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WATER SOLUBLE MESO-TETRARYLPORPHYRIN DIACIDS

A.A. Fernandes* and C.M. Stinson

Department of Chemistry, Talladega College, Talladega, Alabama 35160

and

A. Shamim

Department of Chemistry, Howard University, Washington, D.C. 20059, U.S.A.

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Water soluble porphyrins are of considerable interest for structural and reactivity investigations. Only a few reports have been made for the synthesis and structural studies of *meso*-substituted porphyrin diacids. This report concerns the synthesis, ^1H NMR, IR, UV-visible spectra as well as mass spectra of three *meso*-substituted free-base porphyrins and their diacids.

Key words: Porphyrins; Synthesis and substituted acids.

INTRODUCTION

Synthetic water-soluble porphyrins have acquired considerable importance in porphyrin investigations due to the relative ease of their synthesis and purification. They have been found to be closely related to naturally occurring porphyrins. The question of porphyrins in TFA solution has been under active consideration due to their successive protonation. NMR studies have been undertaken in TFA at variation temperature to observe slow exchange between TPP and its diprotonated form [1,2]. The first molecular and crystal structures of porphyrin diacids were reported by Stone and Fleischer [3]. Their experimental observation indicates that the diacids are highly nonplanar. Ogoshi, *et. al.* characterized the porphyrin monoacid and diacid and discussed the effect of hydrogen-bonding from resonance contributions [4].

The present paper describes the synthesis and spectroscopic studies of three water-soluble substituted *meso*-tetrarylporphyrin diacids and gives a brief method of chemically isolating porphyrin diacids.

EXPERIMENTAL

Synthesis. Tetra (4-methoxyphenyl) porphyrin was prepared by direct condensation method [5] and purified using alumina column. Tetra (4-hydroxyphenyl) porphyrin was prepared by the cleavage of methoxy group with hydro-

bromic acid [6]. Tetra [4-sulphonatophenyl] porphyrin, sodium salt was purchased from Midcentury Chemical Company. The diacids of all free-base porphyrins were prepared by adding equal amounts of porphyrin and concentrated sulphuric acid in a test tube while stirring and ether was added until a green precipitate formed. The precipitate was filtered through the Cuvet filter and washed several times with ether and acetone. It was then air dried.

Mass spectrum was taken using a Varian MAT 112 mass spectrometer equipped with a fast atom bombardment (FAB, Xe atoms accelerated at 8kv). The samples were dissolved in sulphalane and glycerol was added as a mass marker. The spectra were collected, calibrated, and the M^{+1} ion for the free base T(4-OCH₃)PP and T(4-OH)PP were determined.

The proton NMR spectra of diacids, H₂-T(4-SO₃Na)PP, and free base H₂-T(4-OH)PP were obtained in DMSO-d₆ solvent with TMS as an internal standard using high resolution 300MHz WB Nicolet and 200 MHz WP Bruker FT-spectrometers. The spectrum of free base H₂-T(4-OCH₃)PP was taken in CDCl₃ solvent. IR spectra were determined using KBr pellets with a Beckman IR-33 spectrophotometer. Visible spectra were measured on a Beckman DU-8 spectrophotometer.

RESULTS AND DISCUSSION

The three dications I-III (Fig. 1), quite expectedly, were found to be water soluble over a wide range of pH. Table 1 lists the elemental analysis while Tables 2 and 3

*Present Address: Waste Water Management System, 8301 White Road, Muskegon, Michigan 49442, U.S.A.

are respectively for the UV-visible spectra and NMR chemical shifts. It appears that the electron-donating groups (-OH, -OCH₃) activate the benzene ring for the simultaneous *ortho* sulphonation and protonation of the free base porphyrins while the presence of electron withdrawing group (-SO₃⁻ responds to mere protonation. In comparison to -OH and -OCH₃ groups, the powerful electron-donating groups like -N(CH₃)₂ and -NH₂ increase apparent basicity towards protons than the central nitrogen atoms. Sulphuric acid has been used for protonation/sulphonation in porphyrin chemistry for quite sometime [4,7,8]. This work illustrates that due to the presence of electron-donating groups, simultaneous sulphonation and protonation can be accomplished and structural studies made.

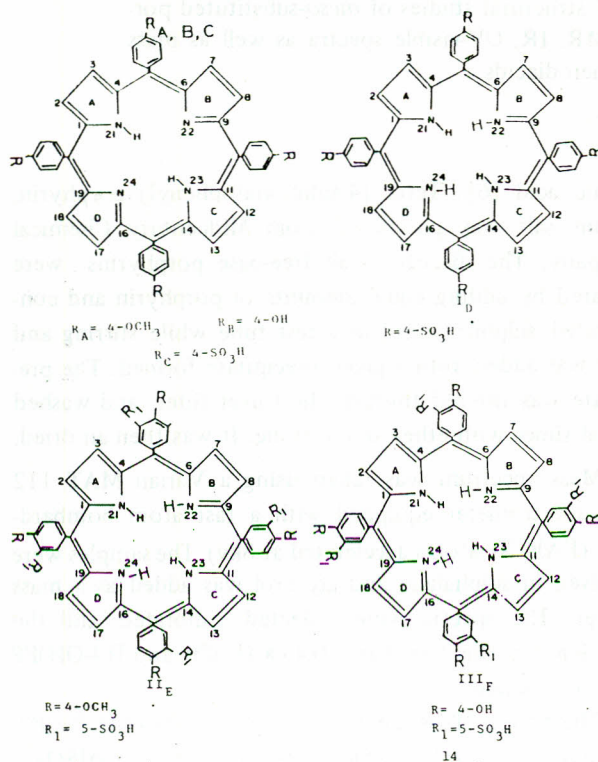


Fig. 1

Table 3 clearly shows that N-H chemical shifts in the tetra (4-hydroxy-5-sulphonatophenyl) porphyrin dication (I) more downfield (-56ppm) as opposed to the free base tetra (4-hydroxyphenyl) porphyrin (-2.89). Similar changes are found for the tetra (4-methoxy-5-sulphonatophenyl) porphyrin dication (II, -.47) when compared with its free base tetra (4-methoxyphenyl) porphyrin (-2.75). Similar but very large changes in chemical shifts are observed for the tetra (4-sulphonatophenyl) porphyrin dication III (+1.15) and tetra (4-sulphonatophenyl) porphyrin sodium salt (-2.92). β -pyrrole resonances for dications I

and II move upfield. β -pyrrole shifts were not significantly changed for dication III. A marked downfield shift was observed for the protons *ortho* (adjacent) to the sulphonate groups. It is also of interest to note that in dication II no splitting was observed between *meta* and *ortho* protons as compared to free base porphyrins and dications I and III. In dication I, a broad doublet was observed due to *ortho* protons adjacent to the sulphonate groups. This is possible due to the coupling which arises from β -pyrrole proton and sulphonate groups with increased planarity of the porphyrin ring system (*vide infra*).

The downfield trend in the N-H chemical shifts for the dications I, II and III, can be seen in the light of ring current theory [9], to be indicative of lesser shielding of the central nitrogen protons. This decrease of N-H chemical shifts is presumably due to the deformation of the porphyrin ring system introduced by the protons to the central nitrogens.

Table 2 shows visible spectral changes for the dications I – III. A Bathochromic Shift (red shift) is observed from dication III (644.75 nm) to dication I (673 nm). Fleischer [3] has observed that the increased red shifts indicate increased planarity (hence increased conjugation) of the porphyrin ring system. This means that between

Table 1.

Dication	Analysis (%)							
	Calcd.				Found			
	C	H	N	S	C	H	N	S
I _a	44.82	4.24	4.75	10.86	45.47	4.31	4.60	10.23
II _b	45.35	4.88	4.41	10.08	45.04	4.79	4.35	9.94
III _c	48.18	4.38	5.11	11.68	49.30	4.30	4.97	11.41

Molecular Formula: (a). C₄₄H₃₂N₄O₁₆S₄(OH)₂ · 8H₂O; (b) C₄₈H₄₀N₄O₁₆S₄(OH)₂ · 10H₂O; (c). C₄₄H₃₂N₄S₄O₁₂(OH)₂ · 7H₂O.

Table 2. Ultraviolet and visible absorption spectra of dications.

Dication	H ₂ O		Soret
	λ max nm	(log(ϵ))	
I	673.08(2.09)	Broad shoulder	444.75 (1.48)
		600-620	
II	670.58(1.99)	Broad shoulder	444.75 (1.77)
		600-620	
III	644.75(1.37)		434.75 (2.22)
	594.75(0.33)		
	552.25(0.11)		

Table 3. Proton chemical shifts(ppm) for free bases and dications.

Compound	N-H	CH ₃	<i>m</i> -H	<i>o</i> -H	β-H	<i>o</i> -H
A	-2.75 (s)	4.10 (s)	7.30-7.28 (d) J _R =8.68 Hz	8.11-8.14 (d) J _R =8.66 Hz	8.86 (s)	—
B	-2.89 (s)	—	7.29-7.32 (d) J _R =8.68 Hz	8.06-8.09 (d) J _R =8.66	8.93 (s)	—
C	-2.92 (s)	—	8.03-8.07 (d) J _R =7.81 Hz	8.17-8.21 (d) J _R =7.81 Hz	8.85 (s)	—
D	1.15 (s)	—	8.22 (s)	8.43 (s)	8.83 (s)	—
E	-0.47 (s)	4.15 (s)	7.76-7.78 (d) J _R =8.5 Hz	8.60-8.63 (m)	—	9.07 (s) Broad
F	-0.56 (s)	—	7.54-7.57 (d) J _R =8.30 Hz	8.59-8.64 (m)	—	8.84-8.90 (bd)

A= H₂-T(4-OCH₃)PP; B= H₂-T(4-OH)PP; C=H₂-T(4-SO₃Na)PP;
D= H₄-T(4-SO₃H)PP; E= H₄-T(4-OCH₃-5-SO₃H)PP;
F= H₄-T(4-OH-5-SO₃H)PP.

the three dications, dication I is probably the most planar (i.e., it has more ring conjugation), while dication III is the least planar due to lesser conjugation in the ring system. Similar changes were observed with the other *meso* substituted phenyl/pyridyl porphyrins [10]. Both the N-H chemical shifts and the visible spectra provide the same conclusion. Dication III is the most deformed, (N-H chemical shifts downfield) least planar (least red shift in the visible spectra) while dication I is least deformed (least N-H downfield shifts) and most planar (highest red shift in the visible spectra).

Marked differences among IR spectra of the free bases and dications have been found in the KBr region. Characteristically intense bands at 1465, 1470, and 1475 were observed in porphyrin dications I, II and III respectively

[3]. The corresponding bands in the free bases were shifted by 10 cm⁻¹ and were much less intense.

Sulphonation and protonation are in agreement with the well-established fact that sulphuric acid is a sulphonating and protonating agent. We believe this synthesis to be interesting in porphyrin chemistry because it accomplishes the sulphonation and protonation in only one step, starting from free bases tetra (4-hydroxyphenyl) and tetra (4-methoxyphenyl) porphyrins.

Because of the fact that porphyrins are highly conjugated and have great affinity for metal ions, a number of water-soluble porphyrins have been synthesized and have found use in the analytical determination of small quantities of metal ions in aqueous systems [11].

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