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Porphins and Their Derivatives: XXIV.* *meso*-Tetraphenylporphyrins with β-Pyrazole Rings

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Abstract—A series of 5-substituted 2-(2-phenyl-3,4-dihydro-2*H*-pyrazol-3-yl)porphyrins was prepared by treating with phenylhydrazine tetraphenylporphyrin derivatives containing in the β-position fragments of β-unsaturated ketones or aldehydes. The compounds obtained were oxidized with *o*-chloranil into the corresponding pyrazolylporphyrins.

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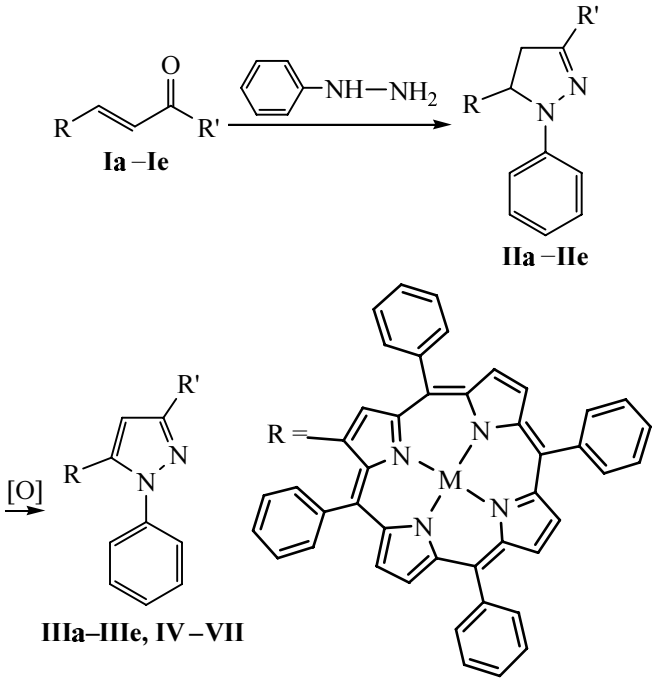
Porphyrin derivatives with pyrazolyl substituents attract much attention due to the versatile modification prospects of the physicochemical characteristics of the macroring. Porphyrin derivatives are known containing pyrazol fragment in the *meso*-positions [2, 3]. A synthesis of pyrazolylporphyrins was also described by reacting substituted phenylhydrazines with deuteroporphyrin **IX** derivatives containing fragments of acetylacetone in the β-position [4].

We recently reported on convenient preparation methods for previously unavailable α,β-unsaturated ketones or aldehydes **I** substituted in the β-position by a tetraphenylporphyrin [1, 5]. In the present paper we describe the synthesis and chemical reactions of pyrazolinylporphyrins **II** formed from compounds **I** and phenylhydrazine.

The course of the reaction strongly depends on the state of the macrocycle coordination center and on the solvent character. Porphyrin as a free base **Ia** did not react with the phenylhydrazine in acetic acid, and although the reaction occurred in the propanol, arising pyrazoline **IIa** was unstable and when subjected to chromatography or at storage in air it gradually decomposed into initial ketone **Ia** and oxidized to pyrazole **IIIa**. Both these compounds were easily removed from pyrzoline **IIa** but were hard to separate because of close R_f values. Besides compounds **Ia–IIIa** the mass spectra measured by FAB method revealed the presence of a product formed by hydrogenation of ketone **Ia** at the exocyclic double bond.

* For communication XXIII, see [1].

The yield of the crude pyrazoline attained 75%, but after the chromatographic purification only 45% of compound **IIa** was recovered.



R' = CH_3 (**a, b**), H (**c**), C_6H_5 (**d**), 2-C_4H_3S (**e**), 5-HO_3S-2-C_4H_2S (**VI**), **IIa, IIIa, IV–VII**, M = 2H; **IIb–IIe**, **IIIb–IIIe**, M = Cu.

We observed a different reaction pattern in the reaction of phenylhydrazine with a copper complex of ketone **Ib**. The process carried out in acetic acid led to the formation of stable pyrazoline **IIb** in a 72% yield, and no

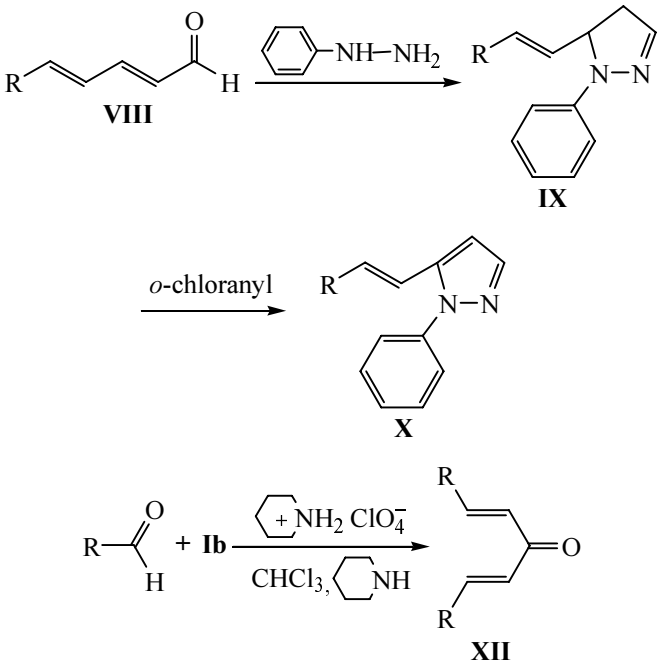
traces of dehydration products were detected in the reaction mixture. Likewise copper complexes of ketones **Id** and **Ie** cleanly entered into the reaction with the phenylhydrazine, but to obtain high yields of pyrazolines **IId** and **IIe** the reaction should be carried out 2–3 times longer than for compound **IIb**. Note that although the reaction time and the phenylhydrazine concentration was increased 2–4-fold the reaction mixture still contained unreacted ketones **Id** and **Ie**.

The oxidation of the copper complexes of pyrazolinylporphyrins **IIb, IId**, and **IIe** into pyrazolylporphyrins **IIIb, IIId**, and **IIIe** occurred the most efficiently and with a high yield at short (1–5 min) boiling in benzene with 3–5-fold excess of *o*-chloranil. In contrast, free base pyrazolinylporphyrin **IIa** under these conditions decomposed into the initial compound **Ia**.

The demetallation of the copper complexes of pyrazolylporphyrins **IIIb–IIId** readily occurred at treating with concn. sulfuric acid giving the corresponding free bases **IIIa, IV**, and **V** in high yields. However in the course of demetallation by this procedure of the copper complex pyrazolylporphyrin **IIIe** the 2-thienyl substituent in the position 5 suffered sulfonation forming sulfoacid **VI** whose molecular weight was proved by the FAB mass spectrometry. The nonsulfonated free base of pyrazolylporphyrin **VII** we obtained by treating the copper complex **IIIe** with moist phosphorus oxychloride. Here we isolated 66% of free base **VII** and 12% of a mixture of unidentified compounds which according to FAB mass spectrrometry were mono- and dichloro derivatives of compound **VII**.

In order to prepare a porphyrin with a pyrazole ring removed from the macroring by one double bond we used as an initial compound the copper complex of α,β,γ,δ-unsaturated aldehyde **VIII** which was a chromatographically unseparable mixture of all possible configurational isomers with *trans*,*trans*-isomer prevailing [5]. In this case the condensation was very fast (30 min), and pyrazolinylporphyrin **IX** was isolated in a high yield. Its oxidation into pyrazole **X** took about 1 h, apparently due to the very low solubility in benzene of pyrazolinylporphyrin **IX**. The long oxidation resulted in a decreased yield of pyrazole **X** (51%). The demetallation of copper complex **X** cleanly led to the formation of free base **XI** which according to ^{1}H NMR spectrum was a pure *trans*-isomer.

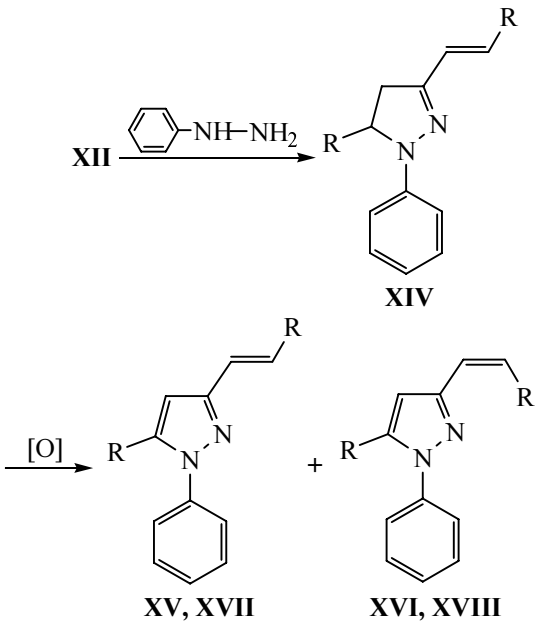
Using the previously developed procedure [1] we carried out a condensation of ketone **Ib** with excess copper complex of 2-formyl-5,10,15,20-tetraphenylporphyrin to



obtain dimeric ketone **XII** in a 52% yield with respect to the taken ketone **Ib**.

The reaction proceeded for 35–40 h till complete disappearance of initial ketone **Ib**. The copper complex of dimer **XII** was demetallated with sulfuric acid to obtain free base **XIII** which according to the ^{1}H NMR spectrum had both double bonds in the *trans*-configuration.

Copper complex **XII** was poorly soluble in acetic acid, and therefore its condensation with the phenylhydrazine was carried out in a mixture acetic acid–pyridine, 5:3, for 20 h, and every 5 h fresh portions of phenylhydrazine



were added. Yet after such a long process 24% of initial ketone **XII** was recovered, and pyrazoline **XIV** was isolated in a 71% yield.

The oxidation of pyrazoline **XIV** with *o*-chloranil yielded two compounds, **XV** and **XVI**, of identical molecular weights suggesting that they are isomers. On increasing the reaction time the more polar compound **XV** completely transformed into the less polar isomer **XVI**. Metal complexes of pyrazolylporphyrins **XV** and **XVI** cleanly underwent demetallation by treating with sulfuric acid into the corresponding free bases **XVII** and **XVIII**. Based on their ^{1}H NMR spectra we identified the more polar substance **XVII** as a *trans*-isomer ($J_{CH=CH}$ 15.74 Hz), and the less polar one **XVIII**, as a *cis*-isomer ($J_{CH=CH}$ 6.2 Hz).

EXPERIMENTAL

^{1}H NMR spectra were registered on a spectrometer Brucker DPX-300 with the operating frequency 300.13 MHz, internal reference TMS, solvent $CDCl_3$. Mass spectra FAB were measured on VC 7070 EQ instrument. The ion desorption was performed with a xenon atoms beam of 8 kW energy from a matrix of a studied compound solution in the 3-nitrobenzyl alcohol. Precise masses of the molecular ions were measured at the mass spectrometer resolution of 10000. Electronic absorption spectra were recorded on a spectrophotometer Specord M – 40 in $CHCl_3$ (C 10^{-5} mol/l). TLC was carried out on Silufol UV-254 plates, eluent benzene and benzene – hexane, 3:1. The column chromatography was performed on silica gel L 40/100. Porphyrin-substituted ketones **Ia–Ie** and formylporphyrin **VIII** were prepared as described in [1] and [5].

5,10,15,20-Tetraphenyl-2-(5-methyl-2-phenyl-3,4-dihydro-2*H*-pyrazol-3-yl)porphyrin (IIa). A mixture of 0.144 g (2.1×10^{-4} mol) of ketone **Ia**, 0.3 ml (3.1×10^{-3} mol) of phenylhydrazine, and 10 ml of propanol was boiled for 5 h. On cooling the reaction mixture the separated precipitate was filtered off, washed with 30% acetic acid and with ethanol, and dried in air. We obtained 0.138 g of crude compound **IIa** that was dissolved in a mixture benzene– tetrachloromethane, 1:2, and applied to a column packed with silica gel (1.5×15 cm), eluent benzene– tetrachloromethane, 1:1. The first fraction obtained contained pyrazoline **IIa**, the eluate was evaporated to a small volume (10–12 ml), and the residue was brought to crystallization by adding 30 ml of 80% methanol. Yield of pyrazoline **IIa** 0.073 g (45%). Electronic spectrum (benzene) λ_{max} (log ε): 425 (5.34), 519 (4.19), 554 (3.87), 597 (3.72), 653 (3.66). Mass spectrum, *m/z*: 773.498 $[M+1]^+$. Then the column was washed with benzene, the solvent was distilled off, and the residue was crystallized from 80% ethanol. We obtained 0.051 g of a mixture of the initial ketone **Ia**, its hydrogenated analog, and pyrazolporphyrin **IIIa**. Mass spectrum, *m/z*: 683.273 $[M+1]^+$, 685.298 $[M+1]^+$, 773.494 $[M+1]^+$.

5,10,15,20-Tetraphenyl-2-(5-methyl-2-phenyl-3,4-dihydro-2*H*-pyrazol-3-yl)porphinatocopper (IIb). A mixture of 0.144 g (1.94×10^{-4} mol) of ketone **Ib**, 0.3 ml (3.05×10^{-3} mol) of phenylhydrazine, and 7 ml of glacial acetic acid was boiled for 5 h. On cooling 10 ml of water was added to the reaction mixture, the separated precipitate was filtered off, washed with 10 ml of 30% acetic acid and with water, dried, dissolved in a mixture benzene–tetrachloromethane, 3:2, and applied to a column packed with silica gel (1×15 cm), eluent benzene–tetrachloromethane, 3:2. The red zone of the main product was collected, eluate was evaporated, and the residue was crystallized from 80% ethanol. Yield 0.116 g (72%). Electronic spectrum, λ_{max} (log ε): 420 (5.47), 542 (4.18). Mass spectrum, *m/z*: 833.241 $[M]^+$.

5,10,15,20-Tetraphenyl-2-(2-phenyl-3,4-dihydro-2*H*-pyrazol-3-yl)porphinatocopper (IIc) was similarly obtained from 0.100 g (1.37×10^{-4} mol) of the copper complex of acroleinylporphyrin (**Ic**), 0.25 ml (2.54×10^{-3} mol) of phenylhydrazine, and 4 ml of glacial acetic acid. Reaction time 0.5 h. Eluent chloroform purified from ethanol. Yield 0.098 g (87.3%). Electronic spectrum, λ_{max} (log ε): 424 (5.22), 551 (4.22), 592 (4.06). Mass spectrum, *m/z*: 819.223 $[M]^+$.

5,10,15,20-Tetraphenyl-2-(2,5-diphenyl-3,4-dihydro-2*H*-pyrazol-3-yl)porphinatocopper (IId). A mixture of 0.143 g (1.78×10^{-4} mol) of ketone **Id**, 0.3 ml (3.05×10^{-3} mol) of phenylhydrazine, and 7 ml of glacial acetic acid was boiled for 5 h, then 0.2 ml (2.03×10^{-3} mol) of phenylhydrazine was added again, and the boiling was continued for another 5 h. Pyrazolinyl **IId** was isolated in the same way as compound **IIb**. First was eluted from the column pyrazolinylporphyrin **IId**, eluent benzene–tetrachloromethane, 1:1. Yield 0.123 g (77.6%). Electronic spectrum, λ_{max} (log ε): 420 (5.61), 542 (4.31). Mass spectrum, *m/z*: 895.257 $[M]^+$. At elution with pure benzene initial ketone **Id** was recovered, yield 0.028 g.

5,10,15,20-Tetraphenyl-2-(2-phenyl-5-thiophen-2-yl-3,4-dihydro-2*H*-pyrazol-3-yl)porphinatocopper (IIe). A mixture of 0.210 g (2.59×10^{-4} mol) of ketone **Ie**, 0.3 ml (3.05×10^{-3} mol) of phenylhydrazine, 8 ml of glacial

acetic acid, and 5 ml of pyridine was boiled for 5 h, then 0.2 ml (2.03×10^{-3} mol) of phenylhydrazine was added again, and the boiling was continued for another 5 h. Compound **IIe** was isolated like pyrazoline **IId**, eluent trichloroethylene. Recovery of initial ketone **Ie** 0.020 g (9.6%). Yield of pyrazoline **IIe** 0.139 g (66%). Electronic spectrum, λ_{max} (log ε): 420 (5.58), 543 (4.30). Mass spectrum, *m/z*: 901.212 $[M]^+$.

5,10,15,20-Tetraphenyl-2-(5-methyl-2-phenyl-2*H*-pyrazol-3-yl)porphinatocopper (IIIb). A mixture of 0.080 g (9.7×10^{-5} mol) of pyrazolinylporphyrin **IIb** and 0.075 γ (3.0×10^{-4} mol) of *o*-chloranil in 10 ml of benzene was boiled for 2 min. Then the reaction mixture was cooled, 3 ml of 15% NaOH was added, and the mixture was stirred for 30 min, then diluted with 20 ml of benzene, the organic layer was separated and washed with water (2×50 ml), evaporated to a minimum volume, and applied to a column charged with silica gel (1×15 cm), eluent benzene. The red zone was collected, the solvent was distilled off, and the residue was crystallized from 90% aqueous methanol. Yield of pyrazole **IIIb** 0.063 g (77.8%). Electronic spectrum, λ_{max} (log ε): 422 (5.63), 544 (4.36). Mass spectrum, *m/z* : 831.232 $[M]^+$.

5,10,15,20-Tetraphenyl-2-(2-phenyl-2*H*-pyrazol-3-yl)porphinatocopper (IIIc). A mixture of 0.077 g (9.4×10^{-5} mol) of pyrazolinylporphyrin **IIc**, 0.070 g (2.8×10^{-4} mol) of *o*-chloranil, and 10 ml of benzene was boiled for 5 min. The workup of the mixture was carried out similarly to compound **IIIb**. Yield 0.036 g (46.8%). Electronic spectrum, λ_{max} (log ε): 422 (5.47), 545 (4.23). Mass spectrum, *m/z*: 817.210 $[M]^+$. We isolated also 0.014 g (20.4%) of aldehyde **Ic**.

5,10,15,20-Tetraphenyl-2-(2,5-diphenyl-2*H*-pyrazol-3-yl)porphinatocopper (IIId) was obtained in a similar way from 0.088 g (9.4×10^{-5} mol) of pyrazoline **IId** and 0.080 g (3.3×10^{-4} mol) of *o*-chloranil. Yield 0.068 g (77.3%). Electronic spectrum, λ_{max} (log ε): 423 (5.68), 544 (4.39), 589 (3.68). Mass spectrum, *m/z*: 893.238 $[M]^+$.

5,10,15,20-Tetraphenyl-2-(2-phenyl-5-thiophen-2-yl-2*H*-pyrazol-3-yl)porphinatocopper (IIIe) was obtained in a similar way from 0.098 g (1.1×10^{-4} mol) of pyrazoline **IIe** and 0.088 g (3.6×10^{-4} mol) of *o*-chloranil. Eluent benzene–tetrachloromethane, 1:1. Yield 0.073 g (74.5%). Electronic spectrum, λ_{max} (log ε): 422 (5.60), 544 (4.33), 587 (3.63). Mass spectrum, *m/z*: 899.209 $[M]^+$.

5,10,15,20-Tetraphenyl-2-(5-methyl-2-phenyl-2*H*-pyrazol-3-yl)porphyrin (IIIa). A mixture of 0.026 g (3.2×10^{-5} mol) of copper complex **IIIb** and 2 ml of concn. sulfuric acid was stirred to complete dissolution of the porphyrin (15–20 min). The reaction mixture was diluted with 50 ml of ice water and neutralized with 25 ml of ammonia solution. Porphyrin **IIIa** was extracted with benzene (2×10 ml). The solution was evaporated to a minimum volume (1–2 ml) and applied to a column charged with silica gel (1×10 cm), eluent benzene. The fractions containing porphyrin **IIIa** were combined, the solvent was evaporated, and the residue was crystallized from 80% aqueous methanol. Yield 0.021 g (84.7%). ^{1}H NMR spectrum, δ, ppm: 8.858 s, 8.798 d.d, 8.746 d, 8.657 s, 8.637 d (7H, β-pyrrole); 8.198 m, 8.043 m, 7.833 d (8H, *o*-phenyl); 7.753 m, 7.653 m, 7.531 m, 6.867 m (12H, *m*-, *p*-phenyl); 7.413 m, 7.201 d.d (5H, phenyl); 5.969 s (1H, pyrazol); 2.269 s (3H, CH_3); –2.672 br.s (2H, NH). Electronic spectrum, λ_{max} (log ε): 424 (5.63), 520 (4.38), 554 (3.92), 596 (3.82), 652 (3.70). Mass spectrum, *m/z*: 771.318 $[M+1]^+$.

5,10,15,20-Tetraphenyl-2-(2-phenyl-2*H*-pyrazol-3-yl)porphyrin (IV) was analogously prepared from 0.028 g (3.5×10^{-5} mol) of compound **IIIc**. Yield 0.023 g (85.8%). ^{1}H NMR spectrum, δ, ppm: 8.87 s, 8.79 d, 8.75 d, 8.68 s, 8.60 d (7H, β-pyrrole); 8.18 m, 8.065 m, 7.78 d (8H, *o*-phenyl); 7.75 m, 7.66 m, 7.48 m, 6.86 m (12H, *m-, p*-phenyl); 7.37 t, 7.20 d.d (5H, phenyl); 7.68 d, 6.27 d (2H, pyrazol); –2.65 br.s (2H, NH). Electronic spectrum, λ_{max} (log ε): 424 (5.57), 519 (4.31), 554 (3.85), 598 (3.74), 654 (3.63). Mass spectrum, *m/z*: 757.299 $[M+1]^+$.

5,10,15,20-Tetraphenyl-2-(2,5-diphenyl-2*H*-pyrazol-3-yl)porphyrin (V) was analogously prepared from 0.027 g (3.0×10^{-5} mol) of complex **IIId**. Yield 0.024 g (97%). ^{1}H NMR spectrum, δ, ppm: 8.86 s, 8.78 s, 8.74 d, 8.62 s, 8.645 d (7H, β-pyrrole); 8.185 m, 8.041 m, 7.87 m (8H, *o*-phenyl); 7.82 m, 7.73 m, 7.63 m, 6.88 m (12H, *m-, p*-phenyl); 7.442 m, 7.33 m (10H, phenyl); 6.455 s (1H, pyrazol); –2.67 br.s (2H, NH). Electronic spectrum, λ_{max} (log ε): 424 (5.62), 520 (4.38), 554 (3.93), 598 (3.82), 652 (3.72). Mass spectrum, *m/z*: 833.341 $[M+1]^+$.

5-[1-Phenyl-5-(5,10,15,20-tetraphenylporphyrin-2-yl)-1*H*-pyrazol-3-yl]thiophene-2-sulfonic acid (VI). A mixture of 0.036 g (4.0×10^{-5} mol) of copper complex **IIIe** and 2 ml of concn. H_2SO_4 was stirred for 10 min to complete dissolution of the porphyrin. The reaction mixture was diluted with cold water (200 ml), the reaction product was extracted into chloroform (2×20 ml), the extract was washed with 1% HCl solution (2×100 ml), evaporated to 5 ml, and applied to a column packed with

silica gel (1×10 cm), eluent chloroform–2-propanol–acetone, 5:1:1. The red-violet zone was collected, the solvent was evaporated on the rotary evaporator, the residue was dissolved in a minimum volume of chloroform and diluted with a 3-fold volume of heptane. The solution was evaporated till the start of crystallization. The reaction product was filtered off and dried in a vacuum (15 mm Hg, 150°C) for 1 h. Yield 0.034 g (92.6%). ^{1}H NMR spectrum, δ, ppm: 8.552 m, 8.36 m (15H, β-pyrrole, *o*-phenyl); 7.964 m, 7.752 m, 6.347 d (12H, *m-, p*-phenyl); 7.33 m, 7.102 m (5H, phenyl); 5.993 s (1H, pyrazol); 5.105 br.s, 4.823 br.s (2H, thiophene); –0.502 br.d (2H, NH). Electronic spectrum, λ_{max} (log ε): 420 (5.37), 544 (4.22), 598.7 (3.94), 666 (3.57). Mass spectrum, *m/z*: 919.247 $[M+1]^+$.

5,10,15,20-Tetraphenyl-2-(2-phenyl-5-thiophen-2-yl-2*H*-pyrazol-3-yl)porphyrin (VII). In 1 ml of $POCl_3$ was dissolved 0.035 g (3.9×10^{-5} mol) of copper complex **IIIe**, 0.1 ml of water was added, and the mixture was shaken for some time. The reaction mixture slightly warmed and was cooled in a water bath. The color of solution quickly changed from red to dingy green. After 5 min 0.1 ml of water was added, and the stirring and cooling continued for another 5 min. The color of solution turned bright green. To the reaction mixture 10–15 g of finely crushed ice was added, the mixture was stirred for 10 min and alkalinized with aqueous ammonia. The reaction products were extracted into benzene (3×10 ml), the benzene extract was evaporated to a minimum volume (1–2 ml), the same volume of tetrachloromethane was added, and the solution was applied to a column packed with silica gel (1×15 cm). First the elution was performed with a mixture benzene–tetrachloromethane, 1:1. The first fraction contained the impurity of chlorinated porphyrin **VII**; on evaporation of the solvent the residue amounted to ~12%. Mass spectrum, *m/z*: 873.251 $[M+1]^+$, 875.259 $[M+1]^+$, 907.201 $[M+1]^+$, 909.219 $[M+1]^+$, 911.220 $[M+1]^+$. The main reaction product **VII** was eluted with a mixture benzene–tetrachloromethane, 3:5, the eluate was evaporated, and the residue was crystallized from 80% ethanol. Yield 0.021 g (66%). ^{1}H NMR spectrum, δ, ppm: 8.874 s, 8.807 d, 8.768 d, 8.693 d, 8.681 s (7H, β-pyrrole); 8.207 m, 8.042 m, 7.887 m (8H, *o*-phenyl); 7.647 m, 7.762 m, 6.909 m (12H, *m-, p*-phenyl); 7.391 m, 7.306 d.d (5H, phenyl); 7.335 m, 7.13 d.d (3H, thiophene); 6.369 s (1H, pyrazole); –2.670 br.s (2H, NH). Electronic spectrum, λ_{max} (log ε): 425 (5.61), 520 (4.37), 555 (3.90), 597 (3.81), 654 (3.7). Mass spectrum, *m/z*: 839.239 $[M+1]^+$.

5,10,15,20-Tetraphenyl-2-[2-(2-phenyl-3,4-dihydro-2*H*-pyrazol-3-yl)vinyl]porphinatocopper (IX). A mixture of 0.131 g (1.7×10^{-4} mol) of aldehyde **VIII**, 0.3 ml (3.1×10^{-3} mol) of phenylhydrazine, and 7 ml of acetic acid was boiled for 30 min till disappearance of initial compound **VIII**. The workup was the same as described for compound **IIb**. Elution with a mixture chloroform – tetrachloromethane, 1:1. The main colored zone was collected, the eluate was evaporated, the residue was crystallized from 80% ethanol. We obtained 0.133 g (91%) of pyrazoline **IX**. Electronic spectrum, λ_{max} (log ε): 426 (5.31), 552 (4.39), 595 (4.34). Mass spectrum, *m/z*: 845.238 $[M]^+$.

5,10,15,20-Tetraphenyl-2-[2-(2-phenyl-2*H*-pyrazol-3-yl)vinyl]porphinatocopper (X). In 20 ml of chloroform was dissolved at boiling 0.051 g (6.0×10^{-5} mol) of porphyrin **IX**, 0.052 g (2.1×10^{-4} mol) of *o*-chloranil and 25 ml of benzene was added. Within 1 h chloroform was slowly distilled off from the mixture till the boiling point of benzene was reached. Then to the reaction mixture 0.01 g (4.0×10^{-5} mol) of *o*-chloranil was added, the mixture was boiled for 30 min, then diluted with 20 ml of benzene, 10 ml of 25% NaOH solution was added to remove the excess *o*-chloranil, and the mixture was stirred for 30 min. The benzene solution was evaporated to 3–4 ml, an equal volume of tetrachloromethane was added, and the solution was applied to a column packed with silica gel (1×25 cm). First the elution was performed with a mixture benzene–tetrachloromethane, 1:1 to remove the impurities, and the main product was eluted with neat benzene. The solvent was distilled off, and the residue was crystallized from ethanol. Yield 0.026 g (51%). Electronic spectrum, λ_{max} (log ε): 426 (5.46), 549 (4.39), 585 (4.01). Mass spectrum, *m/z*: 846.223 $[M]^+$.

5,10,15,20-Tetraphenyl-2-[2-(2-phenyl-2*H*-pyrazol-3-yl)vinyl]porphyrin (XI). A mixture of 0.024 g (2.8×10^{-5} mol) of complex **X** and 2 ml of concn. H_2SO_4 was stirred for 10 min, then 100 ml of ice water was added, and the mixture was neutralized with 25% ammonia solution. Porphyrin **XI** was extracted from the suspension formed into chloroform (2×20 ml), the extract was evaporated to dryness, the residue was dissolved in a hot benzene (~5 ml), and an equal volume of tetrachloromethane was added. The solution was applied to a column packed with silica gel (1×10 cm), elution was performed with benzene, the fractions containing compound **XI** were evaporated to dryness, and the residue was crystallized from 80% ethanol. Yield 0.018 g (81%). ^{1}H NMR spectrum, δ, ppm: 8.82 m, 8.74 d, 8.56 m (7H,

β-pyrrole); 8.20 m, 8.0 m, (8H, *o*-phenyl); 7.77 m (12H, *m-, p*-phenyl); 7.502 m (5H, phenyl); 7.088 d, 6.83 d (2H, *J* 15.9 Hz); 7.67 d, 6.253 d (2H, pyrazole *J* 1.5 Hz,); –2.641 br.s (2H, NH). Electronic spectrum, λ_{max} (log ε): 428 (5.34), 524 (4.31), 562 (3.99), 602 (3.84), 657 (3.43). Mass spectrum, *m/z*: 783.318 $[M+1]^+$.

1,5-Di(5,10,15,20-tetraphenylporphinatocopper-2-yl)penta-1,4-dien-3-one (XII). A mixture of 0.305 g (4.1×10^{-4} mol) of ketone **Ib**, 0.457 g (6.5×10^{-4} mol) of the copper complex of 2-formyl-5,10,15,20-tetraphenylporphyrin, 0.750 g (4.0×10^{-4} mol) of piperidine perchlorate, and 0.012 ml (1.2×10^{-4} mol) of piperidine in 35 ml of chloroform was boiled for 35 h. Then 10 ml of 10% sodium acetate solution was added to the reaction mixture, and the boiling was continued for 10 min. The organic layer was separated, washed with water (3×50 ml), and evaporated to dryness. The residue was dissolved in a mixture tetrachloromethane–benzene, 1:2 (~35–40 ml) and applied to a column packed with silica gel (2.5 × 25 cm). By the initial elution with the same mixture the unreacted copper complex of 2-formyl-5,10,15,20-tetraphenylporphyrin was recovered; the eluate was evaporated, and the residue was crystallized from a mixture chloroform–methanol, 1:5 to obtain 0.074 g (16%) of the initial aldehyde. Then the elution was carried out with a mixture tetrachloromethane–benzene, 1:4. The combined fractions containing compound **XII** were evaporated, and the residue was crystallized from a mixture chloroform–methanol, 1:7. Yield 0.305 g (52%). Electronic spectrum, λ_{max} (log ε): 428 (5.49), 552 (4.61), 593 (4.41). Mass spectrum, *m/z*: 1428.327 $[M]^+$.

1,5-Di(5,10,15,20-tetraphenylporphyrin-2-yl)-penta-1,4-dien-3-one (XIII). A mixture of 0.100 g (7.0×10^{-5} mol) of dimer **XII** and 2 ml of concn. H_2SO_4 was shaken for 3 h, then poured into 100 ml of ice water and neutralized with 25% ammonia solution. The separated precipitate was filtered off, washed with water, and dried. The dry residue was extracted with boiling benzene (4×30 ml), the benzene extract was evaporated to ~50 ml and was subjected to chromatography on a column packed with silica gel (1×30 cm), eluent benzene. The first fraction contained the initial ketone **XII**. Yield 0.002 g (2%). Then the main product **XIII** was eluted. The fractions containing the free base of dimer **XIII** were combined, evaporated to 5 ml, and brought to crystallization by adding 15 ml of ethanol. The precipitate was filtered off, washed with ethanol, and dried at 150°C. Yield of porphyrin **XIII** 0.018 g (20.1%). ^{1}H NMR spectrum, δ, ppm: 9.19 s, 8.88 s, 8.835 m (14H, β-pyrrole); 8.378 m, 8.24 m, 8.16 m (16H, *o*-phenyl); 7.93 m, 7.80 m, 7.58 m (24H, *m-, p*-phenyl); 7.44 d, 6.97 d (4H, *J* 15.74 Hz); -2.50 br.s (4H, NH). Electronic spectrum, λ_{max} (log ε): 429 (5.61), 525 (4.73), 568 (4.42), 603 (4.27), 660 (3.93). Mass spectrum, *m/z*: 1307.517 $[M+1]^+$.

5,10,15,20-Tetraphenyl-2-{2-[1-phenyl-2-(5,10,15,20-tetraphenylporphinatocopper-2-yl)-3,4-dihydro-1*H*-pyrazol-4-yl]vinyl}porphinatocopper (XIV). A mixture of 0.104 g (7.3×10^{-5} mol) of dimeric ketone **XII**, 0.2 ml (2.0×10^{-3} mol)of phenylhydrazine, 5 ml of acetic acid, and 3 ml of pyridine was boiled for 5 h, then 0.1 ml (2.03×10^{-3} mol) of phenylhydrazine was added again, and the boiling was continued for another 5 h. Similarly were added 2 more portions of 0.1 ml of phenylhydrazine with an interval of 5 h. The boiling continued in total for 20 h. On cooling 10 ml of water was added to the reaction mixture, the separated precipitate was filtered off and washed with 30% acetic acid, then with water, the precipitate was dried, dissolved in a mixture tetrachloromethane–benzene, 2:1, and subjected to chromatography on alumina (1×15 cm), eluent tetrachloromethane–benzene, 3:2. The combined fractions containing pyrazoline **XIV** were evaporated, and the residue was crystallized from ethanol. Yield of porphyrin **XIV** 0.062 g (71%). Electronic spectrum, λ_{max} (log ε): 419 (5.84), 544 (4.73), 595 (4.42). Mass spectrum, *m/z*: 1518.394 $[M]^+$. Unreacted initial ketone XII was eluted with neat benzene. Yield 0.025 g (24%).

5,10,15,20-Tetraphenyl-2-{2-[1-phenyl-2-(5,10,15,20-tetraphenylporphinatocopper-2-yl)-1*H*-pyrazol-4-yl]vinyl}porphinatocopper (*trans*-XV, *cis*-XVI). A mixture of 0.097 g (6.4×10^{-5} mol) of pyrazoline **XIV** and 0.073 g (3.0×10^{-4} mol) of *o*-chloranil in 10 ml of benzene was boiled for 1 h, then it was cooled, and 35 ml of 15% NaOH solution was added. The mixture was stirred for 30 min, diluted with 20 ml of benzene, the organic layer was separated, and washed with water (2× 50 ml). According to TLC in the system tetrachloromethane–benzene, 1:1, the mixture contained two well separable compounds. The solvent was distilled off to dryness, the residue was dissolved in a mixture tetrachloromethane–benzene, 2:1, and applied to a column packed with silica gel (1×15 cm). *Cis*-isomer **XVI** was eluted with the same mixture of solvents. The combined fractions containing porphyrin **XVI** were evaporated, and the residue was crystallized from ethanol. Yield 0.069 g (72%). Electronic spectrum, λ_{max} (log ε): 421 (5.95), 545 (4.73), 587 (4.03). Mass spectrum, m/z: 1516.384 $[M]^+$. *Trans*-isomer **XV** was eluted with a mixture tetrachloro-

methane–benzene, 1:1. Crystallization from ethanol. Yield 0.017 g (18%). Electronic spectrum, λ_{max} (log ε): 425 (5.93), 547 (4.69), 581 sh (4.33). Mass spectrum, *m/z*: 1516.373 $[M]^+$. Overall yield 90%.

***trans*-5,10,15,20-Tetraphenyl-2-{2-[1-phenyl-2-(5,10,15,20-tetraphenylporphyrin-2-yl)-1*H*-pyrazol-4-yl]vinyl}porphyrin (XVII).** A mixture of 0.015 g (9.8×10^{-6} mol) of dimer **XV** and 1 ml of concn. H_2SO_4 was stirred with a glass rod grinding the lumps (20 min). Then the mixture was diluted with 50 ml of ice water and neutralized with ammonia solution. Porphyrin **XVII** was extracted into benzene. The extract was evaporated to a minimum volume, and the residue was subjected to chromatography on a column packed with silica gel (1×6 cm), eluent benzene. The combined fractions containing porphyrin **XVII** were evaporated, and the residue was crystallized from a mixture chloroform–ethanol, 1:5. Yield 0.009 g (64%). ^{1}H NMR spectrum, δ, ppm: 9.18 s, 8.96 d, 8.86 m, 8.76 d, 8.69 m (14H, β-pyrrole); 8.24 m (16H, *o*-phenyl); 7.81 m , 6.89 m (24H, *m-, p*-phenyl); 7.40 m, 7.22 m (5H, phenyl); 7.501 d, 6.90 d (2H, *J* 15.75 Hz); 6.14 s (1H, pyrazole); –2.54 s, –2.64 s (4H, NH). Electronic spectrum, λ_{max} (log ε): 426 (5.62), 521 (4.52), 559 (4.18), 599 (4.05), 652 (3.84). Mass spectrum, *m/z*: 1395.548 $[M+1]^+$.

***cis*-5,10,15,20-Tetraphenyl-2-{2-[1-phenyl-2-(5,10,15,20-tetraphenylporphyrin-2-yl)-1*H*-pyrazol-4-yl]vinyl}porphyrin (XVIII).** After treating 0.031 g (2.1×10^{-5} mol) of copper complex **XVI** with 3 ml of concn. H_2SO_4 the workup was performed as with *trans*-isomer **XVII**, elution with the mixture tetrachloromethane–benzene, 1:1. Yield 0.023 g (82%). ^{1}H NMR spectrum, δ, ppm: 9.082 s, 8.779 m, 8.648 d, 8.591 d (14H, β-pyrrole); 8.44 d, 8.18 m, 8.01 m (16H, *o*-phenyl); 7.733 m, 7.63 m, 6.67 m, 6.46 m (24H, *m-, p*-phenyl); 7.54 m, 7.374 m (5H, phenyl); 6.629 d, 5.975 d (2H, *J* 6.2 Hz); 6.392 s (1H, pyrazol); –2.681 s, –2.769 s (4H, NH). Electronic spectrum, λ_{max} (log ε): 423 (5.65), 519 (4.45), 555 (3.99), 597 (3.88), 654 (3.80). Mass spectrum, *m/z*: 1395.557 $[M+1]^+$.

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