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Effect of solvent and pH on the spectral characteristics of *meso*-tetrakis(*p*-hydroxyphenyl) porphyrin in dimethylformamide and dimethylformamide + water mixed solvents

BIDYUT KR. MANNA, SUBHASH CH. BERA and KRISHNA K. ROHATGI-MUKHERJEE†
Physical Chemistry Laboratories, Jadavpur University, Calcutta 700 032, India

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Abstract—The spectral changes in *meso*-tetrakis(*p*-hydroxyphenyl) porphyrin free base *p*-OHTPPH$_2$ are studied in DMF + H$_2$O mixed solvents and DMF alone from pH 2.0 to greater than 12. Drastic changes in spectral characteristics appear at high pH values >12. Besides the modification of Soret and *Q*-bands, a new CT-band develops on the red-side of the *Q*-bands in water rich solvents. In a graded mixture of H$_2$O and DMF, as solvent, mole fraction x_{DMF} varying from 0.04 to 0.7, the *Q*-band as well as the CT-band red shift and increase in intensity with increasing mole fraction of DMF. At $x_{DMF} > 0.7$, i.e. $x = 1$, the spectrum changes dramatically into a single banded broad spectrum of acid type at pH 12 with concomitant disappearance of the CT-band. For *p*-OMeTPPH$_2$, the spectrum transforms to metalloporphyrin type at high pH, but for *o*-OHTPPH$_2$, the spectral characteristics of both *p*-OHTPPH$_2$ and *p*-OMeTPPH$_2$ are observed in DMF as solvent.

1. INTRODUCTION

THE IMPORTANCE of the peripheral substituent in modulating the properties of porphyrins has been studied by a number of workers [1–4]. The electron withdrawing or donating substituents, even in the remote regions such as those on phenyl rings in *meso*-tetraphenyl porphyrins can prevent aggregation, modify redox properties, acid–base character, etc. Porphyrins are in general not very soluble in water. They are made water soluble either by attaching appropriate groups in the peripheral positions or by using aquo-organic solvents.

The *meso*-tetrakis hydroxyphenyl substituted porphyrin as a synthone was first synthesized by MILGROM [5] and studied [6] as a photosensitizer for the photo-chemical electron transfer system for solar energy conversion. The spectral properties of the free base *meso*-tetrakis(*p*-hydroxyphenyl) porphyrins *p*-OHTPPH$_2$ have drawn the attention of many biophysicists [7, 8] also, since it has been found to be a suitable candidate for use in the photodynamic therapy of cancer of internal organs. Its spectral properties differ considerably from those of its *meta*- and *ortho*-isomers and are strongly modified by pH changes. We have observed that the nature of the solvent can have a profound effect on the acid–base characteristics of these compounds and modification of their spectra. Here we report the spectral changes as observed on variation of pH for *p*-hydroxyphenyl substituted tetrakis-porphyrin, *p*-OHTPPH$_2$ in DMF and DMF + H$_2$O (1:1) mixture as solvent. Since the free base porphyrin is neutral at pH between 6 and 7 because of the presence of both acidic and basic groups, pH can be varied on either side of the free base ranging from pH 2 to higher than 12. The spectral changes observed are very dramatic and interesting especially for *p*-OHTPPH$_2$ in DMF + H$_2$O system and DMF alone.

For comparative understanding, *o*-OHTPPH$_2$ was selected for the study of the importance of the steric effect and *p*-OMeTPPH$_2$ to establish the site of pH dependent ionization in *p*-OHTPPH$_2$. The *p*-OHTPPH$_2$ has ionizable Hs which can dissociate as a function of pH, the comparatively acidic phenolic on the four *meso*-hydroxyphenyl substituents in the peripheral region and the inner core pyrrolic-H on the two >NH groups. The imino >NH groups are very weakly acidic [9] pK > 15. Therefore, on titration with strong alkali only the *p*-hydroxyphenyl group is expected to ionize in the high pH range. This has been inferred from the study of *p*-OMeTPPH$_2$ in i-PrOH + H$_2$O solution [10] as a function of pH where peripheral OH groups are blocked. No spectral

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† Author to whom correspondence should be addressed.

changes are observed for p-OMeTPPH$_2$ on variation of pH from 6 to 12 in this solvent mixture suggesting involvement of the phenolic-H in the titration process of p-OHTPPH$_2$.

EXPERIMENTAL

Different substituted porphyrins were prepared by the method of ADLER *et al.* [11]. Purification of p-hydroxyphenyl porphyrin (p-OHTPPH$_2$) free base was described previously [12]. *Ortho*-hydroxyphenyl porphyrin (o-OHTPPH$_2$) was prepared by the hydrolysis of *ortho*-methoxyphenyl (o-OMeTPPH$_2$) prophyrin, following the standard protocol [13]. Alkali and alkaline earth metal hydroxide were from SRL, India and were used without further purification. Solvents like dimethylformamide (DMF), isopropanol (i-PrOH), etc. were of HPLC grade and were used as such.

Two sets of solvent compositions were selected, (1) DMF + H_2O (1 : 1) mixture by volume and (2) DMF only. The concentrations of the the three compounds p-OHTPPH$_2$, o-OHTPPH$_2$ and p-OMeTPPH$_2$ were suitably adjusted to avoid aggregation and at the same time to give reasonably good optical density ($C \simeq 10^{-5}$ M). For pH titration in the alkaline region, pellets of NaOH were dissolved in water–DMF mixture and added dropwise to the neutral solution in appropriate solvents. In the acid range HCl solution was added systematically. To prepare DMF + H_2O solutions of graded composition at pH 12 the solvent composition was varied by mixing DMF and water in different ratios keeping the total volume constant at 10 ml. The concentration of p-OHTPPH$_2$ and NaOH were $C = 5.89 \times 10^{-6}$ and 0.02 M, respectively for the set DMF + H_2O of different composition. To introduce basic and acidic conditions in DMF solvent, two drops each of 0.05 ml 2 M NaOH and two drops of 2.4 M HCl in water were added to 5 ml solution of porphyrin in DMF so that the effective concentrations of NaOH and HCl were 0.02 and 0.024 M, respectively. The pH values of the solution were measured with a digital pH meter model 335 of Systronics (India) Ltd. The absorption spectrum of each solution was measured in a Shimadzu Spectrophotometer model MPS-2000.

RESULTS

DMF + H_2O (1 : 1) *mixtures* (v/v) *as solvent*

The absorption spectrum of p-OHTPPH$_2$ in DMF + H_2O (1 : 1) mixture by volume is presented in Fig. 1. The spectrum is comprised of high intensity Soret band with maximum at 420 nm followed by four-banded Q-region, Y-polarized bands IV [$Q_{y(0,1)}$] and III [$Q_{y(0,0)}$] at 519 and 555 nm, respectively, and X-polarized bands II [$Q_{x(0,1)}$] and I [$Q_{x(0,0)}$] at 595 and 650 nm, respectively. The intensity ratios of the five bands with respect to band IV as unit are 25.8 : 1 : 0.87 : 0.36 : 0.88. The o-OHTPPH$_2$ and p-OMeTPPH$_2$ also give a similar five-banded spectrum but the intensity ratios of the bands differ considerably (Table 1). The X-polarized band I which normally is forbidden and hence of much reduced intensity is considerably enhanced for the p-isomer although for other compounds under study, it is of lower intensity [7].

On systematic drop by drop addition of NaOH in DMF + H_2O solvent (Fig. 1), the Soret band loses much of its intensity although gains in breadth and red shifts to 444 nm at pH 12. The OD for Soret band changes from 2.64 at 420 nm to 1.08 at 444 nm. The changes in the Q-band system are much more drastic. At the same time a new band of moderate intensity develops to the red of the $Q_{x(0,0)}$ band distorting band I. Both the long wavelength bands become well formed at high pH (near 12) with a maximum at 680 nm for the new band and at 655 nm for the modified band I. In the corresponding $Q_{x(0,1)}$ band region, a comparatively high intensity canopy like symmetrical broad band finally develops with λ_{max} at 598 nm and two minima on either side at 640 and 525 nm. The wavelength and log ε values of the bands are given in Table 1. In Fig. 1, the Q-band region is magnified 15 fold in relation to the Soret band to emphasize the details. The optical density of the Soret band at 420 nm is plotted as a function of pH producing a titration curve (inset Fig. 1). A pK of 11.0 is calculated for ionization of the phenolic –OH group in p-OHTPPH$_2$. In Fig. 2 are presented the final contours of the Soret band

and the Q-bands of p-OHTPPH$_2$ at pH > 12 in [NaOH] ≈0.4 M in 1:1 mixtures of (a) DMF + H$_2$O and (b) i-PrOH + H$_2$O. The new bands in the far red region are very well formed and differ only slightly in the two aquo-organic solvents.

The changes are not so drastic for o-OHTPPH$_2$ and only a weak band develops on the red side of the porphyrin band system in DMF + H$_2$O even at high pH. Otherwise the changes are very similar in nature to those of p-OHTPPH$_2$. The peripherally substituted p-OMeTPPH$_2$ which does not have an ionizable hydrogen on the *meso*-substituent, shows no spectral changes at pH 12 in equi-volume DMF + H$_2$O and i-PrOH + H$_2$O solvent system [10]. But at still higher NaOH concentration ≈0.4 M, where pH could not be measured, dramatic changes are observed, the four-banded spectrum in the Q-band region transforms to a two-banded one with maxima at 580 and 625 nm, the latter being of higher intensity (Fig. 2 and Table 1). For the Soret band, when compared with the neutral species a red shift from 420 to 430 nm is observed with enhanced intensity.

DMF *as solvent*

In Fig. 3 are presented the spectra in the neutral, acid and basic forms for the three compounds p-OHTPPH$_2$, p-OMeTPPH$_2$ and o-OHTPPH$_2$ in DMF as solvent. Whereas in the neutral state the spectral changes are normal except for the higher intensity of the $Q_{x(00)}$ band for p-OHTPPH$_2$ but at 0.02 M NaOH concentration, each compound presents a different picture. On the other hand in the acidic solution (0.024 M) the spectra for all the three compounds become identical with one strong absorption band at 702, 696 and 692 nm for the three compounds, respectively and weak shoulders extending towards the shorter wavelength. Interesting observations in the Q-band region in the basic range (0.02 M NaOH) in DMF as solvent for the three systems are:

(1) For p-OHTPPH$_2$ (Fig. 3(A)), there are striking differences in the band observed in basic solution. A single banded and broad spectrum, although very similar to that in the acidic solution, appears slightly blue-shifted at 662 nm with reduced intensity.

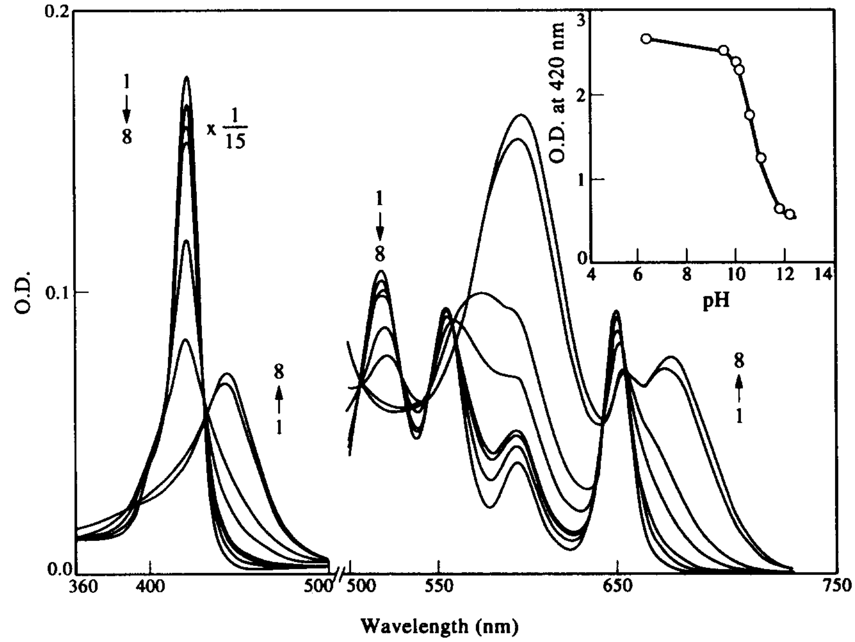


Fig. 1. The effect of pH variation from 6.30 to 12.2 on the spectral characteristics of ~10^{-5} M *meso*-tetrakis(p-hydroxyphenyl) porphyrin in DMF–H$_2$O (1:1, v/v) mixed solvent: pH values are (1) 6.30, (2) 9.50, (3) 9.99, (4) 10.10, (5) 10.54, (6) 11.00, (7) 11.82, (8) 12.2. Inset: Potentiometric titration curve of O.D. at 420 nm as a function of pH. The Q-bands are magnified 15 times with respect to the Soret band to emphasize gradual development of a new band in the long wavelength region at 680 nm.

Table 1. Absorption spectral characteristics of different porphyrins in DMF and DMF–H_2O mixture (λ_{max} in nm and log ε in parenthesis)

p-$OHTPPH_2$	Neutral	422 (5.44)	519 (4.05)	556 (4.00)	596 (3.61)	651 (3.99)
p-$OHTPPH_2$	Acidic	456 (5.38)		640 (3.96)sh		702 (4.56)
p-$OHTPPH_2$	Basic	455 (5.24)		560 (3.87)		662 (4.35)
p-$OMeTPPH_2$	Neutral	420 (5.70)	516 (4.32)	554 (4.20)	594 (3.81)	650 (4.01)
p-$OMeTPPH_2$	Acidic	454 (5.68)		630 (4.16)sh		692 (4.95)
p-$OMeTPPH_2$	Basic	436 (5.84)	540 (3.74)sh		580 (4.31)	626 (4.67)
o-$OHTPPH_2$	Neutral	421 (5.35)	517 (3.92)	554 (3.83)	594 (3.43)	648 (3.60)
o-$OHTPPH_2$	Acidic	455 (5.25)		630 (3.81)sh		696 (4.55)
o-$OHTPPH_2$	Basic	437 (5.08)	455 (4.89)sh		585 (3.74)	648 (4.06)
p-$OHTPPH_2$*	Neutral*	420 (5.46)	518 (4.04)	555 (3.99)	594 (3.59)	649 (3.98)
p-$OHTPPH_2$*	Acidic*	450 (5.32)		630 (3.99)sh		695 (4.62)
p-$OHTPPH_2$*	Basic*	442 (5.05)		596 (4.22)	655 (3.86)	680 (3.99)†

* In DMF–H_2O mixture (1 : 1, v/v).

† new band characteristic of *p*-$OHTPPH_2$ in the presence of water miscible organic solvent, alkaline range (pH > 12).

(2) For *p*-$OMeTPPH_2$ (Fig. 3(B)), the spectrum becomes two-banded ($\lambda_{max} = 580$, 626 nm) like metalloporphyrins where system changes from D_{2h} to D_{4h} symmetry due to the degeneracy in the *Q*-bands. In separate studies it has been observed that the nature of the cations involved in the alkali [LiOH, NaOH, $Ba(OH)_2$] used for the titration of *p*-$OMeTPPH_2$ affects the λ_{max}, as well as the intensities of the two-banded metalloporphyrin like spectra at 0.02 M alkali concentration. The ratios of the intensities of α and β bands are (i) LiOH = 1.1, (ii) NaOH = 1.42, (iii) $Ba(OH)_2 = 1.75$ suggesting the influence of the size of the cation in the central core of the porphyrin ring.

(3) For *o*-$OHTPPH_2$ (Fig. 3(C)), the spectrum at high pH is similar to the spectrum observed in aquo-organic solvent but without the additional red-shifted new band. The wavelength maximum of the canopy shaped spectrum is more shifted towards the red at 648 nm above band 1 with minimum at 604 nm and a weak peak at 685 nm but continuous decrease in the red side. The spectral characteristics of both, *p*-$OHTPPH_2$ as well as that of *p*-$OMeTPPH_2$ are observable. The broad band can be resolved into two peaks one at

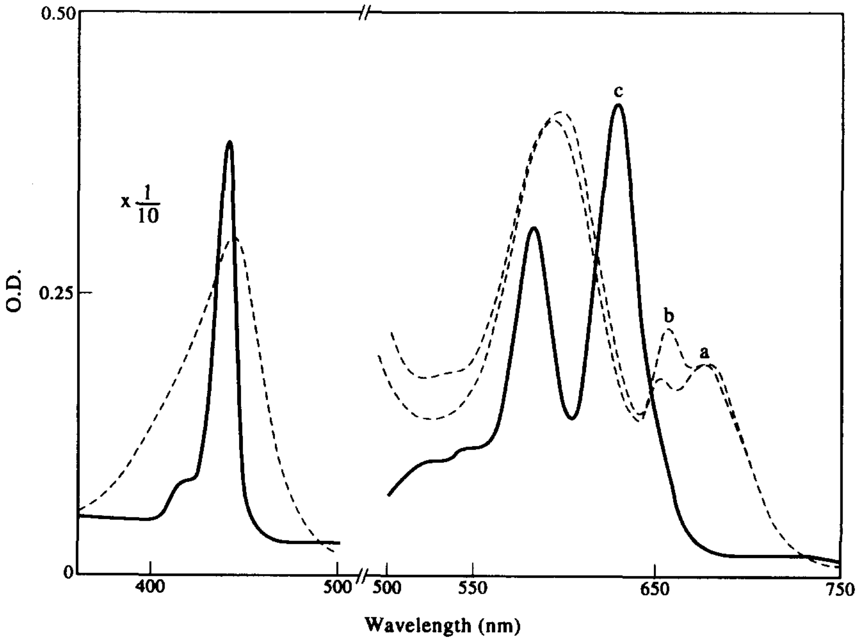


Fig. 2. The Soret band and *Q*-bands at pH > 12 (NaOH = 0.4 M) of *p*-$OHTPPH_2$ (----) in (a) DMF + H_2O, (b) i-PrOH + H_2O and (c) *p*-$OMeTPPH_2$ (——) in DMF + H_2O. All in 1 : 1 solvent mixtures. Magnification of *Q*-bands are 10 times compared to the Soret band.

626 nm and other at 662 nm. The 626 nm peak apparently is the long wave companion peak of metalloporphyrin at 585 nm and the 662 nm peak corresponds to the spectrum observed for *p*-OHTPPH$_2$ in Fig. 3(A).

DMF–H$_2$O *of graded composition as solvent at* pH 12

There is a striking difference in the spectrum of *p*-OHTPPH$_2$ in DMF alone and DMF–H$_2$O mixed solvents. The intensity of the new band in the red region is dependent on the water content of the solvent. To investigate at what composition of the solvent

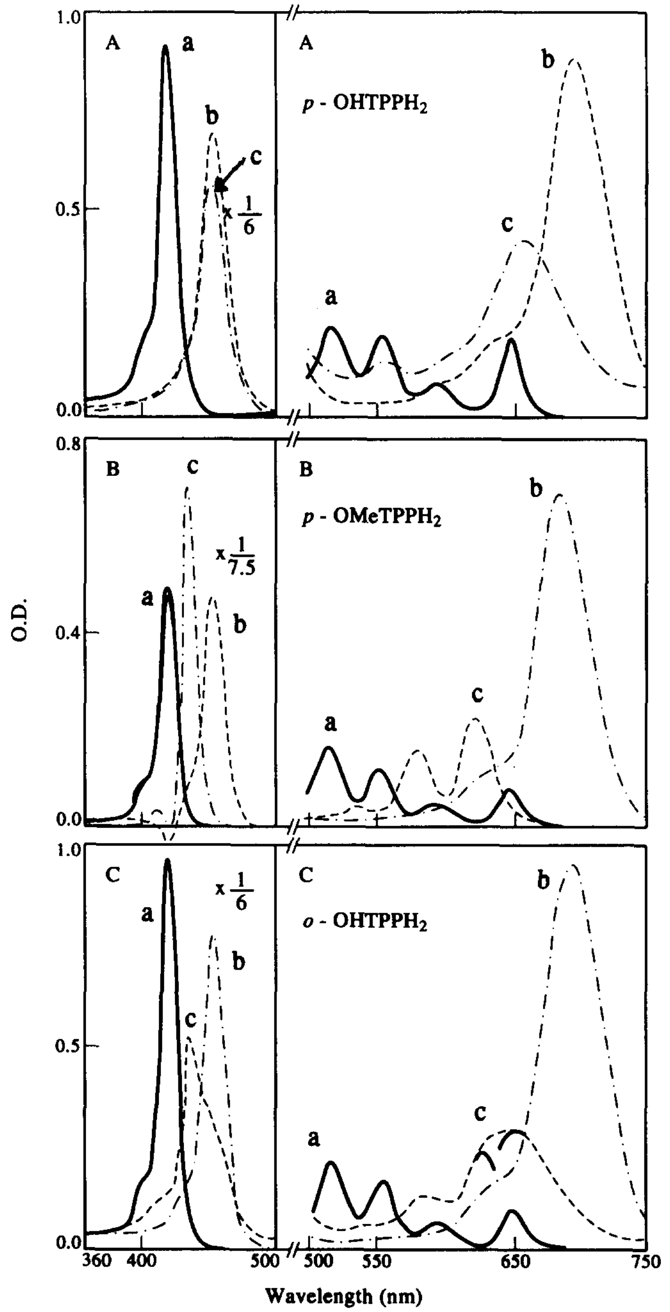


Fig. 3. Spectral characteristics of Soret bands and Q-bands of free base: at pH 6.3 (——), acid forms (0.024 M HCl) (----) and basic forms (0.02 M NaOH) (–·–·–) of (A) *p*-OHTPPH$_2$, (B) *p*-OMeTPPH$_2$ and (C) *o*-OHTPPH$_2$ in DMF solvent. The spectrum in the Q-band region are magnified 6 times for (A), 7.5 times for (B) and 6 times for (C).

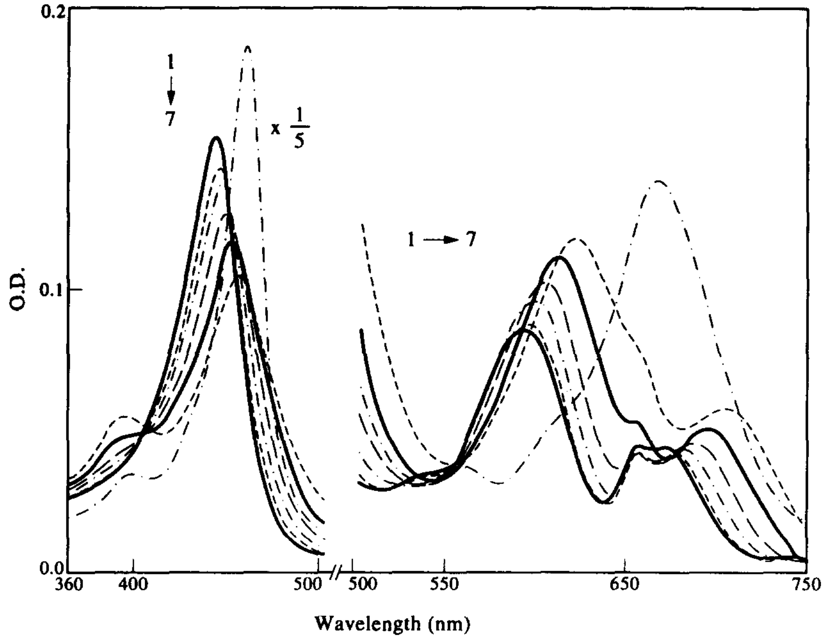


Fig. 4. Spectral characteristics of the Soret band and Q-band region of p-OHTPPH$_2$ at pH = 12 as a function of DMF–H$_2$O composition expressed in x_{DMF} (1) 0.04 (——), (2) 0.09 (----), (3) 0.16 (–––), (4) 0.26) (– – – –), (5) 0.41 (———), (6) 0.68 (–––), (7) 1.0 (———). Dramatic change of spectrum at $x_{DMF} = 1$. Q-bands magnified 5 times with respect to the Soret band.

mixture, the spectrum changes its characteristics, spectral data were obtained for graded composition of DMF–H$_2$O system as solvent at pH 12. The results are very interesting (Fig. 4). On gradual addition of DMF the canopy like spectrum in water-rich solvent gradually gains in intensity with concomitant red shift, together with the new band observed for p-OHTPPH$_2$. Although the spectrum in the Q-band region gradually broadens, the overall contour is still maintained for the mole fraction of DMF, $x_{DMF} \sim 0.7$. But on further increase of DMF, $x_{DMF} = 1.0$, there is complete transformation of the spectrum into a broad single banded acid-like spectrum of the type observed in basic solution, λ_{max} 662 nm, even at high pH (Fig. 4). The solvent dependent red peak at around 680–700 nm apparently disappears. Systematic changes are also observed in the Soret band, initial decrease and band splitting finally gives rise to a sharp high intensity band with a maximum at 454 nm, red shifted from 438 nm. Interestingly the changes are reversible. On addition of water the spectrum regains the characteristics observed in aquo-organic solvents.

DISCUSSION

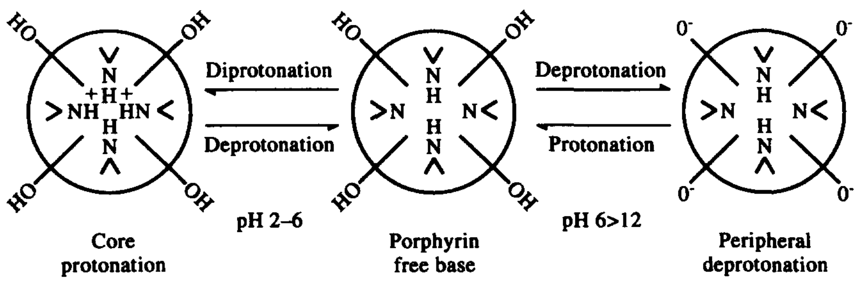
Of the three compounds under study, p-OHTPPH$_2$, o-OHTPPH$_2$ and p-OMeTPPH$_2$, the *para*-derivative is of considerable interest. The reduced intensity but increased breadth of the Soret band and development of a high intensity Q-band in the $Q_{x(01)}$ region with the well defined new band maximum at 680 nm at pH 12 in equivolume DMF + H$_2$O solvent (Fig. 1) needs explanation. The special spectral characteristics of free base p-OHTPPH$_2$, such as enhanced intensity of $Q_{x(00)}$ (band I) as compared to o- and m-derivatives of the free base at neutral pH was observed by Bonnett *et al.* [7, 8] in methanol solution for which they suggested the possibility of effective through bond conjugation in the p-isomer. A possible flow of charge for p- and o-isomers as phenoxides had been demonstrated earlier by Milgrom [5]. The changes in the absorption spectrum on addition of strong alkali have also been reported but there is no report of the formation of the new band in the red region beyond band I, neither any drastic changes in the spectrum as observed in DMF-rich aqueous solvent.

The *p*-OHTPPH$_2$ and *o*-OHTPPH$_2$ have acid–base character at the two centres, the OH groups of the four *p*-hydroxyphenyl substituents in the *meso*-position of porphyrins which can be deprotonated at high pH values and the central core region of porphyrin free base consisting of pyrrolic Ns which can be subjected to protonation–deprotonation equilibrium under appropriate conditions on pH variation. In the free base porphyrins the core region has two types of nitrogens in the five-membered rings, two 'pyrrole type-N' with associated H-atom and two 'pyridine type-N' with no H-atoms, following the nomenclature of GASSMAN *et al.* [4]. On addition of strong acid the pyridine type-Ns are protonated. The consequent overcrowding in the core region of the porphyrin ring causes considerable buckling of the ring resulting in the enhancement of nearly forbidden band I (Fig. 3(A)).

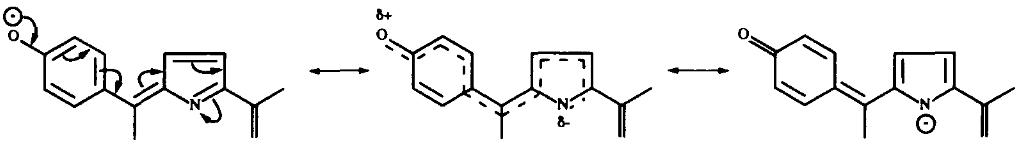
The crystal structure of tetraphenyl porphyrin H$_2$TPP has been worked out by SILVERS and co-workers [14] using the X-ray crystallographic technique. The *meso*-phenyl substituents are observed to be rotated by 60° to the molecular plane. One phenyl group is additionally inclined to this plane by + 9.1° perhaps for improved packing characteristics. In solution, the structure corresponds closely with the hybrid of the two classical resonance forms of the porphyrin molecule. The preferred pathway for delocalization of the π-electrons of the double bonds involves perphery of the macrocycle forming the 18-member cyclic polyene, the NH of the two pyrrol-type rings being not within it. The *p*-phenyl groups of *p*-OHTPP molecules will have considerable rotational freedom and the ionized phenyl groups of the molecule at high pH will find an easy path for delocalization of charges.

The possibility of extensive delocalization of charges from *meso*-*p*-hydroxy phenyl porphyrin to the pyridine-type Ns in the core region will tend to reduce the charge density on the peripheral phenoxide ions. It is difficult to say which phenyl substituent will dissociate first but the reduction in charge density may further facilitate deprotonation of other hydroxyphenyl groups thereby building up charge density on the inner core of pyridine type-N. The titrimetric curve obtained on gradual dropwise addition of 0.20 M NaOH solution (Fig. 1, inset) suggests a p*K* value of 11.0, for the protolytic equilibrium in DMF + H$_2$O (1 : 1) as solvent. A fairly sharp transition curve is observed which suggests that perhaps one or two of the four hydroxyphenyl groups have dissociated near this pH value. At still higher NaOH concentration (~0.4 M), where the pH could not be measured further changes are expected due to dissociation of other phenolic groups also (Scheme 1).

The delocalization of these peripheral charges in solution along the conjugative pathways to the core region causes accumulation of negative charges only on the pyridine-type Ns [5] as has been shown by arrows in Scheme 2. This new charge distribution due to the resonance effect will create a dipole with the positive pole on the phenolic oxygen in the *meso*-positions and negative pole on the N in the centre. Thus a charge transfer state is created. The new band at 680 nm which appears at the red side of the $Q_{x(00)}$ for *p*-OHTPPH$_2$ in (1 : 1) solvent mixtures can be assigned to this CT state. In aquo-organic solvents such as DMF + H$_2$O and i-PrOH + H$_2$O, a CT-band appears in the long wavelength region (Fig. 2). In the ligating solvent such as DMF, no such CT-band is



Scheme 1



Scheme 2

observed (Fig. 3). Appearance of single banded acid type spectra in the basic solution suggests accumulation of enough charge from *meso*-phenoxide ions to the core nitrogen of the pyridine type to cause an acid type spectrum at high pH values. The OH groups in *o*-OHTPPH$_2$ are considerably hindered sterically and consequently resonance effects are small. Therefore, only a weak band is observed (Fig. 3(B)). For *p*-OMeTPPH$_2$, the ionization is also blocked and the peripheral effect on the core region is minimal, giving rise to metalloporphyrins (Fig. 3(C)).

Striking differences in the spectral characteristics observed for *p*-OHTPPH$_2$ in the DMF + H$_2$O system and DMF alone are very clearly brought out by systematic solvent induced changes which appear in the spectrum at high pH (Fig. 4), when the mole fraction of DMF, x_{DMF}, is varied from a very low value to near unity, maintaining all the other conditions the same. The sudden change from the canopy-like spectrum to the acid type spectrum in DMF even at high alkalinity must be due to some critical changes in the reaction medium and charge density requirement. The acid type spectrum appears in general on addition of acid when two of the added protons attach themselves to the two pyridine-type Ns in the centre. The overcrowding thus created in the centre is responsible for the distortion of the π-ring structure of the planar porphyrin. It then seems logical to suggest that increased charge density in the core region transforms the spectrum to acid type expected for D_{4h} symmetry with enhanced intensity for band 1 which is forbidden otherwise. Such an acid type spectrum in a strongly basic solution was first observed by Erdman and Corwin [15] and recently by Milgrom [5] when porphyrin was put in strong base in aqueous solution. This was explained as due to deprotonation of two pyrrole-type Ns which although they leave behind two negative charges in the centre, they destroy the two-fold symmetry of the core region. They report exactly the same wavelength for the acid and basic solutions as is observed in the present study also. But the observations as well as the conditions are not exactly similar to the present case. The changes from CT to acid type appear dramatically when nearly pure DMF is used as solvent. Calculations show that the dielectric constant D of the solvent DMF + H$_2$O system varies linearly as a function of X_{DMF}. The peak energies in cm^{-1} of the Soret band, Q-band and the new band in the red region are plotted as a function of x_{DMF} in Fig. 5. The energy variations are not linear and sharp changes occur in the DMF rich solvent in the Q-band region. The intensity of the Soret band also shows a sharp increase for $x_{\mathrm{DMF}} \sim 1$.

The sudden change at critical value of x_{DMF} can be explained as through-bond flow of peripheral negative charges on the ionized phenolic-oxygens at high pH, also along the resonating structure, to the pyridine-type central Ns as shown in Scheme 2. Further redistribution of the negative charge density on these Ns can occur by tautomerism between pyrrole-type Ns and the pyridine-type Ns. Steric distortion primarily caused by charge accumulation in the centre results in single banded spectrum of the acid type. The observed spectrum at high pH is of higher energy and lower intensity compared to that observed in the acidic medium (Fig. 3(A)) where two additional H-atoms are added to the core region. All the spectral data are recorded in Table 1. What is also striking is that as the solvent composition changes from low value of x_{DMF} to higher values, the Soret band gradually decreases in intensity and shifts to the red. There are changes in other structural features also but beyond $x_{\mathrm{DMF}} \approx 0.7$ the spectrum changes to a high intensity Soret band and broad Q-band of the acid type. The flexibility of the peripheral phenyl groups appears to be restricted and CT-band disappears. At the same time, the Q-band transforms into an acid type band for which sharing amongst the core Ns is predicted [5].

It may be noted that the pK value of phenol has been reported to be greater than 15 in DMF [3, 16].

It is evident from the figure that water-rich solvent behaves differently from the DMF-rich solvent. Water is both a proton donor and proton acceptor, can easily solvate the anions, and form a three-dimensional solvent network but DMF is a dipolar solvent more basic in nature, and strong H-bond acceptor. It has less tendency to form H-bond with the anions and has three reasonating structures [17, 18] one neutral and two dipolar whereby it can interact with Lewis acid as well as ligate the metal ions. The appearance of two-banded spectra for *p*-OMeTPPH$_2$ on addition of alkali can be explained from these considerations. The intensity ratio of the α/β bands and the absorption maxima are observed to depend on the nature of alkali added. The α/β band ratio increases and both the bands are red shifted with increasing size of the cation, $Ba^{2+} > Na^{+} > Li^{+}$. This observation confirms the formation of the respective metalloporphyrins on addition of corresponding metal hydroxide to *p*-OMeTPPH$_2$ in DMF + water as well as in DMF alone as solvents.

Summarizing, the following conclusions become apparent: the appearance of a red-shifted peak in H_2O + DMF mixed solvent at high pH is definitely due to efficient flow of charge from the ionized *p*-phenoxy groups to the pyridine-type Ns in the core region creating a CT state. The combined effect of resonance and tautomerism between the two types of Ns in the centre brings about near equivalence of charge density on these core nitrogens when $x_{DMF} > 0.7$, giving rise to an acid-type spectrum in the alkaline region. For

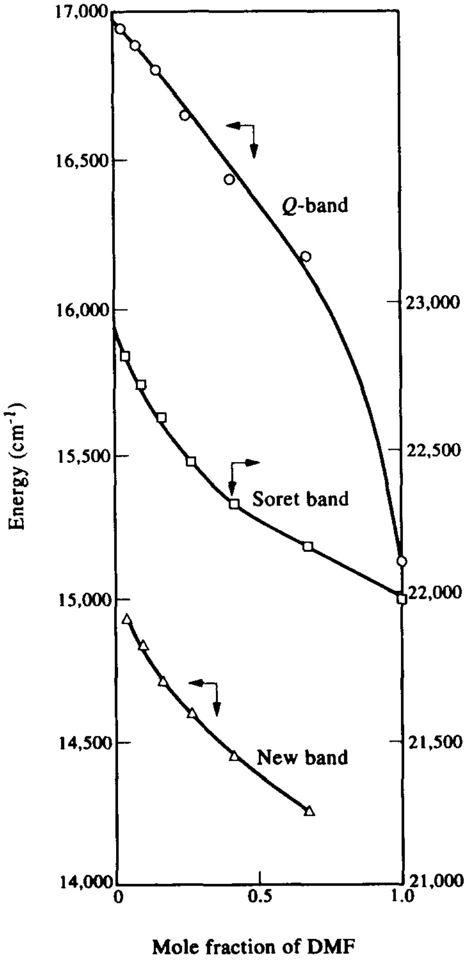


Fig. 5. Solvent induced variation of band maxima. Soret (-□-□-□-), Q-band (-O-O-O-) and the new band (-△-△-△-) as a function of mole fraction of DMF (x_{DMF}) in aquo–DMF solvent mixture.

o-OHTPPH$_2$, lack of suitable coplanarity for *meso*-*o*-hydroxyphenyl groups with the ring due to steric hindrance, prevents enough charge migration and the overall effect is small. The observed spectrum in Fig. 3(C), can be decomposed into contributions from CT type as well as metalloporphyrin type spectra. Perhaps the contribution of the CT type spectrum may be taken as a measure of conjugative interactions between the peripheral phenyl groups and the core region, nearly zero for *p*-OMeTPPH$_2$, very high for *p*-OHTPPH$_2$ and intermediate for *o*-OHTPPH$_2$. Gottwald and Ullman [19] have shown that the *o*-hydroxyphenyl group of *o*-OHTPPH$_2$ is capable of atropoisomerism, i.e. isomerization about an aryl porphyrin bond, when allowed to stand in methanolic solution. They suggest the possibility of distortion of the porphyrin ring in the solution in the transition state. On the other hand for *p*-OMeTPPH$_2$, since the reaction of alkali hydroxides with the *meso*-substituent is blocked and the $-OCH_3$ group is slightly electron withdrawing, the DMF ligated metal ions interact with the core hydrogens of the free base to produce metalloporphyrins [20].

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REFERENCES

[1] J. R. Platt, in *Systematic of the Electronic Spectra of Conjugated Molecules—A Source Book, Papers of Chicago Group, 1949–1964*, pp. 71–123. Wiley, New York (1964).
[2] M. Gouterman, *J. Chem. Phys.* **30**, 1139 (1959).
[3] P. Hambright and E. B. Fleischer, *Inorg. Chem.* **9**, 1759 (1970); A. Stone and E. B. Fleischer, *J. Am. Chem. Soc.* **90**, 2738 (1968).
[4] P. D. Gassman, A. Ghosh and J. Almlof, Univ. Minnesota Super Computer Institute Research Report UMSI 92/106 p. 9; (1992): A. Ghosh, J. Almlof and P. G. Gassman, *Chem. Phys. Lett.* **186**, 113 (1991).
[5] L. R. Milgrom, *J. Chem. Soc. Perkin Trans. I* 2535 (1983).
[6] P. Neta, M. C. Richoux, A. Harriman and L. R. Milgrom, *J. Chem. Soc. Faraday Trans.* **2**, 209 (1986).
[7] R. Bonnett, S. Ioannou, R. D. White, U. J. Winfield and M. C. Berenbaum, from Photophysics to Photobiology, Edited by A. Favre, R. Tyrrell and J. Cadet, Elsevier. *Photobiochem. and Photobiophys. Suppl.* p. 45 (1987).
[8] R. Bonnett, D. J. McGarvey, A. Harriman, E. J. Land, T. G. Truscott and U. J. Winfield, *Photochem. Photobiol.* **48**, 271 (1988) and references therein.
[9] J. H. Fuhrop, in *The Porphyrins*, Vol. II, pt. B, p. 134. Edited by D. Dolphin (1978).
[10] Unpublished work of the authors under preparation.
[11] A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour and L. Korsakoff, *J. Org. Chem.* **32**, 476 (1967).
[12] B. K. Manna, D. Sen, S. C. Bera and K. K. Rohatgi-Mukherjee, *Spectrochim. Acta* **48A**, 1957 (1992).
[13] L. K. Gottwald and E. F. Ullman, *Tetrahedron Lett.* **36**, 3071 (1969).
[14] S. J. Stuart, J. Silvers and A. Tulinsky, *J. Am. Chem. Soc.* **89**, 3331 (1967).
[15] J. G. Erdman and A. H. Corwin, *J. Am. Chem. Soc.* **68**, 1885 (1949).
[16] B. W. Clare, D. Cook, E. C. F. Ko, Y. C. Mac and A. J. Parker, *J. Am. Chem. Soc.* **88**, 1911 (1966).
[17] A. J. Parker, *Quart. Rev.* 163 (1962).
[18] R. C. Paul, in *New Pathways in Inorganic Chemistry* (Edited by E. A. V. Ebsward, A. G. Maddock and A. G. Sharpe, p. 233. Cambridge University Press, London (1968).
[19] L. K. Gottwald and E. F. Ullman, *Tetrahedron Lett.* **36**, 3071 (1969).
[20] G. D. Dorough, J. R. Miller and E. M. Huenkens, *J. Am. Chem. Soc.* **73**, 4315 (1951).