

Ethyl N-Hexafluoroisopropoxyoxamate (XVI). A 0.02-mole sample of NaHCO_3 was added at 0°C to a solution of 4.49 g (0.01 mole) of XV in 20 ml of pyridine, and the mixture was stirred at this temperature for 1 h. The pyridine was then removed *in vacuo*, the residue was extracted with CCl_4 , the filtrate was evaporated, and the residual oil was dissolved in hot CCl_4 . Cooling of the solution yielded crystalline ester XVI.

Hexafluoroisopropylamine Hydrochloride (XVII). A mixture of 2.67 g (0.01 mole) of oxamate XVI and 10 ml of a 30% hydrochloric acid was allowed to stand for 8 h, after which it was evaporated. The crystalline reaction product was washed with ether.

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PORPHYRINS.

18.* SYNTHESIS OF OCTAPROPYLPORPHYRIN BY THE METHOD OF MONOPYRROLE CYCLOTETRAMERIZATION OF 5-CARBOXY-2-METHOXYMETHYL-3,4-DIPROPYLPYRROLE. INVESTIGATION OF THE THERMOLYSIS OF meso-N-METHYLFORMALDIMINEOCTA- PROPYLPORPHYRIN

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UDC 547.749

The synthesis of octapropylporphyrin on the basis of 5-carboxy-2-methoxymethyl-3,4-dipropylpyrrole was realized. It was demonstrated that in the thermolysis of meso-N-methylformaldimineoctapropylporphyrin, 3¹,5¹-cyclo-3¹-ethylidene- and 3¹,5¹-cyclo-3¹-ethyl-5¹-(N-methylimine) derivatives are also formed in addition to 3¹,5¹-cyclo-3¹-ethylhectaporphyrin.

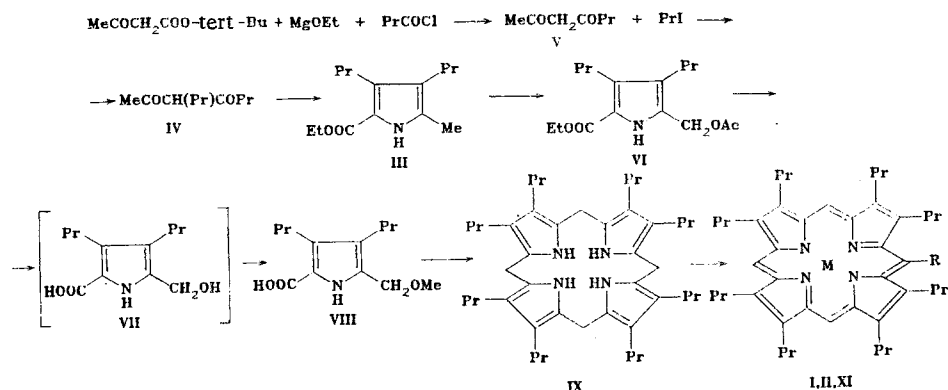
In order to confirm the general character of the thermal decomposition of Schiff bases of meso-formylporphyrins to porphyrins with a cyclopentane ring [2] and to ascertain the effect of the length of the alkyl substituents in the pyrrole rings on the course of the thermolysis, we undertook the synthesis of octapropylporphyrin (I), from which we obtained, in 92% yield, the necessary Schiff base II. To obtain the starting porphyrin I and its derivatives we used the synthetic pathway proposed by Siedel and Winkler [4][†] (see the scheme presented below).

*See [1] for Communication 17.

[†]In [4] it is erroneously assumed that pyrrole III upon oxidation by lead tetraacetate gives immediately the hydroxymethyl derivative, whereas the subsequent action of methanolic alkali leads not only to saponification of the carboxy group but also to cleavage of the carboxy group. However, it was subsequently demonstrated in other derivatives [10] that, in fact, the 2-acetoxymethyl group is, nevertheless, formed; however, the latter group may readily undergo alcoholysis in the case of brief heating in alcohol, as, for example, during recrystallization.

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The basis of the synthesis of porphyrin I consists in the preparation of pyrrole III from the corresponding diketone IV. The latter was synthesized from tert-butyl acetoacetate by condensation initially with butyryl chloride to diketone V, after which the product was treated with propyl iodide. Pyrrole III was obtained by the method in [3] by condensation of diketone IV with isonitrosomalonic ester. The subsequent conversion of pyrrole III to porphin I was accomplished through a step involving the oxidation of pyrrole III with lead tetraacetate to derive VI with subsequent saponification to the expected carboxypyrrole VII which, as has been well known for similar 5-carboxy-2-hydroxymethylpyrroles [4-9], should readily undergo cyclotetramerization in acid media in the presence of an oxidant to porphyrin I. However, during our experiments we established that carboxypyrroles of the VII type are not formed in the saponification of 2-acetoxymethyl-3,4-dialkyl-5-carboxypyrroles with methanolic alkali and that we obtained exclusively 2-methoxymethyl derivatives VIII, which we were unable to isolate in pure form (colorless crystals). The results of elementary analysis and the presence of a narrow singlet of a methoxy group at 3.36-3.37 ppm in the PMR spectra confirm this conclusion (see the experimental section). The cyclotetramerization reaction was carried out with pyrrole VIII.

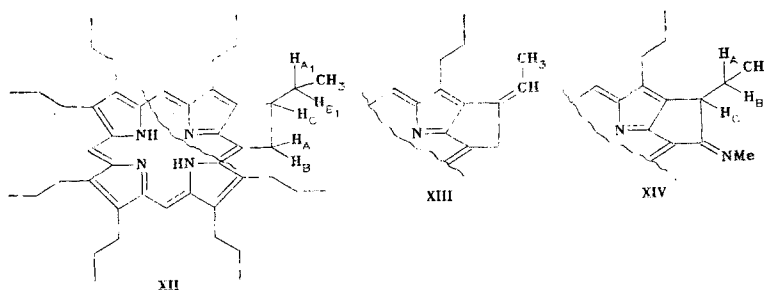


I M=2H, R=H; II M=2H, R=CH=N-CH₃; XI M=Ni, R=CH=N-CH₃

Since the oxidation of porphyrinogen IX by the method in [9] proceeds to give the product in lower yields (60-63%) than for octaethylporphyrin (74-76%), we carried out its oxidation with air oxygen in solution in chloroform. The yield of porphyrin I in this case reaches 80%.*

Vilsmeier formylation was carried out on nickel complex X, since the copper complex dissolves poorly in dichloroethane. The demetallation of the intermediate nickel complex of Schiff base XI by means of concentrated H₂SO₄ proceeds in virtually quantitative yield.

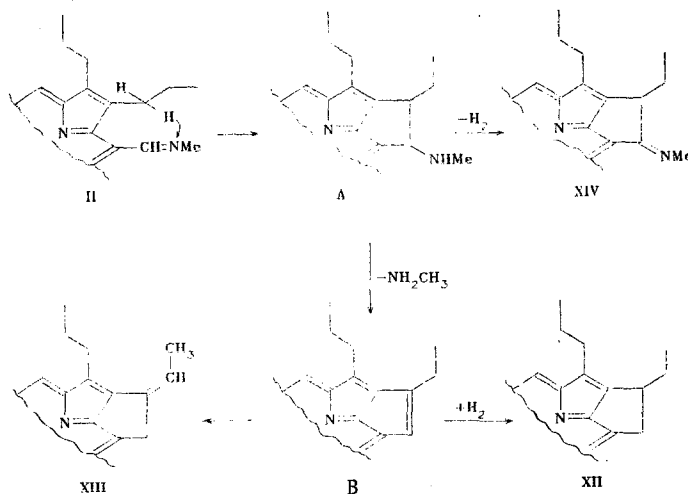
The thermolysis of porphyrin II was carried out by the standard method [2]. However, in contrast to the thermolysis of octaethylporphyrin and etioporphyrin I and II derivatives [2], in addition to the expected porphyrin XII, from the products of thermolysis in this case we also isolated two new porphyrins XIII and XIV, the structures of which were proved on the basis of the results of the electronic, IR, PMR, and mass spectra.



All of the isolated products of the thermolysis of porphyrin II suggest its isomerization to form A. Then, splitting out of methylamine and subsequent hydrogenation lead to product XII, whereas isomerization of intermediate B leads to product XIII. Porphyrin XIV is formed as the principal product of thermolysis in the dehydrogenation of isomer A.

*In a similar reaction of 2-methoxymethyl-3,4-diethyl-5-carboxypyrrole the yield of octaethylporphyrin was 80-83%.

Thus, the thermolysis of the Schiff base of meso-formylporphyrin I (II) can be represented as follows:



EXPERIMENTAL*

Heptane-2,4-dione (V). A). Meldrum's Acid [12]. A 12-ml sample of concentrated H₂SO₄ was added in small portions with stirring to a suspension prepared from 350 g of malonic acid in 360 ml of acetic anhydride, after which 300 ml of dry acetone was added rapidly, during which the temperature rose to 41°C. The solution was allowed to stand at 0°C for 12 h. The precipitated crystals of Meldrum's acid were removed by filtration, washed with cold (~0°C) water, dried in air, and recrystallized from acetone to give 290 g of the acid with mp 95–96°C.

B) tert-Butyl Acetoxyacetate [13]. A 200-ml sample of acetyl chloride was added dropwise with stirring in the course of 30 min at –2°C to a solution of 360 g of Meldrum's acid in a mixture of 500 ml of methylene chloride and 400 ml of pyridine, while maintaining the temperature from –5 to 2°C, after which the mixture was stirred for another 30 min. A mixture of 100 ml of concentrated HCl in 360 ml of water was added, after which the organic layer was separated, washed with water and dried with sodium sulfate, and the solvent was removed *in vacuo*. A 230-ml sample of tert-butanol and 300 ml of dry benzene was added to the bright-yellow precipitate, the mixture was refluxed for 2 h, the benzene was removed *in vacuo*, and the precipitate was fractionated *in vacuo* with collection of the fraction with bp 75–76°C (9 mm) to give 275 g of product, PMR spectrum (in CCl₄): 11.80 (OH, enol), 4.80 (CH, enol), 3.22 (CH₂), 2.16 (CH₃), 1.87 (CH₃, enol), and 1.44 ppm [C(CH₃)₃]. The percentage of the ketone form was 90%.

C) Heptane-2,4-dione [14]. A 52-g sample of magnesium filings was added to a two-liter three-neck flask with a stirrer, and 100 ml of absolute ethanol and 5 ml of CCl₄ were added. After the start of the reaction, 200 ml of dry benzene was added with cooling, and then ethanol and benzene (a total of 300 ml of ethanol and 500 ml of benzene) were added again in portions. To complete the reaction, the mixture was refluxed for 2 h, cooled, treated with 200 ml of dry ether and 320 ml of tert-butyl acetoacetate, the mixture was refluxed for 30 min, cooled to 10–15°C, and 210 ml of butyryl chloride was added with stirring in the course of 30 min. The mixture was refluxed for 1.5 h and allowed to stand for 12 h at room temperature. After this, dilute sulfuric acid (100 ml of concentrated H₂SO₄ and 300 ml of water) was added with stirring to the solution, and water was then added to dissolve the precipitate. The organic layer was separated, washed with a saturated solution of NaCl, the mixture was filtered, the ether and benzene were removed by distillation, 2.4 g of p-toluenesulfonic acid was added, and the mixture was heated at 140–150°C for 2 h with simultaneous removal of the volatile fractions. The residue was fractionated *in vacuo* with collection of the fraction with bp 73–74°C (21 mm) to give 156 g of the product. PMR spectrum (CCl₄): 14.94 (OH, enol), 5.38 (CH, enol), 3.43 (CH₂), 2.11 (s, CH₃), 1.98 (s, CH₃, enol), 2.19 (t), and 1.61 (m) and 0.94 ppm (t, enol, CH₂CH₂CH₃). The percentage of the enol formed was 92–94%.

*The physicochemical investigations were carried out with the apparatuses in [2].

3-Propylheptane-2,4-dione (IV). A mixture of 240 g of potassium carbonate, 216 ml of heptane-2,4-dione, 172 ml of propyl iodide and 270 ml of dry acetone was stirred with heating in the course of 20 h, after which it was cooled and filtered, and the precipitate was washed with acetone. The filtrate was evaporated, the residue was distilled *in vacuo* with collection of the fraction with bp 78–79°C (3 mm) to give 215 g of product. PMR spectrum (in CCl₄): 16.38 (s, enol OH), 3.55 (t, CH), 2.40 (t, 5-CH₂), 2.07 (s, 1-CH₃), 1.78 (q, 3¹-CH₂), 1.54 (sextet, 6-CH₂), 1.20 (m, 3²-CH₂), 0.95 (t, 3³-CH₃), and 0.88 ppm (t, 7-CH₃).

2-Methyl-3,4-dipropyl-5-ethoxycarbonylpyrrole (III). A 150-g sample of anhydrous sodium acetate and 35 g of zinc dust were added to a solution of 90 g of 3-propyl-2,4-heptanedione and 320 ml of acetic acid, after which, with vigorous stirring, 70 ml of a solution prepared from 120 g of isonitrosylmalonic ester, 100 ml of acetic acid, and 50 ml of water was added. The solution heated up very rapidly spontaneously. Zinc dust (105 g) and 210 ml of a solution of isonitrosylmalonic ester were added similarly in parts at 110°C. The solution was refluxed for 3 h, after which the hot solution was poured into water. After 12 h, the precipitate was removed by filtration, washed with water, dried, and recrystallized from hexane to give 51 g (39%) of the pyrrole with mp 101–102°C. PMR spectrum: 8.80 (broad s, NH), 4.26 (q) and 1.34 (t, COOC₂H₅), 2.65 (t), 1.45 (m), and 6.96 (t, 4-CH₂CH₂CH₃), 2.33 (t), 1.45 (m) and 0.92 (t, 3-CH₂CH₂CH₃), and 2.20 ppm (s, 2-CH₃).

2-Acetoxymethyl-3,4-dipropyl-5-ethoxycarbonylpyrrole (VI). A 60-g sample of 2-methyl-3,4-dipropyl-5-ethoxycarbonylpyrrole was dissolved in 600 ml of glacial acetic acid, and 113 g of lead tetraacetate was added with vigorous stirring in portions. After completion of the reaction (as tested by the addition of water), the reaction mixture was poured into water and the precipitate was removed by filtration, washed with water, dried, and crystallized from hexane to give 65 g (87%) of the pyrrole with mp 104–105°C. PMR spectrum: 9.20 (broad s, NH), 5.20 (s, 2-CH₂O), 4.27 (q) and 1.33 (t, 5-COOC₂H₅), 2.65 (t), 1.45 (m) and 0.95 (t, 4-CH₂CH₂-CH₃), 2.40 (t), 1.47 (m) and 0.92 (t, 3-CH₂CH₂CH₃), and 2.05 ppm (3H, s, 2-OCOCH₃).

2-Methoxymethyl-3,4-dipropyl-5-carboxypyrrole (VIII). A solution of 6 g of pyrrole VI dissolved in 12 g KOH in 100 ml of methanol was refluxed for 4 h, after which 40 ml of water was added, and the methanol was removed *in vacuo*. The dark oily precipitate that formed on the surface of the aqueous layer was dissolved by the addition of 70 ml water. The solution was acidified, with ice cooling, with dilute hydrochloric acid (18 ml of concentrated HCl and 80 ml of water, 60–65 ml). The brown precipitate (0.4–0.7 g) was removed by filtration, the filtrate was shaken with activated charcoal (OU-A) and the mixture was filtered. The colorless filtrate was acidified to pH 5.5–6, and the resulting crystalline white precipitate was removed by filtration, washed with water, and dried *in vacuo* over P₂O₅ to give 3.5–3.9 g (72–80%) of a product with mp 141–142°C. PMR spectrum: 11.0 (broad band, 5-CHH), 9.04 (broad s, NH), 4.41 (s, 2-CH₂O), 3.37 (s, 2-OCH₃), 2.70 (t), 1.56 (m) and 0.96 (t, 4-CH₂CH₂CH₃), 2.37 (t), 1.46 (m), and 0.93 ppm (t, 3-CH₂CH₂CH₃). Mass spectrum, m/z (%): 239 (M⁺, 75), 210 (100), 208 (50), 180 (60), 178 (50). Found: C 65.8; H 9.0; N 5.7%. C₁₃H₂₁NO₃. Calculated: C 65.3; H 8.8; N 5.9%.

2-Methoxymethyl-4-methyl-3-ethyl-5-carboxypyrrole. This compound was obtained by refluxing 6 g of the corresponding 2-acetoxymethylpyrrole for 3–4 h under the conditions presented for pyrrole VIII. The yield of product with mp 166–167°C was 3.5–3.7 g (75–79%). PMR spectrum: 10.8 (broad band, 5-COOH), 9.1 (broad s, NH), 4.43 (s, 2-CH₂), 3.36 (s, 2-OCH₃), 2.43 (q) and 1.07 (t, 3-C₂H), and 2.32 ppm (s, 4-CH₃). Mass spectrum, m/z (%): 197 (M⁺, 70), 182 (15), 166 (100), 168 (10), 152 (25), 48 (60). Found: C 60.2; H 7.9; N 6.9%. C₁₀H₁₅NO₃. Calculated: C 60.9; H 7.6; N 7.1%.

2-Methoxymethyl-3,4-diethyl-5-carboxypyrrole. A mixture of 8 g of the corresponding 2-acetoxymethylpyrrole in 120 ml of methanol with 16 g KOH was refluxed for 3 h, after which 50 ml of water was added, and the methanol was removed *in vacuo*. The oily residue was dissolved by the addition of 90–100 ml of water with subsequent treatment as in the case of pyrrole VIII to give 5.1–5.2 g (80.6–82%) of a product with mp 146–147°C. PMR spectrum: 11.3 (broad band, 5-COOH), 9.2 (broad s, NH), 4.41 (s, 2-CH₂), 3.37 (s, 2-OCH₃), 2.70 (q) and 1.14 (t, 4-C₂H₅), 2.37 (q) and 1.07 ppm (t, 3-C₂H₅). Mass spectrum, m/z (%): 211 (M⁺, 70), 196 (15), 182 (10), 180 (100), 166 (30), 162 (77). Found: C 61.9; H 8.2; N 6.4%. C₁₁H₁₇NO₃. Calculated: C 62.6; H 8.1; N 6.6%.

2,3,7,8,12,13,17,18-Octapropyl-21H,23H-porphin (I). A 2.16-sample of pyrrole was dissolved in 80 ml of methanol, 0.45 ml of dilute hydrochloric acid (1:5) was added, and the mixture was heated in a bath for 65°C for 4 min after the formation of the precipitated octa-

propylporphyrinogen IX [note that the specially isolated octapropylporphyrinogen IX, from similar experiments had mp 213–214°C; PMR spectrum: 6.87 (broad s, NH), 3.69 (s, meso-CH₂), 2.32 (t), 1.46 (m), and 0.94 (t, CH₂CH₂CH₃). IR spectrum (in KBr pellets): ν_{bond} 3450 and ν_{as} 3365 cm⁻¹ (NH); (in CCl₄): 3463 and 3442 CN⁻¹], the mixture was neutralized with a sodium acetate solution in methanol, evaporated *in vacuo*, and the residue was treated with 400–450 ml of chloroform. After 3 days, the solution was filtered through a layer of aluminum oxide, and the fraction containing the porphyrin was evaporated and crystallized from chloroform-methanol to give 1.16–1.18 g (79.5–80.6%) of the porphyrin. Electronic spectrum (in CHCl₃): λ_{max} ($\epsilon \cdot 10^{-3}$): 401 (223), 499 (14.3), 503 sh (13.9), 536 (11.0), 568 (7.25), 595 sh (1.24), and 621 nm (5.4). PMR spectrum: 10.09 (s, meso-H), 4.05 (t), 2.37 (sextet), 1.36 (t, CH₂CH₂CH₃), and -3.70 ppm (s, NH). Mass spectrum, m/z (%): 646 (M⁺, 100), 617 (25), 588 (7), 559 (7).

5-(N-Methylformalimine)-2,3,7,8,12,13,17,18-octapropyl-21H,23H-porphin (II). A solution of 1.2 g of nickel acetate in a mixture of 10 ml of acetic acid and 20 ml of DMF was added to a refluxing solution of 3.6 g of octapropylporphyrin I in 150 ml of DMF, after which the mixture was refluxed for 5 min, cooled, and the precipitated crystalline precipitate of nickel complex X in the form of dark-red needles was removed by filtration, washed with methanol, and dried to give the product in quantitative yield. PMR spectrum: 9.75 (s, meso-H), 3.87 (t), and 2.25 (sextet) and 1.29 ppm (t, J = 7.4 Hz, CH₂CH₂CH₃). A 3.85-g sample of complex X and the Vilsmeier complex, obtained from 55 ml of POCl₃ and 40 ml of DMF, were heated in 1.5 liters of dry dichloroethane at 70–75°C for 30 min, after which the solvent was removed *in vacuo*, and the residue was poured over ice. The precipitated "phosphorus complex" was removed by filtration, washed with water, dissolved in 150 ml of chloroform at 40–50°C, 15 ml of 25% aqueous methylamine solution was added, and the mixture was shaken for 5 min. The organic layer was separated, washed with water, and filtered through a 5-cm layer of silica gel. The principal substance was eluted with chloroform-ether (8:1), and the eluate was evaporated to dryness to give complex XI, which was dissolved in 100 ml of concentrated H₂SO₄ with vigorous stirring. After 1 h, the solution was poured over 0.5 kg of finely crushed ice, and the aqueous mixture was neutralized with ammonium hydroxide carefully with cooling. The resulting precipitate was removed by filtration, washed on the filter with water, dried at 70–100°C, and dissolved in the minimum amount of chloroform. The chloroform solution was chromatographed with a column (4 by 10 cm) packed with silica gel by means of chloroform, and, subsequently, chloroform-ether (5:1). A very slight amount of a meso-formyloctapropylporphyrin impurity was isolated initially. The principal fraction was evaporated to a small volume, ethanol was added gradually, and the resulting crystalline precipitate was removed by filtration and air dried to give 3.45 g (83%) of porphyrin II. PMR spectrum: 10.86 (1H, q, J = 1.9 Hz, CH=NMe;), 10.12 (2H, s, meso-H), 9.94 (1H, s, meso-H), 4.09 (3H, d, J = 1.9 Hz, N-CH₃), 4.01–4.03 (12H, overlapped t, CH₂CH₂CH₃), 3.72 (4H, t, CH₂CH₂CH₃), 2.34 (12H, m, CH₂CH₂CH₃), 2.0 (4H, sextet, CH₂CH₂CH₃), 1.36, 1.33, and 1.27 (24H, all t, CH₃), and -3.27 ppm (NH). PMR spectrum of complex XI: 10.70 (broad s, CH=N-Me), 9.48 and 9.47 (2H and 1H, all s, meso-H), 3.79 (s, N-CH₃), 3.75–3.79 (t), 2.10–2.22 (m) and 1.25–1.27 (t, all overlapped, 6-CH₂CH₂CH₃), 3.56 (t), 1.95 (m) and 1.25 ppm (t, all overlapped 2-CH₂CH₂CH₃).

Thermolysis of Porphyrin (II). A suspension of 500 ml of porphyrin II in 10 ml of chloroform was evaporated in an ampul [2], and the residue was heated *in vacuo* (0.05–0.3 torr) for 4 min and 30 sec, after which the mixture was cooled, dissolved in chloroform and chromatographed with a column (2.5 by 50 cm) packed with silica gel. The mobile bright-red zone was separated with chloroform-carbon tetrachloride (1:1) and constituted fraction A. Subsequent elution with chloroform gave the more polar fraction B. The substance from fraction A (286 mg), which consisted of two porphyrins in a ratio of 1:2.5 (according to the PMR spectral data), was subjected to repeated chromatography on silica gel in a chloroform-carbon tetrachloride system (1:2). The more mobile substance (65 mg) was identified as 3¹,5¹-cyclo-3¹-ethylidene-2,7,8,12,13,17,18-heptapropyl-21H,23H-porphin (XIII). PMR spectrum: 10.01 and 9.99 (2H and 1H, all s, meso-H), 6.90 (1H, q, =CH-CH₃), 5.88 (2H, broad s, exocyclic CH₂), 2.46 (3H, d, =CH-CH₃, J = 7.5 Hz), 3.95–4.09, 2.24–2.36, and 1.30–1.41 (7-CH₂CH₂CH₃), and -2.71 and -3.54 ppm (NH). Mass spectrum, m/z (%): 656 (M⁺, 100), 627 (15), 598 (5). The other substance (180 mg) was identified as 3¹,5¹-cyclo-3¹-ethyl-2,7,8,12,13,17,18-heptapropyl-21H,23H-porphin (XII). PMR spectrum: 10.05, 10.00, and 9.99 (3H, all s, meso-H), 5.59 (1H, dd, J_{AB} = 16.5, J_{AC} = 6.6 Hz, H_A), 5.07 (1H, dd, J_{BC} = 2.2 Hz, H_B), 4.50 (1H, m, H_C), 3.97–4.10 (14H, overlapped t, CH₂CH₂CH₃), 2.63 and 2.22 (2H, two m, 3²-CH₂, J_{A₁B₁} = 14.5, J_{A₁C} = 5 Hz), 2.36 (12H, m, CH₂CH₂CH₃), 2.22 (2H, m, 2-CH₂CH₂CH₃), 1.36–1.38 (21H, m, -CH₃), 1.28 (3H, t, 3³-CH₃), and -2.90 and -3.67 ppm (2H, s, H). Mass spectrum, m/z (%): 658 (M⁺, 100), 643 (3), 629 (20), 600 (5).

The substance from fraction B was dissolved in 10 ml of chloroform, 200 mg of zinc acetate in 5 ml of methanol was added, and the mixture was heated for 5 min. It was then filtered through a layer of aluminum oxide (2 cm) and chromatographed with a column (2.5 by 5 cm) packed with silica gel, initially with chloroform to remove the impurities, and then with chloroform-acetone (1:1) to elute the principal substance, which had a bright-green color on the column. Electronic spectrum (in CHCl_3), λ_{max} : 421 (28.0), 556 (1.0), 595 nm (1.2). Demetallation of the zinc complex yielded 55 mg of 3¹,5¹-cyclo-5¹-(N-methylamino)-2,7,8,12,13,17,18-heptapropyl-3¹-ethyl-21H,23H-porphyrin (XIV). Electronic spectrum (in CCl_3), λ_{max} : 417 (14.9), 516 (1.0), 552 (0.43), 581 (0.47), 635 nm (0.78): (in CHCl_3 + 1% CF_3COOH): 428 (13.4), 572 nm (0.47), 605 nm (0.59), 655 (1.11). Mass spectrum, m/z (%): 685 (M^+ , 100), 670 (70), 656 (45), 642 (90). PMR spectrum of zinc complex of porphyrin XIV: 9.97, 9.84, and 9.77 (all s, meso-H), 5.32 (1H, m, 3¹-H), 5.01, 4.11, 2.24, 2.0 (4H, m, 7- $\text{CH}_2\text{CH}_2\text{CH}_3$), 4.05 (s, N-Me), 2.69, 2.59 (2H, m, 3²- CH_2 , $J_{\text{AB}} = 14.5$, $J_{\text{BC}} = 6.6$, $J_{\text{AC}} = 3.6$, $J_{\text{A-CH}_3} = J_{\text{B-CH}_3} = 7.5$ Hz), 1.04 (3H, t, 3³- CH_3), 3.82-3.98 (m), 2.27-2.43 (m), and 1.27-1.39 (t, all overlapped $\text{CH}_2\text{-CH}_2\text{-CH}_3$).

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