UNSYMMETRICAL TETRAARENOPORPHINES

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UDC 547.797.733.147:543.422:548.737

Zinc complexes of unsymmetrical tetraarenoporphines and their oxidized forms were synthesized by condensation of mixtures of phthalic and naphthalene-2,3-dicarboxylic acid imides with sodium acetate or malonic acid in the presence of zinc acetate. Metal-free compounds were obtained by treatment of benzene solutions of the zinc complexes with gaseous hydrogen chloride. The electronic, PMR, x-ray electron, IR, and mass spectra of the synthesized compounds are discussed.

Unsymmetrical arenoporphines are virtually unknown. The only representative of this class is monobenzoporphine, as well as some of its metal complexes [1, 2]. Monobenzoporphine derivatives can be synthesized by diene condensation of protoporphyrin IX dimethyl ester with strongly activated dienophiles with the subsequent elimination of the angular methyl group from the resulting adduct [2]. The range of application of the method is limited, and a search for other synthetic approaches is necessary to obtain unsymmetrical tetraarenoporphines. Our previously proposed method for the synthesis of zinc tetraarenoporphines [3,4] by the template tetramerization of phthalimides in the presence of zinc acetate can also be used for the synthesis of unsymmetrical tetraarenoporphines.

In the present communication we describe the synthesis and some properties of unsymmetrical tetraarenoporphines — tris(4-tert-butylbenzo)-2,3-naphthoporphine zinc (I), tribenzo-2,3-(1-phenylnaphtho)porphine zinc (II), and tris{2,3-(1-phenylnaphtho)]benzoporphine zinc (III), the corresponding metal-free compounds (IV-VI), and the products of their partial oxidation — the oxidized radical forms (ORF) of III (VII), VI (VIII), tri(2,3-naphtho)(4-tert-butyl-benzo)porphine (IX), and its zinc derivative (X).
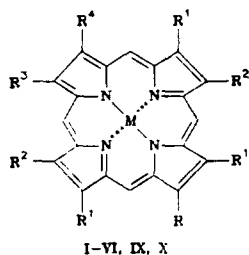
I—VI, IX, X

I—III, X M=Zn, IV—VI, IX M=2H; I, IV R¹R²= 4-tert-butylbenzo, R³R⁴ = 2,3-naphtho;
II, V R¹R²= benzo, R³R⁴ = 2,3-(1-phenylnaphtho); III, VI R¹R² = 2,3-(1-phenylnaphtho),
R³R⁴= benzo; IX, X R¹R² = 2,3-naphto, R³R⁴ = tert-butylbenzo.

Zinc complexes I-III, VII, and X were obtained in up to 35% yields by condensation of phthalic and naphthalene-2,3-dicarboxylic acid imides with sodium acetate or malonic acid at 340-360°C in the presence of zinc acetate. Thus a mixture of I (3%), IX (19%), and tetrakis(4-tert-butylbenzo)porphine zinc (XIII) (3%) was obtained in the reaction of equimolar amounts of the N-potassium derivatives of 4-tert-butylphthalic acid imide (XI) and naphthalene-2,3-dicarboxylic acid imide (XII). Under similar conditions zinc complexes III (35%), VI (9%), II (6.5%), and tetrakis[2,3-(1-phenylnaphtho)]porphine (XV) (7.5%) were obtained from N-potassium derivatives of phthalimide and 1-phenylnaphthalene-2,3-dicarboxylic acid imide (XIV). The yields of I-III depend to a significant extent on the ratio of the starting reagents. Thus 15% III, 10% XV, 5% VI, and traces of zinc tetrabenzoporphine (TBP) and II were obtained when the ratio of XIV to potassium phthalimide was 4:1, while 3% III, 12% VII, 5% II, 10% zinc TBP, and only traces of XV were isolated when the ratio was changed to 1:4.

Compound VII, which is formed in the reaction, is also obtained in the chromatographic purification of III on aluminum oxide as a consequence of its facile oxidation on the sor-

TABLE 1. Electronic Absorption Spectra of Unsymmetrical Tetraarenoporphines I-VI and Their Oxidized Radical Forms (ORF) VII-X in Benzene

| Compound	λ_{max}, nm (log ε) [intensity ratio]
I	650 (4.99), 636 (4.97), 596 (4.28), 430 (5.31)
II	648 [0.42], 635 [0.43], 600 [0.1], 436 [1.0]
III	694 (5.12), 678 (5.18), 442 (5.31)
IV	676 [0.24], 624 [0.29], 610 [0.32], 580 [0.13], 428 [0.92], 422 [1.0]
V	693 (4.47), 656 (4.62), 627 (4.47), 610 sh. (4.28), 447 (4.82), 431 (5.02)
VI	710 (4.54), 670 (4.74), 454 (4.71), 432 (4.79)
VII	660 [0.67], 614 [0.06], 440 [1.0]
VIII	690 [0.44], 655 [0.7], 622 [0.29], 419 [0.98], 431 [1.0]
IX	679 (4.74), 659 (4.35), 628 (4.73), 619 (4.83), 613 (4.84), 560 sh. (4.02), 424 (5.06)
X	660 (4.49), 609 (4.12), 435 (4.79)
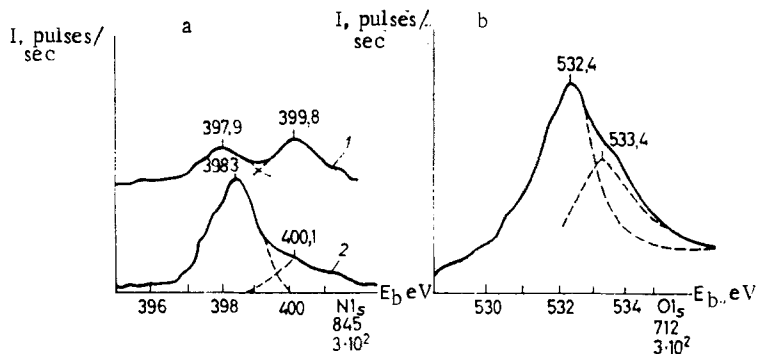
Fig. 1. N1$_s$ (a) and O1$_s$ (b) lines of VIII (1) and its zinc complex VII (2).

bent; to avoid the oxidation of III during purification on this sorbent one must therefore introduce reducing agents such as triethylamine and ethanol into the eluent. The tri(2,3-naphtho)(4-tert-butylbenzo)porphine zinc that is formed under the reaction conditions is oxidized even more readily, and it was therefore isolated only in the form of IX.

Only a singlet band with a g factor of 2.0030 was noted in the EPR spectra of powdered samples of VII-X or solutions of these compounds in toluene; this corresponds to the values of the free radicals of aromatic systems. A cation radical that is spectrally nonidentical to the VIII isolated from the reaction mass is formed in the chemical oxidation of III with silver perchlorate in benzene. Compound III is regenerated when this cation radical is heated in ethanol or triethylamine, while III is not formed from VIII under these conditions. A standard redox potential of 0.41 V (relative to a silver chloride electrode) was determined in the electrochemical one-electron oxidation of o-dichlorobenzene solutions of III on an Au electrode with $(C_4H_9)_4NClO_4$ as the inert electrolyte; this value is in agreement with positioning of III between tetrabenzo- (0.525 V) and tetra(2,3-naphtho)porphine zinc (0.265 V) [5].

Compounds I and II are more resistant to oxidation, and the formation of their oxidized radical forms (ORF) was not noted in the complexing reaction or during chromatographic purification.

The presence of bulky tert-butyl substituents or noncoplanar 1-phenyl substituents in the unsymmetrical tetraarenoporphines leads to a substantial increase in their solubility in organic solvents as compared with the unsubstituted symmetrical analogs. Compounds I-X are crystalline substances with various shades of green that are quite soluble in hexane, in benzene, and chloroform; this facilitates their purification and the investigation of their properties. The synthesized complexes are capable of undergoing hydration and solvation. Their structures were confirmed by their IR, EPR, x-ray electron, and mass spectra.

Thus the electron-impact (EI) mass spectrum of VI was recorded at 150°C. Peaks of low intensity at 888* (12) and 734 (9), which correspond to M and M—2C$_6$H$_5$ ions, are noted in the high region. The ion peak at 507 (100), which is due to the successive loss of a 1-methyl-

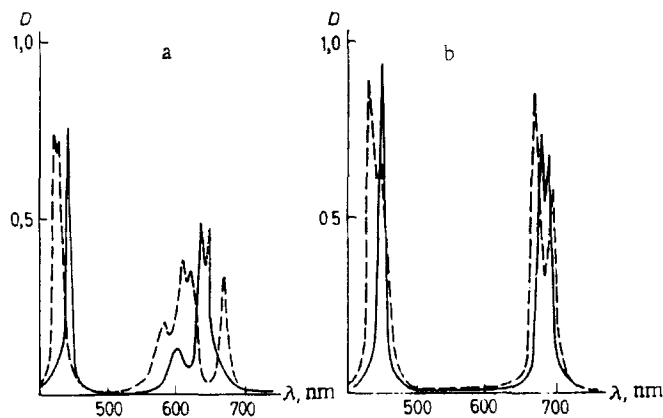*Here and subsequently, the m/z values are given along with the relative intensities in percent (in parentheses).

Fig. 2. Electronic absorption spectra (in benzene): a) VI (---) and its zinc complex III (——); b) IV (---) and its zinc complex I (——).

eneisoindole fragment and the corresponding 4-phenylnaphthalene fragment by the molecular ion, is the most intense peak. Peaks of fragments of medium intensity at 394 (39), 128 (43), 127 (57), and 98 (44), which are due to further fragmentation of the molecule, are also observed in the mass spectrum of this compound.

As in the case of XIII [6], three groups of signals of methylidyne protons at 12.41, 12.66, and 12.94 ppm are observed in the PMR spectrum of zinc complex I at weak field; however, they are shifted ∿0.9 ppm to weak field. The presence of three resonance regions for the meso protons is due to the presence in the molecule of different aromatic environments around the methylidyne groups, as well as position isomers relative to the tert-butyl groups, i.e., the tert-butyl groups of adjacent benzene fragments are located in neighboring or remote positions of the benzene rings relative to the meso proton. The aliphatic protons of the tert-butyl groups give two multiplets at 1.81-1.84 and 1.94-1.98 ppm; this also confirms the existence of position isomers complicated by different aromatic environments. The aromatic-proton region is rather complex; however, in analyzing the spectra of I and comparing them with the spectra of XIII one can isolate several groups of signals of protons that are shifted to weak field (11.20-11.28 ppm). A multiplet signal at 8.58 ppm, which can be ascribed to protons of the naphthalene fragment, is observed at stronger field.

The ratios of the integral intensities of the signals of the protons of the tert-butyl groups and the meso protons, as well as the protons of the benzene and naphthalene fragments, for I are in good agreement with the calculated values.

Four signals of NH protons at −2.47, −2.49, −2.52, and −2.57 ppm, in contrast to the singlet signal of tetrakis(4-tert-butylbenzo)porphine, were recorded in the PMR spectrum of demetallated compound IV in THF at strong field; this is a direct consequence of the asymmetry of the molecule rather than the existence of isomers with different orientations of the tert-butyl groups.

Two peaks with corresponding bond energies of 397.9 and 397.2 eV and 399.8 and 399.6 eV, respectively, are observed in the x-ray electron spectra of VIII (Fig. 1a) and V for the $N1_S$ line. The ratio of the integral intensities of these lines ≈1:1. In analogy with the data in [7], we assigned the peaks with higher energies to the nitrogen atoms of the pyrrole ring and the peaks with lower energies to the nitrogen atoms of the pyrrolenine ring. The $N1_S$ lines for VII (Fig. 1a) and X are somewhat more complex — doublets at 398.3 and 398.4 eV and 400.1 and 400.8 eV, respectively, with a ratio of the integral intensities of the lines of 3:1. The more intense bands in the lower-energy region were ascribed to the nitrogen atoms of naphthalene fragments, while the less intense bands were ascribed to the nitrogen atoms of the isoindole ring. The form of the spectrum makes it possible to conclude that polarization due to redistribution of the electron density from the benzene ring to the naphthalene rings is present in these unsymmetrical structures. The experimental data additionally confirm the structures of unsymmetrical tetraarenoporphines VII and X. The energy state of zinc (Zn $2p_{3/2}$ = 1021.2 eV) corresponds to Zn^{2+} and is in agreement with the data in [7]. The $O1_S$ line was recorded in the spectrum of VII (Fig. 1b) with a bond energy of 532.4 eV and a half width of 3.1 eV; this corresponds to the energically nonhomogeneous state
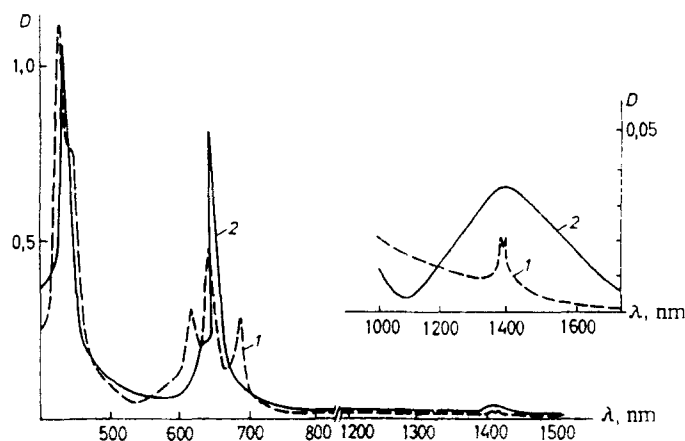
Fig. 3. Electronic absorption spectra in benzene of the oxidized radical forms (ORF) of tris[2,3-(1-phenylnaphtho)]benzoporphine (VIII) (1) and its zinc complex (VII) (2).

of the oxygen atom in this compound. In the graphical expansion of the $O1_S$ line into two components the bond energies for the oxygen atom were 532.4 and 533.4 eV; this corresponds to the oxygen atom of the hydroxy groups of hydration water in the oxidized radical form (ORF), which is also confirmed by the presence in the IR spectra of VII-X (in KCl pellets and in mineral oil) of vibrations at 3400-3500 cm^{-1}, which are characteristic for associated OH groups, as well as the agreement of the results of elementary analysis with the proposed structure.

The electronic absorption spectra of benzene solutions of tetraarenoporphines I-X at 220-750 nm were measured (Table 1, Fig. 2). In contrast to the metal complexes of tetra-benzoporphine (TBP), two bands at 648 and 635 nm ($\Delta\nu$ 320 cm^{-1}) are observed in the absorption spectrum of zinc complex II (Table 1) in the long-wave region, while two bands at 694 and 678 nm ($\Delta\nu$ 350 cm^{-1}) are observed for zinc complex III (Fig. 2a). The Soret band for both compounds is also similarly shifted, but it is represented in the form of a singlet at 436 and 442 nm, respectively. Even greater complication of the electronic absorption spectra occurs on passing from zinc complexes I and III to their metal-free compounds IV and VI (Fig. 2). Thus two bands at 710 and 670 nm ($\Delta\nu$ 330 cm^{-1}) are observed for VI in the long-wave region and for its zinc complex III: however, the Soret band for it is also split into two components at 454 and 432 nm ($\Delta\nu$ 1100 cm^{-1}). Thus substantial differences are observed in the spectra of I-VI as compared with symmetrical tetraarenoporphines [6]: a relative increase in the Q band and a decrease in the B band and their bathochromic shift as a consequence of expansion of the aromatic system of the macrocyclic ligand, as well as splitting of the long-wave band as a consequence of a decrease in the symmetry of the molecule.

Two principal bands at 660 and 440 nm are observed in the spectra of the oxidized zinc complexes VII and X (Fig. 3), while pronounced splitting of both bands is observed for the corresponding metal-free compounds VIII and IX. Thus three bands at 690, 655, and 622 nm are observed for VIII in the long-wave region, while a poorly resolved doublet at 449 and 431 nm (shoulder) is observed in the region of the Soret band.

Broad structureless and low-intensity bands at, respectively, 1200, 1400 (shoulder), and 1400 nm are noted in the near region of the IR spectra (>1000 nm) for X and VII (Fig. 3), whereas two bands at 1380 and 1405 nm, which are characteristic for the radical forms of the porphyrin ring [8], are noted for VIII; however, in contrast to them, they are bathochro-mically shifted because of the more developed conjugation system.

It follows from the information set forth above that in the case of unsymmetrical tetraarenoporphines that contain three naphthalene fragments one observes, in contrast to their mononaphtho analogs, a tendency to form radical oxidized forms that are due to the lower oxidation potential. The differences in their spectra and the spectra of the cation radicals obtained by chemical or electrochemical methods can be associated tentatively with the formation by them of products of covalent addition of an anion such as an hydroxide ion, as is observed in the case of isoporphyrins [9].

The electronic adsorption spectra of solutions of I-X (10^{-5}-10^{-3} M) were measured with SF-4A, Hitachi-356, and Shimadzu-365 spectrophotometers. The EPR spectra of powdered samples and solutions of VII-X in toluene were recorded with a Varian-12 spectrometer. The PMR spectra of I and IV were recorded with a Bruker WM-360 spectrometer (360 MHz, C_5D_5N, tetramethylsilane as the internal standard).

The x-ray electron spectra of V, VII, VIII, and X were recorded with an ES-100 spectrometer using AlK_α emission with E = 1486.6 EV. The spectra were recorded under identical conditions of operation of the spectrometer at 20°C. The pressure in the sample chamber was 133.3•10^{-7} Pa. The Cl_S line, which belongs to the adsorbed hydrocarbons of the diffusion oil, was used as the internal standard. The Cl_S bond energy of the electrons was assumed to be 285 eV. Deconvolution of the unresolved Al $2p_{3/2}$ spectra was carried out using a PDP-11/03 computer.

The mass spectrum of VI was recorded with a Varian MAT-44 mass spectrometer with a source for direct introduction of the samples; the electron-ionization energy was 70 eV, and the samples were introduced at 150°C.

The IR spectra of KCl pellets and mineral oil suspensions of VII-X were recorded with a Perkin-Elmer 598 spectrometer with compensation.

The chromatographic purification and monitoring of I-X were accomplished on Brockmann activity II neutral Al_2O_3.

Reaction of Potassium Derivatives of Imide XII and 4-tert-Butylphthalimide. A mixture of 0.24 g (1 mmole) of potassium 4-tert-butylphthalimide [10], 0.235 g (1 mmole) of the potassium salt of imide XII, 0.5 g (2.28 mmole) of zinc acetate dihydrate, and 1 g (12.2 mmole) of sodium acetate was heated for 1 h at 340-350°C in a helium atmosphere, cooled to 20°C, pulverized in a mortar, transferred to a porous filter, and treated with 500 ml of benzene and 300 ml of acetone. The filtrates were combined, the solvent was removed, and the residue was dissolved in 25 ml of benzene. The solution was transferred to a chromatographic column (3 by 20 cm) and eluted with benzene—pyridine (50:1). The solvent was removed to give 7 mg (3%) of zinc complex XIII with R_f 0.75 [benzene—ethyl acetate (6:1)]. Subsequent elution in the same system gave 7 mg (3%) of complex I with R_f 0.5 [benzene—ethyl acetate (6:1)]. Found: C 78.8; H 6.4; N 6.9; Zn 8.2%. $C_{52}H_{46}N_4Zn$. Calculated: C 78.6; H 6.1; N 7.0; Zn 8.2%.

The column was then washed with benzene—ethanol—chloroform (4:1:1.5) to give a fraction with R_f 0.3. The solvent was removed in vacuo to give 0.05 g (19%) of X with R_f 0.16 [benzene—ethyl acetate (6:1)]. IR spectrum: 3420 cm^{-1} (associated OH). Found: C 82.5; H 6.1; N 5.7%. $C_{52}H_{34}N_4Zn$•OH•$2C_5H_5N$•$6C_6H_6$. Calculated: C 82.7; H 5.7; N 5.9%.

Further elution with ethanol gave 0.01 g (5%) of XIV with R_f 0.8 [pyridine—benzene (1:10)], which was identical with respect to the electronic absorption spectra to the samples obtained by the methods in [4, 11].

Reaction of the Potassium Derivative of Imide XV and Potassium Phthalimide. A mixture of 0.31 g (1 mmole) of the potassium derivative of imide XV [11], 0.185 g (1 mmole) of potassium phthalimide, 0.5 g (2.28 mmole) of zinc acetate dihydrate, and 1 g (12.2 mmole) of sodium acetate was heated for 1 h at 350-360°C in a helium atmosphere, after which the reaction mass was cooled to 20°C, pulverized, and dissolved in 30 ml of benzene—pyridine (50:1). The solution was transferred to a chromatographic column (3 by 15 cm) and eluted in benzene—pyridine (30:1) with collection of the fraction with R_f 0.4 [benzene—triethylamine (50:1)]. The solvent was removed to give 0.02 g (7.5%) of complex XV, which was identical with respect to the spectra to the compound obtained by the method in [11], as well as 0.11 g (35%) of III with R_f 0.3 [benzene—triethylamine (50:1)]. Found: C 81.7; H 4.8; N 7.0; Zn 7.2%. $C_{66}H_{40}N_4Zn$•$2C_5H_5N$. Calculated: C 82.0; H 4.5; N 7.6; Zn 7.3%.

Subsequent elution gave 0.03 g (9%) of VII with R_f 0.8 [benzene—triethylamine—ethyl acetate (56:1:17)], 0.015 g (6.5%) of II with R_f 0.6 [benzene—triethylamine—ethyl acetate (56:1:17)], and 2.5 mg (1.7%) of tetrabenzoporphine zinc [12].

General Method for Demetallation of Zinc Complexes I-III, VII, and X. A stream of gaseous hydrogen chloride was passed into a solution of 0.1 mmole of the zinc complex in 25-30 ml of benzene for 1 h at 20°C, after which the reaction mass was washed with 100 ml

of 5% sodium carbonate and 250 ml of water and dried with sodium sulfate. The solvent was removed, the residue was dissolved in 30 ml of benzene, and the solution was transferred to a chromatographic column (3 by 15 cm) and eluted with benzene—hexane—ethyl acetate (93: 4:3). The solvent was removed to give 75-82% of metal-free compounds IV-VI, VIII, and IX.

Tribenzo[2,3-(1-phenylnaphtho)]porphine (V). This compound was obtained in 82% yield and had R_f 0.3. Found: C 82.7; H 6.9%. $C_{46}H_{28}N_4 \cdot 2(C_2H_5)_3N$. Calculated: C 83.0; H 7.0%.

Tris[2,3-(1-phenylnaphtho)]benzoporphine (VI). This compound was obtained in 75% yield and had R_f 0.5. IR spectrum: 3440 cm^{-1} (associated OH). Found: C 87.2; H 5.0; N 5.7%. $C_{66}H_{40}N_4 \cdot H_2O$. Calculated: C 87.4; H 4.7; N 6.2%.

Compound IX. This compound was obtained in 80% yield and had R_f 0.2. The chromatographic purification of IX was accomplished on aluminum oxide in a hexane—benzene—ethanol system (94:3:3). IR spectrum: 3440 cm^{-1} (associated OH). Found: C 86.0; H 5.5; N 6.9%. $C_{52}H_{36}N_4 \cdot OH \cdot C_6H_6$. Calculated: C 85.8; H 5.3; N 7.0%.

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