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PROGRESS ON THE SYNTHESIS OF MESO-SUBSTITUTED METALLOTETRABENZPORPHYRINS

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BY

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AND
D.E. REMY

NOVEMBER 1986

FINAL REPORT
OCTOB~~ER~~ 1986 - JANU~~A~~RY 1987

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A number of meso-substituted zinc tetrabenzporphyrins were prepared by the reaction of isoindole, zinc acetate, and an aromatic aldehyde. The reaction products were purified and identified by thin-lay chromatography (TLC) and high performance liquid chromatography (HPLC). Additional characterization by NMR and UV/VIS spectroscopy contributed to the establishment of structures for the new compounds. The presence of multiple products was observed with HPLC and the possibility of incomplete meso-substitution as a factor for this observation is discussed.

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PREFACE

The work described in this report was authorized under work unit number 1L161102AH5201019 entitled Energy Absorption and Dissipation Mechanisms in Organic Materials, and covers the period from October 1985 to January 1986. The report describes the progress that was made on the synthesis of meso- substituted metallo-tetrabenzporphyrins during this time period. The authors wish to acknowledge the assistance of Dr. S. Weininger from Worcester Polytechnical Institute and Drs. F. Bissett, J. Cornell and Ms. G. Richard from the Science and Advanced Technology Directorate, U. S. Army Natick Research, Development and Engineering Center.

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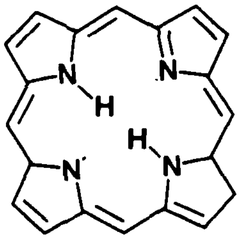
PROGRESS ON THE SYNTHESIS OF MESO-SUBSTITUTED METALLOTETRABENZPORPHYRINS

INTRODUCTION

Porphyrin (1), whose structure is shown below, is an aromatic macrocyclic molecule with four nitrogens. The porphyrins and several closely related classes of compounds, in particular, their metal complexes, are of central importance in biological systems.[1,2] For example, the chlorophylls, cytochromes, and hemes are all biological molecules whose structures are based on the porphyrin system.



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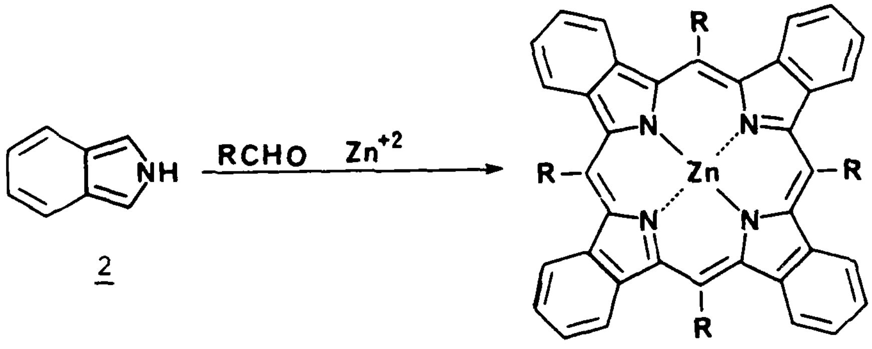
Porphyrins and their analogs are of interest to the military for use as camouflage dyes. The high molar absorptivity of these compounds at wavelengths in the visible spectrum causes them to be intensely colored. The absorption maxima and therefore the color of these compounds can be adjusted by changing the centrally coordinated metal atom or by putting substituents onto the porphyrin ring. Thus, by using the appropriately substituted porphyrin it should be possible to create a dye that is indistinguishable from background vegetation even when using sophisticated spectrophotometric techniques for detection.

Although the porphyrins are one of the most extensively studied classes of substances known, research on the structurally related tetrabenzporphyrins (TBPs) has been slow to progress. In large part this is due to the lack of effective syntheses of tetrabenzporphyrins. Although TBP and some of its metal complexes were prepared in low yield some 45 years ago by Linstead,[3] very little was known about their chemical and physical properties. In 1978, Vogler and Kunkely[4] reported the synthesis of zinc TBP in 17% yield by the reaction of 2-acetylbenzoic acid, zinc acetate and ammonia at 400°C. These syntheses were only useful in preparing the parent TBP.

In 1983, Remy reported that the reaction of isoindole (2), zinc and benzaldehyde at 400°C produces a meso-substituted TBP, zinc 5,10,15,20-tetraphenyltetrabenzporphyrin (3a) (R = phenyl).[5]



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3a: R = Phenyl
3b: R = 1-Naphthyl
3c: R = 9-Anthracenyl
3d: R = p-(N,N-dimethylamino)-phenyl

3e: R = p-Methoxyphenyl
3f: R = p-Cyanophenyl
3g: R = m-Fluorophenyl

The key to this novel synthesis of the TBP structure was the discovery of a facile preparative route that led to (2). Isoindole,[6] although a very simple organic molecule, had defied attempts at synthesis until 1972 when it was prepared independently by Bonnett and Brown,[7] Bornstein, Remy and Shields[8]; and Priestley and Warrener.[9] Isoindole is labile and readily polymerizes, but is sufficiently stable in solution that it can be used immediately after generation to prepare TBP. The synthetic strategy of using isoindole in this procedure is patterned after the Rothemund synthesis[10] of porphyrins in which pyrrole and formaldehyde were heated in the presence of metal salts to give low yields of porphyrin.

The purpose of this segment of the project was to examine the scope of this reaction more completely and to prepare and characterize additional quantities of meso-substituted TBP derivatives from the reaction of isoindole, zinc acetate, and various aromatic aldehydes.

EXPERIMENTAL

General

Reactions were performed under an inert atmosphere of nitrogen, unless otherwise stated. Reagent or HPLC Grade solvents and chemicals were used as received, unless otherwise stated. Infrared (IR) spectra were recorded on a Nicolet 7199 FT-IR or on a Perkin Elmer 735. Nuclear magnetic resonance (NMR) Spectra were recorded on a Varian XL-200 NMR. Ultraviolet (UV)/visible (VIS) spectra were recorded from 350 to 800 nm on a Perkin-Elmer 330 Spectrophotometer. High performance liquid chromatography (HPLC) was performed on a Waters 440 Liquid Chromatograph with a Hewlett-Packard HP1040A Spectrophotometric Detector using an 8-mm i.d. silica gel Radial Pak LC cartridge with 30% tetrahydrofuran (THF) in hexane as solvent.

Analytical thin layer chromatography (TLC) was performed using 250- Whatman Linear K silica gel slides (LK6DF). Preparative TLC was performed using 1000- Whatman Linear K silica gel plates (PLK5F). All glassware was oven-dried for several hours before use.

Preparation of Isoindole.[11]

To a 1000-mL round bottom flask equipped with a magnetic stir bar and a 125-mL pressure-equalizing dropping funnel was added 3.36 g (0.03 mole) of potassium t-butoxide. The solid was dissolved in 75 mL of dry dimethyl sulfoxide (DMSO). To this solution was added a solution of 2-(p-toluenesulfonyl)-dihydroisoindole[12] (m.p.167-172°C) in 75 mL of dry DMSO over a period of 5 minutes. The solution immediately turned purple and after several minutes became dark brown. The reaction mixture was stirred for 60 to 90 minutes at room temperature and then cooled to 0°C in an ice bath. The reaction mixture was hydrolyzed by the addition of 100 mL of cold, degassed, deionized water.

The reaction mixture was transferred to a 1000-mL separatory funnel and extracted with five 100-mL portions of degassed diethyl ether. The ether extracts were combined, washed with two 200-mL portions of cold, degassed, deionized water, and dried over anhydrous potassium carbonate. The resulting orange solution of isoindole was used immediately in the subsequent reaction without further purification.

General Procedure for the Preparation of Meso-substituted Tetrabenzporphyrins.[5]

To a 1000-mL round bottom flask equipped with a vacuum-jacketed air condenser with nitrogen inlet and outlet was added 0.01 mole of zinc acetate dihydrate, 0.01 mole of the appropriate aldehyde and the freshly prepared ether solution of isoindole (0.01 mole). The reaction mixture was rapidly heated by means of an electrical heating mantle so as to drive off the solvent and bring the temperature up to 400°C for 10 to 50 min. After cooling to room temperature, the reaction mixture was taken up in 75 mL of hot pyridine and filtered. Pyridine was removed by spin evaporation in vacuo to give a dark green solid. The crude product was purified by flash chromatography[13] on silica gel with 20-30% tetrahydrofuran (THF) in hexane. The green fractions containing the TBP products were analyzed chromatographically using TLC and HLPC and spectroscopically using UV/VIS, IR, and NMR. Data on individual compounds are given below. Yields were generally 40 to 50% with the exception of (3c) (R = 9-anthracenyl) and (3f) (R = p-cyanophenyl), in which cases the yields were only 16% and 2%, respectively.

In a separate experiment a simplified "one-pot" procedure for synthesizing TBPs was investigated briefly. To a THF solution of 2-(p-toluenesulfonyl)dihydroisoindole was added 1 equiv. of diethylzinc in hexane followed by 1 equiv. of benzaldehyde. The mixture was heated to 400°C for 45 minutes. Analysis of the reaction mixture by TLC and UV/VIS indicated that (3a) was produced, but the yield was low (11% estimated from UV/VIS data).

Zinc Tetraphenyltetrabenzporphyrin (3a)

The green solid isolated from flash chromatography was recrystallized from chloroform/methanol and dried in vacuo at 0.1 mm and 110°C. The latter crops obtained from the recrystallization are purer by HPLC*.

---

*All HPLC runs were conducted with 30% THF/Hexane as eluant solvent unless otherwise noted. When different from this eluant solvent, the solvent used to dissolve the sample and for injection is noted in parenthesis.

TLC: Rf = 0.36 (20% THF in hexane)

HPLC: ET = 2.1 min (sample in THF)
ET = 3.0 min (sample in pyridine)
ET = 2.1, 3.0 min (sample in a mixture of THF and pyridine, two components).

UV/VIS: 658, 615, 473 (Soret band), 447 (sh) nm (pyridine)
653, 608, 462 (Soret), 437 (sh) nm (benzene)
636, 595, 462 (Soret), 446 (sh) nm (chloroform)

^{1}H-NMR ($CDCl_3$,): Phenyl; H_o 8.21 (m, 8H); $H_{m, p}$ 7.90, 7.79 (m, 12H)
Benzo; $H_{1,4}$ 7.25 (m, 8H); $H_{2,3}$ 7.09 (m, 8H)

Zinc Tetra(1-naphthyl)tetrabenzporphyrin (3b)

TLC: Rf = 0.46, 0.38, 0.31, 0.26, 0.23 (30% THF in hexane)

HPLC: ET = 1.7, 2.0, 2.3, 2.9, 3.1, 3.5 min.

From the TLC and HPLC data, there are at least five green components present in the reaction mixture. These were only partially separable by flash chromatography. UV/visible spectral data is given for two of the components that were obtained in reasonably pure form.

UV/VIS: (Rf = 0.46) 631, 585, 460, 439, 429(sh) nm ($CDCl_3$)
(Rf = 0.38) 633, 587, 463, 440 nm.

Zinc Tetra(9-anthracenyl)tetrabenzporphyrin (3c)

TLC: Rf = 0.15, 0.24, 0.36 (30% THF in hexane)

HPLC: ET = 1.8, 2.1, 2.3 min

The two major components (ET = 2.1 and 2.3 min) were partially overlapping. Soret bands for the 2.1-min peak appeared at 445 and 465 nm. For the 2.3-min peak the band appeared at 430 nm.

Zinc Tetra(p-N,N-dimethylaminophenyl)tetrabenzporphyrin (3d)

TLC: Rf = 0.47, 0.37, 0.31, 0.24, 0.18 (30% THF in hexane)

HPLC: ET = 1.9, 2.2, 2.6 (435 nm) 3.3 (450 nm), 4.2 (475 nm), 5.0, 6.5 min. The latter two peaks in the HPLC were very weak compared to the first five.

Attempts were made to separate the components of the reaction mixture by preparative TLC and by extraction of an ether solution of (3d) into aqueous HCl. Preparative TLC on silica gel with 20% THF in hexane afforded only partial separation of the first three HPLC bands. In addition, the recovery of material from the preparative TLC plate was very poor. Extraction of the material into HCl, followed by neutralization with base and reextraction into ether failed to achieve any significant separation.

Zinc Tetra(p-methoxyphenyl)tetrabenzporphyrin (3e)

TLC: Rf = 0.23, 0.30, 0.36 (30%, THF in hexane)

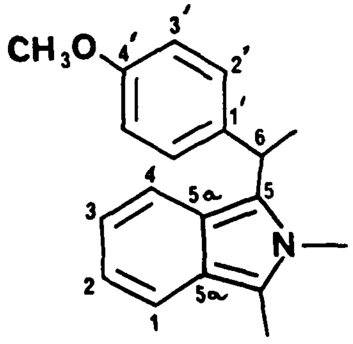
HPLC: ET (major peaks) = 3.1 (445 nm) and 4.0 min (465 nm, Soret bands)
ET (minor peaks) = 1.8, 2.0 and 2.5 min

An attempt was made to purify (3e) by preparative TLC on silica gel with 30% THF in hexane. The only component that could be obtained in pure form corresponded to the ET = 2.5 min peak in the HPLC analytical run. This component had a maximum absorption at 435 nm, which accounted for its detection as a minor peak in the analytical HPLC run (monitored at 450 nm). In spite of poor recovery from the plate, the yield of this component was approximately 10%.

Interestingly, most of the crude (3e) that was placed on the plate remained at the origin during the elution.

The ^{13}C NMR spectrum ($CDCl_3$) of the crude sample of (3e) could be tentatively assigned as follows:

Carbon	Chemical Shift (ppm)
1,4	143
2,3	124
5a	138
5	142
6	113
1'	124
2'	134
3'	122
4'	159
OCH_3	55



3e

Zinc Tetra-(p-cyanophenyl)tetrabenzporphyrin (3f)

TLC: Rf = 0.41 (30% THF in hexane)
HPLC: ET = 1.6, 3.5 min
UV/VIS: 630, 427 nm ($CHCl_3$)
IR ($CHCl_3$ solution): 2240 cm^{-1} (C=N stretch)

The TBP (3f) was the minor product of the reaction with p-cyanobenzaldehyde. The major product was not identified, but it is not a tetrabenzporphyrin. This major product is a dark purple solid which is insoluble in water, pyridine, and other organic solvents. The solid did give a purple solution in aqueous ammonia and aqueous t-butylamine. The UV/visible spectrum in 3M ammonia showed absorption maxima at 679 and 473 nm, but unlike the spectra of the tetrabenzporphyrins run in organic solvents the higher wavelength band was more intense. The IR spectrum (KBr) showed very little absorption in the cyano or carbonyl region.

Zinc Tetra-(m-fluorophenyl)tetrabenzporphyrin (3g)

TLC: Rf = 0.51 (30% THF in hexane)
HPLC: ET = 1.9 min
^{13}C-NMR ($CDCl_3$): C-F, 162.5 ppm (J,C-F = 257 Hz)

Although (3g) appears to contain only one component, careful analysis of the spectra at the leading edge, apex and trailing edge of the HPLC peak revealed three components which have absorption maxima at 437, 445 and 458 nm. Partial resolution of the single HPLC peak containing (3g) could be achieved by decreasing the solvent flow rate from 3.0 to 0.8 mL/min.

DISCUSSION

It has been shown that a number of meso-substituted zinc tetrabenzporphyrins can be prepared by the reaction of isoindole, zinc acetate and an aromatic aldehyde at 400°C. Most aldehydes gave moderate yields of tetrabenzporphyrins but the more bulky 9-anthraldehyde gave a poor yield, which is not surprising considering the steric crowding in the product. The tetrabenzporphyrins could be identified by their green colors and their characteristic UV/visible absorption spectra.

The appearance of multiple green bands in the TLCs and HPLCs of the products (3b-g) was unexpected since this phenomenon was not observed initially in the case of the phenyl substituted TBP (3a). There are at least five explanations that could be postulated for the appearance of multiple components in the TLC and HPLC:

1. Degradation of the tetrabenzporphyrin molecules

during work-up, possibly by photo-oxidation.

2. Aggregation of TBP molecules into their dimers, trimers, and higher aggregates.
3. Products resulting from exchange of apical ligands on the TBP.
4. Atropisomerism of the biphenyl type, which could occur with products from unsymmetrically substituted benzaldehydes.
5. Lack of complete meso substitution - i.e., the presence of tri-, di-, and mono-substitution products in addition to the tetra-substituted TBP.

Each of these possibilities was examined. It is possible to make some statement with regard to the presence or absence of these phenomena in some of the cases examined, although the evidence may be indirect.

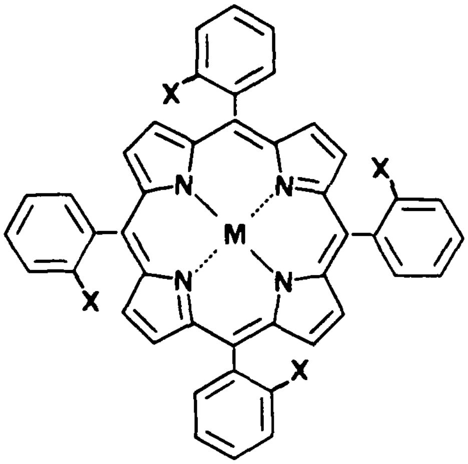
With regard to degradation of the tetrabenzporphyrin molecules, it is clear that a solution of the tetraphenyl derivative (3a) will decompose on standing in air when exposed to light. A dilute chloroform solution of (3a) changed color from green to yellow after a three-hour exposure to a high-intensity light source. At first we thought this decomposition was being catalyzed by HCl present in the chloroform. However, when the degradation studies were carried out in benzene, similiar results were obtained. After one hour the bands due to TBP had decreased and two new bands at 391 and 532 nm had appeared. After 7 hours the TBP bands had completely disappeared and the 391 and 532 nm bands had increased in intensity. Within 24 hours the solution was colorless and there was very little absorption in the 350 to 800 nm region. During the degradation reaction, the color of the solution changed from green to yellow to pink to colorless. When (3a) was photodegraded in pyridine, the material was much more resistant. After 17 hours a new band at 524 nm had appeared but was small in comparison to the TBP bands. This difference in behavior between benzene and pyridine suggests that good donor ligands like pyridine may inhibit photodegradation by complexing with the metal.

Aggregation of porphyrin molecules is known to exist in some systems. It was thought that it would be unlikely in the case of these meso-substituted TBPs because the steric bulk of the aryl substituents would prevent the close approach of two molecules that would be required for effective overlap between the benzporphyrin rings. The degree of aggregation should depend on the concentration of the solute and one would expect to observe changes in the HPLC chromatogram or the absorption spectrum of the TBP on dilution. When concentrated solutions of (3a) and (3e) in 30% THF in hexane were chromatographed on the HPLC, then diluted five to tenfold and reinjected, there was no change in either the HPLC trace or the spectra. Thus, we concluded that aggregation was not a serious problem in these systems.

In most metalloporphyrins, there are empty orbitals of the metal above and below the plane of the macrocycle. It is well known that these apical sites can be occupied by ligands with basic nitrogen or oxygen atoms whose lone pairs of electrons can be donated to the metal to form a complex. Complex formation is pictured as being a dynamic equilibrium in which stronger ligands (more powerful electron donors) may easily displace weaker ones. That this process does occur was demonstrated with (3a), tetraphenyl TBP. When (3a) was dissolved in THF and injected onto the HPLC, one peak with an elution time of 2.1 min was observed. When (3a) was dissolved in pyridine and injected, one peak with an elution time of 3.0 min was observed. When (3a) was dissolved in a 50:50 mixture of pyridine and THF, two peaks with elution times of 2.1 and 3.0 min were observed, with the latter peak consituting greater than 95% of the total area.

Although apical ligand exchange can certainly occur, it is not thought to be a major cause of the multiplicity of peaks in the HPLC traces of the other derivatives (3b-g) since they were prepared under conditions such that THF should be the only potential apical ligand present on HPLC injection.

Atropisomerism resulting from hindered rotation about single bonds has been demonstrated for at least two different meso-tetraaryl porphyrins with substituents in the ortho positions, e.g., 4a-b.



4a: X= OH

4b: X= NH_2

4

In 1969, 4a was prepared and separated into four stereoisomers by TLC on silica gel.[14] In a study of "picket fence porphyrins" in 1975, Collman[15] reported the synthesis and separation of (4b) which was also separated into four isomers. This atropisomerism would be even more likely to occur with tetrabenzporphyrins because of the additional steric bulk of the four benzo rings. There is some evidence that this phenomenon is occurring, although it is not conclusive. While the symmetrical systems (3a) and (3c), where the aryl substituents are phenyl and 9-anthracenyl, show one and three components by HPLC, the compound (4b) in which the substituent is an unsymmetrical 1-naphthyl shows six components by HPLC. It is thought that some of these additional components are due to this biphenyl type atropisomerism.

The final cause of multiple products in these reactions is the possibility of lack of complete meso-substitution*. Although, it is difficult to state anything definitive about the mechanism of the reaction in which isoindole, zinc acetate, and an aldehyde are converted to a TBP at 400°C, at some point in the reaction the carbon atoms that become the meso-carbons and are bonded to a hydrogen and an aryl group must lose one of those groups. If loss of hydrogen occurs every time, then a tetra-substituted product results. If loss of an aryl group is competetive with loss of hydrogen, then products with less substitution will result.

In the present study the only reaction that yielded a single TBP product was the reaction with benzaldehyde. If the loss of an aryl group occurs by some type of radical process, it is understandable that the unsubstituted phenyl group should be the most resistant to this type of cleavage.

CONCLUSIONS

Several new meso-substituted derivatives of the tetrabenzporphyrins have been prepared. This has helped to further define the scope of the isoindole-based synthesis of these compounds, and it has permitted a more complete characterization of the properties of these

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*When acetaldehyde was reacted with isoindole and zinc acetate under similar conditions, the proton NMR of the product showed several signals in the region of the spectrum where meso-protons are known to occur. These were attributed to the trimethyl, dimethyl, and monomethyl tetrabenzporphyrin products.

macrocycles to be made. Of particular importance has been the development of an HPLC analytical method for the determination of product composition and purity. This methodology has led to a more thorough examination of the problem of multiple product formation found for some of the meso-substituted derivatives.

We concluded that the most serious causes of multiple product formation were lack of complete meso-substitution, photodegradation of products and, in the case of ortho and possibly meta-substituted aldehydes, atropisomerism of the biphenyl type. Of these, the first problem may be alleviated by changing the reaction conditions (possibly using ketones rather than aldehydes in the reaction so that the substituents at the meso-position would be identical, and loss of either would give the same product). The degradation problem might be eliminated or at least slowed down by more stringent handling of samples.

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