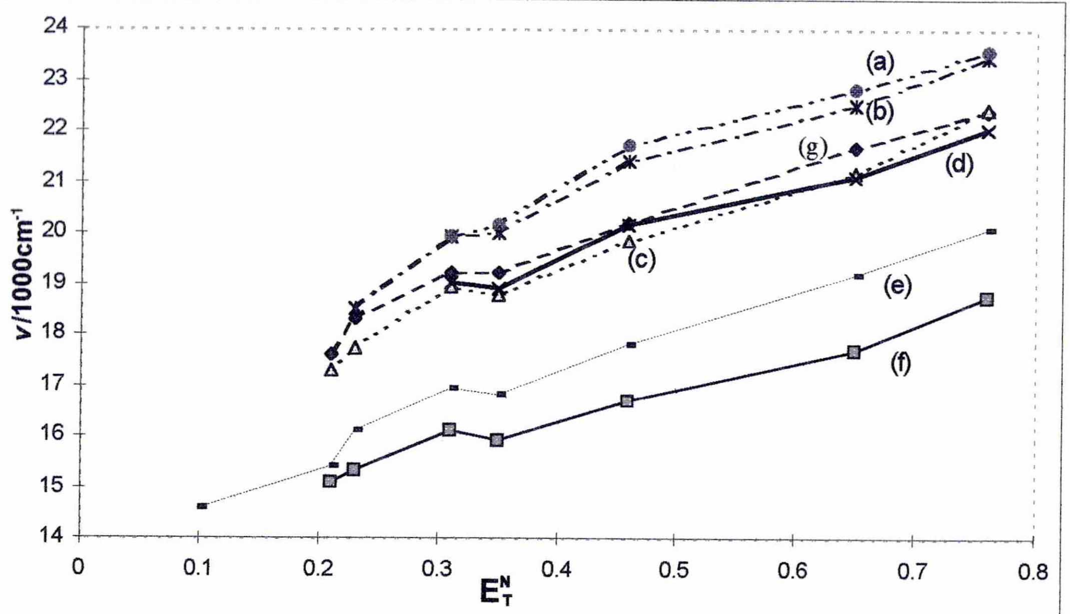


fig.1 Key to compounds: a:R=Bu,X=Br; b:R=Bu,X=Cl; c:R=Ph, X=Cl; d:R=Ph,X=Br; e:R=Ph, X=Ph; f:R=Ph, X=Bu^t; g: betaine(g)

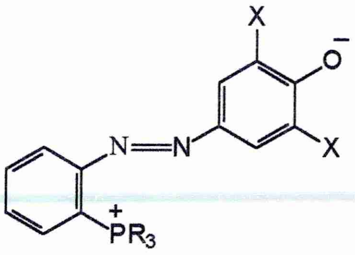
The plot reveals a negative solvatochromic behaviour which correlates reasonably well with that observed for the Reichardt betaine. Measurement points lie nearly on straight line with positive slope. Significantly, the plot is fairly linear over the range of solvent polarity from methanol to acetone. All the plots show similar solvatochromic behaviour in solvents of different polarity, which implies that all the betaines are similarly solvated in all solvents.

It can been seen that various betaines exhibit different positions of the absorption band in a given solvent , with the colour ranging from yellow to green, depending on the type of substituents in the betaines. Thus, introduction of electron-withdrawing substituents such as chloro or bromo into the phenolate moiety of the betaine leads to a hypsochromic shift of the CT absorption band, due to their stabilization effect on the more dipolar ground state. Replacing chloro by electron-donating substituents such as t-butyl groups causes a bathochromic shift due to the effect of destabilization of the dipolar form. For example, dichloro betaine (a) showed an absorption band at $\lambda_{max} = 446$ nm, whereas the dibutyl betaine (c, $\lambda_{max} = 532$nm) brings about a red shift of 86nm.

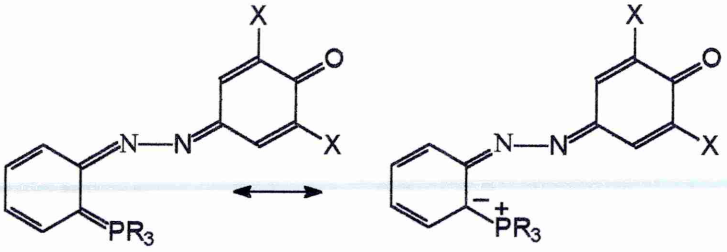
However, in the *ortho* position of the benzylimino moiety of the betaine, the effect of replacing phenyl groups at phosphorus by electron-donating groups such as n-butyl or *p*-methoxyphenyl causes a hypsochromic shift of the CT absorption band because they stabilise the dipolar form.

4.3. The solvatochromism of N-(o-phosphoniophenylazo) phenolate betaines.

The effect on the solvatochromic properties of phosphonio-phenolate betaines of replacing the imino group in the phosphonio-iminophenolates by azo has also been studied. These betaines (2) also exhibited negative solvatochromism. The observation of negative solvatochromism again reflects the stabilisation in the more polar solvents of the dipolar betaine form (ground state, 2A), relative to the less polar forms (exited state, 2B), similar to the phosphonio imino betaines:



(2A)



(2B)

4.3.1. UV/Visible absorption characteristics of N-(o-phosphoniophenylazo) phenolate betaines

The longest-wavelength absorption band λ_{max} and the ε_{max} of each betaine are listed below:

a. *4-(o-Triphenylphosphoniophenylazo)-2,6-difluorophenolate*

Table 4-8

solvent	**colour**	**wavelength λmax, nm**	**$\varepsilon_{max}\times10^4$ (M^{-1} cm^{-1})**
ethanol	**orange**	**508**	**3.545**
acetonitrile	**orange**	**536**	**2.857**
dichloromethane	**red**	**548**	**2.342**
ethyl acetate	**purple**	**552**	**4.201**
Toluene	**purple**	**566**	**2.027**

The absorption band of the difluoroazo betaine moved from 566nm in toluene to 508nm in ethanol, a shift of -2020cm^{-1} (58nm).

b. *4-(o-Triphenylphosphoniophenylazo)-2,6-dichlorophenolate*

Table 4-9

solvent	**colour**	**wavelength λmax, nm**	**$\varepsilon_{max}\times10^4$ (M^{-1} cm^{-1})**
ethanol	**orange**	**514**	**3.134**
acetonitrile	**orange**	**532**	**2.040**
dichloromethane	**red**	**548**	**3.365**
ethyl acetate	**red-purple**	**558**	**3.979**
Toluene	**purple**	**572**	**1.296**

The absorption band of the dichlorophenate betaine moved from 572nm in toluene to 540nm in ethanol, a shift of -1980cm^{-1} (58nm).

c. *4-(o-Triphenylphosphoniophenylazo)-2,6-dimethylphenolate*

Table 4-10

solvent	colour	wavelength λmax, nm	$\varepsilon_{max} \times 10^4$ (M^{-1} cm^{-1})
ethanol	**red**	**550**	**3.134**
acetonitrile	**red**	**560**	**2.040**
dichloromethane	**red**	**568**	**3.365**
ethyl acetate	**red-purple**	**564**	**3.979**
Toluene	**purple**	**570**	**1.296**

This betaine exhibited an absorption band shift of -640cm^{-1} (20nm), from 570nm in toluene to 550nm in ethanol. It showed a significantly smaller degree of negative solvatochromism than the related difluoro- and dichloro- azo dyes and the methyl substituents (electron donating groups) caused a bathochromic shift. Presumably, the electron-withdrawing fluoro and chloro substituents stabilise the dipolar form of each betaine, whereas the electron-donating effect of the methyl groups would be expected to have the opposite effect.

4.3.2. Discussion

The solvatochromism of the phosphonioarylazophenolate betaines was also comparable to that of the Reichardt dye. The normalized empirical solvent polarity parameters E_T^N of the Reichardt dye, the longest-wavenumber intramolecular CT absorption ν_{max} ($=1/\lambda_{max}$) x 10^3 cm^{-1} of betaines above, and their corresponding transition energies, E_T kcal/mol, are shown in table 4-11:

Table 4-11

Solvent	$E_T(30)$	X=F		X=Cl		X=CH_3	
	E_T^N	ν_{max}	E_T	ν_{max}	E_T	ν_{max}	E_T
Ethanol	0.65	19.69	56.28	19.46	55.62	18.18	51.98
Acetonitrile	0.46	18.66	53.34	18.80	53.74	17.86	51.06
Dichloromethane	0.31	18.25	52.17	18.25	52.17	17.61	50.34
Ethyl acetate	0.23	18.12	51.80	17.92	51.34	17.73	50.69
Toluene	0.10	17.67	50.51	17.48	49.98	17.54	50.16
$\Delta\nu_{max}$ 2) ΔE_T		-2.02	5.77	-1.98	5.64	-0.64	1.82

From the results of the UV/Visible absorption study of the azophenolate betaines, we can see the phosphonioazophenolate betaines also exhibit negative solvatochromism , but, compared to the related phosphonioiminophenolates, the solvatochromic range is not as great. For example, the absorption band of the dimethyl azophenolate betaine (X = CH_3) only shifts by -640cm^{-1} (20nm), corresponding to an increase in its molar transition energy E_T value of only 1.82kcal/mol from toluene to ethanol. However, all the phosphonioazophenolate betaines exhibited much more intense colours in solution as shown by the greater molar extinction coefficient ε_{max} than for the corresponding phosphonioiminophenolates .

For each of above compounds, a plot of wavenumber ν for the longest wavelength visible absorption band of the phosphonium betaine against the normalised solvent polarity parameter E_T^N for the Reichardt betaine is shown as fig.2:

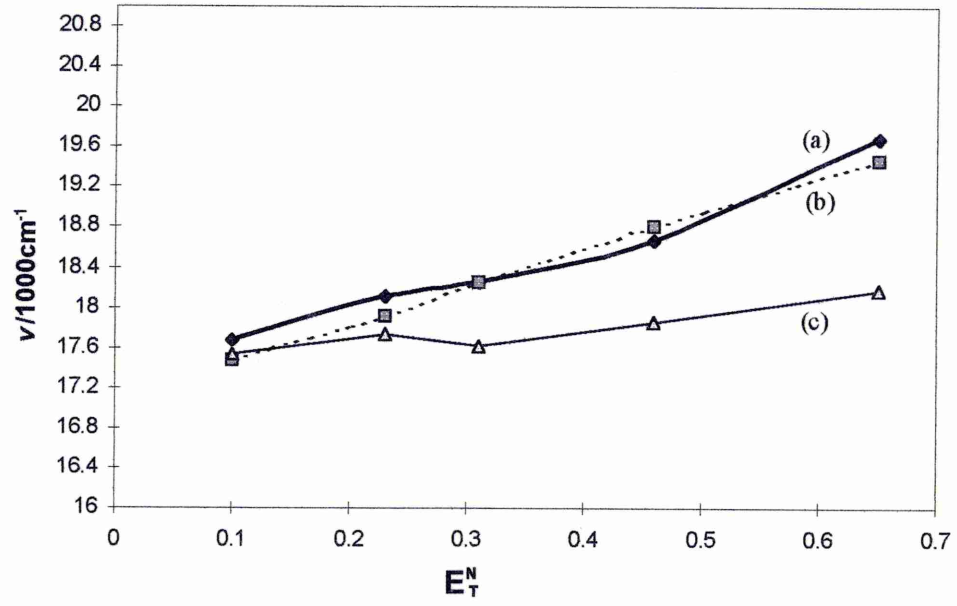
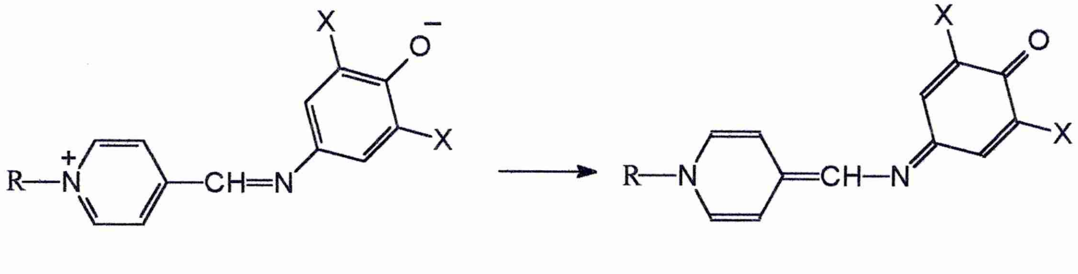


fig.2 Key to compounds: a: X=F; b:X=Cl; c:X=CH_3

The plot demonstrates the analogous solvent-dependent behaviour of phosphonioazophenolate betaines with respect to the standard Reichardt dye by the linear correlation between the E_T^N values of Reichardt dye and the wavenumber ν of the phosphonioazophenolate betaines, revealing a negative solvatochromism with the observed hypsochromic band shift as a consequence.

4.4. The solvatochromism of N-pyridinium betaines

It was of interest to compare the solvatochromic properties of the above phosphonioiminophenolate betaines with those of the pyridinium iminophenolate betaines, for which the possibility of internal charge-transfer between the dipolar form (3A) and the less polar form (3B) would be expected to be more significant than in the above phosphoniophenolate systems. The parent member of the pyridinium series (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[2].



(3A) (3B)

(R = CH_3 , $C_{16}H_{33}$; X = Cl, Br, Bu^t)

4.4.1. UV/Visible absorption characteristics of pyridinium imino- phenolate betaines.

The pyridinium iminophenolate betaines were studied in a variety of solvents of different polarity. The longest-wavelength intramolecular CT absorption bands λ_{max} and the corresponding extinction coefficient ε_{max} of these betaines are listed below:

a. *4-(1-Methylpyridinium-4-methylidene)amino-2,6-dichlorophenolate*

Table 4-12

solvent	**colour**	**wavelength λmax, nm**	$\varepsilon_{max}\times10^{4}$ (M^{-1} cm^{-1})
methanol	**red**	**510**	**2.530**
ethanol	**red -purple**	**540**	**2.315**
acetonitrile	**purple**	**578**	**2.048**
acetone	**blue**	**590**	**1.065**

This compound exhibited negative solvatochromic behaviour. Its intr

CT absorption band undergoes a hypsochromic shift of about -2660c

from 590nm in acetone to 510nm in methanol.

b. 4-(1-Methylpyridinium-4-methylidene)amino-2,6-dibromophenolate

Table 4-12

solvent	**colour**	**wavelength λmax, nm**	$\varepsilon_{max}\times10^{4}$ (M^{-1} cm^{-1})
methanol	**red**	**512**	**2.530**
ethanol	**red -purple**	**540**	**2.315**
acetonitrile	**blue**	**572**	**2.048**
acetone	**blue**	**600**	**1.065**

This betaine shows very similar solvatochromism to compound(a), in

λ_{max} 600nm(in acetone) to λ_{max} 512nm (in methanol), a shift of -2860cm *c. 4-(1-Methylpyridinium-4-methylidene)amino-2,6-di-t-butylphenolate*

Table 4-13

solvent	**colour**	**wavelength λmax, nm**	**$\varepsilon_{max} \times 10^4$ (M^{-1} cm^{-1})**
methanol	**green**	**616**	**1.412**
ethanol	**green**	**618**	**1.364**
acetonitrile	**blue-green**	**634**	**1.129**
acetone	**blue**	**664**	**1.193**
dichloromethane	**blue**	**634**	**0.855**
chloroform	**blue**	**630**	**0.829**
ethyl acetate	**blue**	**626**	**1.001**
THF	**blue**	**620**	**1.315**
Toluene	**violet**	**610**	**1.757**

This di-t-butylphenate exhibits an unusual reverse solvatochromic behaviour i.e., changing from a positive (bathochromic shifts of λ_{max} with increasing solvent polarity) to a negative solvatochromism as the polarity of the medium is increased. This is likely to be due to the varying contributions of the two extreme structures, i.e., the dipolar structure (see 3A, R = CH_3, X = Bu^t) and nonpolar quinonoid structure (see 3B, R = CH_3, X = Bu^t). In solvents of low polarity, the nonpolar form (3B) will predominate and the dipolar form (3A) becomes increasingly stable in polar media. Hence this betaine shows negative solvatochromism in the more polar solvents, and then a significant trend to positive solvatochromism in the less polar solvents. From 610nm in toluene to

664nm in acetone, it exhibits a bathochromic shift of +1330cm^{-1} (54nm) and from 664nm in acetone to 616nm in methanol, a hypsochromic shift of -1170cm^{-1} (48nm).

In the UV/Visible spectrum , it was noticed that the longest-wavelength absorption bands of this betaine were accompanied by the appearance of shoulders and splitting of the bands. The appearance of split bands has been reported in some papers[3]. In the present work, only the longest wavelength bands λ_{max} were considered as the true solvatochromic bands.

d. 4-(1-n-hexadecylpyridinium-4-methylidene)amino-2,6-dichlorophenolate

Table 4-14

solvent	**colour**	**wavelength λmax, nm**	**$\varepsilon_{max} \times 10^4$ (M^{-1} cm^{-1})**
methanol	**red**	**516**	**2.854**
ethanol	**red-purple**	**544**	**1.760**
acetonitrile	**violet**	**578**	**0.735**
acetone	**blue**	**606**	**1.223**
dichloromethane	**green**	**646**	**2.292**
THF	**blue**	**648**	**1.388**

Like most of the betaines, this compound also showed a negative solvatochromism. Thus on changing from THF (λ_{max}= 644nm) to methanol (λ_{max}= 516nm), the longest-wavelength band undergoes a hypsochromic shift of -3947cm^{1}(130nm). The presence of the long alkyl chain improved the solubility of the betaine in the less polar solvents, enabling the observation of a wider solvatochromic range.

e. 4-(1-n-hexadecylpyridinium-4-methylidene)amino-2,6-dibromophenolate

Table 4-15

solvent	**colour**	**wavelength λmax, nm**	**$\varepsilon_{max} \times 10^4$ (M^{-1} cm^{-1})**
methanol	**red**	**518**	**0.652**
ethanol	**purple**	**546**	**0.720**
acetonitrile	**violet**	**576**	**0.710**
acetone	**blue**	**602**	**0.840**
dichloromethane	**blue**	**632**	**0.921**
THF	**blue**	**640**	**1.983**

This betaine also displayed a negative solvatochromism. The absorption band shift was -3680cm^{-1}(122nm) between methanol and THF. Again, the presence of the long alkyl chain improved solubility, and extended the range of solvents studied.

f. 4-(1-n-hexadecylpyridinium-4-methylidene)amino-2,6-t-butylphenolate

Table 4-16

solvent	**colour**	**wavelength λmax, nm**	**$\varepsilon_{max} \times 10^4$ (M^{-1} cm^{-1})**
methanol	**green**	**626**	**1.086**
ethanol	**green-blue**	**630**	**1.423**
acetonitrile	**blue**	**662**	**1.750**
acetone	**blue**	**626**	**3.251**
dichloromethane	**blue**	**622**	**1.064**
THF	**blue**	**626**	**1.361**
Toluene	**blue**	**606**	**1.550**

Like betaine (c), this compound also exhibited a reverse solvatochromism , i.e., in nonpolar solvents, it showed a positive solvatochromism and a negative branch in the high polarity region. From 606nm in toluene to 662nm in acetonitrile, it presented a bathochromic shift of +1390cm^{-1} (56nm) and from 662nm in acetonitrile to 626nm in methanol, a hypsochromic shift of -860cm^{-1} (36nm).

4.4.2. Discussion

The normalized empirical solvent polarity parameters E_T^N for the Reichardt dye, the longest-wavenumber intramolecular CT absorption ν_{max} ($=1/\lambda_{max}$) x 10^3 cm^{-1} of the pyridinium betaines , and their corresponding transition energies, E_T kcal/mol, are tabulated as below:

Table 4-17

Solvent	$E_T(30)$	R=Me; X=Cl		R=Me; X=Br		R=Me; X= Bu^t		R=$C_{16}H_{33}$; X=Cl		R=$C_{16}H_{33}$; X=Br		R=$C_{16}H_{33}$; X= Bu^t	
	E_T^N	ν_{max}	E_T	ν_{max}	E_T	ν_{max}	E_T	ν_{max}	E_T	ν_{max}	E_T	ν_{max}	E_T
Methanol	0.76	19.6	56.1	19.5	55.8	16.2	46.4	19.4	55.4	19.3	55.2	16.0	45.7
Ethanol	0.65	18.5	52.9	18.5	52.9	16.2	46.3	18.4	52,6	18.3	52.4	15.9	45.4
Acetonitrile	0.46	17.3	49.5	17.5	50.0	15.8	45.1	17.3	49.5	17.4	49.6	15.1	43.2
Acetone	0.35	17.0	48.5	16.7	47.7	15.1	43,1	16.5	47.2	16.6	47.5	16.0	45.7
Dichloromethane	0.31					15.8	45.1	15.5	44.3	15.8	45.2	16.1	46.0
THF	0.21					16.1	46.1	15.4	44.1	15.6	44.7	16.0	45.7
Toluene	0.10					16.4	46.9					16.5	47.2
$\Delta\nu_{max}$ ΔE_T		-2.7	-7.6	-2.9	-8.1			-4.0	-11.3	-3.7	-10.5		

For each of the methylpridinium betaines, a plot of wavenumber v for the longest wavelength visible absorption band against the normalised solvent polarity parameter E_T^N for the Reichardt betaine is shown in fig.3. For the sake of comparison, the variation of v with E_T^N for the compound (X = H)^2 is also given in the graph:

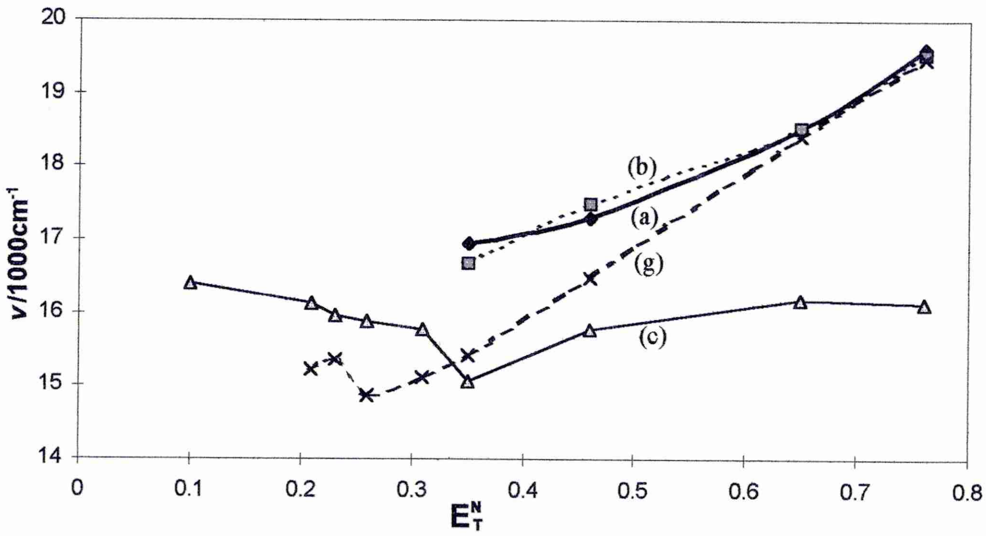


fig.3 Key to compounds: a: X=Cl; b:X=B; c:X=Bu^t; g=H

The solvatochromism behaviour of the pyridinium betaines is somewhat different from that of the related phosphonium betaines because the position of the absorption bands is influenced by the nature of the betaines. The range of polarity variation was narrow for betaines (a) and (b). This is because they are insoluble and could not generate any colour in media of lower polarity than acetone. This seems to be a general limitation for the pyridinium dyes^4. The curves of the betaines (a) and (b) have similar shapes and slopes which shows that they have similar solvatochromic behavior. Like the betaine (g), the reverse solvatochromism of the betaine (c) is evident in the plot where the minima in the curve occurs at the "aprotic" solvent acetone. From the nonpolar solvent toluene to acetone, it shows positive solvatochromism, and then trends to negative solvatochromism from acetone to the more polar solvents, exhibiting a reverse solvatochromism.

For each of n-hexadecylpridinium betaines, a plot of wavenumber v for the longest wavelength visible absorption band against the normalised solvent polarity parameter E_T^N for the Reichardt betaine is shown in fig.4:

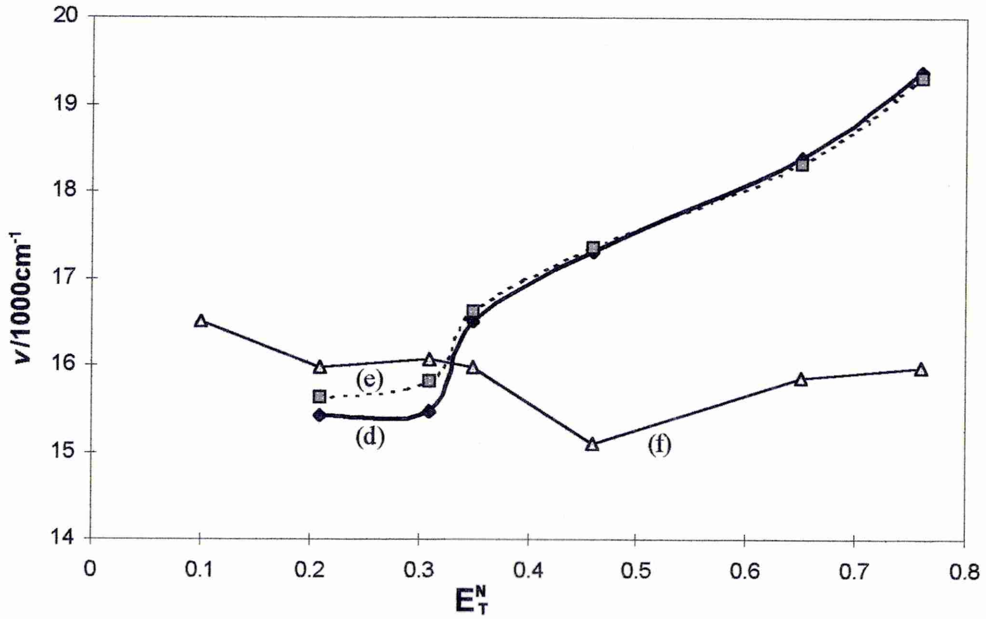


fig.4 Key to compounds: R = $C_{16}H_{33}$; d: X=Cl; e:X=Br; f:X=Bu^t

The betaines (e) and (d) show very similar solvatochromic behaviour. Both display a large negative solvatochromism in polar solvents. However, in the less polar solvents , they appear to show the beginnings of a trend to positive solvatochromism. The betaine (f) show a reverse solvatochromism like the betaine (c), i.e., with increasing solvent polarity, the solvatochromic behaviour of this betaine changed from a positive to a negative solvatochromism in which its minima in the curve occurs at acetonitrile. It was noticed that the reversion in the solvatochromism of both betaines (c) and (f) occurs at almost the same constant E_T value of about 43.1 kcal/mol, below and above which the ν_{max} values increase. In general, as expected, the replacement of the methyl group at nitrogen of the pyridinium unit by the hexadecyl group has little effect, apart from improving solubility and increasing the range of colours displayed. However, the nature of the subsituents in the phenolate unit has a greater influence on the position of the absorption bands. Introduction of a butyl group causes a bathochromic shift of the CT absorption bands, relative to the related dichloro and dibromo betaines. Thus, the betaine (R = CH_3, X = Cl) shows an absorption band at 510nm in methanol. Replacing the dichloro substituents by the dibutyl groups (λ_{max} = 616nm) gives a red shift of 106nm in the same solvent. Similarly, where R was $C_{16}H_{33}$, introducing dibutyl substituents into the betaine (λ_{max} = 626nm) causes a strong red shift of 110nm relative to the related dichloro betaine (λ_{max} = 516nm), with the colour changing from red to green .

4.5. Halochromism properties of phosphonio- and pyridinium- phenolate betaines

All three types of betaines also exhibited a salt-induced negative halochromism on treatment with alkali and alkaline-earth metal ions in various solvents, which stems from an ion-pairing between the cation, delivered from the salt added, and the phenoxide part of the betaine. The halochromism of the betaines can be easily demonstrated by a simple test-tube experiment because of their light absorption within the visible range of the spectrum. In present work, the halochromism of the betaines has been studied in acetonitrile, employing lithium iodide, sodium iodide, and potassium iodide as salts. For example, treatment of a ca.10^{-4} M solution of betaine (a) in acetonitrile (λ_{max} = 504 nm, red solution)with ca.10^{-2}M lithium iodide caused a distinct colour change from red to yellow (λ_{max}= 458 nm, salt-induced shift $\Delta\lambda$ = 46nm). The long-wavelength UV/Visible absorption maxima λ_{max} of betaines [$c_{(betaine)} \approx 1x10^{-4}$ mol/cm^3], measured in acetonitrile without and with added salts, as well as the salt-induced band shifts $\Delta\lambda$ after the addition of various iodides, is shown in table 4-18:

Halochromic Properties of Phosphonio- and Pyridinium-Phenolate Betaines in Acetonitrile

(Table 4-18)

Added Salt [1)]	Concentration (mol dm^{-3})	λmax (nm)	$\Delta\lambda$(nm)[2)]
a) . *4-N(o-Triphenylphosphoniobenzylidene)amino-2,6-dichlorophenolate*			
without salt	-	504	-
LiI	10^{-4}	476	28
LiI	2 x 10^{-4}	464	40
LiI	1 x 10^{-2}	458	46
LiI	10^{-1}	438	66
NaI	10^{-2}	478	26
NaI	10^{-1}	460	44
KI	10^{-1}	484	20
b) . *4-(o-Triphenylphosphoniophenylazo)-2,6-dichlorophenolate*			
without salt	-	576	-
LiI	10^{-2}	518	58
LiI	10^{-1}	512	64
NaI	10^{-2}	556	20
KI	10^{-2}	572	4

c). *4-(1-Methypyridinium-4-methylidene)amino-2,6-dichlorophenolate*

without salt	-	534	-
LiI	10^{-2}	500	34
LiI	10^{-1}	498	36
NaI	10^{-2}	526	8
KI	10^{-2}	534	0

1). Salts in order of increasing effective charge

2). $\Delta\lambda = \lambda_{max}$(without salt) - $\lambda_{max(}$ with salt)

In all cases, hypsochromic salt-induced band shifts were obtained on addition of electrolytes to solutions of the betaines which were dependent on the nature of the cation and the concentration of the salt[5].

As would be expected, the magnitude of the effect decreased in the order $Li^+ > Na^+ > K^+$, as the polarising power of the cation decreased. For example, on addition of various salts with same concentration ($c = 1x10^{-2}$ M) into solution of the betaine (a) in acetonitrile, a continuous increase of halochromic shift with increasing effective charge ($K^+ < Na^+ < Li^+$) of the cation added was observed ($\Delta\lambda = 20 \rightarrow 46$nm).

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 ion . For example, the longest-wavelength band of betaine (a) continued to shift to 438nm from 504nm with increasing concentration of lithium iodide (up to $c_{salt} = 0.1$M). However, for most betaines, smaller changes in the spectra were observed when larger concentrations of salt were added. The longest wavelength absorption band of betaine (b) moved from 576nm to 518nm ($\Delta\lambda$ =58nm) when ca 10^{-2} M lithium iodide was added, but it only moved to 512nm when concentration of lithium iodide increased up to ca 10^{-1} M. This indicates that the betaines interact strongly with the cation of the added salt and form a complex that is no longer sensitive to a subsequent polarity change of the environment on adding further electrolyte.

4.6. Langmuir-Blodgett (L-B) film of 4-(1-n-hexadecylpyridinium-4-methylidene) amino - 2, 6- dichlorophenolate — a report from Professor G. Ashwell of Cranfield University

L-B films were prepared by spreading this betaine dye from dilute chloroform solution (0.12mg cm^{-1}) onto the pure water subphase of a Langmuir trough (Nima Technology, model 622), left for 10 min at *ca.* 20°C and then compressed at 0.5 $cm^2\ s^{-1}$ (ca. 0.1% s^{-1} of compartment area). The pressure-area (π-A) isotherm show a slight transition at $\pi \approx 19$ mN m^{-1} and A $\approx$ 40 Å^2 molecule^{-1} with the onset of collapse at $\pi \approx 35$ mN m^{-1} and A $\approx$ 28 Å^2 molecule^{-1}(fig. 5). The latter is consistent with the mean van der Waals cross-sectional area of the chromophore and indicates that the molecules are closely packed at the air-water interface. L-B films were obtained by passing a glass slide through the floating monolayer at 80 $\mu m\ s^{-1}$ to deposit on the upstroke at 20 mN m^{-1}.

Spectra of a 20 layer L-B film of this betaine dye before (right) and after (left) exposure to HCl vapour were shown in fig. 6. The 4-(1-n-hexadecylpyridinium-4-methylidene)amino-2,6-dichlorophenolate betaine has an intramolecular charge transfer axis and is SHG-active whereas the protonated form shows no SHG.

iodide was added, but it only moved to 512nm when concentration of lithium iodide increased up to ca 10^{-1} M. This indicates that the betaines interact strongly with the cation of the added salt and form a complex that is no longer sensitive to a subsequent polarity change of the environment on adding further electrolyte.

4.6. Langmuir-Blodgett (L-B) film formation by 4-(1-n-hexadecylpyridinium-4-methylidene) amino - 2, 6- dichlorophenolate — a report from Professor G. Ashwell of Cranfield University

L-B films were prepared by spreading this betaine dye from dilute chloroform solution (0.12mg cm^{-1}) onto the pure water subphase of a Langmuir trough (Nima Technology, model 622), left for 10 min at *ca.* 20°C and then compressed at 0.5 cm^2 s^{-1} (ca. 0.1% s^{-1} of compartment area). The pressure-area (π-A) isotherm show a slight transition at $\pi \approx 19$ mN m^{-1} and A ≈ 40 Å^2 molecule^{-1} with the onset of collapse at $\pi \approx 35$ mN m^{-1} and A ≈ 28 Å^2 molecule^{-1}(fig. 5). The latter is consistent with the mean van der Waals cross-sectional area of the chromophore and indicates that the molecules are closely packed at the air-water interface. L-B films were obtained by passing a glass slide through the floating monolayer at 80 μm s^{-1} to deposit on the upstroke at 20 mN m^{-1}.

Spectra of a 20 layer L-B film of this betaine dye before (right) and after (left) exposure to HCl vapour are shown in fig. 6. The 4-(1-n-hexadecylpyridinium-4-methylidene)amino-2,6-dichlorophenolate betaine has an intramolecular charge transfer axis and is SHG-active whereas the protonated form shows no SHG.

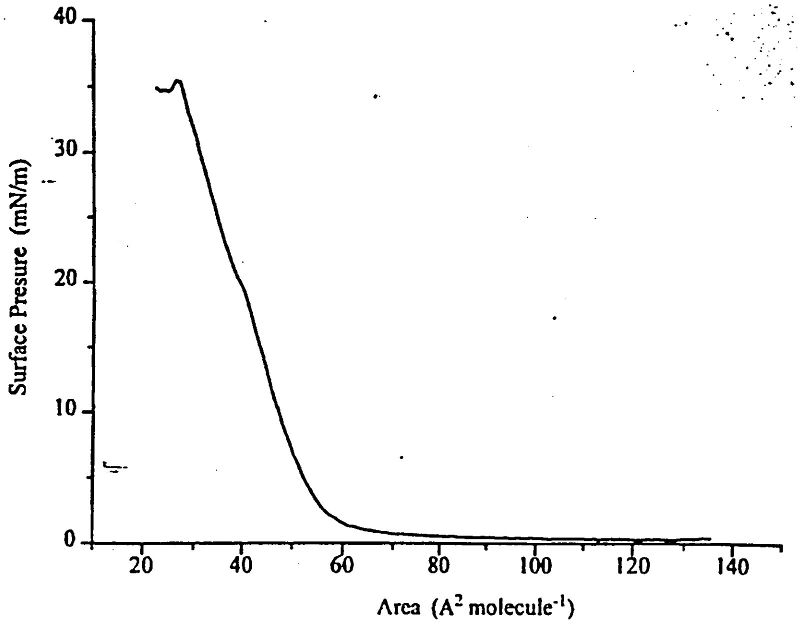


fig. 5 Plot of surface pressure versus area isotherm

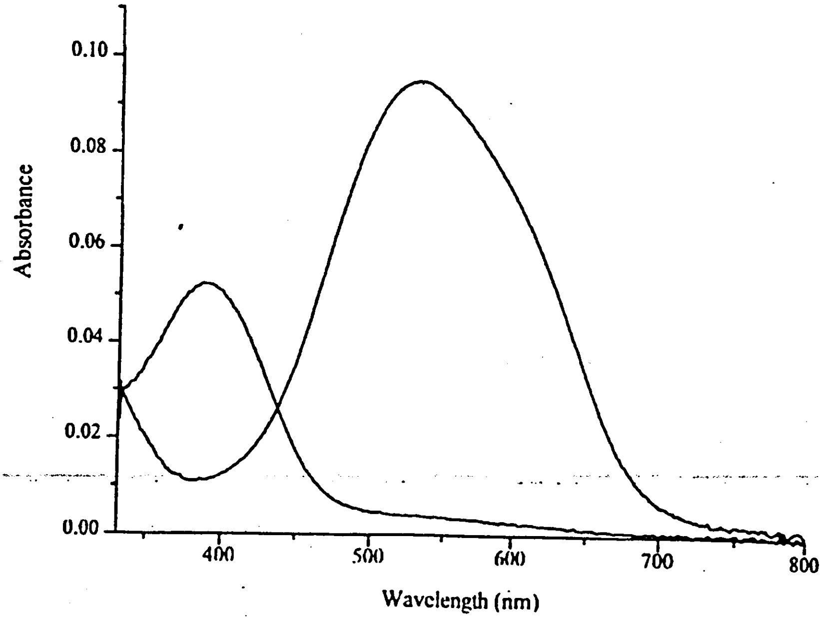


fig. 6 UV/Visible spectra of a 20 layer L-B film
before (right) and after (left) exposure to HCl vapour

The UV/Visible spectra shows that the L-B film has maximum absorption at $\lambda max \approx 530nm$. After exposure to HCl vapour, it has a maximum absorption at $\lambda max \approx 395nm$, undergoing a hypsochromic shift about 135nm due to its protonation.

4.7. Experimental

Solvato- and Halo-chromic measurements:

The UV/Visible absorption spectra were measured on UNICAM UV_2-100 spectrophotometer, with a matched pair of quartz cells of 1cm thickness. The absorption spectrum of each solution was obtained in the range 200nm to 800nm by using one cell containing pure solvent as the reference. All analytically pure organic solvents were of reagent grade , dried over 3Å molecular sieves for over 24 hours prior to use because the betaine dyes are very sensitive to traces of water. The presence of even small amount of water may cause a significant shift in absorption maximum, especially in nonpolar solvents[6].

For the halochromic measurements, salt solutions of different concentration were prepared by dilution of a stock solution containing the electrolyte.

The concentrations of solutions used in the experiments ranged between 10^{-5} and 10^{-4} mol/dm^3 and their visible spectra were recorded immediately after preparation of the solution.

All measurements were carried out at room temperature.

References:

(1). C. Reichardt. *Solvents and solvent Effects in Organic Chemistry,* 2nd ed.; VCH Publishers: Weinheim, 1988. p.363.

(2). Clodoaldo M . *J. Chem.Soc. Perkin Trans. 2* , 1994 , 2539

(3). a). I. Gruda and F. Bolduc. *J. Org. Chem.*, 1984, *49*, 3300

b). V. Luzhkov and A.Warshel. *J, Am. Chem. Soc.*, 1991, *113*, 4491.

(4). a). P.Jacques, *J. Phys. Chem.*, 1986, *90*, 5535.

b). S. T. Abdel-Halim, *J. Chem. Soc., Faraday Trans.*, 1993, *89*, 55.

(5). C. Reichardt, E. Harbusch-Cornert, *Liebigs Ann. Chem.* 1988, 839

(6). C. Reichardt, *Chem.Rev.* 1994, *94*, 2319

Chapter 5

Conclusions and Further Work

5.1. Conclusions

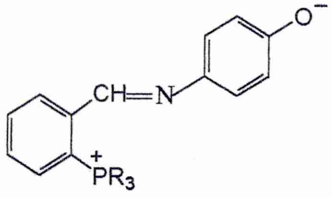
In this work , the synthesis and characterisation of two new solvatochromic phosphonium betaine systems is reported. Both 4-N-(o-triorganophosphonio-benzylidene) aminophenolate and 4-(o-triphenylphosphoniophenylazo) phenolate betaines exhibit negative solvatochromism. The solvatochromic properties of these compounds have been compared with those of a related series of pyridinium iminophenolate betaines which exhibit negative or reverse solvatochromism, depending on substituents and solvent polarity. Halochromism is also observed on treating the phosphonium betaines with alkali metal ions in acetonitrile solution.

The investigation has revealed that some of the betaines exhibited strong solvatochromism and it was demonstrated that their absorption maxima ν_{max} showed a good correlation with the standard $E_T(30)$ values of the Reichardt betaine. It is suggested that such betaines could be used as an indicators of solvent polarity. However, some of the betaines prepared would not be appropriate as probes of solvent polarity due to their relative insensitivity, low solubility or reverse solvatochromic behaviour.

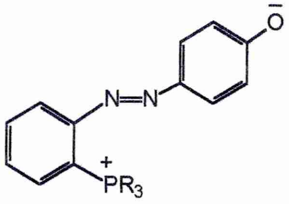
One of the pyridinium betaines which conjugated long chain was made into L-B film and it displayed non-linear optical properties as expected.

5.2. Further work

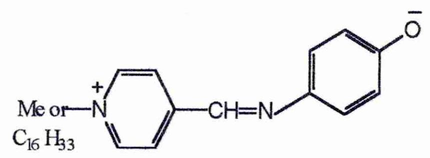
There is clearly scope for further work to expand the membership of each family of betaines, so as to give a more complete picture of their properties and perhaps to find some more effective solvatochromic compounds. For example, it would be of interest to study the betaines (a)-(c) in which there are no substituents adjacent to the phenolate centre.



(a)

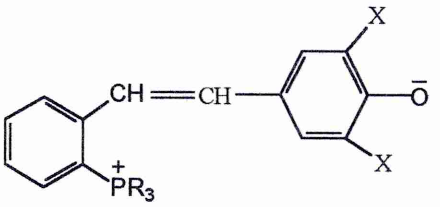


(b)



(c)

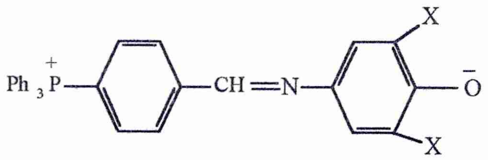
It isalso necessary to compare the two solvatochromic phosphonium betaine systems prepared, i.e., the 4-N-(o-triorganophosphonio- benzylidene) iminophenolate and 4-(o-triphenyl- phosphoniophenylazo) phenolate betaines with the as yet unknown phosphonium betaine system (d):



(d)

This comparison will allow an overall view of these series of dyes, as the unsaturated group joining the two rings is changed from CH=CH to CH=N and N=N.

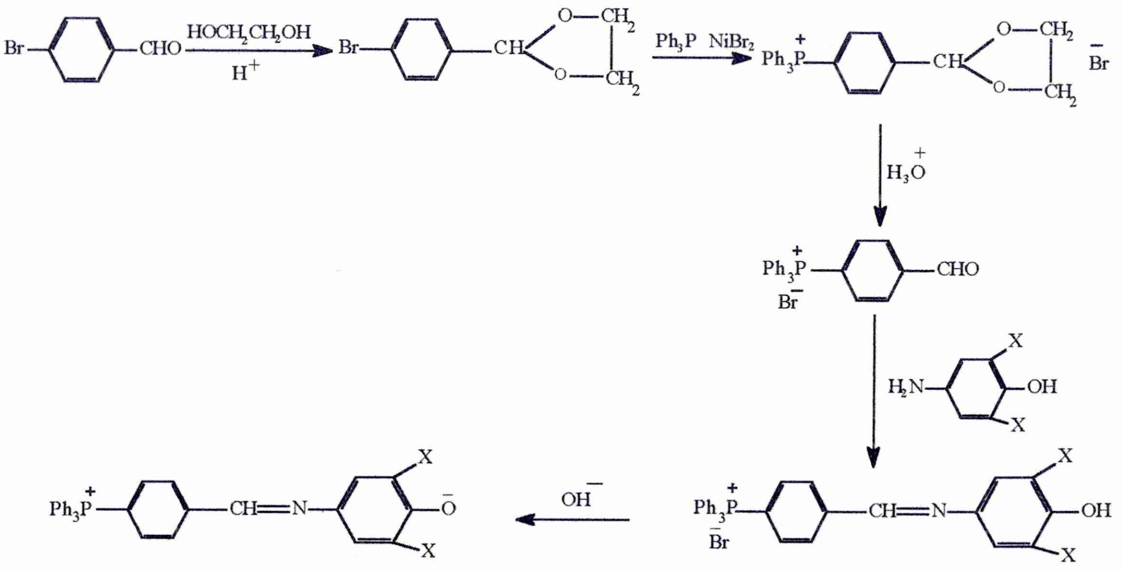
In order to extend the observations on the solvatochromism of the phosphonioiminophenolates, it would be of interest to synthesis the related *para*-substituted phosphonium betaines (e) which are likely to have a larger dipole moment in the ground state, and so may have improved solvatochromic properties.



(e, X= Cl, Br, Bu^t, Ph)

One of the parent compounds 4-N(p-bromobenzylidene)amino-2.6-dichlorophenol has already been synthesised in the present study from 4-bromobenzaldehyde and 4-amino-2, 6-dichlorophenol (in ethanol, under nitrogen). The ^{1}H nmr spectrum and mass spectrum provided confirmation of the identity of this product. However, *para* substituted aryl halides of this type do not react with phosphines under the same conditions as the related *ortho* compounds because these *para* substituted compounds cannot act as coordination templates[1] when the phosphine group (R_3P) is introduced. It is necessary to use much higher temperatures than provided by refluxing ethanol. Thus, an attempt to prepare the related *para*-salt was made using either the reaction of the halide with triphenyl phosphine and nickel(II) bromide in the melt (150 ~ 200°C) or by their reaction under reflux in benzonitrile (200°C)[2] . However, it was found impossible to produce the pure phosphonium salt. The product formed was a brown solid with multiple components as shown by TLC.

Clearly, a new route (see scheme 5-1) for the synthesis of the betaines (d) is required in order to investigate how the isomeric substitution might affect the solvatochromic properties.

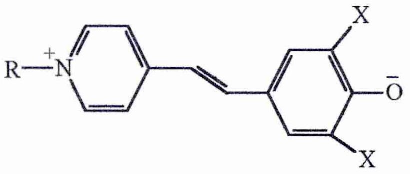


(e)

Scheme 5-1

Because *p*-bromobenzaldehyde is very easily oxidised and the phosphine may also attack the carbonyl group, it must first be protected by converting it to an acetal which is then heated with the tertiary phosphine and nickel bromide (200°C). The acetal can be hydrolysed to regenerate the aldehyde by treating it with aqueous acid, and the phosphonioaldehyde is then heated with the respective 4-amino, 2,6-disubsituted phenol to give the related salt. Finally, the betaine (e) could be obtained by shaking the salt with aqueous alkali.

Since merocyanine dyes constitute a class of compound whose solvatochromism has attracted great interest, it seemed interesting to compare the pyridinium betaines which have been synthesised in this thesis (see chapter 3) with other merocyanine dyes (f) and (g):



(f)

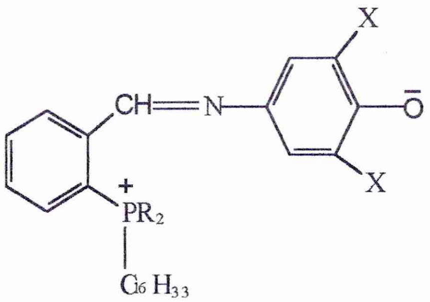
(g)

Among them, betaine(f, R=CH_3, X=H) has been described by Brooker *et al* [3] and shows reverse solvatochromism. Betaine (g, R=CH_3, X=H) has been synthesised by Buncel *et al* [4] and shows positive solvatochromism, being used as the basis of the π^*_{azo} scale. Further members in each series need to be studied to establish substituent effects, which could lead to more interesting solvatochromic compounds.

This comparison will also allow an overall view of these series of dyes, as the unsaturated group joining the two rings is changed from CH=CH to CH=N and N=N.

Besides solvatochromism and halochromism, other possible properties of the phosphonium and pyridinium betaines such as thermochromism[5] or piezochromism[6] should also be investigated.

More extensive synthetic work on solvatochromic materials should also be carried out to find more suitable compounds for L-B film formation and for studying the nonlinear optical (NLO) properties of such films for second-harmonic generation (SHG)[7]. For example, betaine (h) may be a promising class of compound for L-B formation and SHG study in which the long alkyl chain $C_{16}H_{33}$ are attached to the phosphine .



(h)

There is a connection between solvatochromism and SHG. Those structural features that give rise to large β tensor terms usually also give rise to strong solvatochromism[8]. Thus, the measurement of the solvatochromic effect will first allow the determination of both the ground and excited-stated dipole moments (μ_g and μ_e, respectively) and then lead to an estimation of the second-order hyperpolarizability β of the solvatochromic molecule [9].

References

1. D W Allen and P E Cropper,*J. Organomet. Chem.*, 1992, 435, 203.
2. L. Horner and U.M.Duda, *Tetrahedron Letters, 5177(1970)*
3. L. G. S. Brooker, G. H. Keyes, *J. Am. Chem. Soc., 1951, 73, 5350.*
4. E. Buncel and S. Rajagopal. *J. Org. Chem., 1989, 54, 789.*
5. R. I. Zalewski, C. Reichardt, C. *J. Chem. Res.(S) 1990, 280; bid.(M) 1990, 2157.*
6. W.S. Hammack, D. N. hendrickson, *J. Phys, Chem, 1989, 93, 3483.*
7. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D.S., Zyss, J., Eds.; Acadmic press: Orlando, FL, 1987; Vol.1.

8. Reichardt, C. *Solvents and solvent Effects in Organic Chemistry,* 2nd ed.; VCH Publishers: Weinheim, 1988.

9. Paley, M. S.; Harris, J. M. *J. Org. chem. 1991, 56, 568; 1989, 54, 3774.*