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Substitution effects on the UV–vis and ^1H NMR spectra of the dications of *meso* and/or β substituted porphyrins with trifluoroacetic acid: Electron-deficient porphyrins compared to the electron-rich ones

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ABSTRACT

Spectral shifts upon core protonation of a series of electron-rich and electron-deficient porphyrins with five and six membered rings at the *meso*-positions have been studied by UV–vis and ^1H NMR spectroscopy. The direction of the shift of the Q(0,0) band of different porphyrins depends on the electron-donating or electron-withdrawing character of the *meso*-substituent and therefore it may be used to evaluate the relative electron donor ability of the substituents. Also, the shift of the Soret bands was found to be influenced to a lesser extent by the electron donor ability of substituted groups at the porphyrin periphery. Although, large red shifts of the Soret band of $H_4T(o\text{-}NO_2)P^{2+}$, $H_4T(p\text{-}SCH_3P)P^{2+}$ and $H_4T(p\text{-}NO_2P)P^{2+}$ indicate a significant out-of-plane deformation of porphyrin core, negligible upfield shifts of the β protons in their ^1H NMR spectra show that the practice of using the change in the chemical shift of the β protons as an indicator of structurally induced changes in the porphyrin ring current should be approached with more caution. Interestingly, high level *ab initio* and DFT calculations demonstrate that in spite of the better electron donating ability of $-OCH_3$ to benzene ring compared to that of $-SCH_3$, *meso*-(p-SCH_3)phenyl group is a clearly better electron donor to the porphyrin core than *meso*-(p-OCH_3)phenyl one.

1. Introduction

Interaction of porphyrins with weak and strong σ and/or π acceptors has been extensively studied from various viewpoints [1–9]. In the porphyrin structure, the two pyrrolenine nitrogen atoms bearing lone pairs of electrons ($pK_b \sim 9$) can be protonated easily with acids such as trifluoroacetic acid [10]. Although Aronoff's spectrophotometric titration of H_2tpp with CF_3COOH in nitrobenzene has given an intermediate spectrum attributed to a monoprotonated moiety, H_3TPP^+, there has been no evidence for a monoprotonated intermediate between the free base and the diprotonated porphyrin in chloroform and dichloromethane [1–3,6,7,11–13]. Core protonation of porphyrins is accompanied with the out-of-plane deformations of porphyrin core and the decrease of the dihedral angle between the *meso*-aryl substituents and the porphyrin mean plane [2,3,6,10]. Accordingly, it may be used to induce nonplanar distortion in the porphyrin macrocycle with a concomitant reduction in the dihedral angle between the *meso*-aryl substituents and the porphyrin mean plane. This in turn leads to increased resonance interactions between the aryl groups and porphyrin π system. For the free base *meso*-tetraphenylporphyrin (H_2TPP), dihedral angles of 60–85° between the phenyl and porphyrin mean planes were found in solids, and angles of about 40° were calculated by Wolberg in solution [2,14,15]. Several spectral signatures of the porphyrins including those detected by resonance Raman, ^1H NMR and UV–Vis spectroscopies, have been found to be significantly affected by out-of-plane deformations of the macrocycle [16]. With the exception of substantially nonplanar porphyrins, the Soret and Q bands of free base porphyrins with different substituents at *meso*- and β-positions appear at nearly the same wavelengths [6,8]. On the other hand, different shifts of the Soret and Q(0,0) bands of various porphyrins upon protonation with a protic acid, lead to clearly distinguishable spectra for different porphyrins [3,6,8]. In other words, core protonation of porphyrins enhances the influences of the steric and electronic effects of the substituents on the position of the bands in the UV–vis spectra.

Shifts of the Q(0,0) band and to some extent the Soret band of *meso*-tetraarylporphyrins upon protonation with $HClO_4$ and their basicity have been shown to correlate with the π-donor ability of the aryl substituents [2]. On the other hand, electronic properties of the peripheral substituents control the redox properties of metal centers and consequently the catalytic activity of metalloporphyrins [17,18]. In this regard, the redox potential of metal centre depends on the basicity and planarity of the porphyrin ring and consequently the dihedral angle between the *meso*-aryl substituents and porphyrin mean

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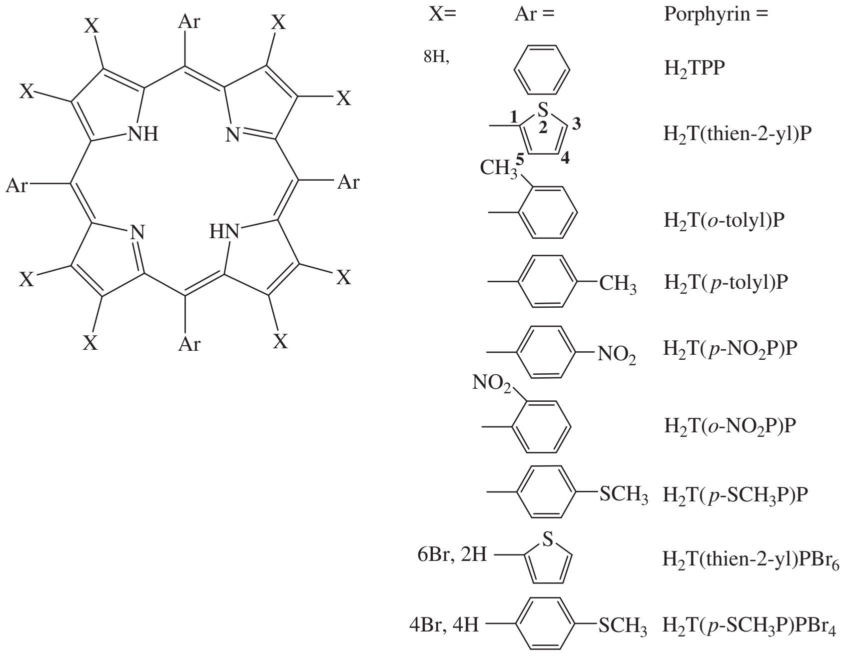

Fig. 1. Porphyrins used in this study.

plane [2,18–23]. For the e_g orbitals the electron densities are distributed on the pyrrole carbon atoms, the methane bridges and the central nitrogen atoms, but the a_{2u} electron densities are equally distributed between the methene carbons and pyrrole nitrogens [24]. Therefore, due to the coordination of nitrogen atoms to the metal centre, the M(III)/M(II) and M(IV)/M(III) reduction potentials of metalloporphyrins may be tuned by electronic properties of the groups attached to the methane and β carbons [17,18]. The aim of the present work is to find the correlation between the magnitude of spectral shifts and the electronic effects of the peripheral substituents upon protonation of a series of electron-rich and electron-deficient porphyrins (Fig. 1). The changes of the chemical shifts of the β protons were used to obtain information on the out-of-plane deformation of porphyrin core and the extent of decrease in the ring current of the aromatic macrocycle [25].

2. Experimental

H_2TPP [26], $H_2T(p\text{-}OCH_3P)P$ [26], $H_2T(p\text{-tolyl})P$ [26], $H_2T(o\text{-tolyl})P$ [26], $H_2t(p\text{-}NO_2P)P$ [23,27], $H_2t(o\text{-}NO_2P)P$ [23,26], $H_2T(p\text{-}SCH_3P)P$ [26,28] and $H_2T(\text{thien-2-yl})P$ [29] (Fig. 1) were synthesized, characterized and purified according to the literature methods. As have been reported in our previous works [30,31], bromination of $H_2T(4\text{-}SCH_3P)P$ and $H_2T(\text{thien-2-yl})P$ with excess amounts of N-bromosuccinimid (freshly recrystallized from hot water and dried at 80 °C under vacuum) [32] leads to the formation of $H_2T(4\text{-}SCH_3P)PBr_4$ and $H_2T(\text{thien-2-yl})PBr_6$. ^1H NMR and UV–vis spectral data of the compounds are summarized in Tables 1–4.

Porphyrin dictions were prepared by adding excess amounts of CF_3COOH (more than the 2:1 molar ratio of the acid to porphyrin) to the solution of porphyrin in dichloromethane followed by slow evaporation of the solvent and excess acid at room temperature [6,8]. It should be noted that recording the UV–vis spectra of the porphyrin dications in the presence of excess amounts of CF_3COOH (beyond the 2:1 molar ratio of acid to porphyrin) led to no detectable changes in the position and intensity of the absorption bands. As the previous studies showed (*vide supra*), the use of different mole ratios of porphyrin to trifluroacetic acid, gave no evidence for the formation of a monoprotonated species in dichloromethane; Fig. S1 shows the spectrophotometric titration of H_2TPP with CF_3COOH in dichloromethane.

3. Results and discussion

Core protonation of a series of porphyrins (Fig. 1) with CF_3COOH in dichloromethane leads to the shifts of the Soret and Q(0,0) bands in UV–vis spectra and the change of chemical shift of different protons in ^1H NMR spectra (Tables 1 and 2).

3.1. ^1H NMR spectra

Protonation of porphyrins with CF_3COOH usually leads to the upfield shifts of the β protons [6,8,25,33]. In free base porphyrins, chemical shifts of the β protons depend closely on the extent of contribution of the porphyrin ring current effects to deshielding of the ring protons. Accordingly, the upfield shifts of the β protons are

Table 1
^1H NMR resonances of $H_2T(\text{thien-2-yl})P$, $H_2T(\text{thien-2-yl})PBr_6$ and the corresponding dications with CF_3COOH in $CDCl_3$.

Porphyrins and dications	NH	H_β	H_4	H_3	H_5
$H_2T(\text{thien-2-yl})P$	2.66	9.03	7.48–7.51	7.84–7.86	7.91–7.92
$H_4T(\text{thien-2-yl})P(CF_3COO)_2$	1.53	8.58	7.78–7.81	8.27–8.29	8.38–8.39
Δδ	4.19	−0.45	0.30	0.43	0.47
$H_2T(\text{thien-2-yl})PBr_6$	−2.62	8.99	7.52–7.53	7.68–7.70	7.90
$H_4T(\text{thien-2-yl})PBr_6(CF_3COO)_2$	0.0	8.32	7.68–7.70	7.94	8.32
Δδ	2.62	−0.67	0.16–0.17	0.26–0.24	0.42