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2,6- and 1,6-Dihydroxynaphthalenes in the Synthesis of Phosphacyclophanes

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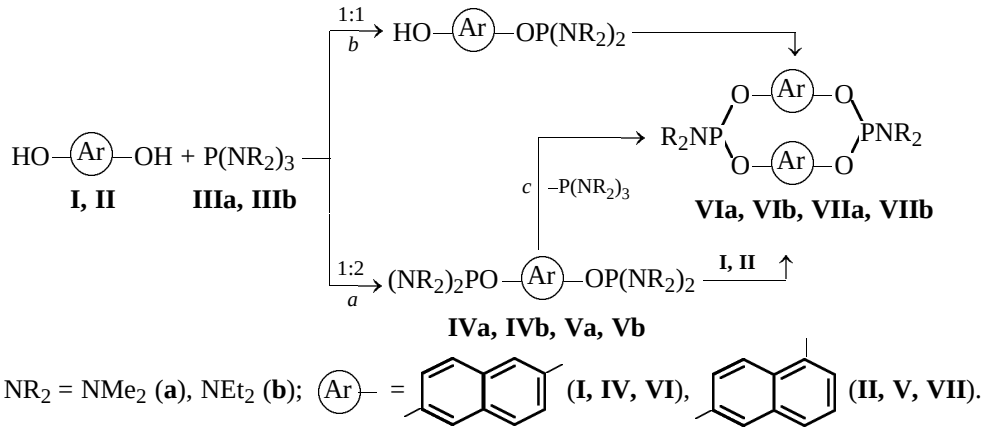
Abstract — Peculiar phosphacyclophanes were prepared from symmetrical 2,6- and unsymmetrical 1,6-dihydroxynaphthalenes. The position of the hydroxy groups in dihydroxynaphthalenes considerably affects their reactivity, the structure of the phosphacyclophanes obtained, and also the disproportionation of bisphosphoramidites. Oxo and thio derivatives of these phosphoramidites as well as their molybdenum complexes were prepared.

We showed recently that the reactions of trihydroxynaphthalenes with phosphorous triamides readily yield previously unknown cyclophanes. In the molecules of these compounds, two naphthalene radicals are bound by phosphorus-containing bridges. Therefore, these compounds were termed phosphocyclophanes [1–3]. It is significant that the structure and properties of phosphacyclophanes are largely determined by the structure of the starting naphthalene derivatives. Therefore, it seems necessary to extend the range of these peculiar structures.

In this work we studied cyclophosphorylation of two structurally related aromatic diols, symmetrical 2,6- (**I**) and unsymmetrical 1,6-dihydroxynaphthalene (**II**), with phosphorous triamides. In the molecules of these compounds, the hydroxy groups in the first ring occupies the β-position, and the other group occupies the most remote α- or β-position in the second ring of the naphthalene system. Such location of hydroxy groups allows formation of "double-decked" phosphacyclophanes based on these compounds. Such cyclophanes are expected to have very interesting chemical properties.

To prepare these bicyclic structures, we used three procedures that proved to be successful in the previous studies. These included molecular assembling (*a*), direct cyclophosphorylation (*b*), and disproportionation of bisphosphorylated naphthodiols (*c*).



All the reactions were carried out in anhydrous acetonitrile at room temperature without special removal of the secondary amine formed in the reaction.

The first stage of molecular assembling was obtaining bisphosphorylated naphthodiols. We have shown that the phosphorylation rate depends on the structures of the naphthodiol and phosphorylating

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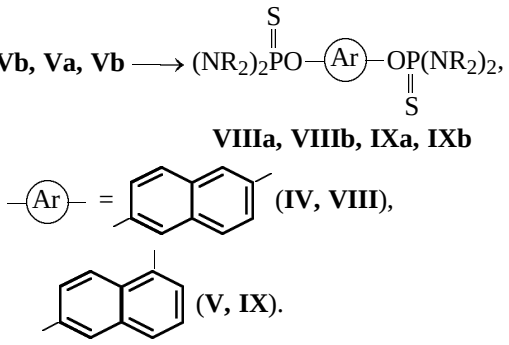
agent, phosphoroamidite. In particular, bisphosphorylation of 2,6-dihydroxynaphthalene with hexaethylphosphorous triamide **IIIb** is complete in 12 min, while with 1,6-dihydroxynaphthalene it takes 1.5 h. At the same time, the reaction with triamide **IIIa** is complete in 4 and 10 min, respectively.

All the synthesized bisphosphorylated naphthodiols **IVa**, **IVb**, **Va**, and **Vb** are unstable compounds tending to disproportionate in solutions. Therefore, they were converted to thiophosphates **VIIIa**, **VIIIb**, **IXa**, and **IXb** which are stable and can be used for identification of the compounds obtained.

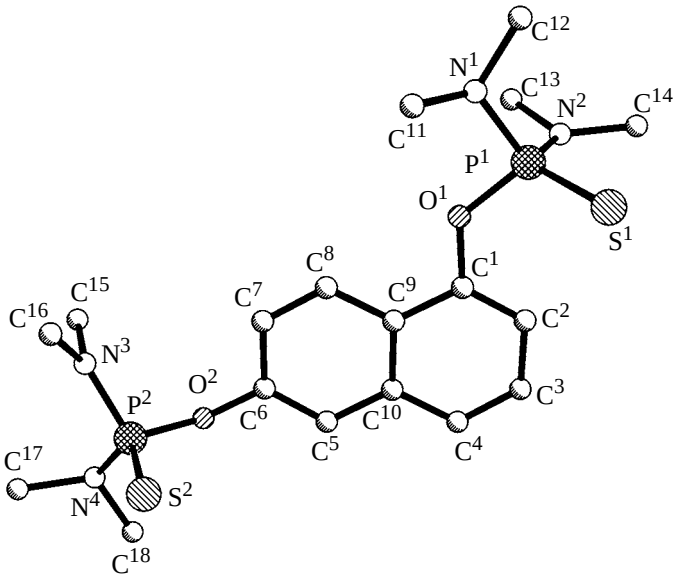


The thiophosphates were purified by column chromatography, and crystalline compounds were obtained. The ^{31}P NMR spectra of the thiophoshates derived from 2,6-dihydroxynaphthalene contained only the singlets in the range characteristic of *O*-phosphoramidothioates, while the compounds prepared from 1,6-dihydroxynaphthalene gave two signals, because of the asymmetry of this molecule (Table 1). The ^{1}H NMR spectra contained the signals of all groups of protons with the consistent ratio of integral intensities. The molecular structure of 1,6-bis(tetramethyldiaminothiophosphoryloxy)naphthalene **VIIIa** was also confirmed by single crystal X-ray diffraction (see figure; Tables 2, 3).

It was shown that the aromatic rings are planar, OPO angles differ from each other by 3°, the sulfur atoms are located on the one side of the plane of the aromatic rings, whereas the phosphorus atoms are located differently: P^1 above the plane and P^2 in the plane of the aromatic rings.

Subsequent cyclization of bisphosphorylated systems with 1 mol of the starting diol, and also the direct synthesis based on the reaction of equimolar amounts of the starting substances yield the same biscyclophosphoramidites **VIa**, **VIb**, **VIIa**, and **VIIb**. The highest yields were attained in the direct synthesis (method *b*, Table 4).

Some features of disproportionation of bisphosphorylated 2,6- and 1,6-dihydroxynaphthalenes should be noted. As shown previously, the reaction depends on the radical at nitrogen, as well as on the solvent used. The process was considered to be complete when the signal of the starting bisphosphoramidite disappeared from the ^{31}P NMR spectrum, and only the signal of the forming phosphorous triamide was observed. For compounds prepared from 2,6-dihydroxynaphthalene (**IVa**, **IVb**), the reaction was complete in acetonitrile in 40 days for the methyl derivative and in 23–30 days for the ethyl derivative. The methyl derivative prepared from 1,6-dihydroxynaphthalene **Va** reacts to only 40% conversion of the starting bisphosphite. Prolonged heating of the reaction mixture does not improve the result, but addition of dimethylammonium chloride allows the reaction to be completed in 10 days. With the ethyl derivative, the disproportionation is complete in 17 days.



Molecular structure of 1,6-bis(tetramethyldiaminothiophosphoryloxy)naphthalene **IXa**.

Using diethyl ether instead of acetonitrile does not change the reaction pattern, but in methylene chloride the reaction sharply accelerates, being complete in 9 days. These results suggest the complex reaction mechanism, which is evidently due to the superposition of such factors as the solvation, removal of the product from the reaction sphere, and formation of supramolecular structures involving the starting compounds and products, and also solvents.

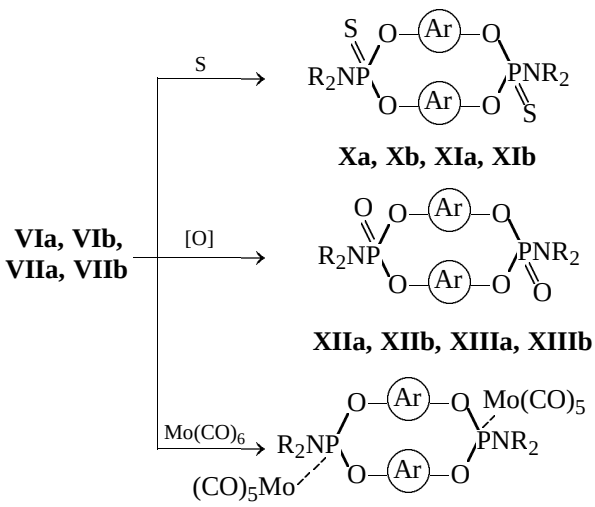
Biscyclophosphoramidites **VIa**, **VIb**, **VIIa**, and **VIIb** obtained in all the three reactions are isolated from the reaction mixture as viscous oils. After drying

Table 1. Parameters of the ^{1}H and ^{31}P NMR spectra of **VIa**–**XVa** and **VIb**–**XVb**

Comp. no.	^{1}H NMR spectrum, δ, ppm (*J*, Hz) (solvent)	^{31}P NMR spectrum, δ_P, ppm (solvent)
VIa	2.87 d (12H, CH_3, $^{3}J_{HH}$ 9.39), 7.24 d, 7.4 s (4H, CH), 7.65 d (2H, CH, $^{3}J_{PH}$ 8.54) ($CDCl_3$)	140.26 (CH_2Cl_2)
VIb	1.12 t (12H, CH_3, $^{3}J_{HH}$ 7.15), 3.31 m (8H, CH_2, $^{3}J_{PH}$ 9.89), 7.25 d (4H, CH, $^{3}J_{HH}$ 8.79, $^{4}J_{HH}$ 2.2), 7.43 s (2H, CH), 7.66 d (2H, CH, $^{3}J_{HH}$ 8.8) ($CDCl_3$)	141.72 (CH_2Cl_2)
VIIa	2.84 d (6H, CH_3, $^{3}J_{PH}$ 9.9), 2.93 d (6H, CH_3, $^{3}J_{PH}$ 11.0), 7.05 d (2H, C^2H, $^{3}J_{H^2H^3}$ 6.6), 7.27 d (2H, C^7H, $^{3}J_{H^7H^8}$ 9.9), 7.34 t (2H, C^3H), 7.47 s (2H, C^5H), 8.17 d (2H, C^4H, $^{3}J_{H^3H^4}$ 9.35), 8.21 d (2H, C^8H, $^{3}J_{H^7H^8}$ 9.9) ($CDCl_3$)	139.27 (CH_2Cl_2)
VIIb	1.17 t (12H, CH_3, $^{3}J_{HH}$ 7.45), 3.41 m (8H, CH_2, $^{3}J_{PH}$ 12.64), 7.13 d (2H, C^2H), 7.33 d (2H, C^7H), 7.46 t (2H, C^3H), 7.52 s (2H, C^5H), 8.21 d (2H, C^4H, $^{3}J_{H^3H^4}$ 7.7), 8.25 d (2H, C^8H, $^{3}J_{H^7H^8}$ 7.69) ($CDCl_3$)	140.89 (CH_2Cl_2)
VIIIa	2.77 d (24H, CH_3, $^{3}J_{PH}$ 12.37), 7.25 d (2H, CH, $^{4}J_{PH}$ 2.05), 7.48 s (2H, CH, $^{4}J_{HH}$ 2.14), 7.74 d (2H, CH, $^{3}J_{HH}$ 8.96) ($CDCl_3$)	81.62 (CH_3CN)
VIIIb	1.17 t (24H, CH_3), 3.27 m (16H, CH_2, $^{3}J_{PH}$ 10.3), 7.29 d, 7.75 s, 7.72 d (6H, CH) ($CDCl_3$)	76.51 (CH_3CN)
IXa	2.73 d (12H, CH_3, $^{3}J_{PH}$ 11.82), 2.78 d (12H, CH_3, $^{3}J_{PH}$ 11.82), 7.16 d.d (1H, C^2H, $^{3}J_{H^2H^3}$ 7.7, $^{4}J_{H^2H^4}$ 2.1), 7.3 d.m (1H, C^7H, $^{3}J_{H^7H^8}$ 9.35, $^{4}J_{H^7H^5}$ 1.1, $^{4}J_{PH}$ 1.2), 7.46 t (1H, C^3H, $^{3}J_{H^2H^3}$ 7.7, $^{3}J_{H^3H^4}$ 8.25), 7.51 s (1H, C^5H, $^{4}J_{H^5H^7}$ 2.2), 7.66 d (1H, C^4H, $^{3}J_{H^3H^4}$ 8.25), 8.1 d (1H, C^8H, $^{3}J_{H^7H^8}$ 9.35) (CD_3CN)	81.46, 80.89 (CH_3CN)
IXb	1.16 m (24H, CH_3, $^{3}J_{HH}$ 12.85), 3.28 m (16H, CH_2, $^{3}J_{HH}$ 12.81, $^{3}J_{PH}$ 7.15), 7.35 d (1H, C^2H), 7.38 d (1H, C^7H, $^{3}J_{H^7H^8}$ 8.8), 7.43 t (1H, C^3H, $^{3}J_{H^2H^3}$ 7.7), 7.57 s (1H, C^5H, $^{4}J_{H^5H^7}$ 2.2), 7.60 d (1H, C^4H, $^{3}J_{H^3H^4}$ 8.25), 8.1 d (1H, C^8H, $^{3}J_{H^7H^8}$ 8.8) (CD_3CN)	76.34, 75.43 (CH_3CN)
Xa	2.78 d (6H, CH_3, $^{3}J_{PH}$ 7.15), 3.05 d (6H, CH_3, $^{3}J_{PH}$ 11.7), 7.4 d (2H, CH, $^{4}J_{HH}$ 1.46), 7.66 s (2H, CH), 7.79 d (2H, CH, $^{3}J_{HH}$ 8.77) ($CDCl_3$)	68.73 (CH_2Cl_2)
Xb	1.17 t (12H, CH_3, $^{3}J_{HH}$ 7.15), 3.51 m (8H, CH_2, $^{3}J_{PH}$ 13.17), 7.40 d, 7.68 s (8H, CH), 7.79 d (4H, CH, $^{3}J_{HH}$ 8.79) ($CDCl_3$)	66.50 (CH_2Cl_2)
XIa	3.08 d (12H, CH_3, $^{3}J_{PH}$ 11.8), 7.38 d (2H, C^2H, $^{3}J_{H^2H^3}$ 7.7), 7.41 d (2H, C^7H, $^{3}J_{H^7H^8}$ 8.25), 7.51 t (2H, C^3H, $^{3}J_{H^2H^3}$ 7.7), 7.54 s (2H, C^5H), 7.65 d (2H, C^4H), 8.01 d (2H, C^8H, $^{3}J_{H^7H^8}$ 8.24) ($CDCl_3$)	67.81 (CH_2Cl_2)
XIb	1.17 t (12H, CH_3), 3.54 m (8H, CH_2, $^{3}J_{PH}$ 14.00), 7.39 d (2H, C^2H), 7.43 d (2H, C^7H), 7.49 t (2H, C^3H), 7.57 s (2H, C^5H), 7.7 d (2H, C^4H), 8.03 d (2H, C^8H, $^{3}J_{H^7H^8}$ 8.25) ($CDCl_3$)	66.84 (CH_2Cl_2)
XIIa	2.79 d (12H, CH_3), 7.41 d (4H, CH, $^{4}J_{HH}$ 1.09), 7.71 s (4H, CH), 7.86 d (2H, CH, $^{3}J_{HH}$ 8.77) ($CDCl_3$)	(CH_2Cl_2)
XIIa	1.05 t (12H, CH_3, $^{3}J_{HH}$ 7.33), 3.27 m (8H, CH_2, $^{3}J_{PH}$ 12.21), 7.39 d (4H, CH, $^{3}J_{HH}$ 9.28), 7.71 s (4H, CH, $^{4}J_{HH}$ 3.91), 7.75 d (4H, CH) ($CDCl_3$)	1.05 (CH_2Cl_2)
XIIIa	2.84 d (12H, CH_3, $^{3}J_{PH}$ 17.6), 7.40 d (2H, C^2H), 7.50 d (2H, C^7H, $^{3}J_{H^7H^8}$ 8.25), 7.58 t (2H, C^5H, $^{4}J_{H^2H^3}$ 1.31), 7.72 t (2H, C^3H, $^{3}J_{H^3H^4}$ 7.7), 8.06 d (2H, C^4H), 8.12 d (2H, C^8H) ($CDCl_3$)	1.78 (CH_2Cl_2)
XIIIb	1.04 t (12H, CH_3), 3.29 m (8H, CH_2, $^{3}J_{PH}$ 11.18), 7.41 d (2H, C^2H), 7.55 d (2H, C^7H), 7.59 t (2H, C^3H), 7.75 s (2H, C^5H), 8.06 d (2H, C^4H), 8.11 d (2H, C^8H) ($CDCl_3$)	1.61 (CH_2Cl_2)
XIVa	2.92 d (12H, CH_3, $^{3}J_{PH}$ 10.46), 7.16 d (2H, CH), 7.40 d (2H, CH, $^{3}J_{HH}$ 8.24), 7.53 s, 7.60 s, 7.68 d (6H, CH), 7.81 d (2H, CH, $^{3}J_{HH}$ 8.25) ($CDCl_3$)	164.31 (dioxane)
XIVa	1.30 t (12H, CH_3), 3.45 m (8H, CH_2), 7.35 d, 7.53 s, 7.76 d (6H, CH), 7.38 d, 7.56 s, 7.81 d (6H, CH) ($CDCl_3$)	163.52 (dioxane)
XVa	2.80 d (6H, CH_3, $^{3}J_{PH}$ 9.9), 2.88 d (6H, CH_3, $^{4}J_{HH}$ 8.8), 6.99 d (2H, C^2H), 7.38 s (2H, C^5H), 7.41 t (2H, C^3H), 7.71 d (2H, C^7H), 7.75 d (2H, C^4H), 8.50 d (2H, C^8H) ($CDCl_3$)	163.13 (C_6H_6)
XVb	1.19 t (12H, CH_3), 3.48 m (8H, CH_2), 7.44 d (2H, C^2H), 7.61 d (2H, C^7H), 7.65 t (2H, C^3H), 7.71 s (2H, C^5H), 8.28 d (2H, C^4H), 8.35 d (2H, C^8H) ($CDCl_3$)	164.35 (C_6H_6)

in a vacuum, they became friable amorphous foams. High (>200°C) melting points of the 2,6-dihydroxynaphthalene derivatives well agree with the same characteristics of the derivatives of symmetrical 1,5- and 2,7-dihydroxynaphthalenes [1], whereas the characteristics of the 1,6-dihydroxynaphthalene derivatives significantly differ from those of the compounds derived from unsymmetrical 1,7-dihydroxynaphthalene [3]. All the structures were determined by the spectroscopic methods and confirmed by elemental analysis.

Construction of the Dreiding models and computer simulation have shown that phosphacyclanes derived from 2,6-dihydroxynaphthalenes are the typical "double-decked" systems. For the unsymmetrical 1,6-dihydroxynaphthalene derivatives, formation of two structural isomers could be expected, similarly to the derivatives of 1,7-dihydroxynaphthalene. However, actually the products obtained from 1,6-dihydroxynaphthalene contained only one isomer irrespective of the synthetic procedure. We believe that the isolated products are 1,6,1,6 isomers, because the computer simulation has shown that formation of the 1,1,6,6 isomers is energetically unfavorable.



Xa, Xb, XIa, XIb

XIIa, XIIb, XIIIa, XIIIb

XIVa, XIVb, XVa, XVb

The compounds obtained were subjected to oxidation, sulfurization, and complex formation. The TLC, ^{1}H, and ^{31}P NMR spectra completely confirmed the purity of the phosphates, thiophosphates, and molybdenum complexes obtained.

The oxidation and sulfurization readily occurred at room temperature. The products, cyclothiophosphates **Xa, Xb, XIa**, and **XIb** and cyclophosphates **XIIa**, **XIIb**, **XIIIa**, and **XIIIb**, after purification by column chromatography or precipitation, respectively, were powder-like substances; the melting points of the

Table 2. Atomic coordinates ($\times 10^4$) and isotropic temperature factors (Å$\times 10^3$) of 1,6-bis(tetramethyldiaminothiophosphoryloxy)naphthalene **IXa**

Atom	*x*	*y*	*z*	U_{iso}
P^1	8995(1)	2111(1)	3210(1)	42(1)
P^2	3990(1)	2178(1)	3749(1)	40(1)
S^1	9444(1)	4404(1)	3282(1)	62(1)
S^2	3954(1)	4554(1)	3466(1)	67(1)
O^1	8187(1)	1913(3)	3467(1)	53(1)
O^2	4870(1)	1586(3)	4296(1)	47(1)
N^1	8588(2)	1280(3)	2384(1)	54(1)
N^2	9651(2)	708(3)	3677(2)	64(1)
N^3	3754(2)	847(3)	3061(1)	54(1)
N^4	3441(2)	1546(3)	4272(1)	54(1)
C^1	8056(2)	2519(4)	4103(1)	43(1)
C^2	8655(2)	3217(4)	4674(2)	55(1)
C^3	8447(2)	3791(5)	5293(2)	59(1)
C^4	7669(2)	3655(4)	5329(2)	54(1)
C^5	6221(2)	2708(4)	4768(2)	42(1)
C^6	5636(2)	1941(4)	4205(2)	39(1)
C^7	5818(2)	1382(4)	3580(2)	42(1)
C^8	6595(2)	1586(3)	3533(2)	39(1)
C^9	7232(2)	2326(3)	4114(1)	36(1)
C^{10}	7033(2)	2903(4)	4743(1)	40(1)
C^{11}	7792(3)	1908(7)	1913(2)	74(1)
C^{12}	9189(3)	1004(7)	1982(3)	83(1)
C^{13}	9409(4)	–1119(6)	3641(5)	115(2)
C^{14}	10528(3)	1007(10)	3997(7)	144(4)
C^{15}	3811(4)	–1008(5)	3193(3)	83(1)
C^{16}	3511(3)	1342(8)	2297(2)	83(1)
C^{17}	2548(2)	1375(7)	3923(3)	82(1)
C^{18}	3667(3)	2167(6)	5030(2)	71(1)

Table 3. Selected interatomic distances (*d*, Å) and bond angles (ω, deg) in 1,6-bis(tetramethyldiaminothiophosphoryloxy)naphthalene **IXa**

Bond	*d*	Angle	ω
P^1–O^1	1.601(2)	$O^1P^1N^2$	105.90(14)
P^1–N^2	1.617(3)	$O^1P^1N^2$	96.48(12)
P^1–N^1	1.651(3)	$N^2P^1N^1$	106.16(16)
P^1–S^1	1.9273(12)	$O^1P^1S^1$	115.11(9)
P^2–O^2	1.604(2)	$O^2P^2N^4$	96.06(12)
P^2–N^3	1.626(3)	$O^2P^2N^3$	107.03(13)
P^2–N^4	1.641(3)	$O^2P^2S^2$	113.70(9)
P^2–S^2	1.9211(12)	$C^1O^1P^1$	128.49(19)
O^1–C^1	1.388(3)	$C^6O^2P^2$	125.33(17)
O^2–C^6	1.392(3)	$C^2C^1O^1$	124.1(3)
		$O^1C^1C^9$	113.9(2)
		$O^2C^6C^7$	120.7(3)
		$C^5C^6O^2$	118.0(3)

Table 4. Yields, melting points, R_f values, and elemental analyses of compounds **VIa**–**XVa** and **VIb**–**XVb**

Comp. no.	Yield, % (method)	mp, °C	R_f (system)	Found, %				Formula	Calculated			
				C	H	N	P		C	H	N	P
VIa	58 (*a*) 61 (*b*) 51 (*c*)	224–226	0.77 (C)	61.45	5.31	6.40	12.91	$C_{24}H_{24}N_2O_4P_2$	61.79	5.18	6.01	13.08
VIb	54 (*a*) 64 (*b*) 55 (*c*)	204–205	0.8 (C)	64.01	6.23	5.42	11.45	$C_{28}H_{32}N_2O_4P_2$	64.35	6.18	5.36	11.82
VIIa	68 (*a*) 70 (*b*) 57 (*c*)	229–230	0.63 (C)	61.58	5.24	6.41	13.18	$C_{24}H_{24}N_2O_4P_2$	61.79	5.18	6.05	13.25
VIIb	62 (*a*) 65 (*b*) 58 (*c*)	101–102	0.75 (C)	–	–	–	11.81	$C_{28}H_{32}N_2O_4P_2$	–	–	–	11.86
VIIIa	39	143–144	0.52 (A)	46.90	6.53	12.19	13.47	$C_{18}H_{30}N_4O_2P_2S_2$	46.93	6.57	12.17	13.46
VIIIb	49	117–118	0.61 (A)	54.50	8.02	9.71	10.78	$C_{26}H_{46}N_4O_2P_2S_2$	54.52	8.09	9.78	10.82
IXa	41	150–151	0.59 (A) 0.22 (B)	46.91	6.54	12.18	13.46	$C_{18}H_{30}N_4O_2P_2S_2$	46.93	6.57	12.17	13.46
IXb	37	[a]	0.52 (B)	54.32	8.10	9.71	10.84	$C_{26}H_{46}N_4O_2P_2S_2$	54.52	8.10	9.77	10.82
Xa	70	137–139	0.77 (C)	54.12	4.49	5.29	11.7	$C_{24}H_{24}N_2O_4P_2S_2$	54.32	4.56	5.28	11.67
Xb	73	144–146	0.81 (C)	57.25	5.41	4.78	10.54	$C_{28}H_{32}N_2O_4P_2S_2$	57.32	5.50	4.77	10.56
XIa	80	110–111	0.91 (C)	–	–	–	11.58	$C_{24}H_{24}N_2O_4P_2S_2$	–	–	–	11.67
XIb	82	138–139	0.82 (C)	57.29	5.48	4.75	10.57	$C_{28}H_{32}N_2O_4P_2S_2$	57.32	5.50	4.77	10.56
XIIa	92	94–95	0.85 (D)	57.84	4.74	5.67	12.40	$C_{24}H_{24}N_2O_6P_2$	57.83	4.85	5.62	12.43
XIIb	94	111–112	0.9 (D)	60.71	5.94	5.11	11.21	$C_{28}H_{32}N_2O_6P_2$	60.64	5.82	5.05	11.17
XIIIa	94	155–156	0.37 (C) 0.69 (D)	57.86	4.83	5.59	12.46	$C_{24}H_{24}N_2O_6P_2$	57.83	4.86	5.07	12.43
XIIIb	93	131–132	0.73 (D)	–	–	–	11.15	$C_{28}H_{32}N_2O_6P_2$	–	–	–	11.17
XIVa	81	112–113 (decomp.)	0.76 (C)	43.71	2.18	–	6.55	$C_{34}H_{24}N_2O_{14}P_2Mo_2$	43.52	2.58	–	6.60
XIVb	85	129–130 (decomp.)	0.79 (C)	45.93	3.28	3.56	6.15	$C_{38}H_{32}N_2O_{14}P_2Mo_2$	45.89	3.24	3.61	6.24
XVa	80	145–146 (decomp.)	0.73 (C)	43.58	2.25	–	6.52	$C_{34}H_{24}N_2O_{14}P_2Mo_2$	43.51	2.56	–	6.59
XVb	79	119–120 (decomp.)	0.78 (C)	–	–	–	6.18	$C_{38}H_{32}N_2O_{14}P_2Mo_2$	–	–	–	6.26

[a] Viscous oily substance.

phosphates were lower than those of the thiophosphates.

Molybdenum complexes **XIVa**, **XIVb**, **XVa**, and **XVb** were prepared by heating of cyclophosphites in benzene or dioxane with $Mo(CO)_6$ in a sealed ampule at 85–95°C for 7–10 h. The complexes, isolated by precipitation, were powders decomposing on heating or storage in the light.

Thus, we have confirmed the conclusions made by us in [1, 2] that the alteration of position of hydroxy groups in dihydronaphthalenes significantly affects their reactivity and also the structure of the resulting phosphacyclophanes.

EXPERIMENTAL

The ^1H NMR spectra were recorded on a Bruker WH-250 (250 MHz) spectrometer relative to TMS. The ^{31}P NMR spectra were measured on a Bruker WP-80 SY spectrometer (32.4 MHz) relative to 85% phosphoric acid.

Adsorption chromatography was carried out on a column packed with silica gel L 100/250. TLC ana-

lysis was performed on Silufol plates, elution with 3:1 hexane–dioxane (A), 7:1 hexane–dioxane (B), 5:1 benzenedioxane (C), 10:1 benzene–dioxane (D), and 5:1 chloroform–ethanol (E). The chromatograms were developed with iodine vapor and by calcination.

Single crystal X-ray diffraction study of VIIIa was performed on an Enraf–Nonius CAD-4 automatic diffractometer with MoK_α radiation. Monoclinic colorless crystal ($C_{18}H_{30}N_4O_2P_2S_2$, *M* 460.52); $0.55 \times 0.30 \times 0.12$ mm, space group $P2_1/n$, *a* 16.973(3), *b* 7.777(2), *c* 19.154(4) Å, β 108.03(3)°, *V* 2404(9) Å^3, *Z* 4, d_{calc} 1.272 mg/cm^3, θ/2θ scanning, θ_{max} 24.96°, 2317 reflections, including 2230 unique reflections [*R*(int) 0.0162] with $F > 2\sigma(F)$. Refinement by the full-matrix least-squares method with respect to F^2. Number of refined parameters 374, *GOF* 0.968, $R_1(F)$ 0.0276, $wR_2(F^2)$ 0.0747.

2,6-Bis(tetraalkyldiaminothiophosphoryloxy)-naphthalenes VIIIa and VIIIb. To a solution of 1.84 mmol of **IIIa** or **IIIb** in 2 ml of anhydrous acetonitrile, a solution of 0.92 mmol of naphthodiol **I** in 8 ml of the same solvent was added with stirring at room temperature to obtain intermediate **IVa** or **IVb**. Then (in 4 min for **IVa** and 12 min for **IVb**), 1.84 mmol of sulfur was added. The mixture was stirred for 3 h. The resulting solution was filtered, the solvent was removed in a vacuum, and the residue was chromatographed on a column, elution with 7:1 dioxane–hexane. The products were dried in a vacuum (1 mm, 70°C) for 2 h.

1,6-Bis(tetraalkyldiaminothiophosphoryloxy)-naphthalenes IXa and IXb. To a solution of 3 mmol of **IIIa** or **IIIb** in 5 ml of dry acetonitrile, a solution of 1.5 mmol of naphthol **II** in 7 ml dry acetonitrile was added with stirring at room temperature to obtain intermediate **Va** or **Vb**. Then (in 10 min for **Va** and 1.5 h for **Vb**), 3 mmol of sulfur was added, and the mixture was stirred for an additional 3 h. Then the solution was filtered, the solvent was removed in a vacuum, and the residue was chromatographed on a column, elution with 10:1 hexane–dioxane. The products were dried in a vacuum (1 mm, 70°C) for 2 h.

Cyclo[2,6-bis(naphthylene dialkylphosphoramidites)] VIa and VIb. *a*. To a solution of 8.4 mmol of **IIIa** or **IIIb** in 6 ml of anhydrous acetonitrile, a solution of 4.2 mmol of naphthodiol **I** in 6 ml of the same solvent was added with stirring at room temperature to obtain intermediate **IVa** or **IVb**. Then (in 4 min for **IVa** and 12 min for **IVb**), additional 4.2 mmol of naphthodiol **I** in 6 ml of acetonitrile was added, and the mixture was left overnight. The precipitate that formed was washed with acetonitrile and dried in a vacuum (1 mm, 70°C) for 2.5 h.

b. To a solution of 6 mmol of **IIIa** or **IIIb** in 5 ml of anhydrous acetonitrile, a solution of 6 mmol of naphthodiol **I** in 5 ml of the same solvent was added. On the next day, the mother liquid was decanted, and the precipitate was washed with acetonitrile and dried in a vacuum (1 mm, 70°C) for 2.5 h.

c. A solution of 2 mol of naphthodiol **I** in 4 ml of dry acetonitrile was added to 4 mmol of **IIIa** or **IIIb**. The reaction mixture was kept for 40 days in the case of **IVa** and 23 days in the case **IVb**. After that, the mother liquor was decanted, and the crystals that formed were washed with acetonitrile and dried in a vacuum (1 mm, 70°C) for 2.5 h.

Cyclo[1,6-bis(naphthylene dialkylphosphoramidites)] VIIa–VIIc. *a*. To a solution of 8 mmol of **IIIa** or **IIIb** in 6 ml of anhydrous acetonitrile, 4 mmol of naphthodiol **II** in 6 ml of the same solvent was added with stirring at room temperature to obtain intermediate **Va** or **Vb**. Then additional 4 mmol of naphthodiol **II** in 6 ml of anhydrous acetonitrile was added (in 5 min for **Va** and 1.5 h for **Vb**), and the mixture was left overnight. The precipitate that formed was washed with acetonitrile and dried in a vacuum (1 mm, 70°C) for 2.5 h.

b. To a solution of 4 mmol of **IIIa** or **IIIb** in 5 ml of anhydrous acetonitrile, a solution of 4 mmol of naphthodiol **II** in 5 ml of the same solvent was added. On the next day, the mother liquor was decanted, and the crystals were washed with acetonitrile and dried in a vacuum (1 mm, 70°C) for 2.5 h.

c. A solution of 2 mmol of naphthodiol **II** in 4 ml of anhydrous acetonitrile was added to 4 mmol of **IIIa** or **IIIb** to obtain intermediate **Va** or **Vb**. The mixture was kept for 10 days, then dimethylammonium chloride was added, and the resulting mixture was kept for additional 17 days in the case of **Va** and 23 days in the case of **Vb**. After that, the mother liquor was decanted, and the precipitate that formed was washed with acetonitrile and dried in a vacuum (1 mm, 70°C) for 2.5 h.

Cyclo[bis(*O,O'*-naphthylene dialkylphosphoramidothioates)] Xa, Xb, XIa, and XIb. To a solution of 4 mmol of **VIa, VIb, VIIa**, or **VIIb** in 7 ml of dry methylene chloride, 8 g of sulfur was added with stirring at room temperature. On the next day, the solution was filtered, the solvent was evaporated in a vacuum, and the residue was chromatographed on a column, elution with 7:1 benzene–dioxane (**Xa**, **XIa**) or 10:1 benzene–dioxane (**Xb**, **XIb**). The products were dried in a vacuum (1 mm, 70°C) for 2 h.

Cyclo[bis(naphthylene dialkylphosphoramidates)] XIIa, XIIb, XIIIa, and XIIIb. To a solution

of 2 mmol of **VIa, VIb, VIIa**, or **VIIb** in 7 ml of dry methylene chloride, 4 mmol of the complex of urea with hydrogen peroxide was added at room temperature. On the next day, the solution was filtered, the solvent was removed in a vacuum, and the residue was precipitated from methylene chloride with hexane. The products were dried in a vacuum (1 mm, 60°C) for 2 h.

μ-Cyclo[bis(naphthylene dialkylphosphoramidite)]bis[pentacarbonylmolybdenum(0)] XIVa, XIVb, XVa, and XVb. To a solution of 1 mmol of **VIa**, **VIb**, **VIIa**, or **VIIb** in benzene or dioxane, 2.5 mmol of $Mo(CO)_6$ was added. The reaction mixture was heated in a sealed ampule at 85–95°C for 10 h. Then the mixture was diluted with benzene or dioxane and filtered. The solvent was evaporated in a vacuum, and the residue was precipitated with hexane. The products were dried in a vacuum (1 mm, 40°C) for 2 h.

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