PORPHYRINS.

14.* SYNTHESIS AND PROPERTIES OF 1-SUBSTITUTED DERIVATIVES OF 5,10,15,20-TETRAPHENYLPORPHYRIN

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The Vilsmeier formylation of the cobalt complex of 5,10,15,20-tetraphenylporphyrin was realized, and its intermediate salt with the dimethylformamide–$POCl_3$ complex was isolated; demetallation of the latter gave 1-formyl-5,10,15,20-tetraphenylporphyrin. Formyltetraphenylporphyrin oxime and its O-acetyl derivative and 1-cyano-5,10,15,20-tetraphenylporphyrin were synthesized. The Wittig reaction with formylporphyrin and its copper and cobalt complexes with methoxycarbonylmethinyltriphenylphosphorane and diethylamidocarbonylmethinylhexamethyltriamidophosphorane was realized, and conditions that affect the ratios of the Z and E isomers of the acrylic derivatives obtained were studied.

Porphyrins and their metal complexes are effective catalysts for many chemical processes. However, the extensive utilization of most of them is hindered by their high cost and the difficulty with which they are obtained. In this respect it is useful to isolate one of the synthetic meso-substituted porphyrins, viz., 5,10,15,20-tetraphenylporphyrin (I). Its symmetrical and relatively simple structure make this compound a convenient model for physicochemical studies, and the accessible starting compounds (benzaldehyde and pyrrole), together with the one-step synthesis, make it possible to obtain it in large amounts.

However, porphyrin I and its metal complexes are only slightly soluble in most organic solvents. Porphyrin does not have functional groups that would make it possible to modify its chemical properties sufficiently to enable one to successfully study its complexes as homogeneous and heterogeneous catalysts. The introduction of a reactive substituent in the β position of the porphyrin ring is therefore of great interest.

In 1973 [2-4] it was demonstrated for the first time that the bromination of porphyrin I gives a mixture of mono-, di-, tri-, and tetrabromo derivatives, from which the corresponding cyanoporphyrins are formed by heating with CuCN.

Exclusively complexes of monoformylporphyrin (IV) were obtained in the Vilsmeier formylation of nickel (II) [3, 5] and copper (III) [6] complexes of porphyrin I. The formyl group in the β position of the pyrrole ring proved to be chemically active; in particular, the Wittig reaction takes place readily at this group to give the products in high yields.

Porphyrin IV was recently synthesized in low yield (13%) by formylation of tetraphenylhemin V for 24 h with subsequent reductive demetallation to the desired product [6]. The low yield of the final product is due to the low reactivity of hemins in the Vilsmeier reaction [7].

The considerably more reactive cobalt complex of tetraphenylporphyrin (VI) undergoes formylation by a method that we proposed. This method shortens the reaction time to 30 min, decreases the amounts of reagents consumed, and lowers the temperature of the process. At the end of the reaction (determined by a chromatographic test) the product is not hydrolyzed, and an intermediate with the structure of a "phosphorus complex" (VII) is isolated [7]. Treatment of the latter with sulfuric acid gave porphyrin IV (65%), the electronic, IR, PMR, and mass spectra of which were in good agreement with the structure and the literature data [6].

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*See [1] for Communication 13.

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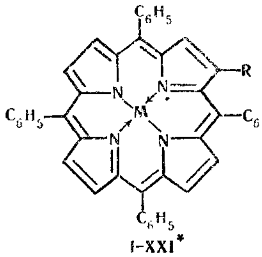
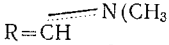
Derivatives that contain diverse substituents in the β position of the porphyrin ring were synthesized from formyl derivative IV. Heating porphyrin IV with excess $NaBH_4$ in tetrahydrofuran (THF) leads to 1-hydroxymethylporphyrin (VIII) in 93% yield. Its electronic spectrum is of the etio type with a 10-20-nm hypsochromic shift as compared with the spectrum of starting porphyrin IV.



I-XXI*

I R=H; II R=H, M=Ni; III R=H, M=Cu; IV R=CHO; V R=H, M=$Fe^{+3}Cl$; VI R=H, M=Co; VII  $R{=}CH\begin{smallmatrix}\cdots N(CH_3)_2\\ \cdots OPOCl_2\end{smallmatrix}$, M=Co; VIII R=$CH_2OH$; IX R=CH=NOH; X R=CN; XI R=CH=$NOCOCH_3$; XII R=CHO, M=Cu; XIII R=CHO, M=Co; XIV R=CH=$CHCO_2CH_3$ (Z isomer); XV R=CH=$CHCO_2CH_3$, M=Cu(Z); XVI R==CH=$CHCO_2CH_3$, M=Co(Z); XVII R=CH=$CHCO_2CH_3$ (E-isomer); XVIII R==CH=$CHCO_2CH_3$, M=Cu(E); XIX R=CH=$CHCO_2CH_3$, M=Co(E); XX R=CH==$CHCON(C_2H_5)_2$ (E isomer); XXI R=CH=$CHCON(C_2H_5)_2$, M=Cu(E)

Porphyrin IV readily forms oxime IX when it is heated with hydroxylamine in pyridine. To obtain cyanoporphyrin X oxime IX was refluxed for 2 h in acetic anhydride as in the synthesis of meso-cyanoporphyrins [7, 8]. However, porphyrin X was isolated in very small amounts, and the principal product (72%) according to data from the PMR, IR, and mass spectra was O-acetyl derivative XI. Its stability is evidently considerably higher than in the case of meso-substituted analogs [8]. In the mass spectrum of XI the molecular-ion peak with m/z 699 has an intensity of 5.8%, while the peak of the $[M - CH_3CO_2H]^+$ fragment has the maximum intensity. Thermolysis of derivative XI to porphyrin X probably occurs in the ion source of the mass spectrometer at 220-240°C.

The corresponding metal complexes XII and XIII were isolated in 98 and 94% yields, respectively, in the formylation of complexes III and VI with subsequent hydrolysis of the reaction mixtures by means of sodium acetate.

Compounds IV, XII, and XIII were used to obtain derivatives that contain carbomethoxyvinyl substituents via the Wittig reaction. Acrylic acid esters, which existed in the Z and E forms (XIV, XV, XVI and XVII, XVIII, XIX, respectively) were obtained in the reaction of porphyrin IV and metal complexes XII and XIII with methoxycarbonylmethinyltriphenylphosphorane (A) [9] in dimethylformamide (DMF) and xylene; the Z and E isomers were readily separated by chromatography.

1-(2-Diethylamidocarbonylvinyl)tetraphenylporphyrin (XX) was isolated in 40% yield in the reaction of porphyrin IV in refluxing xylene with ylid $[(C_2H_5)_2N]_3P{=}CHCON(C_2H_5)_2$ (B) [10].

It is known [11] that in the Wittig reaction the ratio of the Z and E isomers obtained depends on the polarity of the solvent, the presence of several additives (particularly halide ions), and the presence in the ylid molecule of an electron-acceptor group bonded to the ylid carbon atom. We studied the effect of the starting compound (the free porphyrin or the copper or cobalt complex), the solvent (DMF and xylene), and the reagent (phosphoranes A-D) on the ratio of the isomers in the final product. The results are presented in Table 1.

The ratios of the Z and E isomers were measured by direct separation of the reaction products by preparative column chromatography and thin-layer chromatography (TLC). The isomers in the free porphyrins had very close R_f values, and they were therefore converted to the corresponding copper complexes, which were separated by TLC and determined by spectrophotometry.

The assignment of the products of separation to isomers of the Z or E type was made from the PMR data. For this, the separated metal complexes were converted to the corresponding free bases by treatment with concentrated H_2SO_4 or phosphorus oxychloride by the method in [12].

TABLE 1. Ratios of the Z and E Isomers in the Wittig Reaction

Formylporphyrin and its metal complexes IV	Reagent	Solvent	Additives	Z/E
Ni	A	Toluene	None	0,73 [2]
Cu	C[a]	Toluene	,,	0,62 [6]
Cu	A	Xylene	,,	0,73
—	A	The same	,,	0,56
Co	A	,, ,,	,,	No reaction
Co	A	DMF	,,	0,58
Cu	A	The same	,,	0,83
Cu	A	,, ,,	$(C_4H_9)_4NI$	0,75
—	B	Xylene	None	0
Cu	D[b]	$(CH_3OCH_2)_2$	,,	0,05 [6]

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[a] Phosphorane C = $Ph_3P{=}CHCO_2CH_2CH_3$. [b] Phosphorane D = $(C_2H_5O)_3P{=}CHCO_2C_2H_5$.

Reverse transformation of the porphyrins to metal complexes and comparison with the starting compounds showed that decomposition or isomerization of the unsaturated β substituent does not occur during demetallation.

In the case of XVII and XX (the E isomers) the spin–spin coupling constants (SSCC) of the protons attached to the substituted vinyl group were 15.5 and 15 Hz, respectively, as compared with 11.8 Hz for XIV (the Z isomer). This is in good agreement with the published data: 15.4 Hz for the E isomer and 12 Hz for the Z isomer [3].

It is apparent from the data presented in Table 1 that the central metal atoms, the polarity of the solvent, and the addition of tetrabutylammonium iodide did not have a substantial effect on the stereospecificity of the Wittig reaction with formylporphyrin. In all cases the ratio of the Z and E isomers ranged from 0.6 to 0.8. At the same time, changes in the structure of the reagent do have an effect on the ratio of the isomers obtained; the properties of the substituents attached to the phosphorus atom rather than the presence of an electron-acceptor group adjacent to the ylid carbon atom proved to be important in this case. Replacement of the phenyl groups by ethoxy [6] and diethylamido groups led to preponderance of the E isomer in the reaction products, and in the latter case the Z isomer was not detected at all.

EXPERIMENTAL

The electronic spectra of the investigated compounds were obtained with an SF-18 spectrophotometer and are presented in Table 2. The IR spectra of KBr pellets of the compounds were recorded with a Perkin-Elmer model 180 spectrometer. The PMR spectra of solutions of the compounds in $CDCl_3$ were obtained with an HA-100D spectrometer with hexamethyldisiloxane as the internal standard. The signals of the protons of the o-, m-, and p-phenyl substituents in the tetraphenylporphyrin are not presented. The chromatographic mobilities of the compounds were measured on Silufol plates in chloroform–CCl_4 (3:1) (A), chloroform (B), and benzene (C) systems. The mass spectra were obtained with a Varian model MAT-311 spectrometer. The mass spectra of the copper complexes are presented for the signal of the ^{63}Cu isotope.

Cobalt Complex of 1-Formyl-5,10,15,20-tetraphenylporphyrin (XIII). A mixture of 500 mg of complex IV and the complex obtained from 1.9 ml of DMF and 2.25 ml of $POCl_3$ in 300 ml of dichloroethane was heated at 60°C for 30 min, after which it was poured into 0.5 liter of water. The aqueous layer was made alkaline to pH 9-10 and stirred for 4 h, after which the dichloroethane was separated and passed through a layer (3 cm) of activity II aluminum oxide. The solvent was removed by evaporation to dryness, and the residue was crystallized from chloroform–methanol to give 490 mg (94%) of complex XIII with R_f 0.58 (A). IR spectrum: 1670 cm^{-1} (C=O). Mass spectrum, m/z (%): 699 (M^+, 100) and 671 (31). Found: C 76.4; H 3.9; N 7.5%. $C_{45}H_{28}CoN_4O$. Calculated: C 77.3; H 4.0; N 8.0%.

Copper Complex of 1-Formyl-5,10,15,20-tetraphenylporphyrin (XII). A mixture of 5 g of complex III and the Vilsmeier complex from 25 ml of DMF and 30 ml of $POCl_3$ in 1 liter of dichloroethane was refluxed for 6 h. The product was isolated as in the preparation of complex

TABLE 2. Electronic Spectra of the Synthesized Compounds

Compound	Solvent^a	Absorption spectrum, λ_{max}, nm ($\varepsilon \cdot 10^{-3}$)
IV	4	434 (309), 526 (18,8), 568 (8,3), 608 (5,3), 666 (5,5)
VII	2	421 (132), 452 (129), 546 sh (11,8), 572 (12,9)
		431 (143), 583 (13,6)^b
VIII	1	420 (401), 515 (18,4), 548 (5,9), 588 (5,4), 642 (3,4)
IX	1	427 (315), 520 (17,0), 555 (6,7), 594 (5,4), 649 (3,5)
X	2	427 (305), 523 (15,2), 560 (2,9), 602 (4,0), 659 (8,6)
		447 (237), 621 sh (7,5), 677 (35,1)^b
XI	1	428 (326), 522 (21,4), 560 (8,7), 599 (7,6), 656 (4,9)
		439 (293), 618 sh (10,4), 671 (48,6)^b
XII	1	416 (291), 540 (15,5), 586 (4,8)
XIII	1	425 (173), 543 (11,9), 580 (9,4)
XIV	3	426 (225), 519 (19,0), 556 (5,2), 598 (4,2), 655 (2,5)
		449 (231), 614 sh (6,5), 667 (29,9)^b
XV	3	422 (368), 544 (23,0), 580 (5,4)
XVI	3	420 (171), 535 (13,0)
XVII	3	432 (240), 523 (17,5), 563 (7,2), 603 (5,8), 660 (3,7)
		452 (248), 617 sh (8,5), 670 (34,8)^b
XVIII	3	428 (277), 549 (19,8), 588 (9.5)
XIX	3	426 (159), 539 (13,8), 570 sh (7.7)
XX	1	427 (264), 522 (18,0), 559 (7,6), 598 (6,6), 654 (4,2)
		452 (227), 615 sh (9,4), 668 (36,1)^b
XXI	1	426 (386), 548 (23,4), 584 (7,7)

^{a}The solvents were chloroform (1), methylene chloride (2), benzene (3), and toluene (4). ^{b}The spectra were recorded with the addition of 1% CF_3COOH.

XIII to give 5.4 g (99%) of complex XII with R_f 0.80 (A). IR spectrum: 1665 cm^{-1} (C=O). Found: C 76.4; H 3.9; N 7.3%. $C_{45}H_{28}CuN_4O$. Calculated: C 76.7; H 4.0; N 7.9%.

Vilsmeier Salt (VII) Obtained from the Cobalt Complex of 5,10,15,20-Tetraphenylporphyrin. A mixture of 500 mg of complex VI and the Vilsmeier complex from 1.9 ml of DMF and 2.25 ml of $POCl_3$ was heated at 60°C for 30 min, after which the solvent was evaporated *in vacuo*, and 500 ml of cold water was added rapidly to the oily residue. After 10 min, the precipitate was removed by filtration and air-dried to give 620 mg of salt VII, which was subsequently used without additional purification. IR spectrum: 1655 cm^{-1} [broad band, $C{=}\overset{+}{N}(CH_3)_2$]

1-Formyl-5,10,15,20-tetraphenylporphyrin (IV). A 540-mg sample of immonium salt VII was dissolved in 10 ml of concentrated H_2SO_4, and the solution was stirred for 1 h. A saturated solution of sodium acetate and 300 ml of benzene were added, and the mixture was refluxed for 1 h. The organic layer was separated and passed through a layer of aluminum oxide. The solvent was removed by evaporation to dryness, and the residue was crystallized from CCl_4–hexane to give 280 mg of porphyrin IV. Chromatography of the mother liquor (elution with benzene) with a column filled with silica gel gave an additional 30 mg of the reaction product for an overall yield of 65%. The product had R_f 0.63 (B). IR spectrum: 1665 cm^{-1} (C=O). PMR spectrum: 9.33 (1H, s, CHO), 9.16 (1H, s), 8.70–8.80 (6H, m, β-H), and –2.60 ppm (2H, s, NH). Mass spectrum, m/z (%): 642 (M^+, 100) and 614 (18). Found: C 84.3; H 5.0; N 9.0%. $C_{45}H_{30}N_4O$. Calculated: C 84.1; H 4.7; N 8.7%.

1-Formyl-5,10,15,20-tetraphenylporphyrin Oxime (IX). A mixture of 150 mg of porphyrin, 500 mg of hydroxylamine hydrochloride, and 10 ml of pyridine was heated at 80–90°C for 1 h, after which the pyridine was evaporated *in vacuo* and the residue was dissolved in chloroform. The chloroform solution was passed through a layer of aluminum oxide, and the product was crystallized from CCl_4–hexane to give 123 mg (80%) of porphyrin IX with R_f 0.18 (B). IR spectrum: 3520 (OH) and 1600 cm^{-1} (C=N masked by aromatic C=C bands). PMR spectrum: 9.09 (1H, s, –CH=N–), 8.73–8.79 (7H, m, β-H), and –2.76 ppm (2H, s, NH). Mass spectrum, m/z (%): 657 (M^+, 3) and 639 (100). Found: C 81.9; H 4.7; N 10.5%. $C_{45}H_{31}N_5O$. Calculated: C 82.2; H 4.7; N 10.7%.

1-(N-Acetoxy)imino-5,10,15,20-tetraphenylporphyrin (XI). A mixture of 100 mg of oxime IX and 20 ml of acetic anhydride was refluxed for 2 h, after which it was cooled and poured into 200 ml of water. After decomposition of the acetic anhydride, the precipitate was removed by filtration, washed with water, and air-dried. The product was dissolved in chloroform–CCl_4 (3:1) and chromatographed with a column filled with silica gel. The principal fraction was evaporated to dryness, and the residue was crystallized from CCl_4–hexane to give 75 mg (72%) of porphyrin XI with R_f 0.42 (A). IR spectrum: 1775 cm^{-1} (C=O). PMR spectrum:

9.18 (1H, s, —CH=NO—), 8.70-8.77 (7H, m, β-H), 2.13 (3H, s, CH_3), and −2.50 ppm (2H, NH). Mass spectrum, m/z, (%): 699 (M^+, 6), 673 (3), and 639 (100). Found: C 80.4; H 4.8; N 10.0%. $C_{47}H_{33}N_5O_2$. Calculated: C 80.7; H 4.8; N 10.0%. In addition, we isolated a fraction that had a higher R_f value. It was evaporated to dryness to give ~10 mg of 1-cyano-5,10,15,20-tetraphenylporphyrin (X) with R_f 0.56 (A). IR spectrum: 2220 cm^{-1} (C≡N). Mass spectrum, m/z (%): 639 (M^+, 100). Electronic spectrum in CH_2Cl_2, λ_{max} (log ε): 427 (5.48), 523 (4.18), 560 (3.47), 602 (3.61), 659 nm (3.93). According to the data in [4], λ_{max} (log ε): 423 (5.37), 524 (4.07), 560 (3.40), 603 (3.46), 660 nm (3.81).

1-Hydroxymethyl-5,10,15,20-tetraphenylporphyrin (VIII). A mixture of 30 mg of porphyrin IV, 50 mg of $NaBH_4$, and 10 ml of tetrahydrofuran (THF) was heated at 40-50°C for 15 min, after which 50 ml of water was added, and the porphyrin was extracted with chloroform. The solvent was evaporated to dryness, the residue was dissolved in chloroform, and the solution was passed through a layer of aluminum oxide. The solvent was removed by evaporation to dryness, and the residue was crystallized from methylene chloride—pentane to give 28 mg (93%) of porphyrin VIII with R_f 0.41 (B). IR spectrum: 3440 cm^{-1} (OH, broad band). PMR spectrum: 8.86 (1H, s, OH), 8.48-8.77 (7H, m, β-H), 4.80 (2H, s, CH_2), and −2.84 ppm (2H, NH). Mass spectrum, m/z (%): 644 (M^+, 55), 628 (76), and 626 (100). Found: C 83.4; H 5.0; N 8.2%. $C_{45}H_{32}N_4O$. Calculated: C 83.8; H 5.0; N 8.7%.

Z and E Isomers (XV and XVIII) of the Copper Complex of 1-(2-Methoxycarbonylvinyl)-5,10,15,20-tetraphenylporphyrin. A mixture of 210 mg of complex XII and 500 mg of phosphorane A in 10 ml of xylene was refluxed in a stream of nitrogen for 4 h. After the spot of the starting complex no longer appeared on the chromatogram, the mixture was passed through a layer of aluminum oxide, and the solvent was removed by evaporation to dryness. The residue was dissolved in benzene, and the Z (XV) and E (XVIII) isomers were isolated chromatographically with a column filled with silica gel. Crystallization from chloroform—methanol gave 80 mg (35%) of Z isomer XV with R_f 0.62 (C). IR spectrum: 1720 cm^{-1} (C=O). Mass spectrum, m/z (%): 759 (M^+, 100). Workup of the second fraction gave 110 mg (48.5%) of E isomer XVIII with R_f 0.48 (C). IR spectrum: 1710 cm^{-1} (C=O). Mass spectrum, m/z (%): 759 (M^+, 100), 701 (16), and 700 (12). Results of elementary analysis of the mixture of isomers: Found: C 75.5; H 4.2; N 7.2%. $C_{48}H_{32}CuN_4O_2$. Calculated: C 75.8; H 4.2; N 7.4%. The reaction was carried out similarly in DMF. At the end of the reaction, an equal volume of water was added to the reaction mixture, and the precipitate was removed by filtration. Purification and separation gave complexes XV and XVIII in an overall yield of 81% with the isomer ratio indicated in Table 1. The properties of the compounds obtained were in agreement with the properties of the samples described above.

Z and E Isomers (XVI and XIX) of the Cobalt Complex of 1-(2-Methoxycarbonylvinyl)-5,10,15,20-tetraphenylporphyrin. Cobalt complexes XVI and XIX were obtained from complex XIII in DMF by a method similar to that used to prepare corresponding complexes XV and XVIII. The Z and E isomers were separated by means of preparative TLC on plates with silica gel (elution with benzene). Complex XVI was obtained in 11.6% yield and had R_f 0.61 (C). IR spectrum: 1725 cm^{-1} (C=O). Complex XIX was obtained in 18% yield and had R_f 0.47 (C). IR spectrum: 1715 cm^{-1} (C=O). Results of elementary analysis of the mixture of isomers: Found: C 75.5; H 4.3; N 7.3%. $C_{48}H_{32}CoN_4O_2$. Calculated: C 76.2; H 4.2; N 7.5%.

Z and E Isomers (XIV and XVII) of 1-(2-Methoxycarbonylvinyl)-5,10,15,20-tetraphenylporphyrin. 1-(2-Methoxycarbonylvinyl)-5,10,15,20-tetraphenylporphyrin was synthesized in 90% yield in the same way as the isomers of its copper complex (XV and XVIII) by the reaction of porphyrin IV with phosphorane A in xylene. Its Z and E isomers had close R_f values, and we were unable to separate them. Results of elementary analysis of the mixture of isomers: Found: C 82.8; H 5.0; N 8.1%. $C_{48}H_{34}N_4O_2$. Calculated: C 82.5; H 4.9; N 8.0%. Isomers XIV and XVII were obtained from the corresponding copper complexes XV and XVIII. A 12-mg sample of copper complex XV was dissolved in a mixture of 2 ml of $POCl_3$ and 0.2 ml of water. After 1 h, 50 ml of cold water was added, and the mixture was made alkaline to pH 8-9 with ammonium hydroxide. The porphyrin was extracted with chloroform, and the solution was passed through a layer of aluminum oxide and evaporated to dryness. The residue was crystallized from chloroform—methanol to give 10 mg (91%) of porphyrin XIV. IR spectrum: 1715 cm^{-1} (C=O). PMR spectrum: 8.76-8.83 (7H, m, β-H), 6.90 (1H, d, J = 11.8 Hz, $CH=CHCO_2CH_3$), 5.65 (1H, d, J = 11.8 Hz, $CH=CHCO_2CH_3$), 3.55 (3H, s, $-OCH_3$), and −2.55 ppm (2H, s, NH). Mass spectrum, m/z (%): 698 (M^+, 100) and 639 (12). Similarly, 12 mg of copper complex XVIII gave 9.2 mg (84%) of porphyrin XVII. IR spectrum: 1705 cm^{-1} (C=O). PMR spectrum: 8.77-8.97 (7H, m, β-H), 7.41 (1H, d, J = 15.5 Hz, $CH=CHCO_2CH_3$), 6.55 (1H, d, J = 15.5 Hz, $CH=CHCO_2CH_3$), 3.71 (3H, s, OCH_3), and −2.45 ppm (2H, s, NH). Mass spectrum, m/z (%): 698 (M^+, 100), 639 (7), and 349 (M^{2+}, 5).

1-(2-Diethylamidocarbonylvinyl)-5,10,15,20-tetraphenylporphyrin (XX). A mixture of 166 mg of porphyrin IV, 1 g of phosphorane B, and 25 ml of xylene was refluxed for 9 h, after which the solvent was removed *in vacuo*, and the residue was dissolved in chloroform-benzene (1:1) and passed through a layer of aluminum oxide and chromatographed with a column filled with silica gel. Crystallization from a mixture of chloroform with methanol gave 78 mg (40%) of porphyrin XX. IR spectrum: 1650 cm^{-1} (C=O). PMR spectrum: 8.78-8.88 (7H, m, β-H), 7.41 (1H, d, J = 15.0 Hz, **CH**=CHCONEt$_2$), 6.84 (1H, d, J = 15.0 Hz, CH=**CH**CONEt$_2$), 3.48 (2H, q, **CH$_2$**·CH$_3$), 1.26 (3H, t, CH$_2$**CH$_3$**), and −2.49 ppm (2H, s, NH). Mass spectrum, m/z (%): 739 (M^+, 100), 668 (27), 667 (20), 640 (29), and 639 (34). Found: N 8.9%. $C_{51}H_{41}N_5O$. Calculated: N 9.5%. Copper complex XXI, which was found to be an individual compound with R_f 0.34 (C), was obtained to identify the Z and E isomers of porphyrin XX by heating it in chloroform with copper acetate.

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