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PYRIDINE ANALOGS OF TETRAARENOPORPHINS

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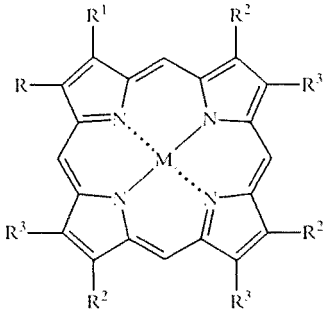
Template tetramerization of quinolinic and cinchomeronic acid imides or their mixtures with the imides of 4-tertbutylphthalic and 1-phenylnaphthalene-2,3-dicarboxylic acids gave the following pyridino zinc complex analogs of the arenoporphins: tetra-2,3-pyridino- and -3,4-pyridinoporphins, tri-2,3-(1-phenylnaphtho)-2,3-pyridino- and -3,4-pyridinoporphins, and tri(4-tertbutylbenzo)-3,4-pyridinoporphin. The desmetal derivatives were obtained for several of these. The electronic absorption spectra are discussed.

Previously, expansion of the aromatic system of tetrabenzoporphin (TBP) has been carried out by symmetric or asymmetric annelation of carbocyclic fragments [1-4]. However, the tetraarenoporphins formed show an increased tendency to oxidation. Structures with a high stability towards oxidation are needed to resolve a number of practical problems. A known method for increasing the stability of tetrapyrrole macrocyclic systems is aza substitution both in the meso position of the macrocycle [5] and in the aromatic fragments [6]. Hence it was interesting to study the effect of aza substitution in the aromatic fragments of the tetraarenoporphins.

In this report we describe the synthesis and certain properties of pyridine analogs of arenoporphins (the zinc complexes of symmetrical tetra-2,3-pyridino- (I) and tetra-3,4-pyridinoporphin (II), unsymmetrical tri-2,3-(1-phenylnaphtho)-2,3-pyridino- (III) and -3,4-pyridinoporphin (IV), tri(4-tert-butylbenzo)-3,4-pyridinoporphin (V), as well as desmetal derivatives of III-V (compounds VI-VIII)).



I–VIII

I—V M = Zn, VI—VIII M = 2H; I $RR^1 = R^2R^3$ = 2,3 piperidino-; II $RR^1 = R^2R^3$ = 3,4- piperidino- III, VI RR^1 = 2,3- piperidino- R^2R^3 = 2,3-(1-phenylnaphtho)- IV, VII RR^1 = 3,4-piperidino- R^2R^3 = = 2,3-(1-phenylnaphtho)-V, VIII RR^1 = 3,4-piperidino- R^2R^3 = 4-tert-butylbenzo-

The zinc complexes I and II were obtained by treating the imides (or N-potassium imides) of quinolinic (IX) or cinchomeronic (X) acids with sodium acetate in the presence of zinc acetate for 1 h at 345-355°C in a helium current [7]. Complex I was also obtained by a known method for TBP [8] via treatment of 3-carboxymethyl-1-oxo-2,3-dihydropyrrolo[4,3-b]-pyridine (XI) [9] with zinc acetate at 360°C for 1 h in a helium current. The yields of I and II did not exceed 6%, probably because of the tendency of the pyridine carboxylic acids to decarboxylate [10]. I and II show a reasonable solubility only in

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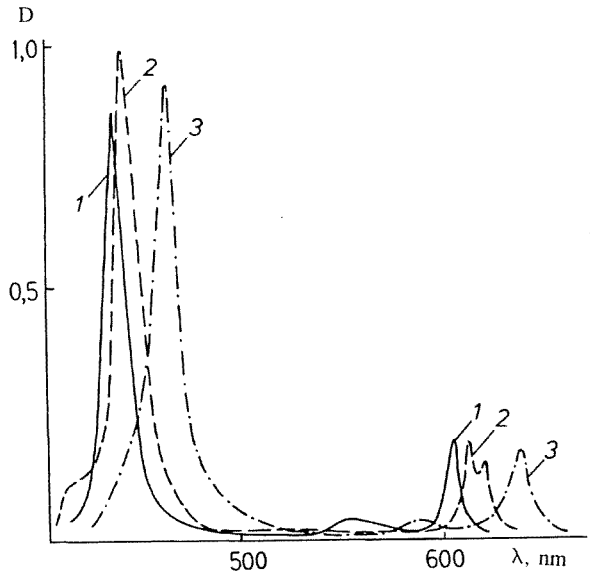

Electronic absorption spectra for zinc complexes of I (1), II (2) and III (3) in pyridine.

highly polar, complex forming solvents, hence they were purified chromatographically on aluminum oxide using pyridine solvent.

The zinc complexes III-V were obtained in up to 10% yields by condensation of mixtures of imide IX or X and the imide of 4-tert-butylphthalic (XII) [11] or 1-phenylnaphthalene-2,3-dicarboxylic acids (XIII) [12] using sodium acetate at 350-420°C with zinc acetate in a helium stream. It was found that imide IX does not react with imide XII and with imide XIII gives complex III in a lower yield than does imide X.

The free compounds VI-VIII were prepared in up to 70% yields by passing gaseous hydrogen chloride through solutions of the zinc complexes III-V in benzene or chloroform. Compounds III-VIII were readily soluble in benzene or chloroform thanks to the presence of the bulky tert-butyl or non planar phenyl groups which make their purification and study easier.

Porphins I-VIII are crystalline materials with different shades of green and inclined to solvation (typical of aza analogs of phthalocyanine [13]).

Exchange of benzene in the TBP molecule for 2,3- or 3,4-pyridine groups leads to a marked increase in the stability of the macrocycle. This is shown by the absence of oxidized radical forms for compounds III, IV, VI, and VII and contrasts with trinaphthobenzoporphins [4]. Solutions of porphins I-VII in benzene or chloroform are stable to the prolonged effects of visible light.

The electronic absorption spectra of I-VIII were measured in solution between 300 and 800 nm. The long wavelength band (Q) in porphin I was shifted hypsochromically by ~20 nm when compared with zinc TBP while the position of the most intense Soret (B) bands is virtually unchanged. By contrast with its 2,3-analog, the spectrum of the 3,4-isomer II in chloroform shows Q and B bands unchanged from their positions in TBP zinc. This spectral behavior upon aza substitution in TBP is similar to that in tetra-2,3- and -3,4-pyridinoporphyrazine [4] in which there is an increase in the energy of the $a_{1u} \rightarrow e_g$ transition (corresponding to the Q Band) upon aza substitution in position 3 of the benzene rings of the phthalocyanine molecule. By contrast with porphin I, the Q band for II in pyridine is split into a doublet at 630 and 618 nm. This is probably due to a lowering of molecular symmetry related to the position of the nitrogen atoms relative to the macrocycle. Confirmation of this needs quantum-chemical investigation. A feature typical of the spectra of I and II when compared with zinc TBP is the hypsochromic change in the Q band related to the decreased oscillator strength of the corresponding electronic transition [15].

In the absorption spectra of the non symmetric pyridine analogs of TBP there are significant differences when compared with the symmetric tetrapyridinoporphins i.e., an increase in the strength of the long wavelength Q band compared with the B band typical for non symmetric arenoporphins [4] together with their splitting due to lower molecular symmetry. Thus the absorption spectrum of the zinc complex V shows a Q band doublet with maxima at 643 and 625 nm ($\Delta\nu_{Q1-Q2} = 450\ cm^{-1}$). Similar but more bathochromically shifted doublets are found for III and IV ($\Delta\nu_{Q1-Q2} = 600\ cm^{-1}$). The maxima of the single

TABLE 1. Parameters for Compounds I-VIII

Compound	Empirical formula	Electronic absorption spectrum	
		solvent	λ_{max}, nm (log ε) (relative intensity)
I	$C_{32}H_{16}N_8Zn \cdot 2\,H_2O$	Pyridine	610 (1,0), 564 (0,2), 432 (0,67)
II	$C_{32}H_{16}N_8Zn \cdot H_2O$	Pyridine	630 (0,2), 618 (0,18), 578 (0,05), 440 (1,0), 410 sh (0,17)
III	$C_{65}H_{37}N_5Zn \cdot (C_2H_5)_3N$	Benzene	694 (0,58), 665 (0,54), 636 sh (0,16), 610 sh (0,11), 451 (1,0)
IV	$C_{65}H_{37}N_5Zn \cdot (C_2H_5)_3N$	Benzene	692 (4,49), 665 (4,48), 632 (4,02), 608 sh (3,60), 454 (4,71), 432 sh (4,60)
V	$C_{47}H_{43}N_5Zn \cdot (C_2H_5)_3N \cdot H_2O$	Benzene	643 (4,84), 625 (4,74), 580sh (4,04), 435 (5,48)
VI	$C_{65}H_{39}N_5 \cdot (C_2H_5)_3N \cdot 4\,H_2O$	Benzene	708 (0,51), 702 sh (0,45), 664 (0,65), 652 sh (0,77), 611 sh (0,15), 452 (1,0), 434 (0,96), 406 sh (0,65)
		DMF	703 (0,47), 663 (0,54), 612 sh (0,16), 448 (1,0), 432 (0,95), 400 sh (0,64)
		DMF + KOH	680 (0,45), 657 (0,46), 626 sh (0,11), 516 sh (0,12), 466 (1,0), 408 sh (0,53)
		CF_3COOH	726 (0,57), 672 (0,24), 478 (1,0), 446 sh (0,77), 414 (0,91)
VII	$C_{65}H_{39}N_5 \cdot (C_2H_5)_3N \cdot 4\,H_2O$	Benzene	710 (1,0), 700 sh (0,86), 664 (1,22), 652 sh (0,77), 608 (0,3), 452 (1,77), 434 (1,68), 408 sh (1,03)
VIII		Benzene	654 (1,0), 609 (1,08), 558 sh (0,32), 428 (4,2), 412 (3,6)

Soret bands for III-V are found at 451, 454, and 435 nm respectively. Change of the benzene ring of TBP for 3,4-pyridine causes a 17 nm bathochromic shift of the Q band in the electronic spectrum. The spectra of the zinc complexes II and V show small differences. Thus the B band of V is shifted hypsochromically by 9 nm from porphyrin II and the Q band doublet is shifted bathochromically by 13 and 7 nm respectively. This points to close symmetry and a similar energy level situation in these porphyrin macroheterocycles.

A further modification in the electronic spectra is seen in going from the metal complexes to the free bases VI-VIII. This is most clear in the spectrum of VIII which is close to that of H_2-TBP. In this compound the Q band is split into two components, the shorter wave of which is a singlet at 609 nm in contrast to H_2-TBP.

The absorption spectra for the free bases of VI and VII do not vary significantly with the position of the nitrogen atoms in the pyridine fragments and their effect is only seen in a small shift of the absorption maxima. Hence both for VII and for its zinc complex IV the Q band is split into components at 710 and 664 nm ($\Delta\nu_{Q1-Q2}$ = 975 cm^{-1}) but, in contrast, the Soret band is split into a doublet at 452 and 434 nm ($\Delta\nu$) = 920 cm^{-1}). Hence the electronic spectra of porphins III, IV, VI, and VII are virtually identical to those for the trinaphthobenzoporphin carbo analogs [4].

The presence of the nitrogen atom on the periphery of the macrocycle does cause a powerful effect on the behavior of the pyridine analogs of TBP in acid–base media. Thus the spectrum of VI is changed in basic media, similar to the zinc derivative, probably as a consequence of the formation of the more symmetrical dianion through deprotonation of the central imino group. However, in acid media (CF_3COOH or CH_3COOH), the Q band is bathochromically shifted by ~20 nm and the splitting is virtually absent, probably a result of protonation of the pyridine nitrogen atom.

Hence introduction of pyridine fragments into symmetric or non symmetric arenoporphin molecules does not cause a significant effect on their electronic absorption spectra but does change properties like solubility, stability towards oxidation, and spectral behavior in acidic media.

EXPERIMENTAL

Electronic absorption spectra for I-VIII were measured on a Hitachi-356 instrument for 10^{-5}-10^{-3} M solutions. IR Spectra were taken on a Perkin-Elmer 598 spectrometer for KCl tablets and vaseline mull. Chromatographic purity control was carried out on neutral Brockmann activity grade II aluminum oxide.

Elemental analytical data agreed with that calculated.

Index X was obtained by [16]. Imide IX was synthesized similarly to X by treating quinolinic acid with ammonium acetate in reluxing acetic anhydride. Phthalimidine XI was prepared by [9].

Tetra-2,3-pyridinoporphin Zinc (I). A mixture of imidine XI (0.1 g, 0.5 mmole) and zinc acetate dihydrate (0.22 g, 1 mmole) was held for 1 h in a helium stream at 360°C. The product was washed with water, hydrochloric acid (1:1), aqueous ammonia, and ethanol. The residue was stepwise extracted with ethanol, benzene, and pyridine. The pyridine extract was chromatographed with the same solvent to give I (5 mg, 6%). IR Spectrum: 3440 cm^{-1} (bound OH).

General Method for Preparation of Tetrapyridinoporphins I,II. A mixture of the N-potassium imide (IX or X, 0.37 g, 2 mmole), zinc acetate dihydrate (0.37 g, 1.7 mmole), and sodium acetate (0.5 g, 6.1 mmole) was held for 1 h at 340-360°C. Treatment as for I gave compounds I or II (5-6%).

General Method for Preparation of Nonsymmetrical Arenoporphins III-V. A mixture of N-potassium imides (IX or X, 1 mmole), N-potassium imide XIII [12] or potassium 4-tert-butyl-phthalimide [11] (1 mmole), zinc acetate dihydrate (0.5 g, 2.3 mmole), and sodium acetate (1 g, 12.2 mmole) was held for 1 h in a helium stream at 350-420°C. The product was washed with water, 5% HCl, 5% NH_4OH, and ethanol. The residue was dissolved in a mixture of benzene–triethylamine–chloroform (1:1:1) to give III-V in yields of 8, 10, and 2% respectively.

General Method for Preparation of Desmethyl Compounds III-V. A stream of gaseous hydrogen chloride was passed into a solution of the zinc complex III (0.1 mmole) in benzene or chloroform (25-30 ml) for 1 h at 20°C. The product was washed with 5% sodium carbonate (100 ml) and water (200 ml) and dried (anhydrous sodium sulfate). The solvent was evaporated and the residue dissolved in benzene (10 ml) and column chromatographed. Elution with hexane–benzene–ethylacetate–triethylamine (450:25:25:1) and removal of solvent gave VI (70%). IR Spectrum: 3450 cm^{-1}.

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