The Synthesis and Some Physical Properties of *ms*-Tetra(pentafluorophenyl)-porphin and *ms*-Tetra(pentachlorophenyl)porphin. (1)

Frederick R. Longo, Margaret Griffith Finarelli (2), and Jean B. Kim.

Chemistry Department, Drexel Institute of Technology

The synthetic *meso*-substituted porphyrins have long been used in porphyrin investigations due to the relative ease of their synthesis and purification. The compound, *ms*-tetraphenylporphin, (TPP), was synthesized by Rothemund through the direct condensation of pyrrole and benzaldehyde (3). As a result of recent mechanistic investigations of this reaction, it is now possible to produce large amounts of relatively pure TPP and other *ms*-substituted porphyrins by acid catalyzed condensation (4,5,6). A report on the application of this method for the synthesis of four porphyrins, two of which are new and have unusual spectra, is presented here. We have also prepared some metallo derivatives of these materials.

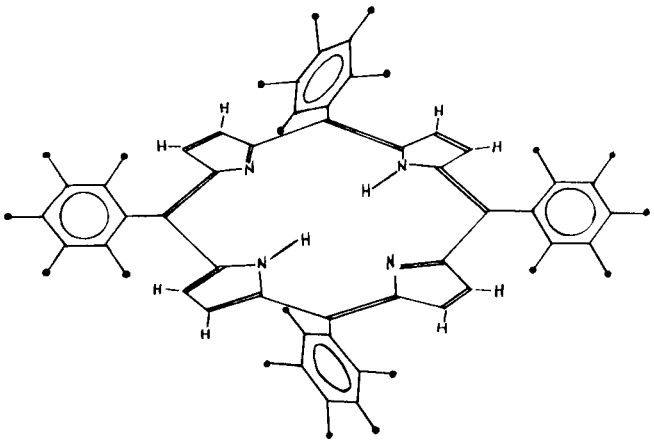

Figure 1. A model of TClPP using bond lengths determined by Fleischer *et al.* (21).

EXPERIMENTAL

Synthesis of Tetra(pentachlorophenyl)porphin, (TClPP). See Figure 1.

TClPP was synthesized by the following route:

$$C_6H_5CH_3 \rightarrow C_6Cl_5CH_3, I \rightarrow C_6Cl_5CHCl_2,$$

$$II \rightarrow C_6Cl_5CHO, III \xrightarrow{\text{pyrrole}} TClPP$$

All intermediates were previously reported. Compound I was prepared from toluene by the method of Silberrad (7a,b). White needles were obtained, m.p. 217-218° (reported 217.5°), 51.5% yield, NMR 2.60 ppm in carbon tetrachloride using the Varian A60D and TMS as an internal reference. Compound II was prepared from I by the method of Lock (8). The tan-colored crystalline product melted at 118-119° (reported 119.5°), 89% yield, NMR 7.65 ppm in carbon disulfide. Compound III was prepared from II by the method of Ross, *et al.* (9). The pale yellow crystalline product melted at 197-199° (reported 196°), yield 66%, NMR 9.65 ppm in deuteriobenzene.

TClPP was synthesized by the acid-catalyzed condensation of III and pyrrole. 6.95 g. (0.025 mole) of III was added to a solution of 5 g. of monochloracetic acid in 125 ml. of benzene. The solution was brought to reflux and a solution of 1.77 ml. (0.025 mole) of pyrrole in 15 ml. of benzene was added dropwise over a three-hour period. The reaction solution was refluxed for an additional

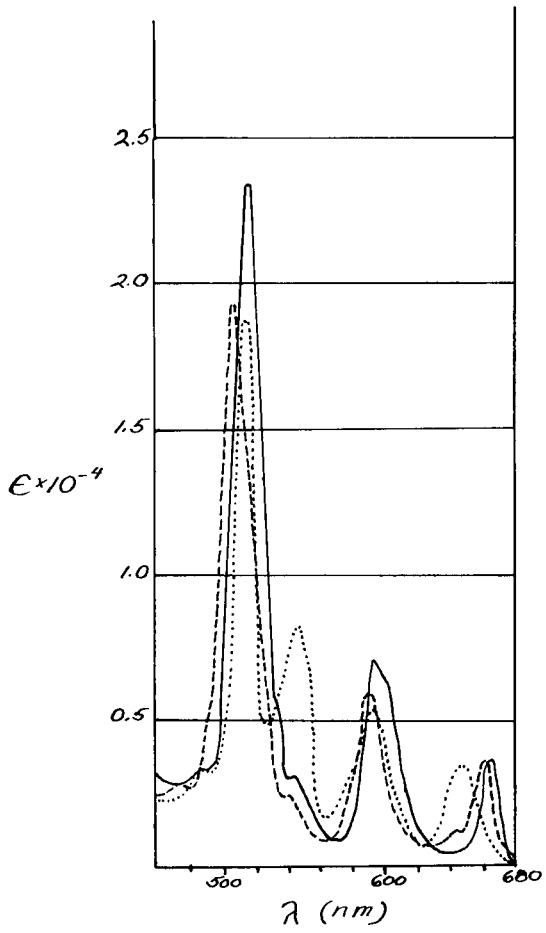

Figure 2. ϵ vs λ for benzene solutions of TClPP (solid line); TFPP (dashed line); and TPP (dotted line).

TABLE I

Electronic Absorption Bands and Extinction Coefficients for the Free Base Porphyrins

Compound	Solvent	Soret	IV	III	II	I
TClPP	Benzene	422 nm ϵ=3.70x10^5	515 nm ϵ=2.35x10^4	---	591 nm 7.02x10^3	663 nm 3.65x10^3
TFPP	Benzene	417 nm ϵ=2.35x10^5	508 nm ϵ=1.91x10^4	---	586 nm 5.81x10^3	659 nm 3.46x10^3
TFPP	DMF	410 nm ϵ=2.6x10^5	504 nm ϵ=1.6x10^4	---	579 nm ϵ=5.1x10^3	654 nm 3.7x10^3
TPyrP	$CHCl_3$	418 ϵ=4.31x10^5	514 ϵ=1.89x10^4	549 ϵ=5.61x10^3	588 ϵ=5.45x10^3	646 ϵ=2.3x10^3
TPyrP (a)	$CHCl_3$	417 ϵ=4.25x10^5	513 ϵ=1.96x10^4	547 ϵ=5.4x10^3	588 ϵ=5.9x10^3	643 ϵ=1.7x10^3
T(CO_2H)PP	Methanol	Not taken ---	510 ϵ=1.63x10^4	543 ϵ=7.22x10^3	585 ϵ=4.73x10^3	641 ϵ=3.6x10^3
T(CO_2H)PP	Pyridine	423 ϵ=1.78x10^5	517 ϵ=1.43x10^4	552 ϵ=7.12x10^3	591 ϵ=4.44x10^3	646 ϵ=3.01x10^3
$\bar{T}$(CO_2H)PP (b)	Pyridine	422 ϵ=1.61x10^5	517 ϵ=1.44x10^4	552 ϵ=7.0x10^3	591 4.3x10^3	649 2.9x10^3
TPP (c)	Benzene	419 nm ϵ=4.7x10^5	514 nm ϵ=1.87x10^4	549 nm ϵ=7.7x10^3	591 nm ϵ=5.4x10^3	647 nm ϵ=3.4x10^3

(a) Ref. 12, (b) Ref. 13, (c) Ref. 18.

TABLE II

Electronic Absorption Bands and Extinction Coefficients for the Metalloporphyrins

Compound	Solvent	Soret			
CuTFPP	DMF	412 nm ϵ=2.2x10^5	503 nm ϵ=4.1x10^3	538 nm ϵ=1.3x10^4	572 nm ϵ=4.6x10^3
CuTClPP	Benzene	419 nm ϵ=2.3x10^5	500 nm slight shoulder	543 nm ϵ=1.0x10^4	577 nm ϵ=3.5x10^3
ZnT(CO_2H)PP	MeOH	429 nm ϵ=3.5x10^5	517 nm ϵ2.9x10^3	556 nm ϵ=1.4x10^4	596 nm ϵ=5.6x10^3
MgTPyrP	$CHCl_3$:MeOH(10:1)	423 nm ϵ=3.8x10^5	515 nm ϵ=4.0x10^3	560 nm ϵ=1.8x10^4	610 nm ϵ=5.2x10^3

30 minutes whereupon the spectrophotometric yield was ~ 7%. The cooled solution was shaken with saturated aqueous sodium bicarbonate, washed with water until neutral, and dried over calcium chloride. Chromatography on neutral alumina (eluting with benzene) yielded seven clearly distinguishable bands. Of these, the first, a green band with slight Soret excited red fluorescence both on and off the column, was the porphyrin with the characteristic Soret absorption peak at 422 nm. The second band, green with yellow fluorescence on the column and red fluorescence off the column, was identified as the acid porphyrin (Soret peak at ~ 440 nm) since stirring the solution over sodium hydroxide pellets converted the spectrum to that of the free base porphyrin. The fifth band, black with yellow fluorescence, exhibited a chlorin-type spectrum and had its Soret peak at about 430 nm. Upon concentration of the first fraction we obtained purple crystals of TClPP. The molecular weight of the product was confirmed by mass spectrometry on the Picker MS-9 Spectrometer at vaporizing temperature of 300° and an ionizing energy of 60 eV. The spectrogram showed a major parent peak at m/e = 1302 in addition to P+1, P+2, P+3, P-1, P-2. We also found groups of peaks corresponding to P – (–C_6Cl_5) and the P – 2(–C_6Cl_5)(10). NMR measurements showed a single peak at 8.66 ppm in deuteriochloroform-trifluoracetic acid using the Jeolco-100 NMR (11).

Anal. Calcd. for $C_{44}H_{10}Cl_{20}N_4$: Cl, 54.33. Found: Cl, 54.28.

The attempted synthesis of TClPP in glacial acetic acid and in propionic acid was successful with a spectrophotometric yield of ~ 11% but contamination was high and we were not successful in purification when these solvents were used.

Synthesis of Tetra(pentafluorophenyl)porphin, TFPP.

TFPP was prepared by refluxing a propionic acid solution, 0.2

TABLE III

Infrared Spectra of Tetra(pentachlorophenyl)porphin and Tetra(pentafluorophenyl)porphin

Band Frequencies (cm^{-1}) and Intensities (a)		
TClPP	TFPP	Assignments (13,16,17,18)
3320 (vw)	3320 (vw)	N–H · · · (stretch)
	3100 (w)	
	2925 (m)	C–H (stretch)
	2855 (m)	
2720 (vw)	2720 (vw)	
	2630 (vw)	
	2540 (vw)	
	1645 (w)	
1595 (w)	1588 (w)	–C=C–skeletal (phenyl)
1555 (w)	1565 (m)	–C=C–skeletal (pyrrole)
1535 (w)	1530 (wsh)	
	1515 (ssh)	
1505 (w)	1512 (s)	–C=C–skeletal (phenyl)
	1495 (s)	–C=C–skeletal (pyrrole)
1465 (m)	1485 (ssh)	–C=N– (stretch)
	1455 (wsh)	
1435 (m)	1435 (m)	C–H (bend)
1395 (w)	1400 (m)	–C=C–skeletal (pyrrole)
	1375 (w)	
	1362 (w)	
1360 (m)	1350 (m)	=C–N– (stretch)
1340 (s)	1340 (m)	
1320 (m)	1320 (w)	
1305 (m)	1305 (vw)	
1270 (m)	1262 (vw)	
1250 (w)	1245 (w)	CH in plane deformation
	1205 (vw)	
1195 (w)	1185 (wsh)	
	1165 (w)	
1150 (w)	1145 (w)	substituted phenyl
1075 (w)	1078 (m)	–C–H in plane deformation or
	1062 (m)	C–F stretch
1050 (vw)	1045 (m)	–C–H in plane deformation
	1040 (ssh)	
1035 (w)	1025 (m)	
975 (m)	985 (s)	N–H deformation
915 (msh)	925 (s)	
910 (m)	918 (s)	–C–H (rock)
	915 (msh)	
	898 (vw)	
828 (m)	828 (w)	–C–H out of plane deformation
810 (m)		
790 (s)	805 (s)	
	785 (w)	
775 (w)	770 (m)	–C–H out of plane deformation
	755 (s)	
730 (w)	725 (s)	
710 (m)	710 (m)	
685 (s)	695 (w)	
635 (w)	630 (vw)	

(a) Infrared band intensities: vw, very weak; w, weak; m, medium; s, strong; sh, shoulder.

molar in both pentafluorobenzaldehyde and pyrrole, for 2 hours. The spectrophotometric yield was ~ 18%. The yield of crude TFPP as obtained by filtration of the cooled reaction mixture was ~ 11%. It was purified in the same manner as was the TClPP. NMR in deuteriochloroform-trifluoracetic acid gave a peak at 9.20 ppm using the Jeolco 100. Using the Hitachi-Perkin Elmer RMU-6 Mass Spectrometer at a vaporizing temperature of 290° and an ionizing voltage of 60 eV we obtained a mass spectrogram that was similar to that of TClPP. The main parent peak was at m/e = 974. Other easily identifiable groupings corresponded to P–(–C_6F_5) and P–2(–C_6F_5).

Anal. Calcd. for $C_{44}H_{10}F_{20}N_4$: F, 38.98. Found: F, 39.03.

Synthesis of *ms*-Tetrapyridylporphin, TPyrP.

TPyrP was previously prepared by Fleischer (12) using the Rothemund conditions. It was found that TPyrP forms in 23.4% yield when a propionic acid solution, 0.24 molar in both pyridine-4-carboxaldehyde and pyrrole was refluxed for 45 minutes. The solvent was flashed off, the residue was washed with DMF which dissolves the tarry by-products and leaves purple crystals. The mass spectrogram (Hitachi Perkin-Elmer RMU-6) gives a parent peak m/e = 618 plus P–(C_5NH_4) and P–2(C_5NH_4). The visible absorption spectrum is in fairly good agreement with that observed by Fleischer (12). See Table I.

Synthesis of *ms*-Tetra(*p*-carboxyphenyl)porphin, T(CO_2H)PP.

T(CO_2H)PP was previously prepared by Datta-Gupta and Bardos (13) by hydrolysis of the corresponding ethyl ester. This compound was prepared directly by refluxing a propionic acid solution, 0.24 molar in both 4-carboxybenzaldehyde and pyrrole, for 2 hours. When the reaction mixture was cooled T(CO_2H)PP precipitated as purple crystals. The yield was 34.5%. The product was relatively pure (95% +); it was further purified by recrystallization from methanol-chloroform solutions. The mass spectrogram (Hitachi PE RMU-6) showed the parent peak (m/e = 791) plus P–(–CO_2H), P–2(–CO_2H), P–(–$C_6H_4CO_2H$), P–2(–$C_6H_4CO_2H$). The visible spectrum agreed well with that reported by Datta-Gupta and Bardos (13). See Table I.

Synthesis of Metalloderivatives.

To a refluxing dimethylformamide solution of TFPP or TClPP (~ 1 x 10^{-4}M) was added a slight excess (10%) of cupric chloride. The reaction was continued until the red fluorescence characteristic of free base porphyrin had ceased (~ 30 minutes). Removal of the solvent left a red crystalline product; the conversion was ~ 100%. The excess cupric chloride was removed by water washing and the product was chromatographed in benzene solutions on neutral alumina.

MgTPyrP and ZnT(CO_2H)PP were prepared in a similar manner. The yields were 23% and 78% respectively. The compounds were purified by chromatographing chloroform solutions on alumina. Mass spectrometric analysis gave the expected parent peak m/e-value for both compounds (14). The four metalloporphyrins reported here are new derivatives. Further details of a general method of metalloporphyrin synthesis using DMF as a solvent have been reported elsewhere (15).

Spectral Properties.

Visible spectra for all porphyrins were taken on the Cary 14 Recording Spectrophotometer. Positions of maximum absorption and the corresponding extinction coefficients are presented in Table I and II. Because the electronic spectra of TFPP and TClPP are rather unusual, plots of ϵ vs λ for these compounds and TPP are shown in Figure 2.

The IR spectra of TFPP and TClPP were taken on the Perkin Elmer 621 Infrared Spectrophotometer. In view of the unusual visible spectra of these compounds we have presented the IR absorption peak positions, relative intensities, and our assignments in Table III.

DISCUSSION

The acid condensation of pyrrole with 4-carboxybenzaldehyde produces a yield of 34% of the corresponding porphyrin. This is the highest yield reported for this kind of synthesis. The yield of *ms*-tetrapyridylporphin was also very good (23.4%).

The most interesting aspect of this study centers around the electronic spectra of TFPP and TClPP. In Figure 2 are plotted ϵ vs λ (nm) for TFPP, TClPP, and TPP (19). The extinction coefficients at the Soret peak differ considerably from TPP but the most remarkable difference is the absence in TFPP and TClPP spectra of peak III at about 550 nm. All tetraphenylporphyrins which have thus far been reported possess an etio spectrum with an absorption peak near 550 nm; the extinction coefficient in this region is always 5000-7000 (20). We must conclude that the electronic structure of these new compounds is very different from TPP.

A clue to the nature of this difference may be present in the IR data. The pyrrole C–H rock energies are appreciably lower in TFPP and in TClPP than in TPP. This may indicate a bond weakening due to halogen interaction with the beta-hydrogen of the pyrrole which could result in bringing the completely halogenated phenyl group nearer to coplanarity with porphyrin nucleus (21).

Unfortunately, the NMR data are not completely consistent with this interpretation. The pyrrole beta-H exhibit sharp singlet peaks on the low field side of benzene as was expected. The TClPP peak was at 8.66 ppm and TFPP: 9.20 ppm; (porphin: 9.92 ppm and TPP: 8.85 ppm (22)). The upfield shift of the beta-H peak in TPP as compared to porphin is attributed to a decrease of ring current. This has been explained by the buckling of the porphyrin nucleus due to *ms*-phenyl substituents (19). The order of ring current strength in the tetraphenyl porphyrins appears to be TFPP> TPP> TClPP. The probable interaction between the beta-H and halogen, resulting in increased coplanarity of TFPP as compared to TPP, could explain these observations. In the case of the larger chlorinated phenyl groups, steric factors are probably paramount and no amount of electrostatic interaction could overcome the effect of the bulk on the buckling of the porphyrin ring. Further speculation regarding these compounds is not warranted at this time. We are preparing a series of *ms*-tetra(monoortho- and diortho-phenyl)porphins in an attempt to find the cause for the anomolous behavior of the porphyrins reported in this note.

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