Chiral Molecular Cavities Based on 1,4;3,6-Dianhydro-*D*-mannite Bis(tetraethylphosphorodiamidite)

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Abstract—The possibility of forming chiral molecular cavities from an accessible bisphosphorylated derivative of 1,4;3,6-dianhydro-*D*-mannite and various bisphenols was examined.

We have studied previously phosphorylation of 1,4;3,6-dianhydro-D-mannite I, a chiral diol in which the hydroxy groups are closely located in space, with amides of trivalent phosphorus acids [1]. An important structural feature of I is that its molecule consists of two fused furanose rings, with the hydroxyls occupying the endo positions relative to the internal chiral cavity. Thanks to this feature, bis-P(III)-phosphorylated derivatives of I are of interest as bidentate ligands with two chelating P(III) atoms located on a bulky chiral matrix [1, 2]. Furthermore, bisphosphoroamidite derivatives of I show promise as synthetic precursors of phosphorus-containing chiral macroheterocycles [3]. Such structures are of particular interest for molecular encapsulation, enantioselective catalysis, synthesis of host-guest complexes, and other lines of supramolecular chemistry [4].

In this context, our goal was to design chiral molecular cavities based on *D*-mannite bis(tetraalkylphosphorodiamidite) **II**, using modern methods of trivalent phosphorus chemistry [5]. The molecules of **II** have a shape of a deep basket with a fixable "grip" (i.e., a bisphenol or diol residue). Therefore, in designing such structures, two problems should be solved. The first is the choice of a "grip," namely, of a bisphenol geometrically suited for formation of a bridge with **II**. Among available bisphenols, we chose six compounds: 2,2'-dihydroxydiphenyl **III**, 2,2'-dihydroxy-5,5'-dimethyl-3,3'-di-*tert*-butyldiphenylmethane **IV**, 2,2-di(*p*-hydroxyphenyl)propane **V**, di(*p*-hydroxyphenyl)diphenylmethane **VI**, 4,4'-dihydroxydiphenyl ether **VII**, and 4,4'-dihydroxydiphenyl sulfide **VIII**. The second problem concerns the selectivity of the process which can, generally speaking, occur by several pathways: (a) diphosphocyclization (each phosphamide group in **II** singly phosphorylates different hydroxyls of the bisphenol to form a diphosphite macroheterocycle); (b) monophosphocyclization (one or both phosphamide groups of **II** doubly phosphorylate the dihydric phenol); and (c) incomplete phosphorylation without formation of phosphocycles (one or both phosphamide groups singly phosphorylate the bisphenol).



The progress of phosphorylation was monitored by ³¹P NMR spectroscopy. Experiments were started from the simplest of the selected dihydric phenols, diphenyl derivative **III**. We showed that the reaction of **II** (138 ppm) with an equimolar amount of **III** follows pathway *b*: After phosphorylation completion, only two signals of equal intensity at 138 and 136 ppm are detected, belonging, respectively, to the phosphorus atoms of the phosphorodiamidite and phosphite moieties of **IX**. Addition of sulfur yields product **X** whose ³¹P NMR spectrum consists of two signals of equal intensity at 79 and 73 ppm, belonging, respectively, to the phosphorodiamidothioate and phosphorothioate moieties. The reaction of the second equivalent of **III** with **IX**, or the reaction of **II** with **III** in a 1 : 2 ratio



yields bisphosphocyclic structures: phosphites **XI** and (after uptake of S) phosphorothioates **XIII**. These compounds give singlets at 136 and 73 ppm, respectively.

bridge and the hydroxyls are sterically shielded by bulky substituents reacts exclusively by pathway c, without formation of phosphocycles.



X = lone electron pair (IX, XI); X = S (X, XII).

Bisphenol **IV** in which the distance between the hydroxyls is larger owing to the additional methylene

X =lone electron pair (XIII, XV); X = S (XIV, XVI).

XV, XVI

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In the spectrum of the reaction mixture in synthesis of **XIII**, after the reaction completion, two signals of equal intensity are observed at 138 and 152 ppm, belonging, respectively, to phosphorus atoms of the phosphorodiamidite and phosphoramidite moieties. After addition of sulfur, we isolated pure unsymmetrical adduct **XIV** in which the phosphorus atoms of the phosphorodiamidothioate and phosphoramidothioate moieties gave, respectively, the signals at 80 and 74 ppm. The suggested structure of **XIV** was also confirmed by the ¹H NMR spectra, e.g., by the relative integral intensities of the proton signals of the ethyl and *tert*-butyl groups.

On treatment of bisphosphite II with two equivalents opf bisphenol IV, we could expect firther substitution of the second amido group at the same P atom and substitution of the amido group at the second P atom. However, disappearance of the signal at 137 ppm and appearance of only one signal at 152 ppm suggest the symmetrical structure of XV and location of the second residue of bisphenol IV at the second P atom. Bis(phosphoramidothioate) XVI also gives a single signal at 74 ppm. On the whole, it should be noted that the P(III)-phosphorylation products IX, XI,¹ XIII, and XV, detected in the reaction mixture, were the major products; other possible products, according to the ³¹P NMR spectra, were present in trace amounts. The corresponding phosphorothioate derivatives X, XII, XIV, and XVI were isolated pure by reprecipitation (X), recrystallization (XII, XIV), and column chromatography (XVI) in 76–85% yields. To conclude, bisphenols III and IV appeared to be unsuitable for formation of macroheterocycles because of unfavorable steric arrangement of the hydroxy groups.

The desired diphosphocyclic structures (pathway *a*) were obtained with bisphenols **V**–**VIII** containing two sterically accessible hydroxyls fairly distant from each other, with dimethylmethylene (**V**), diphenylmethylene (**VI**), oxygen (**VII**), and sulfide (**VIII**) bridges providing a favorable angle $(109^{\circ}-124^{\circ} [6])$ between the central axes of the two phenylene residues.

The phosphorylation products **XVII**, **XIX**, **XXI**, and **XXIII** containing trivalent phosphorus atoms and their sulfide derivatives **XVIII**, **XX**, **XXII**, and **XXIV** give a pair of closely located signals of equal intensity in the ³¹P NMR spectra (ppm): 144.8, 145.2 (**XVII**); 145.7, 146.1 (**XIX**); 144.6, 145.5 (**XXI**); 145.2, 146.1



X = lone electron pair (XVII, XIX, XXI, XXII); X = S (XVIII, XX, XXII, XXIV); Y = CMe_2 (V, XVII, XVIII), CPh_2 (VI, XIX, XX), O (VII, XXI, XXII), S (VIII, XXIII, XXIV).

(XXIII); 71.8, 72.2 (XVIII); 72.0, 72.2 (XX); 71.6, 72.0 (XXII); and 72.1, 72.4 (XXIV). The splitting may be due to the magnetic nonequivalence resulting from different steric orientation of the two phosphorus atoms in these molecules relative to the chiral cavity. A similar splitting is observed in the ¹H NMR spectra of pure phosphorothioates XVIII, XX, XXII, and **XXIV.** Furthermore, in compound **XXII** containing an oxygen bridge between the phenyl groups, which provides the largest angle $(120^{\circ}-124^{\circ} [6])$ between the central axes of the two phenylene residues, the ethyl groups at the same nitrogen atom are also magnetically nonequivalent: Two separate groups of multiplets of the methylene protons of the ethyl groups are observed at 3.10 and 3.22 ppm, and the geminal coupling of the methylene protons in one of the two ethyl groups is clearly detected after decoupling with the methyl protons. This feature of XXII may be due to braked rotation of the *N*-diethyl groups, in contrast to XVIII, XX, and XXIV.

We also attempted to prepare the product of complete substitution of the amido groups by two molar equivalents of bisphenols V-VIII, including the reaction at elevated temperatures (100°C); however, we failed to isolate and identify the reaction products because of tarring.

Bisphenol V also appeared to be a convenient starting compound for preparing more complex macrocyclic systems based on dianhydro-*D*-mannite I and containing three phosphoryl functional groups. In this case, we chose a principally different synthesis strategy, so as to exclude formation of XVII (pathway *a*). The first step of the synthesis was the reaction of two equivalents of the phenol with an equivalent amount of hexaethylphosphorous triamide. The resulting phosphoramidite XXV without isolation was treated with sulfur to obtain phosphoramidothioate XXVI, which was isolated in 95% yield. Compound XXVI was

¹ Compound **XI** was also mentioned in [2], but, in contrast to our procedure [1], it was prepared using 2,2'-binaphthyl phosphorochloridite and was taken in further reactions without isolation.

phosphorylated with a double molar excess of phenyldichlorophosphine in the presence of triethylamine to obtain an original phosphorylated agent **XXVII** capable of cyclophosphorylating dianhydro-*D*-mannite **I**. This reaction was performed in the presence of triethylamine.



R = 2,2-diphenylpropane-*p*,*p*'-diyl; X = lone electron pair (**XXV**), S (**XXVI**); Y = lone electron pair (**XXVIII**), S (**XXIX**).

By addition of sulfur to bisphosphonite XXVIII, we obtained heterocyclic derivative **XXIX** containing three phosphorus functionalities. Compound XXIX was isolated in 76% yield as a colorless powder. Its purity and structure were proved by TLC, ¹H and ³¹P NMR spectroscopy, and elemental analysis. Similar to the above-mentioned phosphorothioates XVIII, XX, **XXII**, and **XXIV**, compound **XXIX** gives in the ${}^{31}P$ NMR spectrum the singlets at 88 and 86 ppm of two magnetically nonequivalent phosphorus atoms of the phosphonothioate moieties directly linked to the dianhydro-D-mannite residue; additionally, it contains the singlet at 67 ppm belonging to the phosphoramidothioate phosphorus atom. The ratio of the integral intensities of these signals is 1:1:1. The ¹H NMR spectrum of XXIX is also complicated by additional splitting (see Experimental).

Thus, starting from accessible dianhydro-*D*-mannite bis(phosphorodiamidites) and bisphenols, it is possible to design original chiral phosphorus-containing cavity systems showing promise for supramolecular chemistry.

EXPERIMENTAL

The ¹H NMR spectra were recorded on a Bruker WP-250 spectrometer, and the ³¹P–{¹H} NMR spectra, on a Bruker WP-80 spectrometer (working frequencies 250 and 32.4 MHz, respectively; ¹H, internal reference TMS; ³¹P, external reference 85% H₃PO₄). All the synthesis were performed in a dry nitrogen atmosphere using dehydrated solvents. Thin-layer chromatography was performed on Silufol UV-366 plates in the systems benzene–dioxane, 6:1 (**A**); benzene–dioxane, 10:1 (**B**); chloroform–ethanol, 3:1 (**C**); chloroform–ethanol, 10:1 (**D**); ethanol–dioxane, 10:1 (**E**); acetone–methanol, 1:3 (**F**); and acetone–dioxane, 1:1 (**G**).

1,4;3,6-Dianhydro-*D*-mannite 2,5-*O*,*O*-bis(tetraethylphosphorodiamidite) **II** was prepared as described in [1].

2-*O*-(4,5;6,7-Dibenzo-2-thioxo-1,3,2λ⁵-dioxaphosphepan-2-yl)-5-O-[bis(diethylamino)thiophosphoryl]-1,4;3,6-dianhydro-D-mannite X. A solution of 0.23 g of bisphenol III in 3 ml of benzene was added with stirring at 20°C to a solution of 0.61 g of II in 7 ml of benzene; the mixture was kept at 75-80°C for 2.5 h in a weak nitrogen flow, with removal of diethylamine. ³¹P NMR spectrum of the reaction mixture (compound IX), δ_{p} , ppm: 137.5 and 138, ratio of integral intensities 1:1. To the reaction mixture, we added 0.0795 g of finely divided sulfur and stirred for 1 h at 80°C; excess sulfur was filtered off, and the solvent was distilled off in a vacuum. The residue was dissolved in 5 ml of benzene, 10 ml of hexane was added, the mixture was stirred, and the light yellow viscous oily precipitate was separated. Yield 0.68 g (92%), R_f 0.8 (A). ¹H NMR spectrum (CDCl₃), δ, ppm: 1.05–1.17 m (12H, CH₃); 3.06– 3.18 m (8H, NCH₂); 3.64–3.71 m, 3.82–3.94 m, 4.09-4.21 m (4H, H^{ĨA}, H^{1B}, H^{6A}, H^{6B}); 4.54-4.66 m, 4.87-5.03 m (2H, H³, H⁴); 4.73-4.83 m, 5.23-5.37 m $(2H, H^2, H^5)$, 7.34–7.56 m (8H, H_{arom}). ³¹P NMR spectrum (C_6H_6), δ_P , ppm: 73 and 79; ratio of integral intensities 1 : 1. Found, %: C 51.75; H 6.15; P 10.39. C₂₆H₃₆N₂O₆P₂S₂. Calculated, %: C 52.16; H 6.06; P 10.34.

2,5-0,0-Bis(4,5;6,7-dibenzo-2-thioxo-1,3,2 λ^{5} -dioxaphosphepan-2-yl)-1,4;3,6-dianhydro-*D*-mannite XII. A solution of 0.23 g of bisphenol III in 3 ml of benzene was added with stirring at 20°C to the reaction mixture containing IX. The mixture was heated at 75–80°C for 2.5 h in a weak nitrogen flow, with the removal of diethylamine. ³¹P NMR spectrum of the reaction mixture (compound XI): δ_{p} 136 ppm. To the reaction mixture, we added 0.08 g of finely divided sulfur; the mixture was stirred for 1 h at 80°C, excess sulfur was filtered off, the solvent was distilled off in a vacuum, and the residue was recrystallized from 3 ml of benzene. Yield 0.65 g (85%), mp 111–112°C, R_f 0.8 (**A**), 0.6 (**B**). ¹H NMR spectrum (CDCl₃), δ, ppm (J, Hz): 3.87 d.d (2H, H^{1A}, H^{6A}, ²J_{1A,1B} 6.4); 4.12 d.d (2H, H^{1B}, H^{6B}, ²J_{6A,6B} 6.4); 4.81 d (2H, H³, H⁴, ³J_{3,4} 3.8); 5.25–5.37 m (2H, H², H⁵, ³J_{HP} 10.3), 7.21–7.58 m (16H, H_{arom}). ³¹P NMR spectrum (C₆H₆), δ_P, ppm: 73. Found, %: C 56.49; H 3.89; P 9.61. C₃₀H₂₄O₈P₂S₂. Calculated, %: C 56.42; H 3.79; P 9.70.

2-O-{O-[2-(2-Hydroxy-5-methyl-3-tert-butylphenylmethyl)-4-methyl-6-tert-butylphenyl]diethylaminothiophosphoryl}-5-O-[bis(diethylamino)thiophosphoryl]-1,4;3,6-dianhydro-D-mannite XIV. A solution of 0.63 g of bisphenol IV in 3 ml of benzene was added with stirring at 20°C to a solution of 0.92 g of II in 7 ml of benzene. The mixture was heated at 75-80°C for 2.5 h in a weak nitrogen flow, with the removal of diethylamine. ³¹P NMR spectrum of the reaction mixture (compound XIII), δ_{p} , ppm: 137 and 152, ratio of integral intensities 1 : 1. To the reaction mixture, we added 0.12 g of finely divided sulfur; the mixture was stirred for 1 h at 80°C, the solvent was distilled off in a vacuum, and the residue was recrystallized from 3 ml of benzene. Yield 1.95 g (85%), mp 55–56°C, $R_f 0.9$ (A), 0.7 (B). ¹H NMR spectrum (CDCl₃), δ, ppm: 1.00-1.16 m (18H, CH₃); 1.37-1.41 m [18H, C(CH₃)₃]; 2.15 s, 2.27 s (6H, C_{arom}-CH₃); 2.90–3.26 m (12H, NCH₂); 3.59–3.94 m (4H, H^{1A} , H^{1B} , H^{6A} , H^{6B}); 4.06–4.12 m (2H, H^3 , H^4); 4.53–4.59 m (2H, C_{arom} –CH₂– C_{arom}); 4.72–4.78 m, 4.89–5.01 m (2H, H², H⁵); 6.45–7.07 m (4H, CH_{arom}). ³¹P NMR spectrum (C_6H_6), δ_P , ppm: 74 and 80, ratio of integral intensities 1:1. Found, %: C 59.23; H 8.36; P 7.39. C₄₁H₆₉N₃O₆P₂S₂. Calculated, %: C 59.61; H 8.42; P 7.5.

2,5-0,0-Bis{O-[2-(2-Hydroxy-5-methyl-3-tert-butylphenylmethyl)-4-methyl-6-tert-butylphenyl]di $ethylaminothiophosphoryl}-1,4;3,6-dianhydro-D$ mannite XVI. A solution of 0.63 g of bisphenol IV in3 ml of benzene was added with stirring at 20°C tothe reaction mixture containing XIII and prepared asdescribed above for synthesis of XIV. The mixturewas heated at 75–80°C for 2.5 h in a weak nitrogenflow, with the removal of diethylamine. ³¹P NMRspectrum of the reaction mixture (compound XV): $<math>\delta_p$ 152 ppm. To the reaction mixture, we added 0.12 g of finely divided sulfur; the mixture was stirred for 1 h at 80°C, the solvent was distilled off in a vacuum, and compound XVI was purified by column chromatography on (alumina, Brockmann grade II; benzene– dioxane, 6 : 1). Yield 1.55 g (76%), mp 95–96°C, R_f 0.9 (**B**). ¹H NMR spectrum (CDCl₃), δ , ppm (*J*, Hz): 1.20 t (12H, CH₃, ³J_{HH} 7.3); 1.41 s, 1.45 s [36H, C(CH₃)₃]; 2.17 s, 2.30 s (12H, C_{arom}–CH₃); 3.15– 3.29 m (8H, NCH₂, ³J_{HP} 7.5); 3.59–3.77 m (4H, H^{1A}, H^{1B}, H^{6A}, H^{6B}); 3.80–4.00 m (2H, H³, H⁴); 4.15– 4.25 m (4H, C_{arom}–CH₂–C_{arom}); 4.57–4.61 m, 4.74– 4.90 m (2H, H², H⁵); 6.47–7.12 m (4H, H_{arom}). ³¹P NMR spectrum (C₆H₆), δ_P , ppm: 74. Found, %: C 65.19; H 8.51; P 5.59. C₆₀H₉₀N₂O₈P₂S₂. Calculated, %: C 65.90; H 8.29; P 5.66.

2,5-0,0-[0,0'-(2,2-Diphenylpropane-*p*,*p*'-diyl)bis(diethylaminothiophosphoryl)]-1,4;3,6-dianhydro-D-mannite XVIII. A solution of 1.18 g of II in 10 ml of benzene was added with stirring to a solution of 0.55 g of bisphenol V in 20 ml of benzene; the mixture was heated at 75°C for 2 h in a weak nitrogen flow, with the removal of diethylamine. ³¹P NMR spectrum of the reaction mixture (compound XVII), $\delta_{\rm P}$, ppm: 145 and 146, respectively; intensity ratio 1:1. To the reaction mixture, we added 0.15 g of finely divided sulfur; the mixture was stirred for 2 h at 20°C, excess sulfur was filtered off, and the solvent was distilled off in a vacuum. The residue was dissolved in 15 ml of acetone, 20 ml of water was added, the mixture was stirred, and the precipitate was separated. Yield 0.93 g (60%), mp 75–77°C. R_f 0.1 (C). ¹H NMR spectrum (acetone- d_6), δ , ppm (J, Hz): 1.05 m (12H, CH₂CH₃); 1.22 s (3H, CH₃); 3.28 m (8H, NCH₂, ${}^{3}J_{HP}$ 14.5); 3.68 m (2H, H^{1A}, H^{6A}, ${}^{2}J_{1A,1B}$ 17.9, ${}^{3}J_{1A,2;6A,5}$ 8.9); 3.93 m (2H, H^{1B}, H^{6B}, ${}^{2}J_{6A,6B}$ 17.1, ${}^{3}J_{1B,2;6B,5}$ 8.5); 4.58 m (2H, H³, H⁴); 4.85 m $(2H, H^2, H^5)$; 7.07 m, 7.12 m (8H, H_{arom}). ³¹P NMR spectrum (C₆H₆), $\delta_{\rm P}$, ppm: 71.8 and 72.2; ratio of the integral intensities 1:1. Found, %: C 54.41; H 6.66; P 9.64. $C_{29}H_{42}N_2O_6P_2S_2$. Calculated, %: C 54.36; H 6.60; P 9.66.

2,5-0,0-[0,0'-(Tetraphenylmethane-p,p'-diyl)bis(diethylaminothiophosphoryl)]-1,4;3,6-dianhydro-D-mannite XX. A solution of 0.57 g of bisphenol VI in 3 ml of dioxane was added with stirring at 20°C to a solution of 0.8 g of **II** in 7 ml of dioxane. The mixture was heated at 75-80°C for 2.5 h in a weak nitrogen flow, with the removal of diethylamine. ³¹P NMR spectrum of the reaction mixture (compound **XIX**), $\delta_{\rm p}$, ppm: 144 and 146; ratio of the integral intensities 1:1. To the reaction mixture, we added 0.1 g of finely divided sulfur; the mixture was stirred for 1 h at 80°C, excess sulfur was filtered off, the solvent was distilled off in a vacuum, and the residue was recrystallized from 3 ml of benzene. Yield 1.08 g (88%), mp 141–142°C, $R_f 0.1$ (C). ¹H NMR spectrum $(CDCl_3)$, δ , ppm (J, Hz): 1.00–1.12 m (12H, CH₃);

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3.20–3.40 m (8H, NCH₂, ${}^{3}J_{HP}$ 13.7); 3.66–3.78 m, 4.00–4.12 m (4H, H^{1A}, H^{1B}, H^{6A}, H^{6B}); 4.51–4.61 m (2H, H³, H⁴); 4.83–4.99 m (2H, H², H⁵); 7.05–7.20 m (18H, H_{arom}). ${}^{31}P$ NMR spectrum (C₆H₆), δ_{P} , ppm: 72.0 and 72.2; ratio of the integral intensities 1 : 1. Found, %: C 60.29; H 6.21; P 8.25. C₃₉H₄₆N₂O₆P₂S₂. Calculated, %: C 61.24; H 6.06; P 8.09.

 $2,5-0,0-\{0,0'-[(Diphenyl oxide)-p,p'-diyl]bis(di$ ethylaminothiophosphoryl)}-1,4;3,6-dianhydro-Dmannite XXII. A solution of 2.22 g of II in 10 ml of dioxane was added with stirring to a solution of 0.91 g of bisphenol VII in 20 ml of dioxane. The mixture was heated at 75°C for 2 h in a weak nitrogen flow, with the removal of diethylamine. ³¹P NMR spectrum of the reaction mixture (compound XXI), $\delta_{\rm P}$, ppm: 145 and 146; ratio of the integral intensities 1:1. To the reaction mixture, we added 0.29 g of finely divided sulfur; the mixture was stirred for 2 h at 75°C, excess sulfur was filtered off, and the solvent was distilled off in a vacuum. The residue was dissolved in 15 ml of acetone, 30 ml of water was added, the mixture was stirred, and the viscous oily precipitate was separated. Yield 2.4 g (90%), mp 74-75°C, $R_f 0.6$ (F), 0.9 (G). ¹H NMR spectrum (CDCl₃), δ , ppm (J, Hz): 1.09 m (12H, NCH₂CH₃); 3.08–3.12 m ^{PPIII} (3, 112): 1.05 m (1211, 10CH₂CH₃); 5.08–5.12 m (4H, NCH₂CH₃, ${}^{3}J_{HP}$ 11.5); 3.30–3.34 m (4H, NCH₂CH₃, ${}^{3}J_{HP}$ 20.66, ${}^{2}J_{HH}$ 12.0); 3.7–3.75 m (2H, H^{1A}, H^{6A}, ${}^{2}J_{1A,1B}$ 8.11); 4.05–4.09 m (2H, H^{1B}, H^{6B}, ${}^{2}J_{1A,1B}$ 8.11); 4.05–4.09 m (2H, H^{1B}, H^{6B}, ${}^{2}J_{1A,1B}$ 8.11); 4.05–4.09 m (2H, H^{1B}, H^{6B}), $^{2}J_{6A,6B}$ 6.97); 4.54–4.56 m (2H, H³, H⁴); 4.91–4.95 m (2H, H², H⁵); 7.15–7.20 m (8H, H_{arom}). ³¹P NMR spectrum (dioxane), $\delta_{\rm P}$, ppm: 71.6 and 72.0; ratio of the integral intensities 1:1. Found, %: C 50.71; H 5.86; P 10.04. $C_{26}H_{36}N_2O_7P_2S_2$. Calculated, %: C 50.81; H 5.90; P 10.08.

2,5-0,0-{0,0'-[(Diphenyl sulfide)-p,p'-diyl]bis-(diethylaminothiophosphoryl)}-1,4;3,6-dianhydro-**D-mannite XXIV.** A solution of 1.67 g of **II** in 5 ml of dioxane was added with stirring to a solution of 0.74 g of bisphenol VIII in 15 ml of dioxane. The mixture was heated at 75°C for 2 h in a weak nitrogen flow, with the removal of diethylamine. ³¹P NMR spectrum of the reaction mixture (compound XXIII), $\delta_{\rm P}$, ppm: 145 and 146; ratio of the integral intensities 1:1. To the reaction mixture, we added 0.11 g of finely divided sulfur; the mixture was stirred for 2 h at 75°C, excess sulfur was filtered off, the solvent was distilled off in a vacuum, and the product was purified by column chromatography (alumina, Brockmann grade II; dioxane-ethanol, 1:10). Yield 1.32 g (44%), mp 84–85°C, $R_f 0.8$ (**D**), 0.1 (**E**). ¹H NMR spectrum (CDCl₃), δ, ppm: 1.12 m (12H, NCH₂CH₃); 3.21-3.42 m (8H, NCH₂CH₃, ${}^{3}J_{HP}$ 11.5); 3.7–3.8 m (2H, H^{1A}, H^{6A}); 4.05–4.12 m (2H, H^{1B}, H^{6B}); 4.54–

4.59 m (2H, H³, H⁴); 4.89–4.95 m (2H, H², H⁵); 7.10–7.14 m (4H, H_{arom}); 7.24–7.30 m (4H, H_{arom}). ³¹P NMR spectrum (dioxane), δ_P , ppm: 72.1 and 72.4; ratio of the integral intensities 1 : 1. Found, %: C 49.61; H 5.86; P 9.94. C₂₆H₃₆N₂O₆P₂S₃. Calculated, %: C 49.51; H 5.75; P 9.82.

2,5-0,0-{Diethylaminothiophosphorylidenebis-[p-(2-p-oxyphenylprop-2-ylphenoxy)(phenyl)thiophosphoryl]}-1,4;3,6-dianhydro-D-mannite XXIX. A solution of 2.09 g of bisphenol V was added to a solution of 2.27 g of hexaethylphosphorous triamide in 40 ml of benzene. The mixture was stirred for 6 h at 75°C, after which an additional 2.09 g of V was added, and the mixture was stirred for 6 h at 75°C. ³¹P NMR spectrum of the reaction mixture (compound **XXV**): $\delta_{\mathbf{P}}$ 140 ppm. To the solution, we added 0.29 g of finely divided sulfur; the mixture was stirred for 2 h at 75°C and cooled, excess sulfur was filtered off, the filtrate was evaporated in a vacuum, the residue was dissolved in 15 ml of acetone, the precipitate of sulfur was filtered off, and the filtrate was vacuum-evaporated. Yield of O,O-diaryl phosphoramidothioate XXVI 2.97 g (95%); light brown viscous oily substance. ³¹P NMR spectrum (CDCl₃): δ_{P} 67 ppm. A solution of 2.7 g of XXVI and 1.04 g of triethylamine in 15 ml of benzene was added with stirring to a solution of 1.7 g of dichlorophenylphosphine in 10 ml of benzene, cooled to 5°C. The mixture was stirred for 2 h at 20°C; the precipitate of triethylamine hydrochloride was filtered off and washed with benzene $(2 \times 2.5 \text{ ml})$. ³¹P NMR spectrum of the reaction mixture (compound **XXVII**), $\delta_{\rm P}$, ppm: 67 and 172; ratio of integral intensities 1 : 2. To the combined filtrates, we added with stirring 0.638 g of 1,4;3,6-dianhydro-D-mannite I and 1.04 g of triethylamine; the mixture was stirred for 1 h at 20°C, and the precipitate of triethylamine hydrochloride was filtered off and washed with benzene $(2 \times 5 \text{ ml})$. ³¹P NMR spectrum of the reaction mixture (compound **XXVIII**), $\delta_{\rm P}$, ppm: 67 and 157; ratio of integral intensities 1:2. To the combined filtrates, we added 0.288 g of finely divided sulfur; the mixture was stirred for 1 h at 20°C, excess sulfur was filtered off, the filtrate was vacuum evaporated, the residue was dissolved in 15 ml of acetone, undissolved sulfur was filtered off, and the filtrate was vacuum-evaporated. The resulting viscous oily product was triturated in a mortar with a small amount of water until a colorless powder formed, which was filtered off, washed with water, and dried in a vacuum. Yield of **XXIX** 3.5 g (76%); mp 96–97°C, $R_f 0.2$ (C). ¹H NMR spectrum (CDCl₃), δ , ppm: 1.10 (6H, NCH₂CH₃); 1.61 (12H, CH₃); 3.40 (4H, NCH₂CH₃); 3.7-4.0 (4H, H^{1A}, H^{1B}, H^{6A}, H^{6B}); 4.39-4.61 (2H, H³, H⁴); 4.92-5.14 (2H, H², H⁵); 7.08-7.14 (16H, $\begin{array}{l} H_{arom}); \ 7.42-7.58 \ (6H, \ H_{arom}); \ 7.76-8.03 \ (4H, \ H_{arom}) \\ ({}^{3}J_{PN} \ 13.8 \ Hz). \ {}^{31}P \ NMR \ spectrum \ (CHCl_{3}), \ \delta_{P}, \ ppm: \\ 67, \ 86, \ and \ 88; \ ratio \ of \ the \ integral \ intensities \ 1:1:1. \\ Found, \ \%: \ C \ 61.79; \ H \ 5.64; \ P \ 9.21. \ C_{52}H_{56}NO_{8}P_{3}S_{3}. \\ Calculated, \ \%: \ C \ \ 61.71; \ H \ \ 5.58; \ P \ \ 9.18. \end{array}$

REFERENCES

- Grachev, M.K., Anfilov, K.L., Bekker, A.R., and Nifant'ev, E.E., *Zh. Obshch. Khim.*, 1995, vol. 65, no. 12, p. 1946.
- 2. Reetz, M.T. and Neugebauer, T., Angew. Chem., Int.

Ed. Engl., 1999, vol. 38, no. 1/2, p. 179.

- Kurochkina, G.I., Grachev, M.K., Vasyanina, L.K., Piskaev, A.E., and Nifant'ev, E.E., *Dokl. Ross. Akad. Nauk*, 2000, vol. 371, no. 2, p. 189.
- 4. Lehn, J.M., *Supramolecular Chemistry*, New York: VCH, 1995.
- 5. Nifantiev, E.E., Grachev, M.K., and Burmistrov, S.Yu., *Chem. Rev.*, 2000, vol. 100, no. 10, p. 3755.
- 6. Gordon, A.J. and Ford, R.A., *The Chemist's Companion. A Handbook of Practical Data, Techniques, and References,* New York: Wiley, 1972. Translated under the title *Sputnik khimika,* Moscow: Mir, 1976, p. 132.