

Solvent effects on some new *meso*-aryl substituted octabromoporphyrins

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Abstract. A series of porphyrins with tolyl and naphthyl substituents at the *meso* positions, their octabromoderivatives (OBP) with Br substituents at *b*-pyrrole positions are synthesised and characterised by chemical analysis, ¹H NMR and electronic spectral studies. It is seen that all the OBPs exhibit pronounced red shifts in both the Soret and *Q* bands of their electronic spectra compared to their non-brominated form in various polar and nonpolar solvents, the energy difference $\Delta\bar{\nu}$ being in the range 2300–2700 cm⁻¹. The high energy *B* band of naphthyl porphyrins (both brominated and nonbrominated) are found to be more red-shifted than that of tolyl porphyrins, owing to the noticeable mesomeric effect of the naphthyl groups. Detailed spectral studies reveal that while none of the nonbrominated porphyrin show solvent-dependent change in their *B* and *Q* bands, all the OBPs manifest significant shifts depending on the nature of solvents. Solvent–solute interaction can be considered to be of strong dipole–dipole nature for OBPs with polar solvents and of *p*–*p* type with aromatic non-polar solvents. In the brominated form we find two categories of porphyrins exhibiting distinctly different absorption phenomena in aromatic solvents. The OBPs having *meso*-groups not shielding the porphyrin *p*-framework exhibit additional absorption peaks (split Soret peaks and broadened *Q* bands) in some aromatic solvents. This could be explained in terms of *p*–*p* type donor–acceptor (DA) complex formation between such bromoporphyrins (acceptor) and the aromatic solvent molecules (donor) that is not possible for OBPs that have bulky *meso* groups that block the approach of aromatic solvent molecules close to the porphyrin framework.

Keywords. Electronic spectra; tetratolylporphyrins; tetranaphthylporphyrins; octabromoporphyrins; solvent effects; donor–acceptor complex.

1. Introduction

The structure and dynamical behaviour of molecular aggregates is a subject of active current interest. Theoretical efforts regarding aggregate systems have focussed on excitonic coupling, often with the hope of clarifying DNA probing interactions and other biological substrates.^{1–3} Artificial reaction centres designed to investigate photoinduced charge separation have been targetted to mimic the events in natural photosynthesis and enzymatic studies.^{4–8} It is recognised that model systems involving porphyrins with well-defined donor–acceptor combinations with specific distance and geometries are essential

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to engineer the efficiency of photoinduced charge separation in these systems. The sensitivity of porphyrins to specific molecular environments has been the focus of intense studies recently owing to their relevance in photodynamic therapy, catalysis and enzyme mimicking.^{9,10} We have been interested in studying some of these aspects and also developing catalysts which mimic enzymes like peroxidase and catalase.^{11–18} We also looked into the specific disposition, the nature and effect of porphyrin-acceptor interactions by single crystal X-ray diffraction studies¹⁹ which was, surprisingly, different from what was reported in solution.²⁰

Recently we reported a new class of brominated and nonbrominated free-base porphyrins and demonstrated that the electronic and redox properties of the porphyrins are significantly influenced by the *meso*-aryl substituents and Br atoms at the *b*-pyrrole positions.^{21,22} The importance and special significance of bromoporphyrins which are known for their non-planarity have been well-documented.^{23,24} While studying the absorption spectra of some of these porphyrins under consideration, we could notice that the absorption characteristics were significantly different in some solvents. We report here the optical absorption features of these free-base porphyrins (brominated and nonbrominated) in different solvents of varying polarity.

2. Experimental

Pyrrole (Fluka) was distilled over KOH pellets, under reduced pressure before use. *a*-Naphthaldehyde and *b*-naphthaldehyde (E-Merck) were used as received. All the solvents employed in the present study were of spectral grade and were distilled before use. Liquid Br₂ procured from Ranbaxy and basic Al₂O₃ obtained from Acmes were used as received. The ¹H NMR spectra were recorded at 300 MHz with CDCl₃ as the solvent using Bruker-300 MHz spectrometer. Elemental analysis were done using a Perkin-Elmer CHN analyzer. The UV-Vis spectral measurements were carried out with a Shimadzu Model 160A UV-Vis spectrophotometer.

3. Preparation

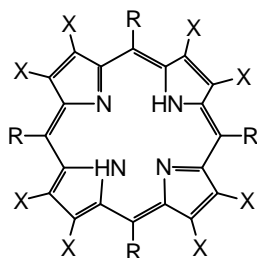
3.1 Free-base porphyrins

Non-brominated free-base tolyl (H₂TTHP) and naphthyl (H₂TNHP) porphyrins were synthesised by Alder's method involving condensation between pyrrole and the respective aldehyde in propionic acid solvent. Brominated free-base tolyl (H₂TTBP) and free-base naphthyl porphyrins (H₂TNBP) were prepared by brominating the Cu²⁺ derivatives of the porphyrins using reported procedure.^{22,25}

4. Results and discussion

The brominated and nonbrominated free-base porphyrins prepared are summarised in table 1. The specifications are based on the substituents on **1**.

All the brominated and non-brominated porphyrins which are purified by column chromatography are characterised by ¹H NMR and electronic spectra.²² In the non-brominated porphyrins the *b*-pyrrole protons are found to occur as singlets in the region 8.5–8.9 ppm while the aryl protons appear as multiplets in the range 7.9–8.7 ppm. The brominated porphyrins do not have any peaks characteristic of pyrrolic hydrogens revealing that all the pyrrolic protons are substituted with Br atoms. The aryl protons in

**1****Table 1.** The substituted free-base porphyrins employed in the present study.

R	X	Porphyrin
	H	H ₂ TN a HP
	Br	H ₂ TN a BP
	H	H ₂ TN b HP
	Br	H ₂ TN b BP
	H	H ₂ TT o HP
	Br	H ₂ TT o BP
	H	H ₂ TT m HP
	Br	H ₂ TT m BP
	H	H ₂ TT p HP
	Br	H ₂ TT p BP

the brominated porphyrins are seen to resonate in the range 7.6–8.8 ppm with marginal shift towards higher δ compared to non-brominated porphyrins, which is expected because of the deshielding effect of the electron-withdrawing Br atoms. We find noticeable deshielding in the NH protons also in the bromoderivatives (δ at –1.3 to –1.65 ppm compared to –2.0 to –3.0 ppm for the non-brominated porphyrins) caused by electron-withdrawing Br atoms. The measured electronic spectra for the non-brominated porphyrins in chloroform show typical four-line bands for *Q* and a strong *B* band. The bromoderivatives, however, show only three bands for *Q* which are all red-shifted by about 50 nm as compared to the corresponding non-brominated porphyrins. Similar red-shifts are seen for *B* bands also. The bromoporphyrins giving red-shifted *B* and *Q* bands as compared to the non-brominated porphyrins can be explained in terms of the cumulative effect of the severe distortion brought about by the bulky Br atoms and also

due to the electronegativity of the eight Br atoms. The lowering of LUMOs of the bromoporphyrins as compared to the respective nonbrominated porphyrins is evident from the easy reduction possible for OBPs.²² The reason for the red-shift in the electronic spectra which are essentially due to HOMO–LUMO transitions is evident from the lowered LUMOs. It is seen that the *B* bands of both brominated and non-brominated naphthyl porphyrins are found to be more red-shifted than the tolyl porphyrins. This could be attributed to the mesomeric effect possible in naphthyl derivatives from the *meso* substituent (naphthyl group). The possibility of naphthyl groups bringing about some amount of distortional change could also be a contributing factor. The energy differences between the *B* bands of brominated and non-brominated free-base compounds in chloroform are summarised in table 2. The nature of the shift and the number of absorption peaks of brominated porphyrins are comparatively well-understood.^{22,25–27}

However in one of our routine measurements of the electronic spectra of the porphyrins we found some interesting observations. In some categories of solvents, some of the brominated porphyrins exhibit unusual absorption features in both *B* and *Q* band regions. This preliminary communication is intended to report those observations. Given in tables 3 and 4 are the *B* and *Q* bands absorption peak maxima for the brominated and nonbrominated porphyrins in CHCl₃, CH₂Cl₂, DMF, benzene and toluene. It is seen that the absorption changes of the porphyrins under study are significant enough in some solvents. The solvents chosen are such that their dielectric constants come in a wide range and include both polar and non-polar types and also aromatic solvents. Carefully measured spectral data permit us to compare the solvent dependent change in the absorption spectra.

Noted below are some of the significant observations. (1) All the non-brominated porphyrins show typical four-line peaks for *Q* bands and intense *B* bands in the higher energy region. In all the solvents under study, almost the same *B* and *Q* band absorption maxima with similar features are observed for the non-brominated porphyrins. However for the OBPs prominent red-shifts are observed for all the peaks in DMF. This is consistent with the reported data.²⁷ Marginal shifts are observed for these porphyrins in other solvents also, but the shifts are seen to be increasing with increase in dielectric constants of the solvents. We could not, however, find any linear dependency of the red-shift with polarity of the solvents.²⁷ The observation of the solvent-dependent change for OBPs which is not seen for the corresponding non-brominated porphyrins is very

Table 2. Energy difference between the Soret bands of brominated and nonbrominated free-bases in chloroform at 298 K.

Porphyrin	Soret band	ΔI (nm)	$\Delta \bar{\nu}$ (cm ⁻¹)
H ₂ TToHP	418	48	2480
H ₂ TToBP	466		
H ₂ TTmHP	418	52	2600
H ₂ TTmBP	470		
H ₂ TTpHP	418	53	2700
H ₂ TTpBP	471		
H ₂ TNaHP	425	48	2380
H ₂ TNaBP	473		
H ₂ TNbHP	425	48	2380
H ₂ TNbBP	473		

Table 3. Absorption spectral values (nm) of Soret bands of brominated and nonbrominated porphyrins in various solvents.

Porphyrin	Toluene	Benzene	CHCl ₃	CH ₂ Cl ₂	DMF
H ₂ TToHP	417	417	418	417	416
H ₂ TTmHP	416	417	418	418	416
H ₂ TTpHP	420	420	418	418	417
H ₂ TNaHP	423	423	424	424	422
H ₂ TNbHP	426	425	424	424	425
H ₂ TToBP	467	468	465	464	473
H ₂ TTmBP	476, 497	421, 472	470	470	487
H ₂ TTpBP	472, 498	422, 472	471	468	487
H ₂ TNaBP	479	480	478	478	483
H ₂ TNbBP	470, 508	419, 474	473	473	490

Table 4. Absorption spectral values (nm) of Q bands of brominated and non-brominated porphyrins in various solvents.

Compound	Toluene	Benzene	CHCl ₃	CH ₂ Cl ₂	DMF
H ₂ TToHP	512	511	514	514	516
	545	545	546	546	547
	590	590	588	588	591
	651	650	648	648	647
H ₂ TTmHP	514	518	516	516	514
	548	548	551	551	548
	593	590	588	588	591
	648	648	648	648	646
H ₂ TTpHP	516	516	517	517	516
	551	551	551	551	551
	592	592	592	591	592
	651	651	648	648	649
H ₂ TNaHP	515	516	515	515	511
	552	551	550	550	551
	589	589	589	589	596
	654	649	647	647	649
H ₂ TNbHP	518	517	519	518	518
	554	553	556	556	554
	595	595	592	592	593
	651	652	650	650	650
H ₂ TToBP	564	564	563	562	646 (<i>br</i>)
	612	614	610	610	759 (<i>br</i>)
	721	722	724	724	
H ₂ TTmBP	625 (<i>br</i>)*	571 (<i>br</i>)	567	564	679 (<i>br</i>)
	733 (<i>br</i>)	627 (<i>br</i>)	631	628	800 (<i>br</i>)
	78 (<i>br</i>)	745 (<i>br</i>)	741	743	
H ₂ TTpBP	629 (<i>br</i>)	574 (<i>br</i>)	568	564	667
	742 (<i>br</i>)	631 (<i>br</i>)	632	629	769
	791 (<i>br</i>)	750 (<i>br</i>)	745	748	916
H ₂ TNaBP	564	568	567	567	655 (<i>br</i>)
	622	625	623	623	765 (<i>br</i>)
	733	733	734	736	
H ₂ TNbBP	620 (<i>br</i>)	572 (<i>br</i>)	566	564	684 (<i>br</i>)
	740 (<i>br</i>)	631 (<i>br</i>)	629	629	792 (<i>br</i>)
	786 (<i>br</i>)	745 (<i>br</i>)	734	736	

**br* – broad

interesting. This can be explained in terms of dipole–dipole interaction between the solvents (CHCl_3 , CH_2Cl_2 and DMF) and OBPs. Compared to non-brominated porphyrins OBPs have better charge polarisation and hence would be better dipoles. The extent of polarity would greatly affect the nature of solvent–solute interaction and would therefore modify the geometry and electronic properties of the porphyrins. While the non-brominated porphyrins are poor dipoles, OBPs can act as strong dipoles because of both Br substitution and severe structural distortion. In the case of non-polar solvents like benzene and toluene, the interaction involved can be considered as of *p-p* type. (2) In the case of brominated porphyrins we find two distinct classes of porphyrins with regard to their absorption features. They are H_2TToBP and H_2TNaBP (category I) and H_2TTmBP , H_2TTpBP and H_2TNbBP (category II). The categorisation was done based on the unique nature of absorption spectra in aromatic solvents. This is illustrated in figure 1 for H_2TNaBP and H_2TTpBP in toluene. (3) The spectra of H_2TToBP and H_2TNaBP (category I) are seen to be similar in all the five solvents including benzene and toluene. The marginal red-shift observed in them is also consistent with the order of the polarity of solvents. Unlike the above bromoporphyrins, H_2TTmBP , H_2TTpBP and H_2TNbBP (category II) are seen to have unique solvent-dependent features in their electronic spectra. While in solvents like CHCl_3 , CH_2Cl_2 and DMF these three bromoporphyrins give similar spectra as in category I, they show the emergence of new *B* bands and red-shifted broadened *Q* bands in both toluene and benzene. This is evident in figure 2 where the absorption spectra of H_2TTpBP in two solvents CHCl_3 and toluene are shown. The peak at 472 nm is common in both solvents. In toluene along with the peak at 472 nm observed in CHCl_3 we find the new band at 498 nm while in benzene the extra peak (other than the peak at 472 nm) is at 422 nm (table 3). We have verified the values by repeated measurements and found that the new peaks are seen only in the case of H_2TTpBP , H_2TTmBP and H_2TNbBP in benzene and toluene only.

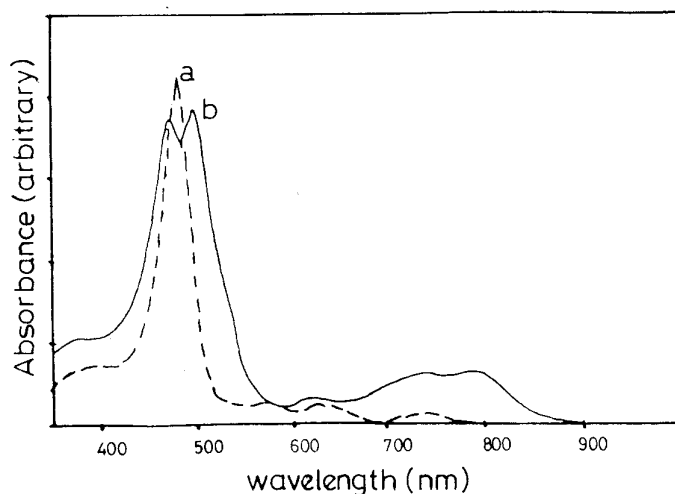


Figure 1. Optical absorption spectra of (a) H_2TTpBP and (b) H_2TNaBP in toluene at 298 K.

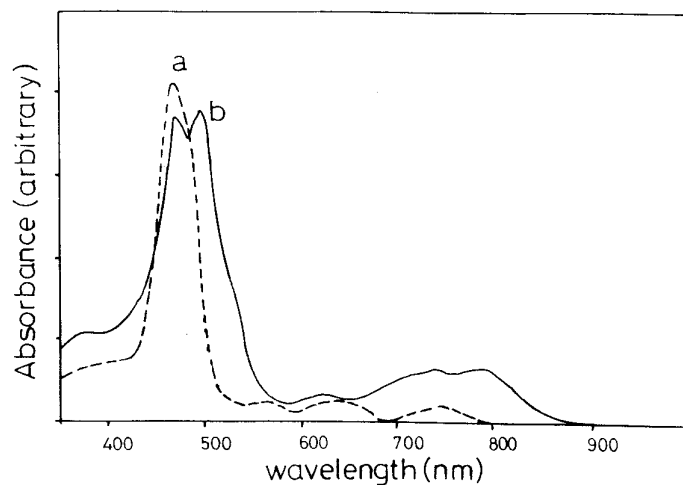
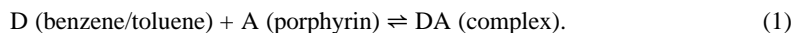


Figure 2. Optical absorption spectra of H_2TTPBP in (a) chloroform and (b) toluene at 298 K.

The significant observation seen in the case of H_2TTPBP , H_2TTmBP and H_2TNbBP in benzene and toluene compared to that in other solvents could be explained as follows. It is seen that special solvent effects are found only in the case of the brominated form of these aryl porphyrins. It may be noted that all the bromoporphyrins have strongly electron-withdrawing Br atoms at *b*-pyrrole positions which would make their *p*-framework comparatively electron-deficient. Unlike $CHCl_3$, CH_2Cl_2 and DMF, benzene and toluene are aromatic systems having *p*-electron clouds. So it can be expected that the electron-depleted bromoderivatives would interact strongly with electron-rich benzene and toluene by *p-p* overlap. The result would be the formation of a strong donor-acceptor complex between benzene/toluene and octabromoporphyrins as given below.



Since such donor-acceptor complexes are known to be comparatively weak, DA, D and A components would coexist based on the above equilibrium. So any porphyrin system which is involved in the donor-acceptor interaction would give the spectra characteristic of both complexed and uncomplexed forms of the porphyrin. Comparison of the spectra of H_2TTPBP in toluene and $CHCl_3$ shows that the peak at 472 nm is common in both the solvents (figure 2). As evident from the spectra of the brominated porphyrin in solvents like $CHCl_3$ this peak can be assigned to the non-complexed porphyrin system and the one at higher wavelength to the DA component. It is also seen that the sum of the intensities of the peaks at 498 and 472 nm in toluene match with the intensities of the peaks expected for the total porphyrin taken. We assign the peak at 498 nm in toluene and the peak at 422 nm in benzene to the Soret band of the porphyrin in the DA complex in each case (table 3). The broadened *Q* bands of these OBPs observed in toluene and benzene are also indicative of the DA complex formation.

For strong donor–acceptor complex formation by **p–p** overlap, it is necessary that the donor (benzene/toluene) and acceptor (OBPs) be in close proximity facing each other. In H₂TToBP and H₂TNaBP the orientation of the *meso*-substituents would be in such a way that they have the groups disposed above the **p**-frame work of the porphyrin preventing aromatic molecules like benzene or toluene from approaching closer to the porphyrin **p**-framework. In such systems no donor–acceptor complex between *D* and *A* is possible. In the other three porphyrins (category II) the *meso*-substituents would be disposed in such a way that the porphyrin **p**-frame work is less hindered. This would enable the benzene or toluene molecule to approach closer to the porphyrin framework to form the DA complex.

We have made some attempt to look at the possible interaction between porphyrin and donor molecules in the DA complexes considered above. The relevant orbitals are the LUMOs of the porphyrin (because it acts as an acceptor) and HOMOs of benzene/toluene (because they are donors). Detailed ¹H NMR²⁰ and single crystal X-ray diffraction studies¹⁹ have demonstrated the nature of disposition of donor–acceptor species involving porphyrins and aromatic acceptor molecules. We believe that the structure of DA complex between H₂TTpBP, H₂TTmBP and H₂TNbBP and benzene are similar to the ones reported.^{19,20} Orbital symmetry considerations¹⁹ of the bromoporphyrins and the benzene molecule in such a disposition would result in an interaction involving *eg*(**p**^{*}) and HOMOs of benzene pushing the LUMOs of porphyrin up in energy. Consequently, the energy gap between the *a_{2u}* (HOMO) and *eg*(**p**^{*}) (LUMO) would be enhanced. The blue-shifted bands (around 422 nm) observed for H₂TTpBP, H₂TTmBP and H₂TNbBP in benzene could therefore be assigned to such a DA complex. The presence of the 472 nm peak along with the one at 422 nm indicates the existence of uncomplexed porphyrins also as required by (1) (see table 3). Even though one would expect similar orientation and interaction between toluene and category II porphyrins (H₂TTpBP, H₂TTmBP and H₂TNbBP) the presence of –CH₃ group in toluene moiety would make it difficult to have the same structural disposition, since –CH₃ group would sterically interact with the two **b**-pyrrole Br atoms. Consequently toluene is expected to orient in a different manner as compared to benzene. Such a disposition can be expected to result in an interaction¹⁹ of *D* and *A* molecules such that the HOMO–LUMO gap between the *a_{2u}* and *eg*(**p**^{*}) gets decreased. In such a case the Soret band should appear at lower energy region for the DA complex which is consistent with the experimental data (peaks around 500 nm observed for category II porphyrins, see table 3). As in the earlier case, the peaks due to the uncomplexed porphyrin in each case is seen around 472 nm in addition to the peak for the DA complex mentioned above in toluene.

As mentioned earlier for the bromoporphyrins like H₂TToBP and H₂TNaBP which have bulky *meso* groups that can block the approach of planar benzene/toluene molecule to have the **p–p** interaction there is no possibility of formation of the DA complex and hence no additional peak can be expected. Our experimental data confirm this point (table 3).

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