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Phosphorylation of the 2,2′−Dihydroxy−1,1′−dinaphthylmethane and Synthesis of Phosphamacrocycles on its Basis

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Phosphorylation of 2,2'-dihydroxy-1,1'-dinaphthylmethane with diamidophosphites with different substituents at phosphorus atom was investigated. It was demonstrated that leaving of either two amide groups or phenyl group occurs upon formation of 1,3,2-dioxaphosphacine. Phosphamacrocyclic systems containing fragments of 2,2'-dihydroxy-1,1'-dinaphthylmethane and aromatic diols – resorcinol and 1,3-dihydroxynaphthalene – were synthesized, their low stability in solution is specified. Oxidation reactions of the synthesized compounds were studied.

Keywords: Phosphorylation, 2,2'-dihydroxy-1,1'-dinaphthylmethane, diamidophosphites, aromatic diols, molecular assembly, NMR spectroscopy, X-ray.

Фосфорилирование 2,2′−дигидрокси−1,1′−динафтилметана и синтез фосфомакроциклов на его основе

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Проведено фосфорилирование 2,2'-дигидрокси-1,1'-динафтилметана диамидоэфирами фосфористой кислоты с различными заместителями у атома фосфора; показана принципиальная возможность ухода как двух амидных групп, так и фенильного заместителя при образовании 1,3,2-диоксафосфацина. Синтезированы фосфомакроциклические системы, содержащие в своей структуре остатки 2,2'-дигидрокси-1,1'-динафтилметана и ароматических диолов − резорцина и 1,3-дигидроксинафталина, отмечена их низкая устойчивость в растворах. Рассмотрены окислительные реакции синтезированных систем.

Ключевые слова: Фосфорилирование, 2,2'-дигидрокси-1,1'-динафтилметан, диамидофосфиты, ароматические диолы, молекулярная сборка, спектроскопия ЯМР, рентгеноструктурный анализ.

Introduction

Active studies of phosphorylation of naphthalene derivatives with two distal hydroxy-groups with di- and triamides of phosphorus acid were performed over last decade.[1-6] As a result, there were synthesized macrocyclic compounds containing several fragments of macrocyclic diols and derivatives of phosphorous and phosphoric acids, which can be referred either as phosphacyclophanes or as benzocrown ethers.[7] Such compounds can be used in synthesis of polynuclear complexes with transition metals for catalytic purposes, as well as supramolecular receptors which can capture ions and small molecules, and for structural tasks of modern organoelemental chemistry.

2,2'-Dihydroxy-1,1'-dinaphthylmethane **1** was investigated in reactions with derivatives of trivalent phosphorus together with other diatomic phenols. It was shown that application of alkyleneamidophosphites and other cyclic derivatives of P^{III} has afforded open-chain molecules, which have been used as ligands for asymmetric catalysis.[8,9] Phosphorylation of **1** with triamidophosphites and other acyclic derivatives have resulted in formation of cyclic products – 1,3,2-dioxaphophacines.[10-12] At the same time, compound **1** has never been applied as a building block in synthesis of macrocyclic systems.

Therefore, the aim of the present investigation was to study applicability of **1** in synthesis of phosphamacrocycles.

Results and Discussion

At the first step, hexabutyltriamidophosphine (HBTA) **2a** and trimorpholinophosphite (TMF) **2b** were used as phosphorylating agents due to their low rate of phosphorylation in 1,4-dioxane in comparison with other triamides of phosphorous acid.[13] However, even at reagent ratio **1**:**2a,b** = 1:3 the formation of bisamidophosphites was not observed in ^{31}P NMR spectra of reaction mixtures. Instead of them, in both cases 1,3,2-dioxaphosphacines **3a** and **3b** were obtained (δ_P = 140.1 and 134.3 ppm respectively) (Scheme 1). Therefore, even application of phosphorylating agents **2a,b** with bulky substituents did not result in formation of *bis*phosphorylated derivatives.

At the next step, other phosphorylating agents were applied, namely, butyl and phenyl esters of phosphorous acid tetraethyldiamide **4a,b** as well as phenyl ester of phosphorous acid tetrabutyldiamide **4c**. Phosporylation of **1** with these reagents was performed in acetonitrile and 1,4-dioxane (Scheme 2).

In the case of **4a** irrespectively on reagent ratio (1:1, 1:2 or 1:3) in ^{31}P NMR spectra there was observed a singlet with c δ_P = 147.6 ppm corresponding to 1,3,2-dioxaphosphacine **5a** with ester substituent at P^{III} atom. Notably, neither phosphacine **3** or bisphosphorylated system **5** were not formed. Therefore, it can be concluded that upon phosporylation of **1** by diamidophosphite containing aliphatic ester fragment, the leaving of amide groups is favourable. The rate of phosphorylation increases when passing from 1,4-dioxane to acetonitrile, which is common for this type of reactions.

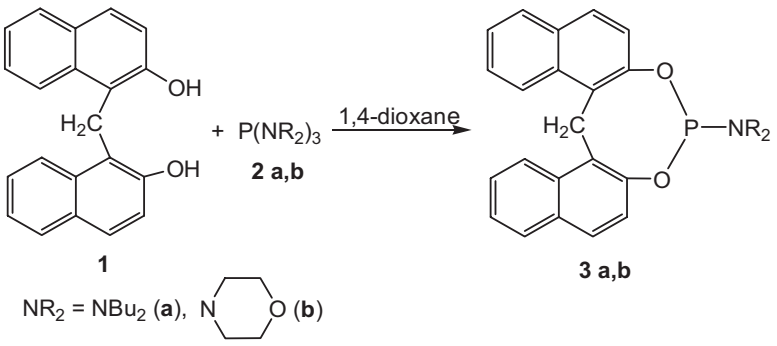
Again, irrespectively on reagent ratio the reaction of bisnaphthol **1** with tetraethyldiamidophenylphosphite **4b** has yielded 1,3,2-dioxaphosphacines **3c** and **5b** together with *bis*phosporylated derivatives **6b** (Scheme 2). The latter compounds were found to be unstable and they gradually have converted into mixture of **3c** and **5b**. Apparently, this process occurs *via* intramolecular dismutation,[14,15] which leads to thermodynamically favourable 8-membered ring system (Scheme 3).

The rate of this cyclization is faster in acetonitrile, while in 1,4-dioxane *bis*phosphorylated derivatives **6b**,**c** are more stable (up to 3 weeks).

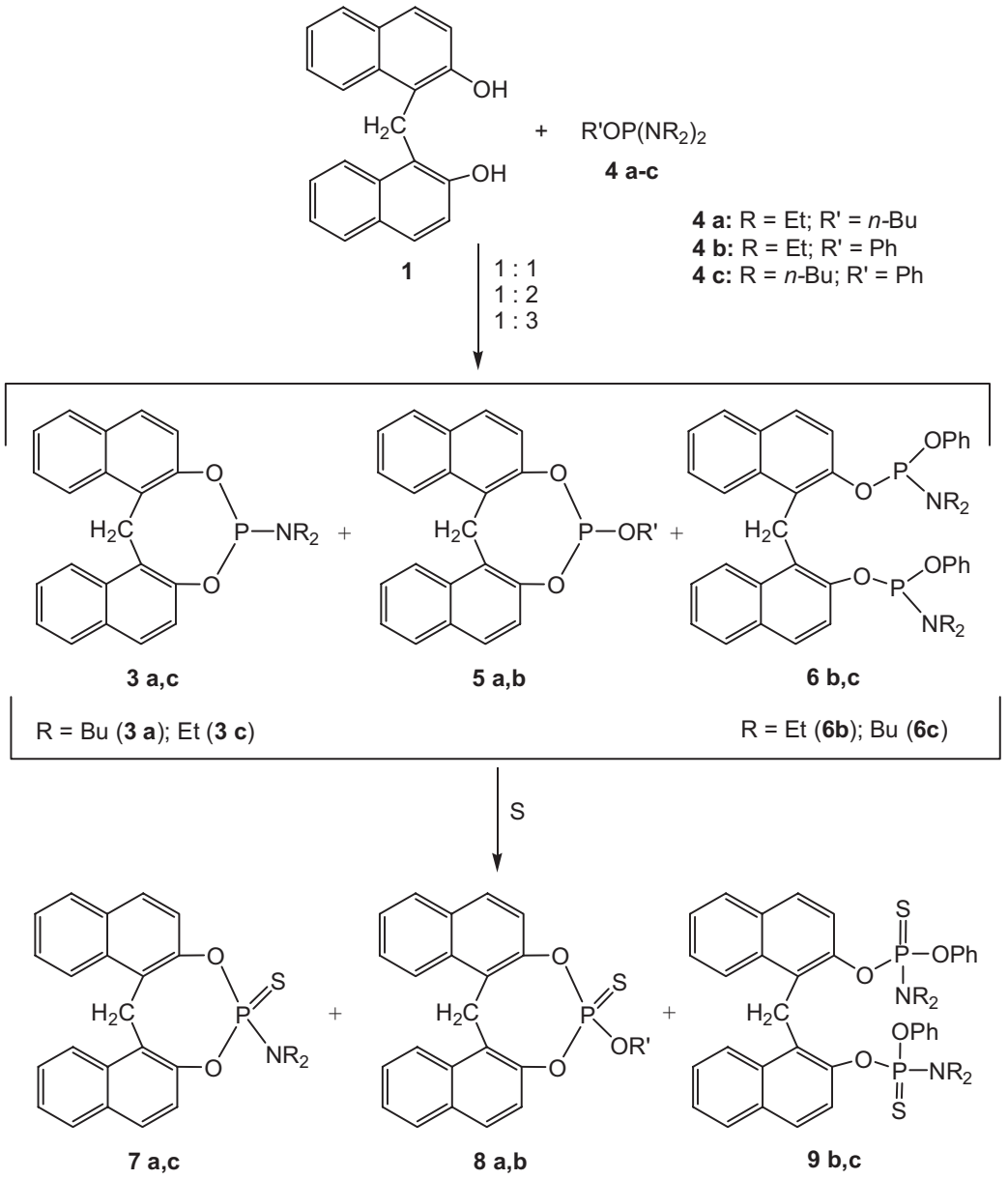
Noteworthy, in contrast to diamidoester **4a**, in the case of **4b** leaving of amide or ester fragments upon phosphorylation is equiprobable independently on reagent ratio as evidenced by ^{31}P NMR spectroscopy. Upon phosphorylation of *bis*naphthol **1** with tetraethyldiamidophenylphosphite **4b** in 1,4-dioxane or reaction mixture in one day after beginning in NMR spectrum there were observed resonance signals δ_P = 133.8 (**6b**) and 132.9 ppm (**4b**), while in one week there were observed resonance signals δ_P = 142.0 (**3c**), 140.6 (**5b**) and 132.9 ppm (**4b**) with integral ratios 1:1:2.

An application of acetonitrile instead of 1,4-dioxane has resulted in increase of reaction rate[16] – in two hours after beginning in ^{31}P NMR spectrum of reaction mixture there was observed only **6b**, however its signal has vanished in NMR spectrum afterwards.

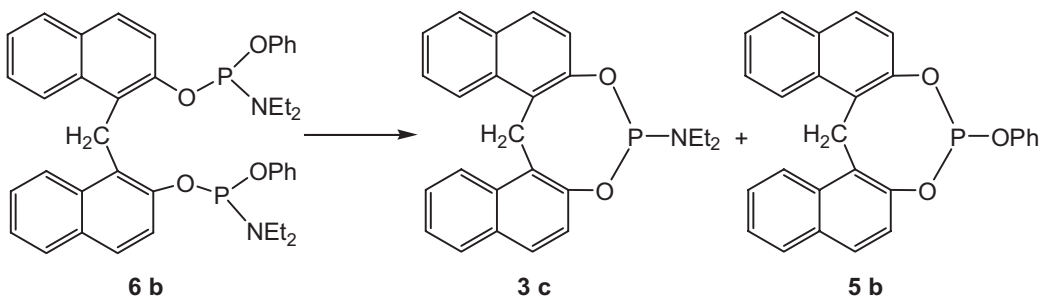
In the case of tetrabutyldiamidophenylphosphite **4c** phosphorylation of **1** was very slow. Even after 1 day in ^{31}P NMR spectrum the most intensive signal was δ_P = 132.5 ppm corresponded to starting diamide **4c**, minor signal with δ_P = 142.6 ppm corresponded to *bis*phosphorylated product **6c** (Scheme 2). The latter have remained in reaction mix-



Scheme 1. Synthesis of 1,3,2-dioxaphosphacines **3a**,**b**.



Scheme 2.

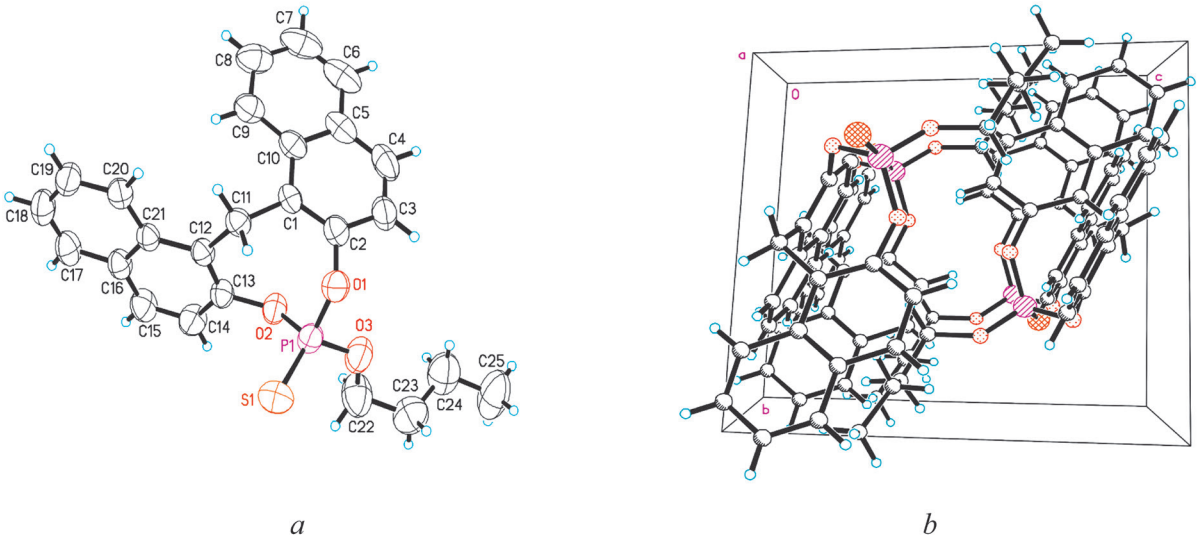


Scheme 3.

ture even after 2 weeks after the beginning of reaction, together with **5b** (δ_P = 141.8 ppm), **3a** (δ_P = 140.5 ppm) and **4c** (δ_P = 132.5 ppm). The integral ratios were 1.5:1:1:6. The slow reaction rate can be explained by lower reactivity of **4c**.

With the aim to separate and identify phosphorylated products, the reaction mixtures were sulfurized and column chromatography was used to isolate 1,3,2-dioxaphosphacines **7a,c** and **8a,b** and *bis*phosphorylated thione derivatives **9b,c**. Because of similarity of solubility and chromatographic mobility, isolation of compounds in pure forms was tedious, so the yields of individual thiones were modest. Physical-chemical properties of **7c** have coincided with the previously reported data.[17]

X-Ray diffraction analysis of crystalline **8a** was performed (Figure 1, Table 1). It has evidenced that the macrocyclic part of the molecule adopts *bath-bath* conformation.[17] Stability of this conformation can be tentatively explained by the presence of bulky butoxy-substituent.



a *b*

Figure 1. Molecular structure of 2-thione-2-*O*-butyl-4,5,7,8-dinaphtho-1,3,2-dioxaphosphacine **8a** (*a*) and fragment of molecules packing in crystal (*b*).

Table 1. Bond lengths (Å) and angles for 2-thione-2-*O*-butyl-4,5,7,8-dinaphtho-1,3,2-dioxaphosphacine **8a**.

Bond	*d*, Å	Angle	ω, grad
P(1)-O(1)	1.5824(18)	O(3)-P(1)-O(1)	99.95(10)
P(1)-O(2)	1.5845(18)	O(3)-P(1)-O(2)	101.68(10)
P(1)-O(3)	1.5491(19)	O(1)-P(1)-O(2)	105.19(9)
P(1)-S(1)	1.8993(11)	O(3)-P(1)-S(1)	118.82(9)
O(1)-C(2)	1.414(3)	O(1)-P(1)-S(1)	112.23(8)
O(2)-C(13)	1.403(3)	O(2)-P(1)-S(1)	116.79(7)
O(3)-C(22)	1.422(4)	C(13)-O(2)-P(1)	128.02(14)
C(1)-C(2)	1.365(3)	C(22)-O(3)-P(1)	124.12(18)
C(1)-C(11)	1.517(3)	C(2)-C(1)-C(10)	117.8(2)
C(2)-C(3)	1.393(3)	C(2)-C(1)-C(11)	119.5(2)
C(11)-C(12)	1.521(3)	C(10)-C(1)-C(11)	122.7(2)
C(12)-C(13)	1.370(3)	C(1)-C(2)-O(1)	118.3(2)
C(13)-C(14)	1.400(3)	C(3)-C(2)-O(1)	117.6(2)
C(22)-C(23)	1.509(4)	C(1)-C(11)-C(12)	114.39(17)
C(23)-C(24)	1.466(5)	C(13)-C(12)-C(21)	117.02(18)
		C(13)-C(12)-C(11)	121.49(18)
		C(12)-C(13)-C(14)	123.7(2)
		C(12)-C(13)-O(2)	122.08(18)
		C(14)-C(13)-O(2)	114.10(19)
		O(3)-C(22)-C(23)	108.3(2)
		C(24)-C(23)-C(22)	114.3(3)

The observed formation of phosphacines upon phosphorylation of **1** with acyclic amidophosphites has precluded formation of macrocycles containing two fragments of *bis*-naphthol. Therefore, we have proposed two-step approach to 14-membered macrocyclic systems,[18] containing a fragment of *bis*naphthol **1** and a fragment of resorcinol **10** or 1,3-dihydroxynaphthalene **11**. This approach implies synthesis of primary *bis*phosphorylation of diols **10** and **11** with hexaethyltriamidophosphite (HETA) **2c** with subsequent cyclization of resulting *bis*phosphorylated derivatives **12** and **13** with *bis*naphthol **1** (Scheme 4).

Reactions were performed in 1,4-dioxane. The completion of *bis*phosphorylation of diols **10** and **11** was confirmed by ^{31}P NMR spectroscopy – there was observed a singlet at $\delta_P = 132.8$ ppm, which is characteristic for diamidoesters of phosphorous esters with aromatic radicals – **12** and **13**. Then, *bis*phenol **1** was added to reaction mixture and the mixture was kept for 3 days. During this time the signal at 132.8 ppm gradually vanished and a new signal at 140.5 ppm became intensive. This signal corresponded to the target amidodiesters.

Resulting macrocycles **14** and **15** were found to be unstable. In solution they have rearranged with the formation of 1,3,2-dioxaphosphacine **3c** and uniform cyclophanes.[3,16]

However, we have tried to isolate target macrocycles. With this aim the reaction mixtures containing products with $\delta_P = 140$ ppm were evaporated to minimal volume and cooled resulting in formation of oily product. The solvent was decanted, the oil was washed with cold acetonitrile and dried *in vacuo*. Their NMR spectra corresponded to the target macrocycles **14** and **15**, however, they also contained resonance signals of 1,3,2-dioxaphosphacine **3c** impurity. Isolation of pure macrocycles was possible only after their conversion into thiones and phosphates.

Sulfurization of cyclophosphites **14** and **15** was performed with elemental sulfur in CH_2Cl_2 during 1 day. Resulting cyclo(*bis*thioneamidophosphates) **16** and **17** were isolated by column chromatography in 30 and 25 % yields respectively as viscous oils. Their ^{31}P NMR spectra contained singlets in 68 ppm region, what corresponded to amidoesters of thionephosphoric acid.

Oxidation of cyclophosphites **14** and **15** was peformed with urea peroxide in CH_2Cl_2 for 1 day. Phosphates **18** and **19** were isolated by precipitation with hexane. They were isolated as low-melting powders in 79 and 65 % yields respectively. Their ^{31}P NMR spectra contained singlets at 1 ppm which corresponded to monoamidophosphates. ^{1}H NMR spectrum of compound **19** revealed some broadening of resonance signals.

Conclusions

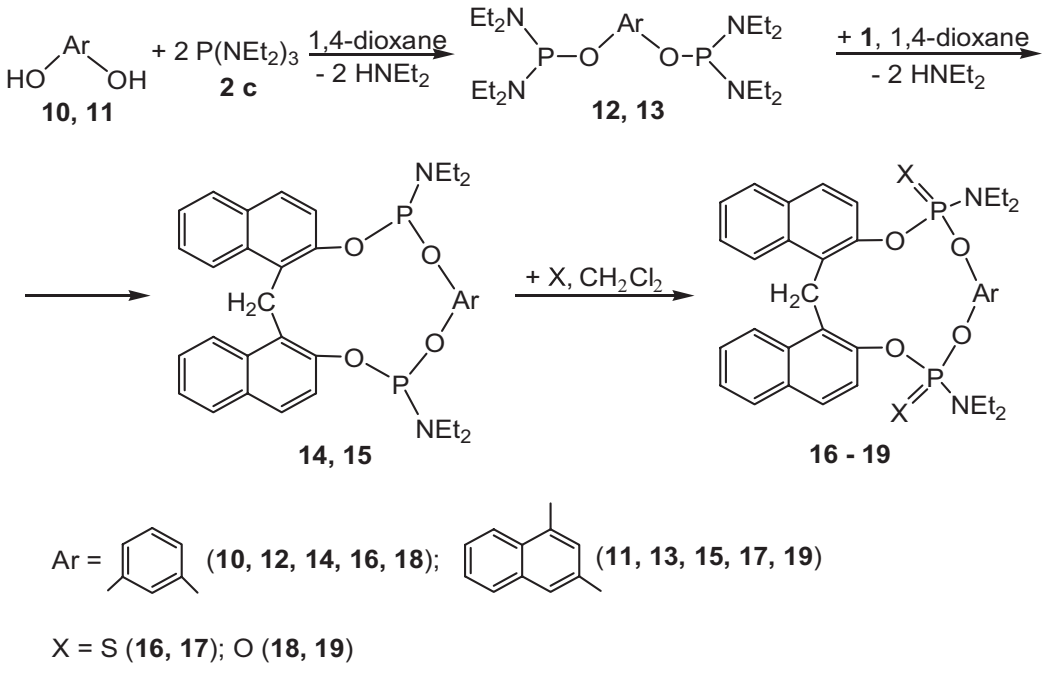
1. We have investigated phosphorylation of 2,2'-dihydroxy-1,1'-dinaphthylmetane with derivatives of P^{III} – hexabutyltriamide, trimorpholinephosphite, tetraethyl- and tetrabutyldiamidophenylphosphites, as well as tetraethyldiamidobutylphosphite.

2. The equiprobable leaving of amide or aromatic ester substituent was found upon formation of 1,3,2-dioxaphosphacine.

3. We have synthesized phosphamacrocyclic systems, containing 2,2'-dihydroxy-1,1'-dinaphthylmethane as a building block, the oxidation reactions of these macrocycles were investigated.

Experimental

All syntheses were conducted in dry solvents under an argon atmosphere. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a JEOL ECX-400 spectrometer operating at 400, 100.5 and 161.8 MHz



Scheme 4.

respectively; ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$; chemical shifts (δ, ppm) were referenced to TMS (^{1}H and ^{13}C) or to 85 % H_3PO_4 (^{31}P). Spin-spin coupling constants (*J*) are given in Hz. Mass spectra were measured on a Bruker Ultraflex MALDI-TOF spectrometer using a nitrogen laser (λ=337 nm) and trihydroxyanthracene as a matrix. Crystals of compound **8a** have obtained by crystallization from hexane. X-ray analysis was performed on an automatic CAD-4 Enraf-Nonius diffractometer (β-filter, λ(Mo-Kα) θ/2θ data collection, θ_{max}=24.88°). Colorless triclinic crystal ($C_{25}H_{23}O_3PS$, *M*=434.46), size 0.56×0.40×0.15 mm, *a*=9.881(2) Å, *b*=10.846(2) Å, *c*=11.482(2) Å, α=87.10(3)°, β=74.82(3)°, γ=71.12(3)°. *V*=1122.9(5) Å^3. *Z*=2. ρ=1.258 mg/cm^3. Number of reflections: 4433, independent reflections: 4172 (*R*(int)=0.0200). *F*(000)=456; $R_1(F)$=0.0431, $wR_2(F^2)$=0.1307. Refinement method: full-matrix least squares on F^2 for non-hydrogen atoms. All hydrogen atoms have included in the refinement with fixed parameters (placed in calculated positions) in the isotropic approximation. Crystallographic data reported in this paper have been deposited with Cambridge Crysrallographic Data Centre (№ CCDC 1052567). Column adsorption chromatography was operated on silica gel L 100/250; TLC was performed on Silufol plates (UV-254) using C_6H_{14}:dioxane, 5:1 (A), C_6H_6:dioxane, 3:1 (B). Detection was achieved using iodine vapor treatment and calcination.

2,2'-Dihydroxy-1,1'-dinaphthylmethane ***1*** was synthesized by the method,[19] *HBTA* ***2a***,[16] *tetraethyl-* and *tetrabutyldiamidophenylphosphites* (***4b,c***),[15] *HETA* ***12***. [20]

2-Dibutylamido-4,5,7,8-dinaphtho-1,3,2-dioxaphosphacine ***(3a)***. A solution of 1.25 g (3 mmol) HBTA (**2a**) in 5 ml of 1,4-dioxane was added to a solution of 0.3 g (1 mmol) of bisnaphthol **1** in 4 ml of 1,4-dioxane. The reaction mixture was kept at room temperature for 2 h. The solvent was evaporated *in vacuo* (12 mm Hg), and the residue was chromatographed on a column, the resulting product was eluted by hexane:dioxane (10:1) system. The resulting material was dried *in vacuo* for 1.5 h (1 mm Hg, 60 ºC). Yield 0.41 g (89 %). R_f 0.69 (A). ^{1}H NMR δ_H ppm: 0.97 (6H, t, $^3J_{HH}$=7.3, CH_3), 1.40 (4H, m, CH_2), 1.62 (4H, m, CH_2), 3.19 (4H, m, $^3J_{PH}$=11.0, N-CH_2), 4.58 (1H, dd, $^2J_{HH}$=16.0, Ar-CH_2), 5.11 (1H, d, $^2J_{HH}$=16.0, Ar-CH_2), 7.18 (2H, d, $^3J_{HH}$=8.7, CH^3), 7.38 (2H, dd, $^3J_{HH}$=6.9; 7.8, CH^7), 7.49 (2H, dd, $^3J_{HH}$=7.8, CH^6), 7.68 (2H, d, $^3J_{HH}$=8.8, CH^4), 7.80 (2H, d, $^3J_{HH}$=7.8, CH^5), 8.22 (2H, d, $^3J_{HH}$=8.7, CH^8). ^{13}C NMR δ_C ppm: 14.1 (CH_3), 20.2 (CH_2), 25.1 (Ar-CH_2), 30.9 (CH_2), 43.7 (d, $^2J_{PC}$=19.1, CH_2-N), 121.9 (d, $^3J_{PC}$=5.8, C^{3}H), 122.6 (d, $^3J_{PC}$=3.8, C^1), 123.4 (C^{8}H), 124.1 (C^{7}H), 126.8 (C^{6}H), 128.4 (C^{5}H), 128.9 (C^{4}H), 130.9 (C^9), 133.0 (C^{10}), 151.8 (C-O). ^{31}P NMR (1,4-dioxane) δ_P ppm: 140.1.

2-Morpholino-4,5,7,8-dinaphtho-1,3,2-dioxaphosphacine ***(3b)***. A solution of 1.86 g (3 mmol) TMF (**2b**) in 5 ml of 1,4-dioxane was added to a solution of 0.3 g (1 mmol) of *bis*naphthol **1** in 4 ml of 1,4-dioxane. The reaction mixture was kept at room temperature for 2 h. The solvent was evaporated *in vacuo* (12 mm Hg); the residue was added to the 5 ml of acetonitrile. After 12 h the crystals precipitated were filtered off, washed with hexane and acetonitrile. The resulting material was dried *in vacuo* for 1.5 h (1 mm Hg, 60 ºC). Yield 0.37 g (90 %). Mp 189–190 °C. R_f 0.32 (A). ^{1}H NMR δ_H ppm: 3.33 (4H, m, $^3J_{PH}$=7.8, $^3J_{HH}$=4.6, N-CH_2), 3.75 (4H, dd, $^3J_{HH}$=4.6, O-CH_2), 4.56 (1H, dd, $^2J_{HH}$=16.1, Ar-CH_2), 5.09 (1H, d, $^2J_{HH}$=16.1, Ar-CH_2), 7.18 (2H, d, $^3J_{HH}$=8.7, CH3), 7.39 (2H, dd, $^3J_{HH}$=7.0; 7.6, CH^7), 7.50 (2H, dd, $^3J_{HH}$=7.0; 8.3, CH^6), 7.69 (2H, d, $^3J_{HH}$=8.7, CH^4), 7.81 (2H, d, $^3J_{HH}$=8.2, CH^5), 8.21 (2H, d, $^3J_{HH}$=8.7, CH^8). ^{13}C NMR δ_C ppm: 25.1 (Ar-CH_2), 44.2 (d, $^2J_{PC}$=17.2, CH_2-N), 68.1 (CH_2-O), 121.9 (d, $^3J_{PC}$=5.7, C^{3}H), 123.4 (C^{8}H), 124.4 (C^1), 126.9 (C^{7}H), 128.6 (C^{6}H), 128.9 (C^{4,5}H), 131.1 (C^9), 132.9 (C^{10}), 151.1 (C-O). ^{31}P NMR (CH_2Cl_2) δ_P ppm: 134.3.

Phosphorylation of 2,2'-dihydroxy-1,1'-dinaphthylmethane ***1*** *with diamidoesters of phosphorous acid* ***4a-c*** *(general procedure)*. Solution of diamidophosphite **4a-c** in 4 ml of acetonitrile or 1,4-dioxane was mixed with solution of 1 mmol of *bis*naphthol **1** in acetonitrile or dioxane respectively, at room temperature and continuous stirring. Molar ratios of *bis*naphthol **1** and diamidophosphite **4a-c** were 1:1, 1:2 or 1:3. In two weeks sulfur was added to reaction mixtures, its amount corresponded to that of used diamidophosphite. In two days the reaction mixtures were evaporated, the residues were dissolved in minimal volume of benzene and chromatographed eluting products with hexane:dioxane, 10:1 mixture. Resulting compounds were dried *in vacuo* (1 mm Hg, 70 °C) for 2 hours.

2-Thione-2-dibutylamido-4,5,7,8-dinaphtho-1,3,2-dioxaphosphacine ***(7a)***. Yield 0.39 g (79 %). M.p. 112-113 °C. R_f 0.57 (A). ^{1}H NMR δ_H ppm: 0.97 (6H, t, $^3J_{HH}$=7.8, CH_3), 1.40 (4H, m, CH_2), 1.70 (4H, m, CH_2), 3.35 (4H, m, $^3J_{PH}$=7.3, N-CH_2), 4.99 (1H, d, $^2J_{HH}$=16.0, Ar-CH_2), 5.12 (1H, d, $^2J_{HH}$=15.6, Ar-CH_2), 7.19 (2H, d, $^3J_{HH}$=9.2, CH^3), 7.44 (2H, dd, $^3J_{HH}$=7.3, CH^7), 7.55 (2H, dd, $^3J_{HH}$=7.3; 8.3, CH^6), 7.73 (2H, d, $^3J_{HH}$=8.7, CH^4), 7.83 (2H, d, $^3J_{HH}$=7.3, CH^5), 8.34 (2H, d, $^3J_{HH}$=8.7, CH^8). ^{13}C NMR δ_C ppm: 14.1 (CH_3), 20.2 (CH_2), 25.1 (Ar-CH_2), 30.7 (CH_2), 46.7 (CH_2-N), 121.9 (C^{3}H), 123.8 (C^1), 124.9 (C^{8}H), 125.1 (C^{7}H), 127.1 (C^{6}H), 128.4 (C^{5}H), 128.9 (C^{4}H), 131.8 (C^9), 132.9 (C^{10}), 149.9 (d, $^2J_{PC}$=11.5, C-O). ^{31}P NMR (1,4-dioxane) δ_P ppm: 67.8.

2-Thione-2-O-butyl-4,5,7,8-dinaphtho-1,3,2-dioxaphosphacine ***(8a)***. Yield 0.087 g (20 %). M.p. 142-143 °C. R_f 0.73 (A). ^{1}H NMR δ_H ppm: 0.98 (3H, t, $^3J_{HH}$=7.3, CH_3), 1.50 (2H, m, CH_2), 1.80 (2H, m, $^3J_{HH}$=6.4; 7.8, CH_2), 4.36 (2H, m, $^3J_{PH}$=12.8, O-CH_2), 4.76 (1H, d, $^2J_{HH}$=16.0, Ar-CH_2), 5.18 (1H, d, $^2J_{HH}$=16.0, Ar-CH_2), 7.22 (2H, d, $^3J_{HH}$=8.9, $^4J_{PH}$=1.4, CH^3), 7.47 (dd, 2H, $^3J_{HH}$=7.3, CH^7), 7.57 (2H, dd, $^3J_{HH}$=7.8, CH^6), 7.77 (2H, d, $^3J_{HH}$=8.8, CH^4), 7.86 (2H, d, $^3J_{HH}$=8.2, CH^5), 8.28 (2H, d, $^3J_{HH}$=8.3, CH^8). ^{13}C NMR δ_C ppm: 13.8 (CH_3), 24.4 (Ar-CH_2), 32.2 (CH_2), 69.5 (CH_2-O), 120.9 (C^{3}H), 123.6 (C^{8}H), 124.6 (d, C^1), 125.5 (C^{7}H), 127.4 (C^{6}H), 129.1 (C^{4,5}H), 132.1 (C^9), 132.8 (C^{10}), 148.9 (d, C-O). ^{31}P NMR (1,4-dioxane) δ_P ppm: 59.5.

2-Thione-2-O-phenyl-4,5,7,8-dinaphtho-1,3,2-dioxaphosphacine ***(8b)***. Yield 0.068 g (15 %). M.p. 158–159 °C. R_f 0.51 (A). ^{1}H NMR δ_H ppm: 4.80 (1H, d, $^2J_{HH}$=16.0, Ar-CH_2), 5.24 (1H, d, $^2J_{HH}$=16.0, Ar-CH_2), 7.20 (2H, d, $^3J_{HH}$=8.8, CH^3), 7.27 (2H, d, Ph), 7.36−7.44 (3H, m, Ph), 7.49 (2H, dd, $^3J_{HH}$=7.3; 7.8, CH^7), 7.58 (2H, dd, $^3J_{HH}$=7.3; 7.8, CH^6), 7.75 (2H, d, $^3J_{HH}$=9.0, CH^4), 7.86 (2H, d, $^3J_{HH}$=8.3, CH^5), 8.29 (2H, d, $^3J_{HH}$=8.7, CH^8). ^{13}C NMR δ_C ppm: 24.4 (Ar-CH_2), 120.8 (C^{3}H), 121.2 (*o*-Ph), 123.6 (C^{8}H), 124.5 (d, $^3J_{PC}$=7.7, C^1), 125.6 (C^{7}H), 125.9 (*p*-Ph), 127.5 (C^{6}H), 129.2 (C^{4,5}H), 129.9 (*m*-Ph), 133.2 (C^9), 132.8 (C^{10}), 150.1 (d, C-O), 153.2 (d, Ph-O). ^{31}P NMR (1,4-dioxane) δ_P ppm: 53.5. Mass spectrum (MALDI) *m/z*: 455.48 [*M*+H]$^+$.

2,2'-Bis(diethylamidophenylthionephosphatoxy)-1,1'-dinaphthylmethane ***(9b)***. Yield 0.06 g (8 %). M.p. 157–158 ºC. R_f 0.63 (A). ^{1}H NMR δ_H ppm: 1.17 (6H, t, $^3J_{HH}$=7.3, CH_3), 1.32 (6H, t, $^3J_{HH}$=7.0, CH_3), 3.46 (8H, m, $^3J_{PH}$=14.3, CH_2), 5.00 (1H, d, $^2J_{HH}$=15.7, Ar-CH_2), 5.14 (1H, d, $^2J_{HH}$=15.7, Ar-CH_2), 7.19 (4H, d, Ph), 7.24 (2H, d, CH^3), 7.32 (4H, t, $^3J_{HH}$=8.0, Ph), 7.36 (2H, m, Ph), 7.49 (2H, dd, $^3J_{HH}$=8.0, CH^7), 7.56 (2H, dd, $^3J_{HH}$=8.0, $^4J_{HH}$=1.1, CH^6), 7.74 (2H, d, $^3J_{HH}$=8.8, CH^4), 7.86 (2H, d, $^3J_{HH}$=7.7, CH^5), 8.35 (2H, d, $^3J_{HH}$=8.8, CH^8). ^{31}P NMR (CH_3CN) δ_P ppm: 66.8. Found, %: P 8.18. $C_{41}H_{44}N_2O_4P_2S_2$. Calculated, %: P 8.21.

Cyclophosphorylation of 2,2'-dihydroxy-1,1'-dinaphthylmethane (general procedure). A solution 0.16 g (1 mmol) of dihydroxynaphthalene **10** or **11** in 6 ml of 1,4-dioxane was added at stirring at room temperature to 0.5 g (2 mmol) HETA **2c**. After 12 h (**10**) or 6 h (**11**) a solution of 0.3 g (1 mmol) of *bis*naphthol **1** in 4 ml of 1,4-dioxane was added to the reaction mixture. The mixture was stirred for 5 h and left for 60 h. The solvent was evaporated *in vacuo* (12 mm Hg); the remaining oily precipitate was washed twice with cold acetonitrile and dried *in vacuo* for 2 h (1 mm Hg, 60 ºC).

1,3(1,2)-Dinaphthalina-7(1,3)-benzena-4,6,8,10-tetraoxa-5,9-di(diethylamidate)phosphacyclodeca-phane ***(14)***. Yield 0.14 g (25 %). Oily substance. R_f 0.80 (B). ^{1}H NMR δ_H ppm: 1.19 (6H, t, $^3J_{HH}$=7.0, CH_3), 1.25 (6H, t, $^3J_{HH}$=7.0, CH_3), 3.31 (8H, m, $^3J_{PH}$=11.0, N-CH_2), 4.55 (1H, d, $^2J_{HH}$=16.2, Ar-CH_2), 5.26 (1H, d,

$^2J_{HH}$=16.2, Ar-CH_2), 6.38 (2H, dd, $^3J_{HH}$=7.9, $^4J_{HH}$=2.3, *o*-CH), 6.79 (1H, s, *o*'-CH), 6.95 (1H, d, *m*-CH), 7.23 (2H, d, $^3J_{HH}$=8.9, CH^3), 7.41 (2H, m, $^3J_{HH}$=7.5, 7.6, CH^6), 7.53 (2H, m, $^3J_{HH}$=7.2, 7.8, CH^7), 7.80 (2H, d, $^3J_{HH}$=8.9, CH^4), 7.88 (2H, d, $^3J_{HH}$=7.6, CH^5), 8.36 (2H, d, $^3J_{HH}$=8.2, CH^8). ^{31}P NMR (1,4-dioxane) δ_P ppm: 140.8.

*Thionephosphoramidates (**16**, **17**) (general procedure).* Sulfur 0.064 g (2 mmol) was added to cyclophosphite (**14**, **15**) in 5 ml of dichloromethane. The mixture was stirred for 3 h at room temperature and left for 24 h. The solution was filtered, the solvent was evaporated *in vacuo* (12 mm Hg), and the residue was chromatographed on a column, the resulting product was eluted by the benzene:dioxane (7 : 1) system. The resulting material was dried *in vacuo* for 2 h (1 mm Hg, 70 ºC).

*1,3(1,2)-Dinaphtholina-7(1,3)-benzena-4,6,8,10-tetraoxa-5,9-di(diethylamidate)thionphosphacyclodeca-phane (**17**).* Yield 0.20 g (30 %). Oily substance. R_f 0.61 (A). ^{1}H NMR δ_H ppm: 1.00 (9H, t, CH_3), 1.02 (3H, t, $^3J_{HH}$=7.2, CH_3), 3.32 (8H, m, $^3J_{PH}$=13.9, N-CH_2), 4.70 (1H, d, $^2J_{HH}$=16.1, Ar-CH_2), 5.14 (1H, d, $^2J_{HH}$=16.8, Ar-CH_2), 6.68 (2H, d, $^3J_{HH}$=8.0, *o*-CH), 6.79 (1H, d, $^4J_{PH}$=4.0, *o*'-CH), 6.85 (1H, m, $^3J_{HH}$= 8.0, *m*-CH), 7.12 (2H, dd, $^3J_{HH}$=8.8, $^4J_{PH}$=1.5, CH^3), 7.38 (2H, dd, $^3J_{HH}$=7.3, 7.8, CH^7), 7.48 (2H, dd, $^3J_{HH}$=7.7, $^4J_{HH}$=1.5, CH^6), 7.66 (2H, d, $^3J_{HH}$=8.8, CH^4), 7.76 (2H, dd, $^3J_{HH}$=8.0, $^4J_{HH}$=1.2, CH^5), 8.19 (2H, d, $^3J_{HH}$=8.0, CH^8). ^{31}P NMR (1,4-dioxane) δ_P ppm: 66.8. Found, %: C, 62.07; H, 5.69; N, 4.12; P, 9.24. $C_{35}H_{38}N_2O_4P_2S_2$. Calculated, %: C, 62.12; H, 5.66; N, 4.14; P, 9.15.

*1,3(1,2),7(1,3)-Trinaphthalina-4,6,8,10-tetraoxa-5,9-di-(diethylamidate)thionphosphacyclodecaphane (**18**).* Yield 0.18 g (25 %). Oily substance. R_f 0.58 ($CHCl_3$). ^{1}H NMR δ_H ppm: 1.17 (12H, t, $^3J_{HH}$=6.9, CH_3), 3.26 (8H, m, $^3J_{PH}$=12.4, N-CH_2), 4.81 (1H, d, $^2J_{HH}$=16.1, Ar-CH_2), 5.26 (1H, d, $^2J_{HH}$=15.4, Ar-CH_2), 7.04 (1H, s, $CH^{2'}$), 7.13 (2H, dd, $^3J_{HH}$=8.8, $^4J_{HH}$=1.1, CH^3), 7.22 (1H, s, $CH^{4'}$), 7.25 (1H, dd, $CH^{6'}$), 7.35 (1H, dd, $CH^{7'}$), 7.48 (2H, dd, CH^6), 7.59 (2H, dd, CH^7), 7.67 (2H, d, $^3J_{HH}$=8.8, CH^4), 7.74 (1H, d, $^3J_{HH}$=8.8, $CH^{5'}$), 7.83 (2H, d, $^3J_{HH}$=8.4, CH^5), 8.12 (1H, d, $^3J_{HH}$=8.0, $CH^{8'}$), 8.20 (2H, d, $^3J_{HH}$=8.4, CH^8). ^{31}P NMR (1,4-dioxane) δ_P ppm: 66.4, 67.0. Found, %: C, 64.34; H, 5.74; N, 3.89. $C_{39}H_{40}N_2O_4P_2S_2$. Calculated, %: C, 64.45; H, 5.55; N, 3.85.

*Phosphoramidates (**18**, **19**) (general procedure).* The urea peroxide (commercial hydroperite) 0.23 g was added to cyclophosphite (**14**, **15**) in 6 ml of dichloromethane. The mixture was left for 24 h at room temperature. Then the solution was cooled to 0 °C and filtered, the solvent was removed *in vacuo* (12 mm Hg) down to a small volume, and 10 ml hexane was added; after 10 min the solution was decanted from precipitate. The procedure was repeated twice. The resulting material was dried *in vacuo* for 2 h (1 mm Hg, 60 ºC).

*1,3(1,2)-Dinaphtholina-7(1,3)-benzena-4,6,8,10-tetraoxa-5,9-di(diethylamidate)oxophosphacyclodeca-phane (**18**).* Yield 0.51 g (79 %). M.p. 89–91 ºC. R_f 0.63 (B). ^{1}H NMR δ_H ppm: 1.03 (9H, t, CH_3), 1.30 (3H, t, $^3J_{HH}$=7.3, CH_3), 3.18 (6H, m, $^3J_{PH}$=12.4, N-CH_2), 3.33 (2H, m $^3J_{PH}$=12.8, N-CH_2), 4.93 (1H, d, $^2J_{HH}$=16.2, Ar-CH_2), 5.16 (1H, d, $^2J_{HH}$=16.2, Ar-CH_2), 6.58 (2H, d, $^3J_{HH}$=7.7, *o*-CH), 6.90 (1H, s, *o'*-CH), 7.05 (1H, t, *m*-CH), 7.21 (2H, d, $^3J_{HH}$=8.5, CH^3), 7.43 (2H, dd, $^3J_{HH}$=6.8, 8.1, CH^6), 7.54 (2H, dd, $^3J_{HH}$=7.7, CH^7), 7.73 (2H, d, $^3J_{HH}$=8.9, CH^4), 7.82 (2H, d, $^3J_{HH}$=8.1, CH^5), 8.28 (2H, d, $^3J_{HH}$=8.5, CH^8). ^{31}P NMR (CH_2Cl_2) δ_P ppm: 0.9. Mass spectrum (MALDI) *m/z*: 645.22 [*M*+H]$^+$.

*1,3(1,2),7(1,3)-Trinaphthalina-4,6,8,10-tetraoxa-5,9-di(diethylamidate)oxophosphacyclodecaphane (**19**).* Yield 0.48 g (81 %). M.p. 98–100 ºC. R_f 0.68 (B). ^{31}P NMR (CH_2Cl_2) δ_P ppm: 1.1, 0.9.

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