

Asymmetrical Porphyrins. I. Synthesis, Characterization and Physicochemical Properties of Phenyl/4-Benzyloxyphenyl 5,10,15,20-Substituted Porphyrins

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A complete series of five phenyl/4-benzyloxyphenyl 5,10,15,20-substituted porphyrin has been synthesized, characterized by analysis, R_f values, and proton-nmr spectroscopy (pmr). Their physicochemical properties, namely ir spectra, absorption spectra, emission spectra, excited state life-times, pK_3 values, reduction potentials, and kinetics of $Cu(+2)$ insertion, have been determined. Attempts have been made to correlate these physicochemical properties with the structures of the porphyrins.

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Introduction.

In recent years a number of reports of the synthesis and characterization of unsymmetrical porphyrins have appeared [1]. Unlike symmetrical tetraphenylporphyrins, unsymmetrical tetraphenylporphyrins provide selectivity in number and positions of functional groups. This type of porphyrins have been used to synthesize covalently linked porphyrin dimers and trimers and their metal complexes [2]. Besides studying the various physicochemical properties [1,3], these porphyrins are also being tested for solar energy conversion [1f]. In this report we would like to present the synthesis and characterization and several physicochemical properties of a new and complete set of the phenyl/4-benzyloxyphenyl 5,10,15,20-substituted porphyrins.

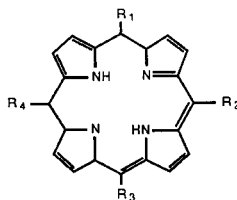
Results and Discussion.

The structure of six porphyrins isolated from the reaction mixture are:

In Table I are listed the R_f values and elemental analysis of porphyrins **A** to **F**.

Table I
Analytical Data

Porphyrins	R_f Values	% C	% H	% N	% C	% H	% N
A	0.90	—	—	—	—	—	—
B	0.70	85.00 (for $C_{51}H_{36}N_4O$)	5.00	7.78	84.86	4.98	7.72
C	0.56	84.26 (for $C_{58}H_{42}N_4O_2$)	5.08	6.78	84.39	5.06	6.67
D	0.35	84.26 (for $C_{58}H_{42}N_4O_2$)	5.08	6.78	84.44	5.11	6.80
E	0.18	83.70 (for $C_{65}H_{48}N_4O_3$)	5.15	6.01	83.57	5.17	5.96
F	0.12	83.24 (for $C_{72}H_{54}N_4O_4$)	5.20	5.39	83.26	5.22	5.35



A	$R_1 = R_2 = R_3 = R_4 =$		(Tetraphenyl porphyrin (TPP))		
B	$R_1 =$		$R_2, R_3 = R_4 =$		(5-(4-Benzyloxyphenyl)-10,15,20-tri(phenyl)porphyrin)
C	$R_1 = R_3 =$		$R_2 = R_4 =$		(5,15-Di(4-benzyloxyphenyl)-10,20-di(phenyl)porphyrin)
D	$R_1 = R_2 =$		$R_3 = R_4 =$		(5,10-Di(4-benzyloxyphenyl)-15,20-di(phenyl)porphyrin)
E	$R_1 = R_2 = R_3 =$		$R_4 =$		(5,10,15-Tri(4-benzyloxyphenyl)-20-phenylporphyrin)
F	$R_1 = R_2 = R_3 = R_4 =$				(5,10,15,20-Tetra(4-benzyloxy)-phenylporphyrin)

Tables II and III contain the uv-visible and the ir absorption bands of the porphyrins respectively. The corrected emission spectral bands, their relative intensities as well as the life-time of the excited states are presented in Table IV. In each table the data for tetraphenylporphyrin, **A**, are included for comparison.

Table II

UV-Visible Absorption Spectral Maxima in DMF Solution

Porphyrins	λ max (nm) ($\epsilon \times 10^{-3}$)					
A	415 (485)	513 (20.82)	547 (9.67)	588 (6.69)	645 (6.05)	
B	421 (634)	516 (21.38)	551 (10.69)	594 (5.88)	650 (4.63)	
C	422 (426)	515 (18.92)	552 (11.87)	593 (6.68)	650 (6.30)	
D	422 (388)	519 (16.80)	555 (11.59)	596 (5.79)	652 (6.88)	
E	421 (523)	518 (17.66)	555 (13.76)	594 (5.51)	652 (6.88)	
F	421 (431)	516 (17.50)	553 (13.48)	593 (5.67)	650 (8.16)	

Table III

Infrared Absorption Bands in Potassium Bromide Matrix

Porphyrins	(Cm^{-1})
A	3310 w, 3050 w, 1590 m, 1500 m, 1470 s, 1445 m, 1350 m, 970 s, 805 s, 705 s
B	3310 w, 3020 w, 1600 s, 1590 m, 1500 m, 1470 s, 1445 m, 1245 s, 1180 s, 970 s, 805 s, 737 s, 705 s
C	3310 w, 3025 w, 1600 m, 1500 m, 1470 w, 1450 w, 1245 s, 1180 s, 970 s, 810 s, 740 s, 705 m
D	3310 w, 3025 w, 1600 m, 1500 m, 1470 m, 1450 w, 1290 m, 1245 s, 1180 s, 970 s, 810 s, 735 s, 705 m
E	3320 w, 3025 w, 1600 s, 1500 s, 1470 m, 1450 w, 1290 m, 1240 s, 1180 s, 970 s, 810 s, 745 s, 705 s
F	3310 w, 3025 w, 1600 s, 1500 s, 1470 m, 1245 s, 1180 s, 970 s, 810 s

s, m, and w indicate relatively strong, medium and weak bands respectively.

Table IV

Corrected Fluorescence Emission Spectra, 1×10^{-6} M in DMF, $\lambda_{\text{ex}} = 420$ nm and the Life Time of their Excited State

Porphyrins	λ em, max, nm, (Relative Intensity)	Life Time of Excited State [a]
A	655 (100) 720 (80)	10.43 ($\pm .16$)
B	656 (100) 723 (74)	10.28 ($\pm .17$)
C	659 (100) 723 (66)	10.17 ($\pm .15$)
D	663 (100) 727 (60)	9.77 ($\pm .10$)
E	661 (100) 726 (59)	9.73 ($\pm .10$)
F	663 (100) 727 (52)	9.43 ($\pm .23$)

[a] 1×10^{-6} M in DMF solutions were used, $\lambda_{\text{ex}} = 420$ nm, $\lambda_{\text{em}} = 650$ nm, frequency = 6 M Hz, average of ten measurements reported.

The pmr spectra between 7 and 9 ppm of the six porphyrins **A-F** are presented in Figure I. The protons are labeled in each compound. The pmr spectrum of tetraphenyl porphyrin, **A**, is identical to that in the literature [5]. The exact chemical shifts in ppm of the protons in ppm for the other porphyrins, together with the important coupling constants, are provided below. For porphyrin **B**: 8.89, 8.87, 8.85 (2H_a , 2H_b , 2H_c and 2H_d), 8.23-8.20 (several peaks, 2H_e , 4H_f), 8.14, 8.10 (doublet, 2H_g , $J = 8.50$ Hz), 7.77-7.73 (a complex of peaks, 4H_d , 2H_e , 2H_d , H_c), 7.63, 7.60 (doublet, 2H_j), 7.52-7.38 (multiplet, 2H_g , 1H_i), 7.36, 7.32 (doublet, 2H_d , $J = 8.56$ Hz), 5.32 (singlet, 2 methylene protons) and -2.75 (singlet, 2 N-H). For porphyrin **C**: 8.67, 8.86 (doublet, 4H_a , $J = 2.9$ Hz), 8.83, 8.82 (doublet, 4H_b , $J = 2.9$ Hz), 8.22-8.18 (several peaks, 4H_c), 8.13, 8.10 (doublet, 4H_e , $J = 8.44$ Hz), 7.77-7.70 (multiplet, 4H_d , 2H_j), 7.64, 7.61 (doublet, 4H_i), 7.64-7.41 (multiplet, 2H_g and 2H_h), 7.36, 7.33 (doublet, 4H_d , $J = 8.60$ Hz), 5.34 (singlet, 4 methylene protons) and -2.77 (singlet, 2N-H). For porphyrin **D**: 8.84, 8.82 (2H_a , 2H_b , 2H_c and 2H_d), 8.63, 8.62, (4H_d), 8.43-8.40 (multiplet, 4H_j), 8.31-8.19 (multiplet, 4H_e , 2H_f , 4H_g), 7.99-7.93 (multiplet, 4H_h , 2H_i), 7.76, 7.75 (4H_e), 5.34 (singlet, 4 methylene protons), and -2.67 (singlet, 2 N-H). For porphyrin **E**: 8.87, 8.86, 8.83, 8.81 (2H_a , 2H_b , 2H_c , 2H_d), 8.23-8.19 (split doublet, 2H_e), 8.14, 8.11 (doublet, 4H_e , 2H_c , $J = 8.4$ Hz), 7.78-7.74 (multiplet, 2H_d , 1H_f), 7.65, 7.62 (4H_e , 2H_c), 7.51-7.38 (multiplet, 6H_f , 3H_g), 7.38, 7.34 (doublet, 4H_d , 2H_j , $J = 8.4$ Hz), 5.35 (singlet, 6 methylene protons), and -2.75 (singlet, 2N-H). For porphyrin **F**: 8.67 (singlet, 8H_a), 8.14, 8.11 (doublet, 8H_b , $J = 8.6$ Hz), 7.67-7.62 (multiplet, 8H_j), 7.51-7.41 (multiplet, 8H_e , 4H_i), 7.38, 7.35 (doublet, 8H_c , $J = 8.6$ Hz), 5.37 (singlet, 8 methylene protons) and -2.75 (singlet 2 N-H).

The R_f values (see Table I) of the porphyrins indicate that addition of benzyloxy groups to TPP makes it increasingly polar. As expected, the symmetrical porphyrin **C** is less polar than its unsymmetrical isomer, **D**. Since various solvents, *viz*, methanol and tetrahydrofuran, were used to make analytical samples in open atmosphere, these solvents and water were needed to balance elemental analysis. These solvents could not be removed even after drying overnight at 100° over phosphorus pentoxide under high vacuum.

All the absorption bands of each of the benzyloxy porphyrins in DMF (see Table II) show slight hyperchromic shift compared to those of TPP. However, this shift as well as the intensities of the bands cannot be correlated to the structures. The infrared spectra of **B** through **F** are very similar (see Table III), and they have two very strong bands at 1245 and 1180 cm^{-1} due to asymmetrical and symmetrical C-O-C stretching, respectively. These bands are absent in TPP. Both the fluorescence emission spectral bands of the benzyloxy porphyrins, like the uv-visible

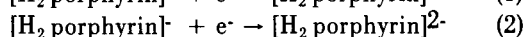
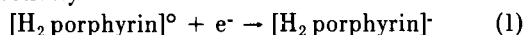
absorption bands, show hyperchromic shift (see Table IV). The ratio of the intensity of the higher wavelength band to the lower wavelength band decreases as the number of benzyloxy groups are increased. The excited life times of these porphyrins also decreases in the same direction. Thus the emission spectral data appear to have interesting correlation with the structure of this series of porphyrins.

The high-resolution pmr spectroscopy (see Figure 1) is the best method for verifying the structural identity of these porphyrins. The spectra of porphyrin **D** and **E** are interesting. Compared to the other porphyrins, the chemical shifts of the pyrrolic- and benzenoid protons fall within the narrowest range for **D**. In **D**, neither the four H_d ,

benzyloxyphenyl groups. Same relationship between the two H_d and four H_d . The H-nmr spectrum, however, shows that the H_c and H_c are magnetically equivalent, so are the H_d and H_d . It should be pointed out that for **E**, the magnetic equivalency is also observed between the protons H_e and H_e , H_f and H_f as well as H_g and H_g .

Figure 1

The reduction potentials $-E_{1/2}(1)$ (volts) and $-E_{1/2}(2)$ (volts) of the porphyrins **A** through **F**, in DMF solution (see Table V) correspond to the electrode reactions 1 and 2 respectively as shown below:



The values for the two reduction potentials, measured by square wave and cyclic voltammetry are close and comparable to literature values for other porphyrins. However, no correlation between the reduction potentials and the structure of the porphyrins is observed. In CV measurements, the separation of anodic and cathodic peaks were between $0.59/n$ to $0.85/n$ and produced somewhat unequal peak currents for the anodic and cathodic processes, indicating that the electrode processes are pseudoreversible under the conditions of experiments.

Kinetics of Cu(+2) insertion (see Table 6) of the porphyrins at three different temperatures have been studied. A clear correlation is observed between the structures of porphyrins **A** through **E** and the rate of Cu(+2) insertion, showing that the rate is maximum as the number of benzyloxy groups are added to the TPP is three. However, the rate falls with **F** containing four benzyloxy groups. We do not have any reasonable explanation for this deviation. However, the pK_3 values of the porphyrins increases as benzyloxy groups are attached to TPP. This means that the benzyloxy group serves as the electron donating group and thus increases the basicity of the porphyrin ring. Studies with other sets of asymmetrical porphyrins are in progress. A new series of asymmetrical porphyrins with phenolic groups have been prepared by facile debenzoylation of **B** through **F** with acid. Through these phenolic groups oligo, as well as polyporphyrins can be easily prepared.

EXPERIMENTAL

To a refluxing mixture of benzaldehyde (12.7 g, 0.12 mole), 4-benzyloxybenzaldehyde (27 g, 0.12 mole) and propionic acid (1.2 lit) was added pyrrole (16.75 g, 0.25 mole) from a dropping funnel. After an half-hour of reflux, the solvent was removed under reduced pressure, the residue neutralized with ammonium hydroxide, filtered and dried under suction. Upon chromatography over silica gel with benzene-hexane mixture, followed by benzene-methylene chloride mixture, all the possible six porphyrins were isolated in mixtures. Final separation of the individual porphyrins was accomplished with thin layer chromatography on silica gel. R_f values of these porphyrins were determined in benzene/hexane (3:1) on Baker-flex Silica Gel 1B sheets. The fastest moving porphyrin was the

Table V

Polarographic Results with Porphyrins in DMF
($1 \times 10^{-4} M$) Containing 0.1 M TBAP at 25°C

Porphyrins	$-E_{1/2}(1)$ [a]	$-E_{1/2}(2)$ [a]	Method
A	1.150	1.565	SWV
	1.093	1.448	CV
B	1.115	1.580	SWV
	1.098	1.545	CV
C	1.155	1.645	SWV
	1.110	1.578	CV
D	1.145	1.650	SWV
	1.107	1.576	CV
E	1.115	1.550	SWV
	1.125	1.524	CV
F	1.145	1.630	SWV
	1.133	1.601	CV

[a] Volts (± 0.005) vs SCE, SWV = square wave voltammetry, CV = cyclic voltammetry.

Table VI

Kinetics of Cu (+2) Insertion in Porphyrins **A** to **F**,
in DMF Solution (min^{-1}) and their pK_3 Values in Nitrobenzene

Porphyrin	Measured at °C			pK_3 (25°) [6]
	23	30	37	
A	0.2229	0.4664	0.9081	3.99
B	0.2663	0.5726	1.0426	4.14
C	0.3814	0.8265	1.3583	4.19
D	0.4963	0.9916	1.8572	4.21
E	0.6518	1.2869	2.3301	4.24
F	0.6001	1.1233	2.0604	4.28

nor the four H_c are magnetically equivalent. Instead of two doublets (with $J = 8.6$), one obtains two distorted triplets, indicating long range coupling between these protons. For porphyrin **E**, one would expect that the two H_c in the middle benzyloxyphenyl group would be magnetically nonequivalent from the four H_c in the two outside

tetraphenylporphyrin and the slowest, the tetra (4-benzyloxy) phenylporphyrin with R_f values 0.90 and 0.12 respectively (see Table I).

The uv-visible, pmr and emission spectra were measured with SLM-AMINCO DW2RC, Bruker Spectrospin 250 M Hz and SLM 4800S instruments respectively. The copper(II) incorporation kinetics were measured following literature procedure [3]. The infrared absorption spectra in potassium bromide matrix were measured with a Perkin-Elmer Model 467 spectrophotometer. The uv-visible and emission spectra have been measured in DMF and the pmr spectra in deuteriochloroform with TMS as indicator. Cyclic voltammetry (CV) was performed with an EG&G Model 264A Polarographic Analyzer/stripping voltammeter, an RE 0089 X-Y Recorder and a Model 303A SMDE. Square wave voltammograms (SWV) were measured with an EG&G PARC Model 173 Potentiostat/Galvanostat attached to a Model 276 Interface and a Model 178 Electrometer connected to an ACC. 178/41 Noise Filter. For SWV, an Apple IIe computer with a monitor and an EPSON printer as well as a software, Model 276 Interface Demonstration Program, Volume II, were used. The Model 276 Interface allowed the potentiostat/galvanostat to be controlled by the Apple IIe computer which incorporates an IEEE-488 Interface. DMF was used as a solvent for the CV and SWV and it was purified following the literature method [4]. A 10^{-4} M porphyrin solution in DMF containing 0.1 M tetrabutyl ammoniumperchlorate (TBAP) was used for all studies and an aqueous saturated calomel electrode (SCE) was used as a reference electrode. The SCE was placed in a bridge tube with vycor tip and was filled with 0.1 M TBAP in DMF. The tip of the bridge tube was placed in the porphyrin solution. Deaeration of the porphyrin solution was achieved by bubbling oxygen free argon saturated with DMF. For SWV, the working electrode was a planar impervious glassy carbon electrode, 7 mm² surface area (EG&G PARC Part #G0197).

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