The synthesis of dimers in which the macrocycles are connected by an ester bond was accomplished starting from tetraphenylporphyrin. Dimers containing the metal in one and two porphyrin rings were obtained. It is shown that exclusively the E isomer of 1-(2-carboxyvinyl)-5,10,15,20-tetraphenylporphyrin is formed in the decarboxylation of 1-(2,2-dicarboxyvinyl)-5,10,15,20-tetraphenylporphyrin.

Covalently bonded bisporphyrins and their metal complexes have recently been the subject of intensive study [1]. Diverse derivatives of dimeric compounds of metalloporphyrins have been synthesized in order to create efficient photocatalysts [2, 3], as well as to study photosynthesis [4]. 5,10,15,20-Tetraphenylporphyrin (TPP) is most often used for these purposes because of its accessibility. Syntheses of bisporphyrins on the basis of TPP, in which connection of the macrocycles occurs at one of the aryl groups, have been described [5-7]. We have synthesized dimers of TPP that are connected by an ester bond at the β positions of the porphyrin ring.

Hydroxy and carboxy derivatives of TPP were obtained for the synthesis of the bisporphyrins. 2-Formyl-5,10,15,20-tetraphenylporphyrin (III) was synthesized by a known method [8] from porphyrin I, while copper complex (IV) was synthesized from porphyrin (II) [9]. The formyl groups of derivatives III and IV were reduced with sodium borohydride to hydroxymethyl groups with the production of 2-hydroxymethyl-5,10,15,20-tetraphenylporphyrin V and its copper complex VI, respectively.

We used the Knoevenagel reaction in the synthesis of the carboxy component [9]. The copper complex (VII) of 1-[2,2-bis(methoxycarbonyl)vinyl]-5,10,15,20-tetraphenylporphyrin was obtained in 63% yield in the reaction of IV with dimethyl malonate. The copper was removed from complex VII by passing hydrogen chloride into a mixture of dichloroethane and
methanol (10:1) in the presence of catalytic amounts of trifluoroacetic acid; the yield of 1-[2,2-bis(methoxycarbonyl)vinyl]-5,10,15,20-tetraphenylporphyrin (VIII) was 93%. Absorption bands corresponding to the stretching vibrations of an ester carbonyl group (1732 cm⁻¹) and a conjugated double bond (1615 cm⁻¹) are present in the IR spectrum of VIII. Compounds VII and VIII were very stable, and we were unable to remove one of the carbomethoxy groups by pyrolysis in pyridine. To obtain IX we carried out a similar Knoevenagel reaction, but with malonic acid in this case. The very high polarity of the copper complex (VIIa) of 2-(2,2-dicarboxyvinyl)-5,10,15,20-tetraphenylporphyrin made it possible to use, for its isolation, chromatography without prior workup of the reaction mass and also made it possible to reuse the unchanged formyl derivative IV.

Because of the low solubility of VIIa in organic solvents, the copper was removed from it by the method in [10] in order to prove the structure. The yield of 2-(2,2-dicarboxyvinyl)-5,10,15,20-tetraphenylporphyrin (VIIIa) was 50% based on IV. It should be noted that the IR spectrum of VIIIa contains absorption bands corresponding to the stretching vibrations of a carboxy C=O group (1705 cm⁻¹) and an ionized carboxy group (1678 cm⁻¹).

The decarboxylation of porphyrin VIIIa was carried out by refluxing in pyridine in the presence of lithium fluoride. 2-(2-Carboxyvinyl)-5,10,15,20-tetraphenylporphyrin (IX) was obtained in 69% yield after workup of the reaction mixture and chromatography on silica gel. According to the data in [11], 2-(2-Carboxyvinyl)-5,10,15,20-tetraphenylporphyrin has a value of 15.5 Hz; this is in good agreement with the data in [8] for the E isomer of the methyl ester of porphyrin IX (15.5 Hz).

The methyl ester of porphyrin IX was previously synthesized [7, 8] on the basis of formylporphyrin III and its copper complex IV by the Wittig reaction in the form of a mixture of the E and Z isomers. Exclusively the E isomer of porphyrin IX is formed in our case. By chromatography of the products of the decarboxylation of porphyrin VIIIa we isolated a compound (4% yield), to which bisporphyrin XV structure with conjugated macrocycles was assigned on the basis of data from the IR, electronic, and PMR spectra. The IR spectrum of bisporphyrin XV does not contain absorption bands corresponding to the stretching vibrations of carbonyl groups but does contain absorption bands that are characteristic for conjugated double bonds. The electronic spectrum contains two Soret bands (437 and 472 nm), and in the visible region the absorption maximum of one of the four bands has a value of 701 nm. According to the data in [11], conjugated bisporphyrins have absorption bands at 700-750 nm. The PMR spectrum also confirms the presence of conjugated double bonds.

Zinc complex XVa was obtained by treatment of dimer XV with a saturated solution of zinc acetate in methanol.

To construct the ester bond in the synthesis of the dimers we selected O-acelation with the use of an acid chloride. Treatment of porphyrin IX with oxalyl chloride gave acid chloride X, which was stable and was isolated and characterized completely. The absorption band at 1775 cm⁻¹ in the IR spectrum of this compound corresponds to the stretching vibrations of the carbonyl group in acid chlorides.

Dimer XI was synthesized by the reaction of acid chloride X in refluxing dichloroethane or pyridine with porphyrin V for 2 h in the presence of 4-N,N-dimethylaminopyridine. The dimer was isolated by preparative TLC on silica gel, and the yield was 21%. The electronic spectrum of dimer XI contains two Soret bands, which correspond to the Soret bands of the monomers that make up the dimer - 419 nm (V) and 436 nm (IX). The PMR spectrum of dimer XI is the sum of the PMR spectra of porphyrins V and IX, from which it was synthesized. For definitive proof of the structure of dimer XI we carried out its alkaline hydrolysis in a mixture of dioxane and an 80% solution of potassium hydroxide in 80% ethanol. After workup of the reaction and chromatography on silica gel we obtained only two reactions products, viz., porphyrins V and IX; this was established by chromatographic comparison of the reaction products with standard monomers, as well as by comparison of their electronic spectra with the spectra of starting porphyrins V and IX, which coincided completely.

Zinc complex XIV was obtained in 91% yield by treatment of dimer XI with zinc acetate in methanol. The electronic spectrum of this compound contains two Soret bands (424 and 434 nm). The PMR spectrum of zinc complex XIV is the sum of the spectra of the monomers that make up the dimer.

To obtain dimers with different metals we synthesized dimer XII, which contains a copper atom in only one porphyrin macrocycle. The condensation of acid chloride X with copper