SYNTHESIS OF TETRA-2,3-QUINOLINOPORPHYRAZINE AND ITS METAL COMPLEXES

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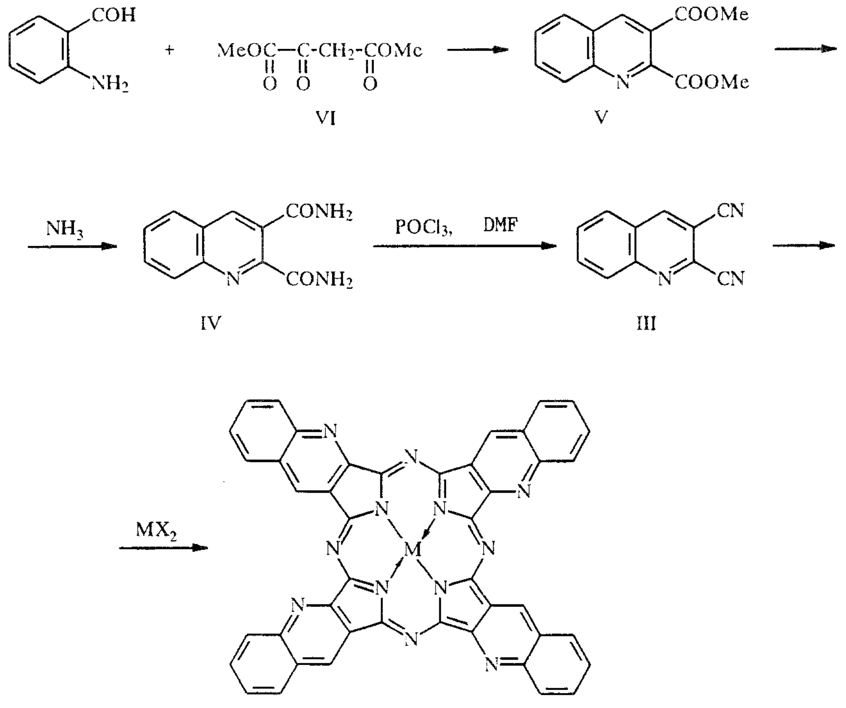
Tetra-2,3-quinolinoporphyrazine and its complexes with a number of metals were synthesized. The electronic and IR spectra of the compounds obtained, which have typical phthalocyanine character, were studied.

Phthalocyanine (PcH_2) and its metal complexes are currently being investigated extensively in order to create new technologically valuable materials based on them. In this connection, the structural modification of the periphery of the molecule directed toward the improvement of a number of the physicochemical properties of the compounds is imperative.

Benzannelation and aza substitution are promising methods for the structural modification of phthalocyanines [1, 2]. At present, the following polyazaphthalocyanines have been described and studied to some extent: tetra-2,3- and tetra-3,4-pyridinoporphyrazines [2, 3], tetrapyrazinoporphyrazines [3], and tetra-2,3- and tetra-6,7-quinoxalinoporphyrazines [3, 4]. The lack of information regarding the synthesis of at least one of the five isomeric tetraquinolinoporphyrazines (the 2,3-, 3,4-, 5,6-, 6,7-, or 7,8-substituted derivatives), with the exception of a single report regarding the production of silicon tetra-2,3-quinolinoporphyrazine [5], is especially surprising.

The synthesis of I and IIa-f was carried out via the following scheme:



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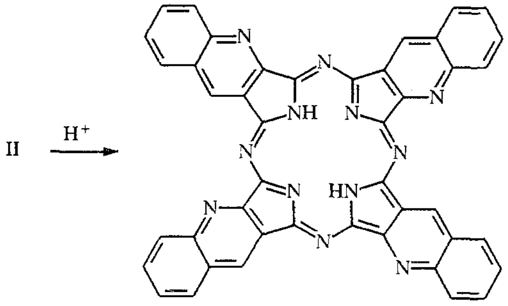

I

IIa M=Mg, b M=Zn, c M=Fe, d M=Cu, e M=Co, f M=Ni; X=Cl, MeCOO

The synthesis of one of these isomers, viz., tetra-2,3-quinolinoporphyrazine (I), for the designation of which we propose the Latin abbreviation 2,3-QlcH_2,* and metal complexes IIa-f (2,3-QlcM) of this compound is reported in the present paper.

The synthesized I and IIa-f are finely crystalline dark-green powders that are insoluble in most organic solvents and do not melt at temperatures up to 500°C.

Like phthalocyanines, they are slightly soluble in DMF and DMSO and moderately soluble in protonating solvents (in the case of sulfuric acid, beginning at a concentration of 5 moles/liter).

Like most phthalocyanines that are aza-substituted along the periphery of the molecule, I and IIa-f form stable hydrates in air; this is confirmed by the results of thermogravimetric and elementary analysis.

The synthesized macroheterocyclic compounds were characterized by their electronic absorption spectra (EAS) (Table 1) and IR spectra (Fig. 1), which have typical phthalocyanine character.

Tetrasubstitution with simultaneous benzannelation leads to a bathochromic shift of the first band in the EAS of the compounds in organic solvents and levels out the spectral manifestations of coordination with metals with different natures.

The IR spectra of I and IIa-f, as compared with the IR spectrum of PcH_2, are presented in Fig. 1. Passing from I to IIa-f does not lead to a qualitative change in the IR spectra, the detailed identification of the bands of which, as in the case of other tetraazaporphines, is difficult because of the loss of their specific characteristics [6].

EXPERIMENTAL

The electronic absorption spectra (EAS) of the compounds were recorded with a Specord M-40 spectrophotometer. The IR spectra of solid solutions in KBr were recorded with a Specord M-80 spectrometer.

Dimethyl oxaloacetate (VI, $C_6H_8O_5$) was obtained by the method in [7] and had mp 75°C (from petroleum ether) (literature mp 74-76°C). The yield was 39%.

Dimethyl quinoline-2,3-dicarboxylate (V, $C_{13}H_{11}NO_4$) was obtained by the method in [8] and had mp 107°C (from methanol) (literature mp 107-108°C). The yield was 58%.

Quinoline-2,3-dicarboxylic Acid Diamide (IV, $C_{11}H_9N_3O_2$). A 4-g (20 mmole) sample of ester V was dissolved in 200 ml of dry methanol, the solution was saturated with dry ammonia for 2-3 h, and the mixture was allowed to stand for 12 h at room temperature. The resulting precipitate was removed by filtration, washed with 20 ml of cold water, and air dried to give 2.5 g (66%) of diamide IV in the form of colorless needles with mp 314°C (mp 314-315°C [8]).

2,3-Dicyanoquinoline (III, $C_{11}H_5N_3$). A 14.4-g (0.07 mole) sample of diamide IV was dissolved in 150 ml of dry dimethylformamide, and 18 ml (0.2 mole) of phosphorus oxychloride was added in small portions with stirring at 20°C. The mixture was stirred for 4 h, allowed to stand for 12 h, and then poured over 100 g of ice. The resulting precipitate was removed by filtration, washed with 100 ml of water, and air dried to give 7.2 g (60%) of dinitrile III in the form of a light-brown powder with mp 220°C (mp 220-222°C [8]).

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*In analogy with phthalocyanine (PcH_2) and naphthalocyanines (2,3-NcH_2 and 1,2-NcH_2), these compounds should be called 2,3-quinolinocyanines, and, consequently, the abbreviation proposed by us has the significance that the periphery of the molecule (2,3-Ql) is initially designated, after which the generic attribute, viz., cyanine (c), is given.

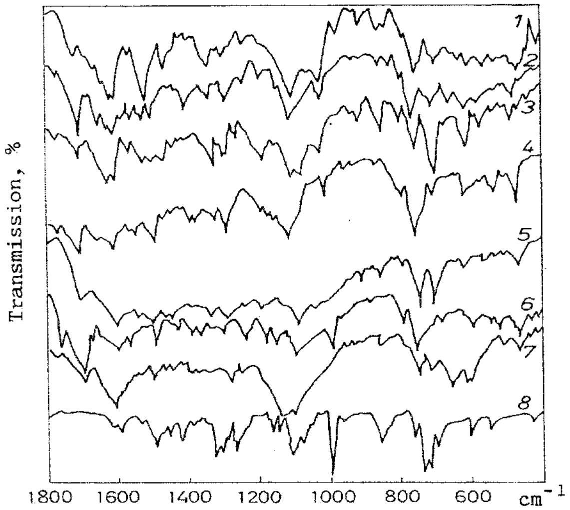

Fig. 1. IR spectra: 1) I; 2) IIa; 3) IIb; 4) IIc; 5) IId; 6) IIe; 7) IIf; 8) PcH_2.

TABLE 1. Characteristics of the Synthesized Compounds

Compound	EAS, λ_{max}, nm (rel. int.), DMSO	Yield, %
I	714 (1,5), 637 (1,0)	58
IIa	714 (6,3), 680 (2,0), 645 (2,0), 444 (1,0), 385 (3,6), 334 (5,5)	53
IIb	714 (3,9), 670 (2,9), 465 (1,0), 333 (6,6)	64
IIc	706 (1,5), 637 (1,0), 444 (1,8), 357 (6,1)	62
IId	695 (1,5), 662 (1,4), 465 (1,0), 333 (4,7)	66
IIe	704 (3,8), 637 (1,0), 444 (2,2), 333 (5,1)	68
IIf	693 (1,0), 654 (2,1), 333 (22,0)	72

Metal Complexes of Tetra-2,3-quinolinoporphyrazine (IIa-f, $C_{44}H_{22}N_{12}M$). A mixture of 1.8 g (10 mmole) of 2,3-dicyanoquinoline (III), 2.5 mmole of a salt of the corresponding metal, and 0.01 g of ammonium molybdate was sintered for 3 h at 220°C. The melt was triturated and washed successively with hot water, 5% HCl, and 5% NH_3 until the filtrates were colorless. The organic impurities were extracted with hot acetone and pyridine in a Soxhlet apparatus until the extract was colorless.

The Cu^{2+}, Zn^{2+}, Fe^{2+}, Ni^{2+}, and Co^{2+} complexes were reprecipitated twice from solutions in concentrated sulfuric acid (1 g in 50 ml) by pouring over 500 g of ice. The purity of the compounds was monitored by means of the constancy of the parameters of the electronic absorption spectra (EAS).

Tetra-2,3-quinolinoporphyrazine (I, $C_{44}H_{22}N_{12}$) (Tetraquinolino[2,3-b;2,3-g;2,3-i;2,3-q]-5,10,15,20-tetraazaporphine). A 0.74-g (1 mmole) sample of IIa was dissolved in 50 ml of 17 M H_2SO_4, the solution was filtered through a Schott filter, and the filtrate was poured over 500 g of ice. The resulting precipitate was washed successively on the filter with water (until the filtrate gave no reaction for H^+), 50 ml of 5% NH_3, and again with water until the filtrate was neutral to give 0.36 g (58%) of I.

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HIGHLY ENANTIOSELECTIVE SYNTHESIS OF 3,3-DISUBSTITUTED 4-PIPERIDONES BY MICHAEL ALKYLATION OF CHIRAL PIPERIDONE IMINES

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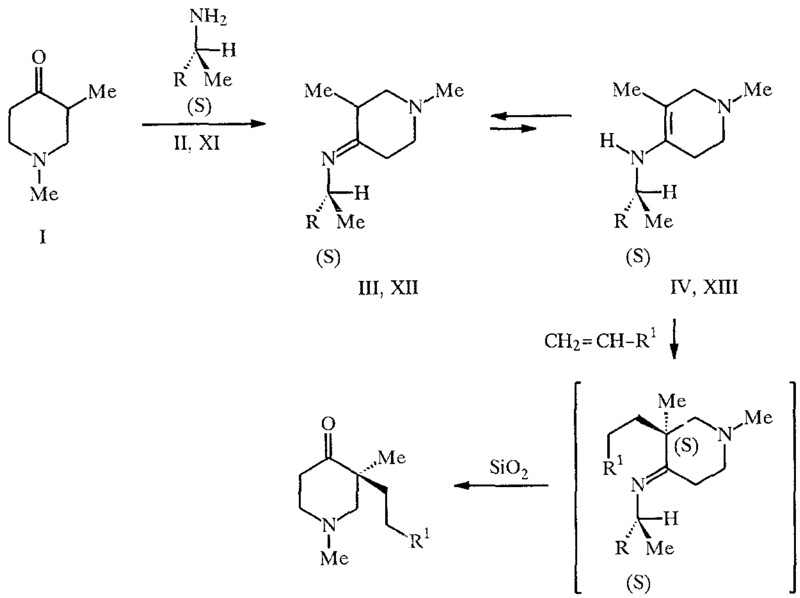
A method for the highly enantioselective synthesis of (3S)- and (3R)-3,3-disubstituted 4-piperidones with an optical purity of 98% based on the "deracemizing" alkylation of 3-substituted 4-piperidones during Michael addition of their chiral imines to electrophilic alkenes was developed.

The great practical value of 3,3-disubstituted 4-piperidones, which are chiral synthones for obtaining natural and synthetic biologically active compounds, has determined the direction of our research in the area of the asymmetric synthesis of chiral derivatives of piperidine that have high optical purity.

A quaternary carbon atom is the key fragment of many alkaloids, aza steroids, and other natural compounds [1]; however, up until now there have been only a few methods that lead to the formation of a quaternary carbon center with high enantioselectivity [2-4]. One of the most elegant methods for the enantioselective formation of a C—C bond consists in the creation of a quaternary carbon center during the "deracemizing" alkylation of α-substituted cycloalkanones by Michael addition of their chiral imines to electrophilic olefins [5].



II—VIII R=Ph; XI—XIII R=CH_2Ph; V, VIII, VIIIa R^1=CN; VI, IX, IXa R^1=COOMe; VII, X R^1=COMe

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