ml of hexane, and the precipitated disulfide was removed by filtration and dried to give a product with mp 145-147°C (ethyl acetate). IR spectrum (KBr): 1660, 1640 cm^{-1} (C=C, C=N). UV spectrum (ethanol), λ_{max}, nm (log ε): 245 (4.27), 294 (4.1 sh). PMR spectrum ($CDCl_3$): 1.09 (6H, s), 1.26 [6H, s, 2,5-$(CH_3)_2$], 2.25 (3H, s, N—CH_3), 5.86 (1H, s, —CH=), 7.2 ppm (5H, m, C_6H_5). ^{13}C NMR spectrum ($CDCl_3$): 23.95, 24.98 [2,5-$(CH_3)_2$]; 26.94 (N—CH_3); 62.97 ($C_{(5)}$); 89.83 ($C_{(2)}$); 113.73 (—CH=); 127.91, 128.32, 128.73, 139.34 (C_6H_5); 142.70 ($C_{(4)}$); 150.54 ppm (=C—). The yield was 0.2 g (70%). PMR spectrum ($CDCl_3$) of V: 1.05 [6H, s, $(CH_3)_2$], 2.41 (3H, br.s, forms B and C), 2.46 (3-CH_3—, form A), 3.56 (3H, br.s, forms B and C), 3.63 (5-CH_2—, form A), 4.05 (br.s, $COCH_2$—, form A), 5.20 (1H, br.s, —C=, forms B and C), 7.2 (3H, m), 7.7 ppm (2H, m, C_6H_5). ^{13}C NMR spectrum ($CDCl_3$): 27.48 [4-$(CH_3)_2$] (B, C); 27.72 [4-$(CH_3)_2$] (A); 34.39 ($C_{(4)}$) (B, C); 36.89 ($C_{(4)}$) (A); 46.22 ($C_{(3)}$) (A); 47.48 ($C_{(3)}$) (B, C); 71.10 ($C_{(5)}$), (B, C); 74.43 ($C_{(5)}$), (A); 85.96 (—CH—), (B, C); 126.53, 128.0, 129.94, 133.52 (C_6H_5) (B, C); 129.12, 128.59 (C_6H_5) (A); 137.02 ($C_{(2)}$) (A); 151.64 ($C_{(2)}$) (B, C); 171.61 (=C—OH) (B, C); 194.06 ppm (C=O) (A).

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SYNTHESIS OF A DONOR-ACCEPTOR PHOTOSYNTHETIC SYSTEM CONTAINING COVALENTLY BOUND AMINE, PORPHYRIN, AND QUINONE

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The synthesis of a diquinone derivative of the amino-containing analog of hematoporphyrin IX, obtained by the sequential modification of the tetramethyl hematoporphyrin IX, was accomplished.

A key stage in photosynthesis is the separation of the charges in the reaction centers with the subsequent stabilization of this state by the transfer of an electron across a series of intermediate acceptors of the chlorine structure to the primary quinone acceptor [1]. Covalently bound porphyrin—quinone compounds containing the main components of the electron transport chain (the photosensitizer and the electron acceptor) serve as convenient synthetic models for the study of the processes associated with the absorption and transformation of solar energy in photosynthesis [2, 3] (see scheme on following page).

Investigations performed recently [4, 5] have shown the principle possibility of the utilization of the diquinone derivatives of deuteroporphyrin IX (Ia, b; IIa, b) for the simulation of the intermediate stage of the primary separation of the charges in photosynthesis — the stage of the transfer of the electron from the pheophytin to the quinone. The main idea of the experiment consisted of the preliminary photoreduction of the porphyrin fragment in the compounds (Ia, b) and (IIa, b) by an electron-donor solvent — triethylamine. The dark transfer of the electron to the quinone fragment was accomplished in the final stage. However, the products of the photoreaction — the anion radicals of the porphyrin and the quinone — could only be detected successfully at a low temperature

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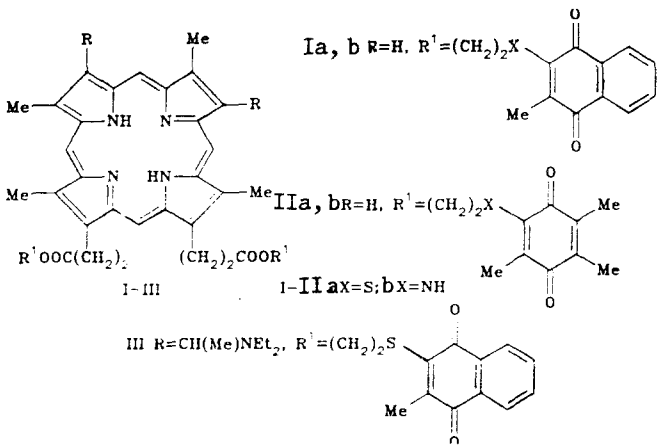
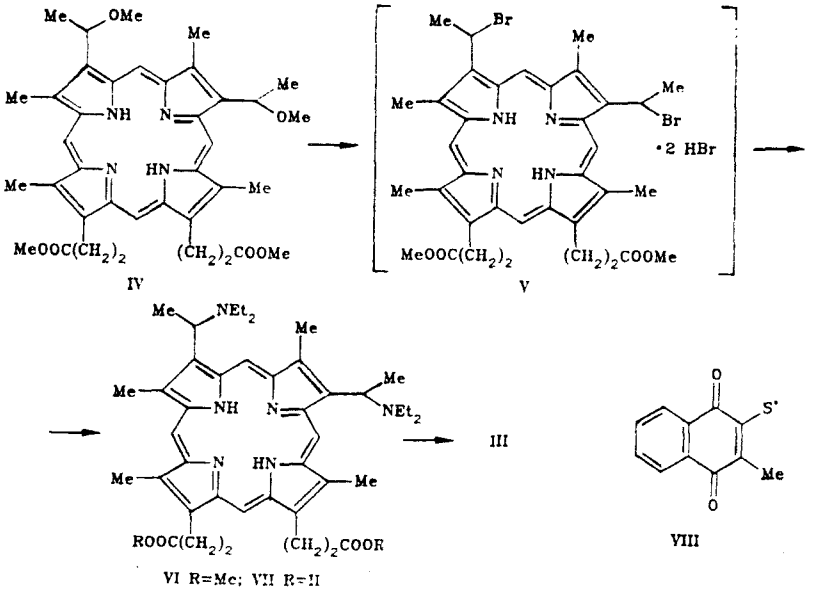


(77 K) in consequence of the lability of this system. The covalent binding of all three components (the porphyrin, the amine, and the quinone on a mutual basis) could both permit a solution to the problem of the stability of the system, and allow a detailed study of the process of the intramolecular transfer of the electron.

We synthesized the model structure (III) based on the amino derivative of hematoporphyrin IX, in which the hydroxyl groups are substituted by diethylamine groups, and where the most effective of the investigated acceptors [5] (2-(2-hydroxyethyl)thio-3-methyl-1,4-naphthoquinone (HNQ) [6, 7]) were introduced as the ester component.

The synthesis of compound (III) was accomplished according to the scheme from the readily available tetramethyl hematoporphyrin IX (IV) [8]. The treatment of the porphyrin (IV) with acetic acid saturated with HBr gave the intermediate dihydrobromide (V), which reacted with diethylamine by a general method [9] and underwent subsequent esterification in $MeOH/H_2SO_4$,* after the distillation of the diethylamine, with the formation of the porphyrin (VI) with the total yield of 53%. The structure of the porphyrin (VI) was shown by the method of PMR and was confirmed by the data of the elemental analysis and the IR spectra. A characteristic feature of the PMR spectrum of the porphyrin (VI) is the splitting of the signals of the α- and β-meso protons into two components, indicating the formation of the equally probable amount of the R- and S-isomers at the 2^1 and 4^1 atoms of the carbon of the $CH(NEt_2)Me$ groups in the process of the synthesis. The diethylamino groups appear in the form of two quadruplets at 3.30 and 3.28 ppm and two closely situated triplets in the region of 1.21 ppm; this indicates the nonequivalence of the magnetic environment of the substituents at positions 2 and 4 of the porphyrin ring.

Scheme



*The process of the esterification can be excluded with small (up to 100 mg) amounts of the porphyrin (IV).

The acid hydrolysis of the porphyrin (VI) led to the isolation of the corresponding diacid (VII), which was condensed with HNQ by the method of mixed anhydrides utilizing the tert-butylpyrocarbonate—4-dimethylaminopyridine system [6, 7]. The purification of product (III) was carried out using preparative TLC on Kieselgel 60 F_{254} (Merck). The yield of the triad molecule (III) comprised 28%.

The structure of compound (III) was confirmed by the data of the UV, IR, and PMR spectroscopy, and mass spectrometry (the method of fast atom bombardment).

The mass spectrum of compound (III) contains the intense peak of the MH^+ ion with the m/z 1169; the molecular mass of this compound is determined on the basis of the value of its mass number. The decomposition of the MH^+ ion proceeds by means of the sequential elimination of the $NHEt_2$ and NEt_2 groups; this leads to the formation of the ions with the m/z 1096 and 1024, correspondingly. The last may lose two thiyl compounds sequentially, forming the ions with the m/z values of 821 and 618, respectively.

It is possible to come to a preliminary conclusion concerning the steric organization of the model structure on the basis of the analysis of the PMR spectral data of the molecule (III). Thus, the shifts of the signals of the quinone protons to the region of high field by 0.35-0.45 ppm by comparison with the initial HNQ for the CH protons of the naphthoquinone ring, and by 0.38 ppm for the CH_3 protons of the quinone, are observed in the PMR spectrum of compound (III). Similar changes are characteristic of porphyrinquinone compounds with a flexible covalent bridge between the chromophores [2, 6, 7], and are the consequence of the effect of the magnetic anisotropy of the porphyrin nucleus.

The UV spectrum of the triad system of (III) is the superposition of the spectra of the porphyrin and the quinone fragments in the region of 200-450 nm without a change in the form and position of the absorption bands; this indicates the absence of significant interactions between the chromophores in the basic state. The UV spectrum is the sum of the spectra of the initial porphyrin and quinone for the majority of the porphyrinquinones with a flexible covalent bridge [2].

EXPERIMENTAL

The condensation reactions were accomplished in dry solvents. The IR spectra were taken on a Shimadzu IR-435 spectrophotometer. The UV spectra were taken on the Shimadzu UV-240 and Beckman DU-8 spectrophotometers. The PMR spectra were registered in deuterochloroform using the Bruker WM-250 instrument with the working frequency of 250 MHz. The internal standard was HMDS. The mass spectrum was obtained on the Kratos MS-50 spectrometer using the bombardment with fast atoms of xenon having the energy of 6-8 KeV. Glycerol was utilized as the matrix.

1,3,5,8-Tetramethyl-2,4-di(1-diethylaminoethyl)-6,7-di(2-methoxycarbonylethyl)porphyrin (VI) ($C_{44}H_{60}N_6$). The solution of 100 mg (0.15 mmole) of the porphyrin (IV) in 2 ml of glacial acetic acid saturated with HBr (d 1.47) is held for 2 h at 20°C prior to the distillation of the solvent in vacuo at the temperature <50°C. The residue is washed with methylene chloride and dried over potassium hydroxide. To the dry bromo derivative (V) are added 15 ml of methylene chloride and 2 ml (20 mmoles) of diethylamine. The mixture is stirred for 1 h at 20°C; the solvent is removed in vacuo, and 15 ml of a 5% solution of H_2SO_4 in methanol are added to the residue. After 3 h, 30 ml of water and 20 ml of a saturated solution of sodium acetate are added to the methanolic solution. The porphyrin is extracted from the reaction mass with chloroform; the organic layer is dried over $MgSO_4$ and chromatographed on a column 15 × 2.5 cm using Al_2O_3 III deg. The porphyrin (VI) (60 mg, 53.3%) is isolated from the main fraction. The electronic spectrum in chloroform [λ_{max}, nm ($\log \varepsilon$)] is as follows: 402 (5.23), 501 (4.11), 534 (3.92), 586 (3.78), and 621 (3.54). The IR spectrum (the tablet with KBr) (ν, cm^{-1}) is as follows: 1740 (CO in ester), 2815, 2870, 2930, 2980 (CH), and 3340 (NH). PMR spectrum (δ, ppm): 11.151 (1/2), 11.139 (1/2), 11.120 (1/2), 11.112 (1/2), 10.065, 10.022 (all s, 4H, meso H), 5.28 (m, 2H, CH—CH_3), 4.42 (t, 4H, CH_2CH_2CO), 3.685, 3.665, 3.65, 3.64 (all s, 18H, $COOCH_3$ and CH_3 porph.), 3.30, 3.28 (two q, 8H, CH_2CH_3), 3.10 (two t, 4H, CH_2CH_2CO), 2.08 (d, 6H, J = 6.1 Hz, CH—CH_3), 1.21 (two t, 12H, J = 6.71 Hz, CH_2CH_3), and −3.72 (s, 2H, NH).

1,3,5,8-Tetramethyl-2,4-di(1-diethylaminoethyl)-6,7-di(2-carboxyethyl)porphyrin (VII). The solution of 40 mg of the porphyrin (VI) in 20 ml of 20% HCl is kept for 12 h prior to the neutralization with ammonia solution to the pH 7. The precipitated residue is filtered, dried in vacuo over P_2O_5, dissolved in the 1:1 mixture of methanol—chloroform, and filtered through a 1-cm layer of silica gel L 40/100; the solvent is removed, and 18.3 mg (47.6%) of the porphyrin (VII) are isolated. The identification of the diacid (VII) was performed by the esterification using 5% H_2SO_4 in methanol and the comparison with the porphyrin (VI). The diester obtained after the esterification was completely identical with the initial porphyrin (VI).

1,3,5,8-Tetramethyl-2,4-di(1-diethylaminoethyl)-6,7-di[2-(2-(3-methyl-1,4-naphthoquinone-2-yl)thioethyl)oxycarbonylethyl]porphyrin (III). To the solution of 10 mg (0.015 mmole) of porphyrin (IV) in the mixture of 5 ml of chloroform and 0.5 ml of pyridine are added 8.7 mg (0.035 mmole) of HNQ prior to the addition of 7.7 mg (0.035 mmole) of tert-butylpyrocarbonate at 0°C and, after 10 min, 1 mg (0.008 mmole) of 4-dimethylaminopyridine; the mixture is stirred for 2 h at 20°C. The reaction mass is poured into 50 ml of 0.5% HCl and extracted with chloroform (3 × 10 ml). The extract is washed with water (3 × 30 ml) and dried with sodium sulfate. The solvent is removed, and the residue is chromatographed on plates (20 × 20 cm) with Kieselgel 60 F_{254} (Merck); the elution is performed with a 50:1 system of chloroform—methanol. The main porphyrin fraction is collected; the solvent is removed. The residue is smoothed out in pentane, filtered, and dried in vacuo over paraffin and P_2O_5. UV spectrum in chloroform [λ_{max}, nm ($\log \varepsilon$)]: 405.9 (5.30), 504.9 (4.22), 539.7 (4.02), 573.1 (3.91), and 627.1 (3.58). IR spectrum (mineral oil, KBr) (ν, cm^{-1}): 3295 (NH), 1731 (CO in ester), 1655 (CO quin.), 1585, and 1550 (C=C quin.). PMR spectrum (δ, ppm): 11.10 (2H), 9.93 (1H), 9.91 (1H, all s, meso H), 7.78-7.69 (4H), 7.34-7.21 (4H, all m, CH arom.), 5.34-5.24 (2H, m, CH—CH_3), 4.33 (4H, t, J = 7.5 Hz, CH_2CH_2CO), 4.27 (4H, t, J = 6.25 Hz, CH_2CH_2O), 3.66 (6H), 3.58 (3H), 3.57 (3H, all s, CH_3 porph.), 3.28-3.04 (16H, m, CH_2CH_2CO, CH_2CH_2O, CH_2CH_3), 2.06 (6H, s, CH_3 quin.), 2.04 (6H, d, J = 6 Hz, CH—CH_3), 1.25 (6H), 1.22 (6H, two t, J = 7 Hz, CH_2CH_3), and −3.7 (2H, s, NH). Mass spectrum [m/z (I_{rel}, %)]: 1169 (MH^+, 50), 1096 (85), 1024 (75), 821 (80), 618 (75), and 446 (100). The yield was 5 mg (28%).

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