SYNTHESIS AND SPECTROSCOPIC PROPERTIES OF SOLUBLE AZA ANALOGS OF PHTHALOCYANINE AND NAPHTHALOCYANINE

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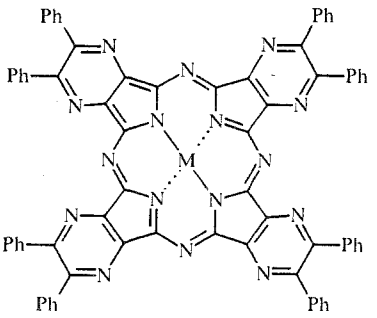
The syntheses of aryl-substituted octaaza analogs of phthalocyanine — tetra-2,3-(4,5-diphenylpyrazino)porphyrazin and its vanadyl complex — and also of the vanadyl complex of tetra-2,3-(4-phenylquinolino)porphyrazin — a tetraaza analog of naphthalocyanine — are described. A modified single-stage method for the synthesis of the previously reported tetra-2,3-(5-tert-butylpyrazino)porphyrazin is put forward. The electronic absorption spectra of the compounds synthesized have been studied in organic solvents and acid media — in sulfuric acid solution and in organic solvents with the addition of phenol or trichloroacetic acid.

Aza analogs of phthalo- and naphthalocyanein have recently become products of interest to research workers as photoinitiators for textile bleaching and the destruction of microorganisms [1], catalysts for the oxidation of mercaptans [2, 3], electrocatalysts for the reduction of oxygen [4], materials for electrochromic displays [5, 6], media for optical storage of information [7], etc.

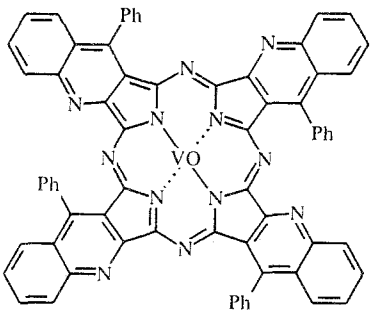
However, unsubstituted aza analogs of phthalo- and naphthalocyanine are known to be difficultly soluble in organic solvents [8, 9], which hinders their purification and limits their potential applications.

The syntheses of alkyl-substituted aza analogs of phthalo- and naphthalocyanine [10-12], which are capable of dissolving in normal organic solvents such as chloroform, and also compounds with isocyanide [13] or axial dialkylsiloxane ligands [14] have previously been carried out. On the other hand, it is known that introduction of aryl substituents into the phthalo- or naphthalocyanine molecule results in a marked improvement in solubility as a result of disruption of the planarity of the molecules [15-17].

In the present study we describe the synthesis and electronic absorption spectra of aryl-substituted octaaza analogs of phthalocyanine — tetra-2,3-(4,5-diphenylpyrazino)porphyrazin (I) and its vanadyl complex (II) — and also the vanadyl complex of tetra-2,3-(4-phenylquinolino)porphyrazin (III) — a tetraaza analog of naphthalocyanine.



I, II



III

I M=HH; II M=VO

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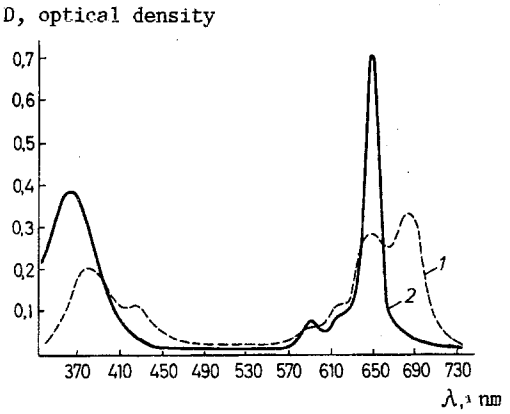

Fig. 1. Electronic absorption spectra of tetra-2,3-(4,5-diphenylpyrazino)porphyrazin I: 1) in 1-chloronaphthalene; 2) in DMF.

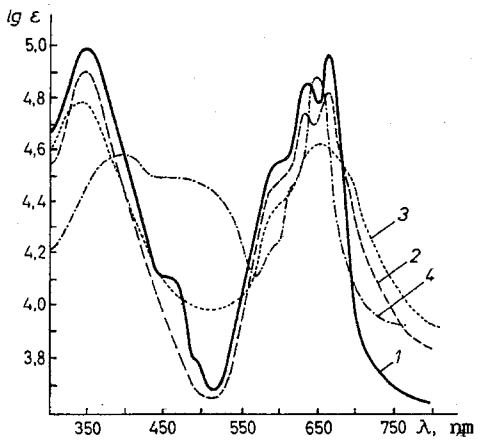

Fig. 2. Electronic absorption spectra of tetra-2,3-(5-tert-butyltetrapyrazino)porphyrazin IV in sulfuric acid solution: 1) 75% H_2SO_4; 2) 82% H_2SO_4; 3) 93% H_2SO_4; 4) electronic absorption spectrum of tetra-2,3-(4,5-diphenylpyrazino)porphyrazin I in 93% H_2SO_4 solution.

Furthermore we describe a modified single-stage method for the synthesis of the previously known tetra-2,3-(5-tert-butylpyrazino)porphyrazin (IV) [18] from diaminomaleonitrile and tert-butylglyoxal in the presence of acetic acid. This is carried out without the usual isolation of the intermediate o-dinitrile (in this case 5-tert-butyl-2,3-dicyanopyrazine) formed by condensation and without the use of traditional catalysts for the template synthesis of phthalocyanine [19] and its analogs [12] from the corresponding o-dinitriles, which are strong organic bases. On heating compound IV in a mixture of chloroform and ethanol with metal salts, the respective complexes are readily formed. Thus, when cobaltous chloride is used, the cobalt complex (V) is obtained.

Compound I is obtained by demetallation of the magnesium or lithium complexes synthesized from 4,5-diphenyl-2,3-dicyanopyrazine (VI) [20], which is a product of the condensation of benzil with diaminomaleonitrile. The vanadyl complex II is synthesized by heating o-dinitrile VI with vanadium trichloride. The copper complex of octaphenylpyrazinoporphyrazin was obtained previously in a similar manner [21] by reaction of compound VI with cuprous chloride, but its properties were not studied.

We used the anhydride (VII) or imide (VIII) of 4-phenyl-2,3-quinolinedicarboxylic acid (IX) as a starting material for preparation of the vanadyl complex of the tetraaza analog of naphthalocyanine III by the urea method. Acid IX is obtained by alkaline hydrolysis of its diethyl ester X, which, in turn, is synthesized in a similar manner to the dimethyl ester [22] by reaction of o-aminobenzophenone with diethyl acetylenedicarboxylate.

The aza analogs of phthalo- and naphthalocyanine that we prepared were purified by means of column chromatography and characterized from their electronic absorption spectra.

A substantial electron-donating effect from the phenyl substituents is suggested by the spectra of compounds I-III in organic solvents. This manifests itself as a bathochromic shift of the principal absorption band by approximately 20 nm relative to the unsubstituted aza analogs. This shift is in the opposite direction to the hypsochromic displacement due to aza substitution at the positions of the benzene rings closest to the macrocycle, which in the case of octasubstitution is 40-45 nm, as was demonstrated previously [18]. Thus, the principal absorption band of the vanadyl complex of tetra-2,3-pyrazinoporphyrazin has a maximum at 635 nm in DMSO [8], its octaphenyl-substituted derivative II has a maximum at 656 nm in the same solvent, while the principal band maximum of its carbocyclic analog — vanadyl tetra(4,5-diphenyl)phthalocyanine — occurs at 700 nm [23].

In the visible region of its electronic spectrum in 1-chloronaphthalene, octaphenyltetrapyrazinoporphyrazin I has two absorption bands that are characteristic of a metal-free phthalocyanine but they partly overlap because of the aggregation of I (Fig. 1). The corresponding spectra of I recorded in DMSO and DMF have a single absorption band, like the spectrum of a metal derivative. Similar spectroscopic evidence of interaction with amines in these solvents was previously found in the case of metal-free phthalocyanines and was attributed to the formation of a dianion — the product of cleavage of the central imino hydrogens [24].

The concerted electron-donating effect from the introduction of phenyl substituents and linear annelation to tetra-2,3-pyridinoporphyrazin manifests itself in the electronic spectrum of compound III as a significant bathochromic shift of the principal absorption band. The maximum occurs at 780 nm in chloroform, whereas the spectrum of the corresponding complex of the unsubstituted tetra-2,3-pyridinoporphyrazin has a maximum at about 645 nm [8], and its annelated analog — tetra-2,3-quinolinoporphyrazin — has a maximum at about 730 nm [14].

Thus, the main characteristics due to the effect of azasubstitution and linear annelation on the electronic absorption spectraof phthalocyanines which we identified previously [18, 25] on series of unsubstituted aza analogs of phthalo-, naphthalo-, and anthracyanines and also their tert-butyl derivatives, which were subsequently confirmed in Freyer's publication [9], are in good agreement with out recent results for aryl-substituted compounds.

We have also recorded the electronic absorption spectra in acid media of the aza analogs synthesized — in sulfuric acid (over a concentration range of 65-93% acid) and in organic solvents with the addition of phenol or trichloroacetic acid.

The behavior of phthalocyanines and their aza analogs in sulfuric acid is known to differ significantly [26]. It was established previously [27] in the case of the dihydroxyltitanium complex of tetra-2,3-pyridinoporphyrazin by means of electronic spectroscopy that in concentrated sulfuric acid this compound is protonated on the peripheral nitrogen atoms, whereas the meso nitrogen atoms of the porphyrazin ring are not affected.

The possibility of multiple protonation, especially for the octaaza analogs, results in the appearance of broad absorption bands with low resolution in their electronic spectra [28].

The compounds synthesized behave similarly in sulfuric acid solution. For the metal-free tert-butyl-substituted analog, with a progressive decrease in concentration of sulfuric acid the long-wavelength band is gradually resolved into a doublet, most likely a result of the decrease in the degree of protonation (Fig. 2).

The octaphenyl-substituted tetrapyrazine phthalocyanine analog I is appreciably hydrophobic and is only soluble in concentrated sulfuric acid, which is not typical of the octaaza analogs. Compounds I and II have the greatest tendency to undergo aggregation even in organic solvents, but because of the increased basicity of the aza analogs, addition of organic acids such as phenol or trichloroacetic acid considerably increases their solubility and alters the nature of their spectrum. At the same time, however, the maximum of the main absorption band is hardly displaced at all, which also points to the absence of protonation on the meso atoms. Previously dissolving mixtures of this type were successfully used to study the acid-base properties of tetraazaporphins and phthalo- and naphthalocyanines [29]. These mixtures are also convenient for spectroscopic studies of the aza analogs, since, in contrast to sulfuric acid, they do not have such a pronounced oxidizing action. Thus, for example, vanadyl complex II rapidly decomposes in concentrated sulfuric acid, whereas in a mixture of phenol and 1,2,4-trichlorobenzene (1:1 by weight) or trichloroacetic acid and 1-chloronaphthalene (concentration of trichloroacetic acid is about 1 mole/liter) this compound is completely stable.

The aza analogs of phthalo- and naphthalocyanine that were synthesized are readily soluble in organic solvents (chloroform, chlorobenzene, DMSO, etc.) as well as in polymer matrices (polymethyl methacrylate, polysulfone, polystyrene, etc.), so that they can be used as absorbers of radiation in the production of various optical materials.

EXPERIMENTAL

Preparative purification of the compounds synthesized was carried out by means of column chromatography using silica gel L 40/100, while Silufol UV-254 plates were used for thin layer chromatography. UV spectra were recorded on a Hitachi-356 spectrophotometer at concentrations of the order of 10^{-6} mole/liter in a cell of width 1 cm. The quantitative spectroscopic parameters in solution were determined when the compounds being studied were sufficiently soluble. In the remaining cases the relative intensities of the absorption bands were recorded.

The elemental analysis data of the products corresponded to the calculated values.

Tetra-2,3-(5-tert-butylpyrazino)porphyrazin (IV). To a solution of 4.56 g (0.04 mole) of the tert-butylglyoxal [30] and 4.25 g (0.04 mole) of diaminomaleonitrile (Janssen Chimica) in 130 ml of ethanol was added 13 ml of acetic acid, and the mixture was boiled for 1 h. The solvent was then evaporated under vacuum at 100°C and 30-40 mm Hg. The green residue was dissolved in benzene and purified on a column. Elution with chloroform gave product IV, which was identical to that obtained by demetallation of the disodium complex. Yield 1.5 g (26%).

Cobalt Tetra-2,3-(5-tert-butylpyrazino)porphyrazin (V). The tetra-2,3-(5-tert-butyltetrapyrazino)porphyrazin IV (0.1 g) was dissolved in 400 ml of chloroform and 150 ml of an alcoholic solution of cobaltous chloride saturated by boiling was added, and the mixture was boiled for 2 min. The solvent was then evaporated under vacuum, and extraction with chloroform from the residue yielded complex V, which was purified on a column. The impurities were eluted with chloroform and compound V was eluted with a mixture of benzene and acetone (2:1). Yield 0.072 g (72%). UV spectrum (in DMSO), λ_{max}, nm (log ε): 616 (4.82), 560 (4.13), 422 (3.89), 334 (4.60).

Tetra-2,3-(4,5-diphenylpyrazino)porphyrazin (I, $C_{72}H_{42}N_{16}$). **A.** A mixture of 0.1 g (0.35 mmole) of 4,5-diphenyl-2,3-dicyanopyrazine VI [20], 0.075 g (0.65 mmole) of anhydrous magnesium sulfate, 0.075 g (3 mmole) of magnesium in the form of fine shavings, 0.4 g of urea, and a catalytic quantity of ammonium molybdate was kept at 270°C for 5 h. The melt was extracted with chloroform and the extract evaporated to dryness. The resulting residue was purified by reprecipitation from concentrated sulfuric acid, and the impurities were then extracted with boiling ethanol. Yield of compound I 0.047 g (47%). **B.** Lithium (0.01 g, 1.6 mmole) was dissolved in 1 ml of redistilled isoamyl alcohol on heating and agitation and the solution was cooled to room temperature and supplemented with 0.15 g (0.53 mmole) of dinitrile VI. The mixture was kept at 120°C, and when an intense green color appeared the heating was immediately removed. After cooling, the reaction mixture was treated with 5% HCl, the organic layer was washed with water until neutral reaction and 2 ml of chloroform was added to it. The precipitate that formed was filtered off and thoroughly washed with acetone and hot ethanol. Compound I was obtained, identical to that obtained by method A. Yield 0.042 g (28%). UV spectrum (in DMF), λ_{max}, nm (log ε): 656 (4.95), 604 sh (4.00), 596 (4.03), 372 (4.68). UV spectrum (in 1-chloronaphthalene), λ_{max}, nm (relative intensity): 678, 654, 614 sh, 590 sh, 420 sh, 376 sh, 366 (3.88:3.68:1.48:1.00:1.63:2.88:3.05).

Vanadyl Tetra-2,3-(4,5-diphenylpyrazino)porphyrazin (II, $C_{72}H_{40}N_{16}VO$). A mixture of 0.1 g (0.35 mmole) of 4,5-diphenyl-2,3-dicyanopyrazine VI and 0.096 g (0.6 mmole) of vanadium trichloride was kept at 260°C for 4 h. The melt was treated with chloroform, the extract was evaporated, and the residue chromatographed on a column. The initial dinitrile and intermediates were eluted with a mixture of hexane and acetone (2:1), and the product was eluted with a mixture of benzene and acetone (25:1). Yield of complex II 0.034 g (34%). UV spectrum (in DMSO), λ_{max}, nm (log ε): 656 (5.19), 595 (4.42), 367 (4.94). UV spectrum (in 1-chloronaphthalene), λ_{max}, nm (relative intensity): 680, 370 (1.0:1.2). UV spectrum (in a mixture of phenol and 1,2,4-trichlorobenzene, 1:1 by weight), λ_{max}, nm (relative intensity): 676, 614, 368 (6.4:1:7.2).

Diethyl 4-phenylacridinate (X, $C_{21}H_{19}NO_4$). A mixture of 11.2 g (0.042 mmole) of diethyl acetylenedicarboxylate and 13 g (0.066 mmole) of o-aminobenzophenone in 330 ml of benzene was boiled for 5 days. The solvent was evaporated and the residue was purified by successive recrystallization from ethanol and hexane. Ester X was obtained, 4.48 g (yield 32%), mp 95-98°C.

4-Phenylacridinic Acid (IX). A mixture of 1.75 g (5 mmole) of diester X and 1.75 g of KOH in 35 ml of absolute ethanol was boiled for 39 min. The precipitate of dipotassium 4-phenylacridinate that formed was filtered off, dissolved in water, acidified with dilute HCl, and product IX was isolated. Yield 0.97 g (66%), mp 200-205°C. According to the literature data [31], mp 200-215°C.

4-Phenylacridinic Anhydride (VII, $C_{17}H_9NO_3$). 4-Phenylacridinic acid (0.52 g, 1.8 mmole) in 6 ml of acetic anhydride was boiled for 1 h. On cooling, product VII precipitated out, and the latter was filtered and washed with hexane. Yield 0.37 g (75%), mp 260-263°C (from chloroform). According to the literature data [32], mp 264-266°C (from benzene).

4-Phenylacridinimide (VIII, $C_{17}H_9N_2O_2$). A mixture of 0.4 g (1.45 mmole) of anhydride VII and 0.87 g (14.5 mmole) of urea was kept at 180°C for 1 h. The melt was treated with hot water and the precipitate of product was filtered and washed thoroughly with water. Yield of imide VIII 0.31 g (78%), mp 298-300°C (from chloroform).

Vanadyl Tetra-2,3-(4-phenylquinolino)porphyrazin (III, $C_{68}H_{36}N_{12}VO$). **A.** A mixture of 0.1 g (0.36 mmole) of anhydride VII, 0.1 g (0.63 mmole) of vanadium trichloride, 0.5 g of urea, 0.2 g of anhydrous sodium sulfate, a catalytic quantity of ammonium molybdate, and 0.5 ml of 1-bromonaphthalene was kept at 250°C for 0.5 h. The melt was cooled and washed with hot water and 50% aqueous ethanol. The residue was chromatographed on an Al_2O_3 column, and complex III was eluted with chloroform. Yield 0.044 g (45%).

B. A mixture of 0.2 g (0.73 mmole) of 4-phenylacridinimide VIII, 0.2 g (1.27 mmole) of vanadium trichloride, 1 g of urea, 0.4 g of anhydrous sodium sulfate, a catalytic quantity of ammonium molybdate, and 0.5 ml of 1-bromonaphthalene was kept at 300°C for 0.5 h. Subsequent treatment of the melt obtained was similar to that described in method A. Yield of compound III 0.098 g (49%). UV spectrum (in chloroform), λ_{max}, nm (log ε): 780 (5.29).

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