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Phosphomacrocyclic Systems Based on 2,2'-Dihydroxy-1,1'-dinaphtylmethane

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Abstract—For the first time phosphomacrocyclic systems were synthesized based on 2,2'-dihydroxy-1,1'-dinaphthylmethane, other aromatic diols, and phosphorous hexaethyltriamide. Spontaneous transformation of the obtained macrocycles into the more stable 1,3,2-dioxaphosphacyn and cyclobisamidophosphite was established.

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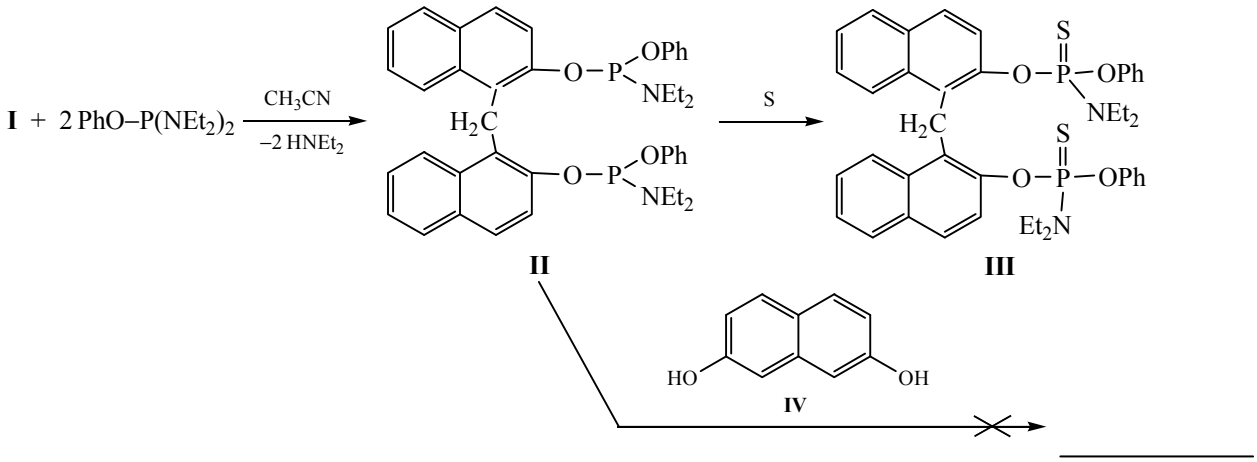
In recent years active study was initiated of the phosphorylation of dibasic aromatic systems with two sterically distant hydroxy groups using the trivalent phosphorus acids di- and by triamides. These studies resulted in the syntheses of macrocyclic constructions containing several residues of aromatic diols and derivatives of phosphorous and phosphoric acids, which can be related both to the class of phosphacyclophanes and benzocrown ethers [1]. Such compounds can be used for the synthesis of polynuclear complexes of transition metals interesting as effective catalysts, for obtaining supramolecular systems due to the capture of ions and neutral molecules, and also in the development of the structural problems of contemporary organoelemental chemistry.

Among other diatomic phenols, in the reactions with the trivalent phosphorus compounds 2,2'-dihydroxy-1,1'-dinaphthylmethane (**I**) was examined. It was established that it reacted with alkyleneamidophosphites and other cyclic derivatives of trivalent phosphorus to form open bisphosphorylated systems. The latter were used as the ligands in the catalysts of asymmetric synthesis [2, 3]. At the phosphorylation of bisnaphthol **I** with phosphorous acid triamides and with the compounds of acyclic structure occurred formation of intramolecular rings, 1,3,2-dioxaphosphacyns [4–6]. However, the use of bisnaphthol **I** as a building block for creating the macrocyclic constructions has not been studied.

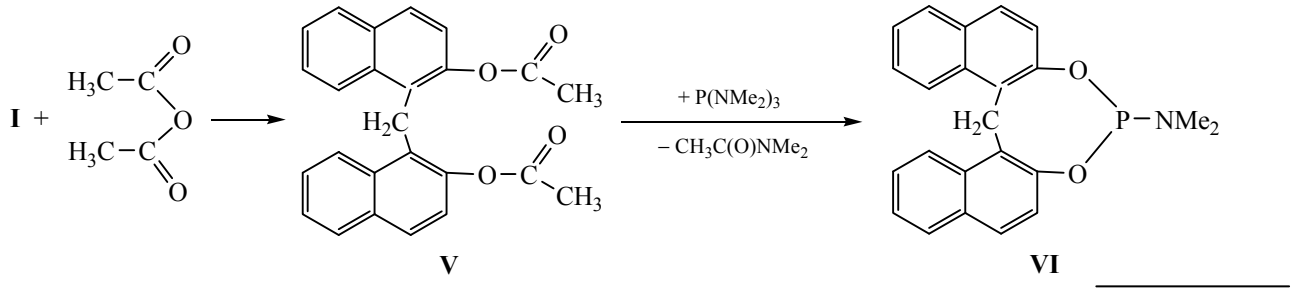
In this connection we decided to examine a possibility of application of the accessible bisnaphthol **I** as a structural element for the creation of phosphomacrocycles. For the phosphorylation of diol **I** we used phenyl phosphorous tetraethyldiamide, the amidoester that we had used earlier in the analogous syntheses [7–9]. The synthesis was performed in two stages. In the reaction of phenyl tetraethyldiamidophosphite with bisnaphthol **I** in the acetonitrile at room temperature for 2 h occurred the formation of diesteroamide (**II**), as testified the disappearance in the ^{31}P NMR spectrum of signal of the initial diamidophosphite (132.6 ppm) and the appearance of a signal at 140.4 ppm, which corresponded to compound **II**. The sulfurizaion of the reaction mass was carried out to prove its structure. The thionamidophosphate (**III**) obtained was isolated by column chromatography. In its ^{31}P NMR spectrum appeared a signal with the chemical shift 66.7 ppm. The structure of product **III** was proved by ^{1}H NMR method.

The second stage of the synthesis consisted in the reaction of bis(diesteroamide) **II** with the dibasic phenol 2,7-dihydroxynaphthalene (**IV**). The reagents **II** and **IV** were heated at 70–75ºC. Unfortunately, the desired macrocycle was not obtained, probably because of the absence of the three-dimensional correspondence between the reagents **II** and **IV**.

Acyl derivatives of phenols are known to enter into the reaction with complete phosphorous amides with



the lower reaction rate than unprotected hydroxy systems [10, 11]; therefore we decided to slow down the process of bisphosphorylation using acyl derivatives of bisnaphthol **I**. For this purpose bisnaphthol **I** was acylated by acetic anhydride and then the obtained acyl derivative (**V**) was phosphorylated with phosphorous hexamethyl- and hexaethyltriamides (HMTA and HETA). Dioxane was used as a solvent.

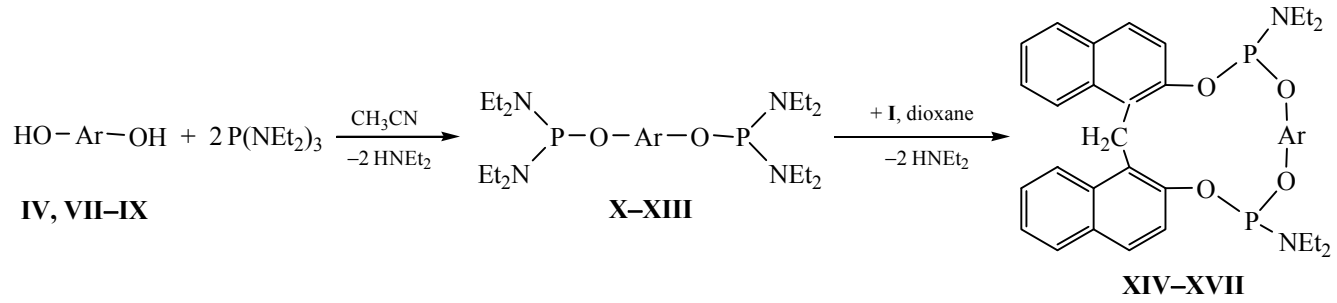


We found that the reaction with HETA does not occur even at 100ºC, whereas with HMTA it began already at 70ºC and was completed in 12 h. The reaction was considered completed when in the ^{31}P NMR spectrum of the reaction mixture disappeared the signal with the chemical shift 122.4 ppm (HMTA) and accumulated the signal with the chemical shift 138.8 ppm. At the analysis of the obtained products of phosphrylation by physicochemical methods (TLC, ^{31}P NMR, and ^{1}H NMR) we showed that regardless of the ratio of the initial reagents (1 : 2 or 1 : 3) the reaction product was 1,3,2-dioxaphosphacyn (**VI**) that had been synthesized earlier [4–6]. Thus, the initially planned reaction did not lead to the expected results and thus this scheme of synthesis could not be used to obtain the bisamidophosphites on the basis of 2,2'-dihydroxy-1,1'-dinaphthyl methane **I**.

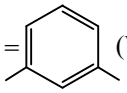
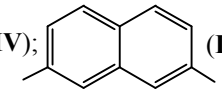
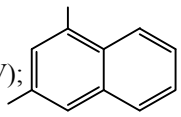
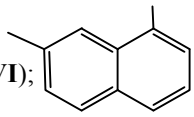
Continuing the research, we assumed that the desired macrocyclic systems would be obtained at the reverse order of the condensation: the primary phosphorylation of aromatic diols and the subsequent cyclization by reaction with one mole of bisnaphthol **I**. As the second structural blocks were selected resorcinol (**VII**) and 2,7- (**IV**); 1,3- (**VIII**) and 1,7-dihydroxynaphthalenes (**IX**), the aromatic diols with the hydroxy groups reciprocally remote in the space. Acetonitrile was selected as a solvent for the first stage of the assembling, since the reaction of bisphosphorylation in this solvent proceeds rapidly enough. For the second stage 1,4-dioxane was taken, in which the reaction products most slowly undergo the spontaneous transformation that will be considered below.

The reaction course was monitored by ^{31}P NMR spectroscopy. The first stage was regarded as complete when in the ^{31}P NMR spectrum of the reaction system only one signal in the region 132 ppm (phosphorous diamidoesther **X–XIII**) was observed. With all the selected diols this stage continued from 20 min (with 2,7-dihydroxynaphthalene) to 6 h (with resorcinol).

The second stage of the synthesis consisted in cyclophosphorylation of dinaphthylmethane **I** by the



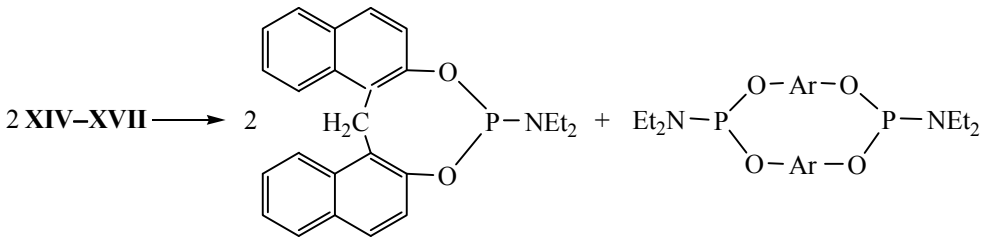
IV, VII–IX **X–XIII** **XIV–XVII**

Ar =  (**VII, X, XIV**);  (**IV, XI, XV**);  (**VIII, XII, XVI**);  (**IX, XIII, XVII**).

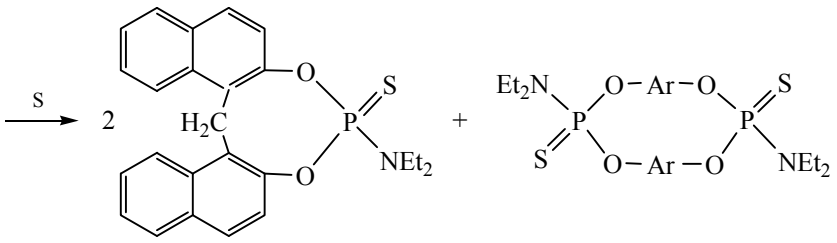
formed bisamidophosphites **X–XIII**. In the ^{31}P NMR spectrum of the reaction solution the signal in the region of 132 ppm (phosphorous diamidoester **X–XIII**) disappeared and appeared a signal in the region of 140–141 ppm. (phosphorous diesteroamide **XIV–XVII**). The phosphacyclization proceeded on the average over 3 days.

However, after a certain time from the beginning of the phosphacyclization, in the ^{31}P NMR spectrum besides the signals in the region of 140–141 ppm, began to increase the signals in the region of 142–143 ppm, characteristic of 1,3,2-dioxaphosphacyns. They grew the fastest in the case of derivative **XV**, the less in the case of derivative **XVI**. As a result, after a certain time from the solution were separated crystalline substances that according to their physicochemical characteristics were completely identical to 1,3,2-dioxaphosphacyn on the basis of 2,2'-dihydroxy-1,1'-dinaphthylmethane **I**.

Further it was shown that the selection of solvent plays a significant role in this spontaneous transformation. When the reaction mixture in acetonitrile, dioxane, or methylene chloride was left for a week, the bis(cycloamidophosphite) (**XIV–XVII**) did not remain in the solution. Most rapidly this process occurs in methylene chloride (3 days), and most slowly in dioxane (more than 8 days). We assume that the process in the solution can be described by the following scheme:



XVIII **XIX–XXII**

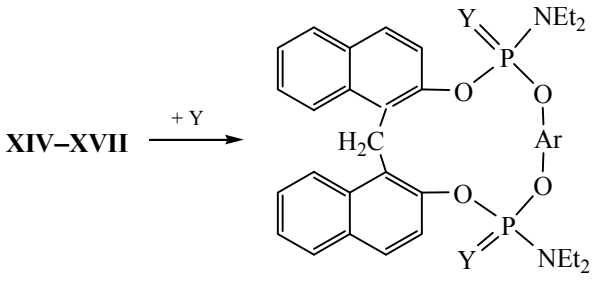


XXIII **XXIV–XXVII**

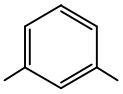
To confirm the structure of macrocycles **XVIII–XXII** the sulfurization of reaction mixture was carried out, which supported our assumptions. As a result, by column chromatography were isolated two compounds, one of which was 1,3,2-thionodioxophosphocyn (**XXIII**), and another, cyclo(bisthionoamidophosphate) **XXIV–XXVII** on the basis of aromatic diol **V–VIII**. Structure and individuality of these compounds were confirmed by the physicochemical methods (^{1}H and ^{31}P NMR spectroscopy and TLC), and the characteristics of synthesized thionoamidophosphates **XXIII–XXVII** completely coincided with those obtained earlier [12–16]. We assumed that the transformation of cycloamidophosphites **XIV–XVII** into 1,3,2-dioxaphosphacyn **XVIII** and cyclobisamidophosphites **XIX–XXII** is energetically more advantageous process, since it was shown earlier that the formation of the systems mentioned above proceeds very easily with the decrease in the steric energy [4, 13, 15].

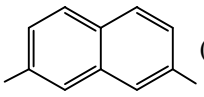
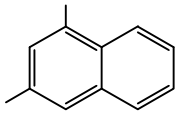
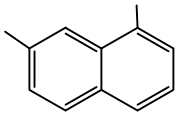
We succeeded to isolate individually on the phosphate level only the derivatives **XIV** and **XV**. Their structure and individuality were confirmed by TLC and ^{31}P, ^{1}H NMR spectroscopy. In favor of the formation of the cyclic structures **XIV** and **XV** attests the presence in the ^{1}H NMR spectrum of the characteristic splitting of the signals of methylene (bridging) protons, which appears as an AB system: two doublets with $\Delta\delta$ = 0.7 ppm and $^2J_{HH}$ ~16 Hz. At the same time, in the acyclic systems, for example, **III** and **IV**, the signals of methylene (bridging) protons are singlets. These data are completely consistent with those published for similar systems [16–18].

For the additional identification of the synthesized cyclophosphites **XIV–XVII** we carried out their sulfurization and oxidation. The sulfurization was carried out in methylene chloride by keeping for 1 day at room temperature, and the obtained substances were separated by column chromatography. The isolated cyclo(bisthionamidophosphates) **XXVIII–XXXI** are viscous oily substances. The oxidation was carried out in methylene chloride at room temperature for 1 day. As the oxidant hydropyrite was used. Phosphates (**XXXII, XXXIII**) were separated by reprecipitation to hexane.



XXVIII–XXXIII

Y = S (**XXVIII–XXXI**), O (**XXXII, XXXIII**); Ar =  (**XIV, XXVIII, XXXII**),

 (**XV, XXIX, XXXIII**),  (**XVI, XXX**),  (**XVII, XXXI**).

The isolated compounds **XXVIII–XXXIII** were characterized by the physicochemical methods (^{1}H, ^{13}C, and ^{31}P NMR, TLC, molecular weight, and elemental analysis). The ^{1}H NMR spectra of compounds **XXVIII–XXXIII** are analogous to those of respective phosphite derivatives **XIV, XV**.

Thus, for the first time we obtained phosphamacrocyclic systems containing both pentavalent and trivalent phosphorus on the basis of 2,2'-dihydroxy-1,1'-dinaphthyl methane, dibasic phenols, and phosphorous hexaethyltriamide.

EXPERIMENTAL

All syntheses were carried out with the use of anhydrous solvents in an atmosphere of dry nitrogen.

The ^{1}H and ^{31}P NMR spectra were registered on a Bruker AC-200 instrument (200 and 50 MHz

respectively) relative to internal reference TMS. The ^{31}P NMR spectra of compounds were recorded on a Bruker WP-80SY instrument at the frequency 32.4 MHz relative to 85% H_3PO_4. The mass spectra were taken on a Bruker Ultra Flex instrument (solvent $CHCl_3$, matrix dibenzoic acid). The adsorption column chromatography was accomplished on the silica gel L 100/250. The TLC analysis was carried out on the Silufol plates with the use of the systems: benzene–dioxane, 5:1 (A), benzene–dioxane, 10:1 (B), hexane–dioxane, 5:1 (C), chloroform (D). The detection of substances was achieved by iodine vapor and by calcination.

2,2'-Dihydroxy-1,1'-dinaphthylmethane **I** is obtained by the procedure [19], tetraethyldiamidophenylphosphite, by the procedure [20], phosphorous hexaethyltriamide, by the procedure [21].

2,2'-Bis (diethylamidophenylthionophosphatoxy)-1,1'-dinaphthylmethane (II). A solution of 0.363 g of bisnaphthol **I** in 10 ml of acetonitrile was added to 0.6 g of tetraethyldiamidolphosphite at room temperature, at the continuous stirring. After 4 h to the reaction mass was added 0.08 g of sulfur, and it was left standing for 2 days. Then the solvent was distilled off in a vacuum, the residue was subjected to column chromatography eluating the product with benzene. The obtained substance was dried in a vacuum for 2 h (1 mm Hg, 70ºC). Yield 85%, mp 157–158ºC, R_f 0.50 (C). ^1H NMR spectrum δ, ppm ($CDCl_3$): 1.17 t (6H, CH_3, $^3J_{HH}$ 7.3 Hz), 1.32 t (6H, CH_3, $^3J_{HH}$ 7.0 Hz), 3.46 m (8H, CH_2, $^3J_{PH}$ 14.3 Hz), 5.00 d [1H, CH_2 (bridge), $^2J_{HH}$ 15.7 Hz], 5.14 d [1H, CH_2 (bridge), $^2J_{HH}$ 15.7 Hz], 7.19 d (4H, Ph), 7.24 d (2H, CH), 7.32 t (4H, Ph, $^3J_{HH}$ 8.0 Hz), 7.36 m (2H, Ph), 7.45 m (2H, CH, $^3J_{HH}$ 8.0 Hz), 7.56 m (2H, CH, $^3J_{HH}$ 8.0 Hz, $^4J_{HH}$ 1.1 Hz), 7.74 d (2H, CH, $^3J_{HH}$ 8.8 Hz), 7.84 d (2H, CH, $^3J_{HH}$ 7.7 Hz), 8.35 d (2H, CH, $^3J_{HH}$ 8.8 Hz). ^{31}P NMR spectrum, δ, ppm (CH_3CN): 66.8. Found, %: P 8.18. $C_{41}H_2O_4P_2S_2$. Calculated, %: P 8.21.

2,2'-Diacetoxy-1,1'-dinaphthylmethane (V). 20 ml of acetic anhydride was poured to 3 g of bisnaphthol **I**, and the mixture was refluxed for 2 h. The obtained solution was left to slow cooling. The precipitated colorless crystals of diacetate **IV** were filtered 1 day later, washed with diluted acetic acid, then with ice water, and dried in a vacuum for 1 h (1 mm Hg, 80ºC). Yield 95%, mp 210–212ºC, R_f 0.85 (A). ^1H NMR spectrum, δ, ppm [$(CD_3)_2SO$]: 2.49 s (6H, CH_3), 4.69 s [2H, CH_2 (bridge)], 7.21 d (2H, CH, $^3J_{HH}$ 8.9 Hz), 7.45–7.50 m (4H, CH), 7.84 d (2H, CH, $^3J_{HH}$ 8.9 Hz), 7.95 t (2H, CH, $^3J_{HH}$ 9.2 Hz, $^4J_{HH}$ 2.4 Hz), 8.18 t (2H, CH, $^3J_{HH}$ 9.2 Hz, $^4J_{HH}$ 3.4 Hz).

Cyclobisamidophosphites (XIV–XVII) (*general procedure*). To 2 mmol of HETA at room temperature at the continuous stirring was added 1 mmol of diol **IV, VII–IX** dissolved in 4 ml of acetonitrile. In 6 h (in the case of derivative **X**), 20 min (for derivative **XI**), 1.5 h (for derivative **XII**), and 40 min (in the case of **XIII**) the solvent was rapidly distilled off and to the formed oily product **X–XIII** was poured the solution of 1 mmol of bisnaphthol **I** in 5 ml of dioxane. The solvent was distilled off 3 days later, the reaction mixture was then diluted with acetonitrile, and cooled. Then the solvent was rapidly decanted from the oily residue, which was dried in a vacuum for 2 h (1 mm Hg, 70ºC).

1,7-Diethylamido-11,11-dihydro-3,4,5-benzo-9,10; 12,13-di(1,2-naphtho)-2,6,8,14-tetraoxy-1,7-diphosphacyclotetradecane (XIV), yield 35%, oily substance, R_f 0.8 (A). ^1H NMR spectrum, δ, ppm ($CDCl_3$): 1.19 t (6H, CH_3, $^3J_{HH}$ 7.0 Hz), 1.25 t (6H, CH_3, $^3J_{HH}$ 7.0 Hz), 3.31 m (8H, CH_2, $^3J_{PH}$ 11.0 Hz), 4.55 d [1H, CH_2 (bridge), $^2J_{HH}$ 16.2 Hz], 5.26 d [1H, CH_2 (bridge), $^2J_{HH}$ 16.2 Hz], 6.38 d.d [2H, CH (resorcinol)], $^3J_{HH}$ 7.9 Hz, $^4J_{HH}$ 2.3 Hz), 6.79 s (1H, CH resorcinol), 6.95 m (1H, CH resorcinol), 7.23 d (2H, CH, $^3J_{HH}$ 8.9 Hz), 7.41 m (2H, CH, $^3J_{HH}$ 7.6 Hz, $^3J_{HH}$ 7.5 Hz, $^4J_{HH}$ 1.2 Hz), 7.53 t (2H, CH, $^3J_{HH}$ 7.8 Hz, $^3J_{HH}$ 7.2 Hz, $^4J_{HH}$ 1.2 Hz), 7.80 d (2H, CH, $^3J_{HH}$ 8.9 Hz), 7.88 d (2H, CH, $^3J_{HH}$ 7.6 Hz), 8.36 d (2H, CH, $^3J_{HH}$ 8.2 Hz). ^{31}P NMR spectrum δ, ppm (1,4-dioxane): 140.8.

1,9-Diethyl-13,13-dihydro-3,4,5,6,7-naphtho-11,12; 14,15-di(1,2-naphtho)-2,8,10,16-tetraoxy-1,9-diphosphacyclodecahexane (XV), yield 52%, oily substance, R_f 0.77 (A). ^1H NMR spectrum, δ, ppm ($CDCl_3$): 1.25 t (12H, CH_3, $^3J_{HH}$ 6.9 Hz), 3.31 m (8H, CH_2, $^3J_{PH}$ 11.0 Hz), 4.55 d [1H, CH_2 (bridge), $^2J_{HH}$ 16.1 Hz], 5.25 d [1H, CH_2 (bridge), $^2J_{HH}$ 16.1 Hz], 7.17 d (2H, CH), 7.22 d (2H, CH, $^3J_{HH}$ 9.1 Hz), 7.41 m (2H, CH, $^3J_{HH}$ 6.2; 6.9 Hz), 7.45 s (2H, CH), 7.52 m (2H, CH, $^3J_{HH}$ 6.9 Hz, $^4J_{HH}$ 1.5 Hz), 7.64 d (2H, CH), 7.79 d (2H, CH, $^3J_{HH}$ 8.4 Hz), 7.88 d (2H, CH, $^3J_{HH}$ 8.0 Hz), 8.36 d.d (2H, CH, $^3J_{HH}$ 8.4 Hz, $^4J_{HH}$ 1.5 Hz). ^{31}P NMR spectrum, δ, ppm (1,4-dioxane): 141.3.

Sulfurization (*general procedure*). To 1 mmol of cyclophosphite (**XIV–XVII**) in 5 ml of anhydrous CH_2Cl_2 was added 2 mmol of sulfur at continuous stirring at room temperature. The solvent was distilled

off 2 days later, and the residue was subjected to column chromatography eluating products with the system benzene–dioxane (7: 1). The obtained substances were dried in the vacuum for 2 h (1 mm Hg, 70ºC).

1,7-Dithiono-1,7-diethylamido-11,11-dihydro-3,4,5-benzo-9,10;12,13-di(1,2-naphtho)-2,6,8,14-tetraoxy-1,7-diphosphacyclotetradecane (XXVIII), yield 30%, oily substance, R_f 0.61 (C). ^{1}H NMR spectrum, δ, ppm ($CDCl_3$): 1.09 br. t (9H, CH_3, $^3J_{HH}$ 7.2 Hz), 3.40 m (8H, CH_2, $^3J_{PH}$ 14.2 Hz), 4.49 d [1H, CH_2 (bridge), $^2J_{HH}$ 16.2 Hz], 4.95 d [1H, CH_2 (bridge), $^2J_{HH}$ 16.2 Hz], 6.66 d [2H, CH (resorcynol)], 6.76 s (1H, CH (resorcynol)], 7.05 d (2H, CH), 7.14–7.86 m (8H, CH), 8.29 d (2H, CH, $^3J_{HH}$ 7.7 Hz). ^{31}P NMR spectrum, δ, ppm (CH_2Cl2): 66.8. Found, %: C 62.14; H 5.64; N 4.11; P 9.18. $C_{35}H_{38}N_2O_4P_2S_2$. Calculated, %: C 62.12; H 5.66; N 4.14; P 9.15.

1,9-Diethylamido-1,9-dithiono-13,13-dihydro-3,4,5,6,7-naphtho-11,12;14,15-di(1,2-naphtho)-2,8,10,16-tetraoxy-1,9-diphosphacyclodecahexane (XXIX), yield 34%, oily substance, R_f 0.75 (A), 0.65 (B). ^{1}H NMR spectrum, δ, ppm ($CDCl_3$): 1.30 t (12H, CH_3), 3.38 m (8H, CH_2, $^3J_{PH}$ 12.8 Hz), 4.45 d [1H, CH_2 (bridge), $^2J_{HH}$ 16.1 Hz], 5.32 d [1H, CH_2 (bridge), $^2J_{HH}$ 16.1 Hz], 7.17 d (2H, CH), 7.22 d (2H, CH, $^3J_{HH}$ 9.1 Hz), 7.40–7.68 m (10H, CH), 7.82 d (2H, CH, $^3J_{HH}$ 8.2 Hz), 8.38 d.d (2H, CH, $^3J_{HH}$ 8.4 Hz). ^{31}P NMR spectrum, δ, ppm (1,4-dioxane): 66.6. 1,7-dithiono-1,7-diethylamido-11,11-dihydro-3,4,5-naphtho-9,10; 12,13-di(1,2-naphtho)-2,6,8,14-tetraoxy-1,7-[diphosphacyclotetradecane] (**XXX**), yield 25%, oily substance, R_f 0.70 (B), 0.58 (D). ^{1}H NMR spectrum, δ, ppm ($CDCl_3$): 1.17 t (12H, CH_3, $^3J_{HH}$ 6.9 Hz), 3.26 m (8H, CH_2, $^3J_{PH}$ 12.4 Hz), 4.81 d [1H, CH_2 (bridge), $^2J_{HH}$ 16.1 Hz], 5.26 d [1H, CH_2 (bridge), $^2J_{HH}$ 15.4 Hz], 7.04 d (1H, CH, $^3J_{HH}$ 8.7 Hz), 7.13 d.d (1H, CH, $^3J_{HH}$ 8.8 Hz, $^4J_{HH}$ 1.1 Hz), 7.22 d (2H, CH), 7.35 m (1H, CH), 7.43 m (1H, CH, $^4J_{HH}$ 3.3 Hz), 7.48 m (2H, CH), 7.59 m (2H, CH), 7.67 d.d (1H, CH, $^3J_{HH}$ 8.8 Hz, $^4J_{HH}$ 3.3 Hz), 7.74 d (2H, CH, $^3J_{HH}$ 8.8 Hz), 7.83 d (2H, CH, $^3J_{HH}$ 8.4 Hz), 8.12 d (1H, CH, $^3J_{HH}$ 8.0 Hz), 8.20 d (2H, CH, $^3J_{HH}$ 8.4 Hz). ^{31}P NMR spectrum, δ, ppm (1,4-dioxane): 66.4; 67.0. Found, %: C 64.34; H 5.74; N 3.89; P 8.48. $C_{39}H_{40}N_2O_4P_2S_2$. Calculated, %: C 64.45; H 5.55; N 3.85; P 8.52.

1,8-Dithiono-1,8-diethylamido-12,12-dihydro-3,4,5,6-naphtho-10,11;13,14-di(1,2-naphtho)-2,7,9,15-tetraoxy-1,8-diphosphacyclopentadecane (XXXI), yield 15%, oily substance, R_f 0.75 (B). ^{31}P NMR spectrum, δ, ppm (1,4-dioxane): 66.2; 67.1.

Oxidation (*general procedure*). To 1 mmol of compound **XIV, XV** in 5 ml of anhydrous methylene chloride was added 2 mmol of $(NH_2)_2CO{\cdot}H_2O_2$, and the mixture was left for 1 day. Then solution was filtered, the solvent was distilled off to a minimum quantity, and 12 ml of hexane was added. After 1 h from the solution above the precipitate was decanted and the substance was twice washed with hexane and dried in a vacuum for 2 h (1 mm Hg, 70ºC).

1,7-Dioxo-1,7-diethylamido-11,11-dihydro-3,4,5-benzo-9,10;12,13-di(1,2-naphtho)-2,6,8,14-tetraoxy-1,7-diphosphacyclotetradecane (XXXII), yield 79%, mp 89–91ºC, R_f 0.63 (A). ^{1}H NMR spectrum, δ, ppm ($CDCl_3$): 1.03 br. t (9H, CH_3), 1.30 t (3H, CH_3, $^3J_{HH}$ 7.3 Hz), 3.18 br.m (6H, CH_2, $^3J_{PH}$ 12.4 Hz), 3.33 m (2H, CH_2, $^3J_{PH}$ 12.8 Hz), 4.93 d [1H, CH_2 (bridge), $^2J_{HH}$ 16.2 Hz], 5.16 d [1H, CH_2 (bridge), $^2J_{HH}$ 16.2 Hz], 6.58 d [2H, CH (resorcynol), $^3J_{HH}$ 7.7 Hz], 6.9 s [1H, CH (resorcynol)], 7.05 br.t [1H, CH (resorcynol)], 7.21 d (2H, CH, $^3J_{HH}$ 8.5 Hz), 7.43 t (2H, CH, $^3J_{HH}$ 6.8 Hz, $^3J_{HH}$ 8.1 Hz), 7.54 t (2H, CH, $^3J_{HH}$ 7.7 Hz, $^3J_{HH}$ 7.7 Hz), 7.73 d (2H, CH, $^3J_{HH}$ 8.9 Hz), 7.82 d (2H, CH, $^3J_{HH}$ 9.1 Hz), 8.28 d (2H, CH, $^3J_{HH}$ 8.5 Hz). ^{31}P NMR spectrum, δ, ppm (CH_2Cl2): 0.9. Found: *M* (MALDI–TOF), *m/z*: 645 $[M + H]^+$. Calculated: *M* 644.

1,9-Diethylamido-1,9-dioxo-13,13-dihydro-3,4,5,6,7-naphtho-11,12;14,15-di(1,2-naphtho)-2,8,10,16-tetraoxy-1,9-diphosphacyclodecahexane (XXXIII), yield 85%, mp 149–150ºC, R_f 0.56 (A). ^{1}H NMR spectrum, δ, ppm ($CDCl_3$): 1.31 t (12H, CH_3, $^3J_{HH}$ 7.0 Hz), 3.33 m (8H, CH_2, $^3J_{PH}$ 12.8 Hz), 4.94 d [1H, CH_2 (bridge), $^2J_{HH}$ 16.2 Hz], 5.16 d [1H, CH_2 (bridge), $^2J_{HH}$ 16.2 Hz], 7.21 d (2H, CH, $^3J_{HH}$ 9.2 Hz), 7.31 d (2H, CH), 7.39 s (2H, CH), 7.44 m (2H, CH, $^3J_{HH}$ 7.9 Hz, $^4J_{HH}$ 1.2 Hz), 7.54 m (2H, CH, $^3J_{HH}$ 7.6 Hz, $^4J_{HH}$ 1.2 Hz), 7.67 d (2H, the CH), 7.73 d (2H, CH, $^3J_{HH}$ 8.9 Hz), 7.82 d (2H, CH, $^3J_{HH}$ 7.6 Hz), 8.30 d (2H, CH, $^3J_{HH}$ 8.2 Hz). ^{13}C NMR spectrum, δ_C, ppm ($CDCl_3$): 13.9 d (4C, CH_3, $^3J_{PC}$ 20.7 Hz), 23.9 s [1C, CH_2 (bridge)], 39.9 d (4C, CH_2, $^2J_{PC}$ 24.2 Hz), 109.9 s (2C, CH), 116.1 s (2C, CH), 119.7 s (2C, CH), 120.0 d (2C, CH, $^3J_{PC}$ 5.2 Hz), 123.3 s (2C, CH), 124.8 s (2C, CH), 127.0 s (2C, CH), 127.9 s (1C, C), 128.7 s (4C, CH), 129.2 s (2C, C), 129.5 s (2C, CH), 132.6 s (2C, C), 134.5 s (1C, C), 149.1 d (2C, CO), 149.6 d (2C, $^3J_{PC}$ 9.5 Hz). ^{31}P NMR spectrum, δ, ppm (CH_2Cl_2): 1.1. Found, %: C 67.34; H 5.74; N 4.05; P 8.22.

$C_{39}H_{40}N_2O_6P_2$. Calculated, %: C 67.43; N 5.80; N 4.03; P 8.92.

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