Unusual Solvent Effect on Absorption Spectra of Nonplanar Dodecaphenylporphyrin Caused by Hydrogen-Bonding Interactions

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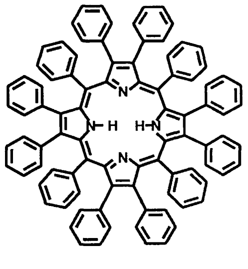
UV-vis absorption spectra of nonplanar dodecaphenylporphyrin H_2DPP show a strong solvent dependence caused by the hydrogen-bonding interactions of pyrrole NH protons and pyrrolenine nitrogen lone pairs with solvent molecules.

Nonplanar porphyrin ring systems are currently of considerable interest because of their occurrence in ferrochelatase[1] and some haemproteins as active centers[2] and because of their fascinating properties disclosed in model porphyrins.[3] Dodecaphenylporphyrin (H_2DPP)[3,4] has a permanently and highly distorted macrocycle and is a well suited model for characterizing "nonplanar effect" on various chemical and physical properties of porphyrin macrocycles. Here we report that the UV-vis absorption spectrum of the free base H_2DPP is strongly solvent dependent. This is in marked contrast with the situation found in numerous planar porphyrin free bases; their spectra are virtually insensitive to solvents. The solvent effect observed for H_2DPP is interpreted in terms of hydrogen(H)-bonding interactions of the internal pyrrole NH protons and the pyrrolenine nitrogen lone pair electrons, both of which are forced out of plane by the nonplanar distortion of DPP macrocycle.



H_2DPP

The UV-visible absorption spectra of H_2DPP in hexane and pyridine are shown in Figure 1. Very distinct differences in the Soret (or the B) and Q bands are noticed. The spectrum in hexane exhibits a sharp Soret band at 458 nm, while that in pyridine, a broadened Soret band shifted to longer wavelength at 476 nm. The solvent dependence in the Q band region is more complicated. It is well known that planar porphyrin free bases exhibit four Q bands designated $Q_x(0,0)$, $Q_x(1,0)$, $Q_y(0,0)$, and $Q_y(1,0)$ in order of increasing transition energy.[5] For H_2DPP in hexane, four Q bands are indeed observed, although $Q_x(1,0)$ is not well resolved but identified as a shoulder peak (Figure 1). However, as the solvent goes from hexane to pyridine, the two Q_y bands shift to red with greater extent than the two Q_x bands, and the $Q_x(1,0)$ is concealed behind the strong $Q_y(0,0)$ to give the apparent three-banded spectrum. Control experiments have established that the solvent effect on the planar porphyrin free bases, *meso*-tetraphenylporphyrin (H_2TPP) and octakis(*p*-isopropylphenyl)porphyrin ($H_2OiPrPP$),[6] is very small. Thus, the solvent effect observed for H_2DPP is likely caused by the nonplanarity of the porphyrin macrocycle. The red-shifts are observed for a variety of solvents.

To know whether the spectral shifts are caused by simple solvation effect or special solute-solvent interaction, the spectra of H_2DPP and H_2TPP in thirty-seven different neat solvents have been measured and analyzed using the method of Valentine.[7]

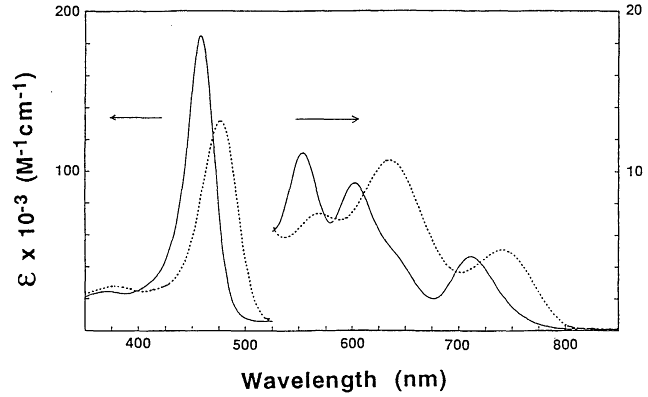


Figure 1. UV-visible absoporption spectra of H_2DPP in hexane (——) and pyridine (·····).

Figure 2 shows a plot of the Soret band energies (E_B) vs the function $(n^2-1)/(2n^2+1)$, where n is the refractive index of the neat solvent. This plot has been successful in elucidating solvent effect for a variety of organic dyes as well as for zinc porphyrin.[7] The E_B values of H_2TPP show a linear dependence on this function, indicative of simple solvation effect. For H_2DPP, a linear dependence with similar slope but with more scatter is also obtained for the solvents with non H-bonding properties.[8] On the other hand, the E_B values of H_2DPP in the solvents with H-bonding properties show greater shifts from the linearity. The latter solvents include proton acceptor (amines, amides and sulfoxide) and donor (alcohols) solvents. Moreover, the E_B values in these solvents are dependent on the steric hindrance of solvent molecules. For example, the red shifts in a series of substituted pyridines are in the order; pyridine ~ 4-picoline > 2-picoline > 2,6-lutidine ~ 2,4,6-collidine (35, 34 → 28 → 31, 30 in Figure 2). Similar steric effect is observed for amides (20 → 18 → 21 → 22), alcohols (19 → 10 → 7 → 6 → 8)[9] and aliphatic amines (24 → 9 → 13 → 12 and 9 → 3). It is noted that the E_B values are also correlated with donor number of the solvents except for such hindered solvent molecules (not shown in Figure).

The result can be explained in terms of H-bonding interactions between the pyrrole NH protons and the lone pair electrons of the solvent molecules (amines, amides and sulfoxide). These solvents act as good proton acceptors toward NH protons to form H-bonds such as $>N\text{-}H\cdots N<$ and $>N\text{-}H\cdots O{=}S(CH_3)_2$. It is well known that pyrrole itself H-bonds to DMSO and pyridine.[10] On the other hand, alcohols act as good proton donors to form H-bonds with pyrrolenine type nitrogens.

X-ray results of H_2DPP show a saddle-shaped deformation of the porphyrin macrocycle in which the four pyrrole rings are alternatively tilted up and down, and this conformation must be maintained in solution.[3] Thus, the nonplanar conformation is

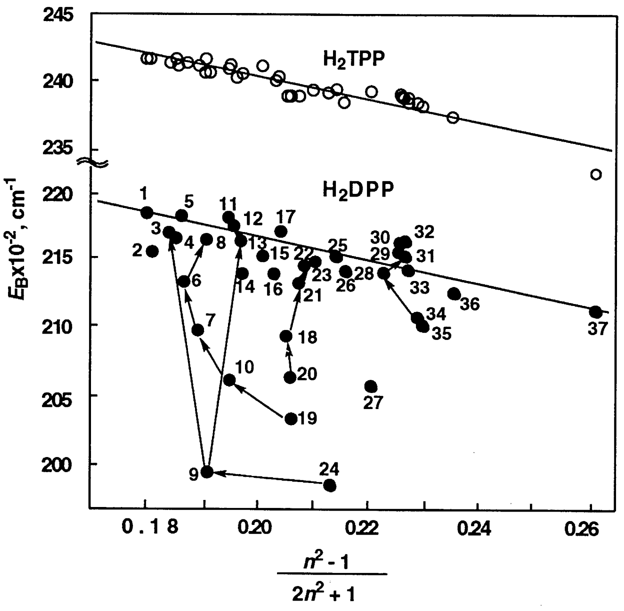


Figure 2. Plots of the Soret band transition energy (E_B) of H_2TPP and H_2DPP vs the function $(n^2-1)/(2n^2+1)$, where n is the refractive index of the neat solvent: 1, pentane; 2, acetone; 3, t-butylamine; 4, ethyl acetate; 5, hexane; 6, 2-propanol; 7, 1-propanol; 8, t-butanol; 9, 1-propylamine; 10, 1-butanol; 11, heptane; 12, triethylamine; 13, dipropylamine; 14, THF; 15, butylonitrile; 16, dichloromethane; 17, cyclohexane; 18, DMF; 19, ethyleneglycol; 20, methylformamide; 21, dimethylacetamide; 22, dimethylpropionamide; 23, chloroform; 24, ethylenediamine; 25, HMPA; 26, carbon tetrachloride; 27, dimethyl sulfoxide; 28, 2-picoline; 29, toluene; 30, 2,4,6-collidine; 31, 2,6-lutidine; 32, mesitylene; 33, benzene; 34, 4-picoline; 35, pyridine; 36, benzonitrile, 37, carbon disulfide. Arrows indicate a series of the same type of solvents, as described in the text.

sterically favorable for the formation of H-bonds between the pyrrole NH protons or pyrrolenine N lone pairs and the solvent molecules. However, sterically hindered solvent molecules such as 2,6-lutidine, triethylamine, dimethylpropionamide and *t*-butanol are unable to form such H-bonds. Thus, the spectra of H_2DPP in sterically hindered solvents are similar to that in hexane, exhibiting the four-banded visible absorptions. Similar steric effects have been observed in the H-bonded association between pyrrole and pyridines.[11] The planar porphyrin free bases such as H_2TPP are not capable of forming H-bonds, because the N-H bonds and the lone pairs lying in the porphyrin plane are not accessible to attack by solvents. ^{1}H NMR spectra also support the H-bonding interactions. The resonance of NH protons in DMSO-d_6 (δ = 1.0 ppm) appears at noticeably lower field than in CD_2Cl_2 (δ = -1 ppm). The strong deshielding of the NH protons leaves no doubt of the formation of H-bonds between H_2DPP and DMSO.[12]

The nonplanar conformation described above is also important in relation to the metal incorporation into porphyrin macrocycles. The ring deformation causes both the basicity of the pyrrolenine nitrogens and the acidity of the pyrrole NH protons to increase. These bifunctional properties of nonplanar porphyrins lead to rate acceleration of metalation in ferro-chelatase[1] and model systems.[4,13] Further studies on the solvent effect of a series of phenyl-substituted planar to nonplanar porphyrins (hexa-, octa-, deca- and undecaphenylporphyrins)[14] are now underway.

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8 The scattered plot is probably due to saddle type conformation of H_2DPP. Some weak electrostatic interaction must be presented for the solvent molecules near the cavity.

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