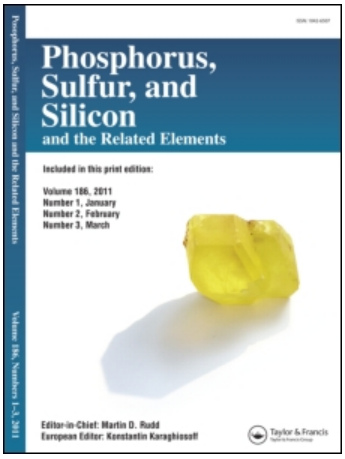

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Anthracene Diols in the Synthesis of Phosphacyclophanes

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To cite this Article Nifantyev, Edward E. , Petrov, Arkady V. , Stach, Adam I. and Rasadkina, Elena N.(2007) 'Anthracene Diols in the Synthesis of Phosphacyclophanes', Phosphorus, Sulfur, and Silicon and the Related Elements, 182: 6, 1413 — 1424
To link to this Article: DOI: 10.1080/10426500701196481
URL: http://dx.doi.org/10.1080/10426500701196481

Phosphorus, Sulfur, and Silicon, 182:1413–1424, 2007

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500701196481

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The first phosphacyclophanes have been synthesized from anthracene derivatives. For this purpose, the reactions of 2,6-anthracene diol and 9,10-diacetoxy anthracene with phosphorous acid triamides have been studied. Some chemical properties of the obtained compounds have been investigated.

Keywords Bisphosphorylated dihydroxyanthracenes; phosphacyclanes; properties; structure; synthesis

INTRODUCTION

The phosphorylation of anthracene phenols is poorly understood. Only data on the phosphorylation of monophenols have been published up to now.[1] In continuation of our earlier studies of the reactions of dihydroxynaphthalenes with hexamethyl (**1a**) and hexaethyl (**1b**) phosphorous triamides,[2] we have investigated the reactions of these phosphamides with dihydroxyanthracenes.

Received October 14, 2006; accepted December 4, 2006.
This work was supported in part by the Grant of the President of the Russian Federation for the Support of Leading Scientific Schools (NSh-560.2003.3).
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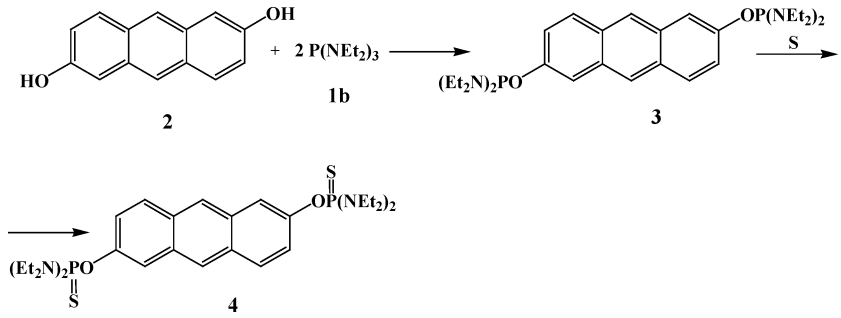


SCHEME 1

RESULTS AND DISCUSSION

First the phosphorylation of 2,6-dihydroxyanthracene (**2**) with phosphamide **1b** was studied. We found that the diol **2** reacts with the amide **1b** in a molar ratio of 1:2 to form the bisamidophosphite **3** (Scheme 1).

The formation of bisamidophosphite **3** was indicated by ^{31}P NMR spectroscopy. This compound was characterized as thiophosphate **4**, which was isolated as a pure compound. The spatial orientation of thiophosphate **4** was determined by single crystal X-ray diffraction. A view of the molecular structure of **4** is shown in Figure 1; selected geometrical parameters are given in Table I. The X-ray study showed that the compound **4** is crystallized as a centrosymmetrical *trans* isomer, in

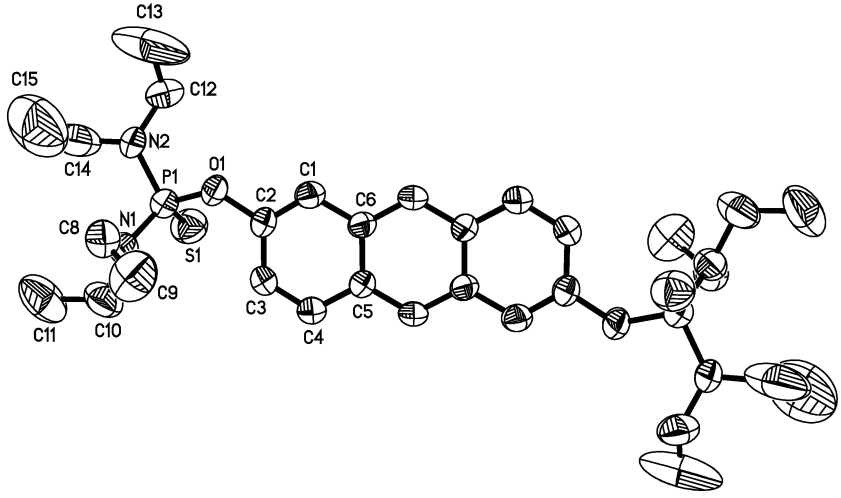


FIGURE 1 ORTEP view of the molecular structure of **4** in the crystal. Thermal ellipsoids are shown at the 50% probability level.

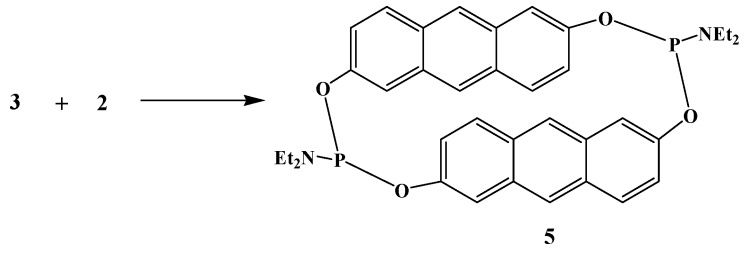
TABLE I Selected Bond Lengths (Å) and Angles (°) for 4

S(1)—P(1)	1.9358(19)	O(1)P(1)N(2)	96.82(18)
C(1)—C(2)	1.340(6)	O(1)—P(1)—N(1)	106.2(2)
C(1)—C(6)	1.431(6)	N(1)—P(1)—N(2)	106.4(2)
C(2)—C(3)	1.418(6)	N(1)—P(1)—S(1)	113.97(15)
C(3)—C(4)	1.357(6)	N(2)—P(1)—S(1)	117.79(18)
C(4)—C(5)	1.417(6)	C—(2)C—(1)C—(6)	120.1(4)
C(5)—C(7)*	1.402(5)	C—(2)C—(3)C—(4)	120.2(4)
C(5)—C(6)	1.427(5)	C—(3)C—(4)C—(5)	120.5(4)
C(6)—C(7)	1.402(5)	C—(4)C—(5)C—(6)	119.0(3)
C(7)—C(5)*	1.402(5)	C—(7)C—(6)C—(5)	119.3(3)
		C(7)*—C(5)—C(6)	119.1(3)
		C(7)*—C(5)—C(4)	121.9(4)
		C(5)*—C(7)—C(6)	121.6(3)
P(1)—N(2)	1.660(4)		
P(1)—N(1)	1.618(4)		
N(1)—C(8)	1.465(7)		
N(1)—C(10)	1.476(6)		
N(2)—C(12)	1.444(7)		
N(2)—C(14)	1.595(13)		

Symmetry transformations used to generate equivalent atoms: *$-x + 1, -y + 1$, and $-z + 1$.

which the phosphorus moieties are located on opposite sides of the aromatic plane. The two diethylamido groups in the thiophosphate moiety appreciably differ from each other. The sums of angles at atoms N(1) and N(2) are 359.1(1)° and 343.2(1)°, respectively. The different configurations result in a variation of the P–N bond lengths. Shortening of the P(1)–N(1) bond by 0.042 Å in the flattened NEt_2 group suggests the conjugation of the P═S bond with the lone electron pair of the atom N(1).

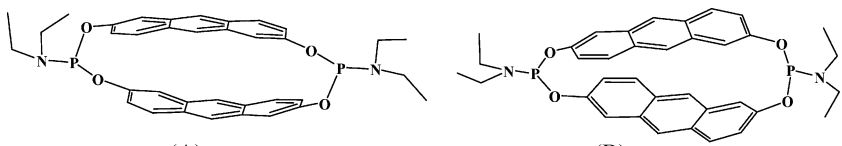
The reaction of bisamidophosphite **3** with an equimolar amount of the diol **2** was studied. It results in the formation of the first anthracene phosphacyclophane **5**, which is isolated with a yield of 39% (Scheme 2).



5

SCHEME 2

The ^{31}P NMR spectrum of this product showed a singlet ($\delta = 151.7$ ppm) in the region typical for monoamidophosphites, which suggested



(A) (B)

FIGURE 2 Calculated (MM2) conformations of phosphacyclophane **5**.

the symmetry of the molecule. A set of signals from all proton groups with the corresponding integral intensity was observed in the proton NMR spectrum. Its dimer structure was supported by molecular mass measurements.

Cyclophane **5** was also synthesized by the direct cyclophosphorylation of the diol **2** with an equimolar amount of the amidophosphite **1b** and isolated with a 52% yield.

$$2\,\mathbf{2} + 2\,\mathbf{1b} \rightarrow \mathbf{5} \qquad (1)$$

We also showed that the bisamidophosphite **3** spontaneously dismutates when stored in an acetonitrile solution with the formation of **5** and **1b**.

$$2\,\mathbf{3} \rightarrow 5 + 2\,\mathbf{1b} \qquad (2)$$

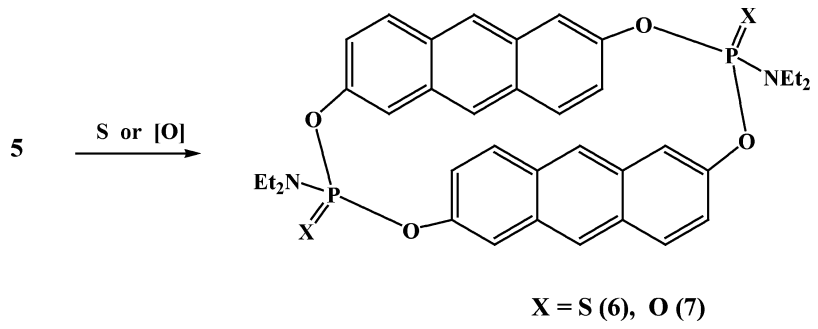
It was found that this process readied equilibrium in 60 days. According to the ^{31}P NMR data, the equilibrium composition contained 28% of **5**, 36% of **3**, and 36% of **1b**.

A computer calculation of the steric energies using the MM2[3] method showed that compound **5**, similar to analogous products prepared earlier from 1,4-hydroquinone and 1,5-dihydroxynaphthalene,[4] can occur in a fully (**A**) or partially (**B**) eclipsed conformation with E_{ster} of 5.26 and 1.6 eV, respectively (Figure 2). This suggests that the compound most probably adopts structure **B**, which has lower energy.

The phosphorus(III) cyclophane **5** was subjected to oxidation and sulfurization, which resulted in the corresponding cyclobisamidophosphate **6** and thiophosphate **7** (Scheme 3).

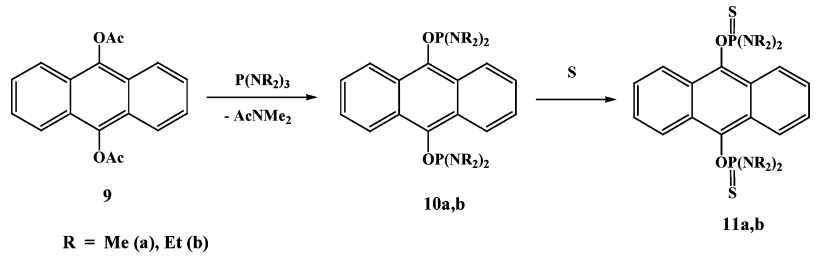
Thiophosphate **6** and the phosphate **7** are powders, which are readily soluble in organic solvents; however, they rapidly lost their solubility under storage conditions, which we attribute to an increasing stress in the cycle and, hence, a loss of its stability. An MM2 calculation of the steric energies for these compounds also showed that they are significantly higher for thio and oxo derivatives (25.6 and 24.58 eV, respectively) than for cyclophosphite **5** (0.9 eV).

In the second part of the investigation, the phosphorylation of 9,10-dihydroxyanthracene (**8**) was studied. At the beginning we



SCHEME 3

were faced with a problem of diol instability. We substituted 9,10-diacetoxyanthracene **9** for diol **8**. This decision was based on the reported indication of the possible phosphorylation of one of the simplest acetates with phosphamide **1a**.[5] We showed that the reaction of bis(acetate) **9** with two equivalents of phosphamides **1a**,**b** gives the bisamidophosphites **10a**,**b** (Scheme 4).



SCHEME 4

The reaction products were transformed into the corresponding thiophosphates **11** by oxidation with sulfur. The structure of all resulting products was supported by ^{1}H and ^{31}P NMR spectroscopy and by single crystal X-ray diffraction in the case of **11a**. A view of the molecular structure of **11a** in the crystal is shown in Figure 3; selected geometrical parameters are given in Table II. It is worth noting that the difference between the sums of angles at atoms N(1) and N(2) in the molecule of **11a** is 9.79°, which is significantly lower than in compound **4**, and the difference between the P—N bonds is decreased to 0.0115 Å. It should also be noted that bond lengths C(1)–C(2), C(4)–C(5), and C(5)–C(6) in the aromatic ring are longer; the bonds lengths C(1)–C(6), C(2)–C(3), and C(6)–C(7) are shorter; and the length of the C(3)–C(4) bond has remained unchanged compared to the parameters of compound **4**. A P,H coupling constant of 12.2 Hz was observed for the methyl protons in the

TABLE II Selected Bond Lengths (Å) and Angles (°) for11a

S(1)—P(1)	1.9271(7)	O(1)P(1)N(2)	97.62(7)
C(1)—C(2)	1.355(2)	O(1)—P(1)—N(1)	109.72(7)
C(1)—C(6)	1.425(2)	N(1)—P(1)—N(2)	102.97(8)
C(2)—C(3)	1.405(3)	N(1)—P(1)—S(1)	113.08(6)
C(3)—C(4)	1.357(3)	N(2)—P(1)—S(1)	119.32(7)
C(4)—C(5)	1.427(2)	C—(2)C—(1)C—(6)	121.07(16)
C(5)—C(7)*	1.391(2)	C—(2)C—(1)C—(3)	120.28(16)
C(5)—C(6)	1.433(2)	C—(2)C—(3)C—(4)	121.03(17)
C(6)—C(7)	1.399(2)	C—(3)C—(4)C—(5)	120.85(17)
C(7)—C(5)*	1.391(2)	C—(4)C—(5)C—(6)	120.85(17)
		C—(7)C—(6)C—(5)	118.83(13)
		C(7)*—C(5)—C(6)	123.07(15)
		C(7)*—C(5)—C(4)	118.82(13)
		C(5)*—C(7)—C(6)	122.35(14)
P(1)—N(2)	1.6451(15)		
P(1)—N(1)	1.6336(15)		
N(1)—C (8)	1.460(3)		
N(1)—C (9)	1.446(3)		
N(2)—C(11)	1.481(2)		
N(2)—C(10)	1.448(2)		

Symmetry transformations used to generate equivalent atoms: *−x + 1, −y + 1, and −z + 1.

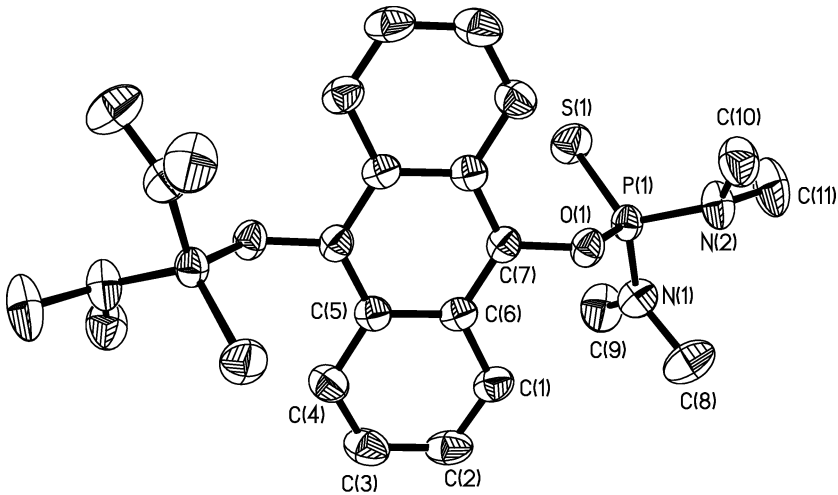
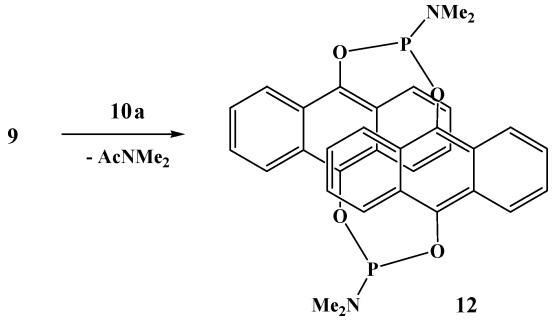


FIGURE 3 ORTEP view of the molecular structure of **11a** in the crystal. Thermal ellipsoids represent the 50% probability.

^{1}H NMR spectrum of **11a**, and two coupling constants ($^3J_{PH}$ = 11.6 Hz and 12.2 Hz) were observed for the methylene protons of the ethyl groups in compound **11b**. This is probably due to the diastereotopy of the mehtylene protons of amide groups.

We used the new method of phosphorylation to synthesize product **12**, in which two anthracene moieties are linked to positions 9 and 10 by amidophosphite bridges (Scheme 5).



SCHEME 5

The reaction proceeded at 20°C and was completed in 4 days. Compound **12** was isolated with a yield of 42%. The product was found to be unstable in solution forming anthraquinone. MM2 calculations showed that the molecule of **12** has a rigid structure. The lowest steric energy for this compound is 15.36 eV, the largest deviation of the lateral rings from the anthracene plane is 3.74 Å, and the shortest distance between the central rings is 3.3 Å. From these data, it can be suggested that this heterocycle is unstable.

Compound **12** was also synthesized by two other methods, reacting equimolar amounts of **1a** and **9** and via dismutation of compound **10a**. The reaction was completed in 4 and 6 days with yields of 68% and 40%, respectively. This difference in the yields is related to the smaller amount of byproducts resulting from the direct synthesis.

The oxidation of cyclic phosphite **12** with sulfur resulted in the destruction of the heterocycle; anthraquinone was isolated as one of the products. Because of decreasing valence angles, the aromatic cycles in these compounds come closer than the distance of stacking interaction, which results in their destruction.

Thus, it was shown that phosphacyclophanes can be synthesized from dihydroxyanthracenes; however, they are unstable compounds. It was also shown for the first time that acetoesters of aromatic systems can be used in phosphorylation with phosphorous acid amides. Previously inaccessible phosphorylated systems based on 9,10-dihydroxyanthracene were synthesized by this route.

EXPERIMENTAL

^{1}H NMR spectra were recorded on a Bruker AC-200 instrument at 200 MHz in $CDCl_3$. ^{31}P NMR spectra were recorded on a Bruker WP-80 SY instrument at 32.4 MHz (85% H_3PO_4 was used as an external standard). Mass spectra were recorded on a Bruker Reflex III instrument using $CHCl_3$ as a solvent and 2,4,6-trihydroxyacetophenone as a matrix.

Column chromatography was carried out on L 100/250 silica gel; TLC was performed on Silufol plates using (A) benzene–dioxane 3:1, (B) hexane–dioxane 5:1, and (C) benzene–dioxane–hexane 5:1:2 as eluents. The detection of the compounds was achieved by iodine vapor treatment and calcination.

All syntheses were performed in dry solvents under a dry argon atmosphere.

Single crystal X-ray diffraction analysis of compound **4** was performed on an Enraf–Nonius CAD-4 diffractometer using Mo-K_α radiation ($\theta/2\theta$ scan, $\theta \leq 24.97^\circ$). Orange plate crystal ($C_{30}H_{48}N_4O_2P_2S_2$, $M = 622.78$), size $0.30 \times 0.12 \times 0.08$ mm, monoclinic, space group P2(1)/n, $a = 7.247$ $b = 16.154$ $c = 14.669$, Å, $\alpha = 90^\circ$, $\beta = 102.59(3)^\circ$, $\gamma = 90^\circ$ $V = 1676.0(5)$ Å^3, $Z = 2$, $d_{calc} = 1.234$ g/cm^3, 3248 observed reflections with $I > 2\sigma(I)$, 2928 independent reflections [$R_{int} = 0.0164$]. The final values of divergence parameters were $R_1(F) = 0.0634$, $wR_2(F) = 0.1910$. The structure was solved by direct methods and refined by full-matrix least-squares method in an anisotropic approximation for non-hydrogen atoms. Hydrogen atoms were located from difference Fourier syntheses.

Single crystal X-ray diffraction analysis of compound **11a** was performed on an Enraf–Nonius CAD-4 diffractometer using Mo-K_α radiation ($\theta/2\theta$ scan, $\theta < 25.08^\circ$). Yellow prism ($C_{22}H_{32}N_4O_2P_2S_2$, $M = 510.58$), size $0.50 \times 0.35 \times 0.30$ mm, monoclinic, space group P2(1)/n, $a = 8.009(2)$ Å, $b = 13.714(3)$ Å, $c = 11.530(2)$ Å, $\alpha = 90^\circ$ $\beta = 92.50(3)^\circ$, $\gamma = 90^\circ$ $V = 1265.2(5)$ Å^3, $Z = 2$, $d_{calc} = 1.340$ g/cm^3, 2481 observed reflections with $I > 2\sigma(I)$, 2241 independent reflections [$R_{int} = 0.0122$]. The final values of divergence parameters were: $R_1(F) = 0.0279$, $wR_2(F^2) = 0.0838$. The structure was solved by direct methods and refined by full-matrix least-squares method in an anisotropic approximation for non-hydrogen atoms. The positions of the hydrogen atoms were determined from difference Fourier syntheses and refined by least squares in an isotropic approximation. Further details on the single crystal X-ray structure determinations can be obtained free of charge on application to the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, U.K., (Fax: + 44 (0)

1223 336033; e-mail: deposit@ccdc.cam.ac.uk) quoting the depository no. CCDC 625806 for **4** and CCDC 625807 for **11a**.

Hexamethyl phosphorous triamide was synthesized as described in[6]; hexaethyl phosphorous triamide was synthesized as described in.[7]

Hexaethyl phosphorous triamide was purified from diethylamide hydrochloride as described in.[8] 9,10-diacetoxyanthracene was prepared by reductive acylation.[9]

2,6-Bis(tetraethyldiamidothiophosphatoxy)anthracene (4)

Hexaethyl phosphorous triamide 0.74 g (3 mmol) was added to a solution of 0.32 g (1.5 mmol) of 2,6-dihydroxyanthreacene (**2**) in 10 mL of acetonitrile. The mixture was stirred for 30 min; 0.096 g (3 mmol) of sulfur was added, and the mixture was stirred for an additional 2 h at room temperature. The solution was filtered and the solvent evaporated in vacuo; the residue was subjected to column chromatography, compound **4** being eluted with 10:1 benzene/dioxane. The resulting product was dried in vacuo for 2.5 h (1 mm Hg, 60°C). Yield 0.36 g (38%); m.p. 120–s125°C, R_f 0.67 (B). ^{1}H NMR ($CDCl_3$): δ 1.19 (t, $^3J_{HH} = 7.0$ Hz, 24H, CH_3), 3.29 (m, 16H, CH_2), 7.34 (d, $^3J_{HH} = 9.1$ Hz, 2H, 3,7-H), 7.71 (m, 2H, 1,5-H), 7.90 (m, 2H, 4,8-H), 8.31 (m, 2H, 9,10-H). ^{31}P NMR (CH_2Cl_2): δ 76.3. $C_{30}H_{48}N_4O_2P_2S_2$: Calcd.: C 57.85, H 7.77, N 9.00, P 9.95%; found: C 57.65, H 7.83, N 9.13, P 9.67%.

Cyclo[Bis(2,6-anthracenyldiethylamidophosphite)] (5)

(a) Molecular Assemblage

Hexaethyl phosphorous triamide (0.2 g; (0.8 mmol) in 2.5 mL of acetonitrile was added to a suspension of 0.084 g (0.4 mmol) of 2,6-dihydroxyanthracene (**2**) in 1 mL of acetonitrile at room temperature and with constant stirring. After 24 h, 0.084 g (0.4 mmol) more of 2,6-dihydroxyanthracene in 0.5 mL of acetonitrile was added to the reaction mixture. The solution was decanted from the precipitate formed; the precipitate was washed with acetonitrile and dried in vacuo for 2 h (1 mm Hg, 70°C). An amorphous yellow-brown powder was obtained after drying. Yield 0.097 g (39%); m.p. 301–303°C, R_f 0.82 (A); ^{1}H NMR (CD_2Cl_2): δ 1.15 (q, $^3J_{HH} = 7.0$ Hz, 12H, CH_3), 3.40 (d, $^3J_{PH} = 10.0$ Hz, 8H, NCH_2), 7.29 (d, $^3J_{HH} = 8.8$ Hz, 4H, 3,7-H), 7.59 (s, 4H, 1,5-H), 7.91 (d, $^3J_{HH} = 9.1$ Hz, 4H, 4,8-H), 8.26 (s, 4H, 9,10-H); ^{31}P NMR (CH_2Cl_2): δ 141.2; $C_{36}H_{36}N_2O_4P_2$: Calcd.: C 69.45, H 5.83, P 9.95%, $M = 622.63$; found: C 69.48, H 5.87, P 9.71%, $M = 623$.

(b) Direct Synthesis

Hexaethyl phosphorous triamide (0.5 g 2 mmol) was added to 0.42 g (2 mmol) of 2,6-dihydroxyanthracene in 30 mL of acetonitrile and stirred for 5 h at room temperature. After 24 h, the solution was decanted from the oily product formed on the bottom; the residue was washed with acetonitrile and dried in vacuo for 3 h (1 mm Hg, 50°C). Yield 0.65 g (52%).

(c) Dismutation

Hexaethyl phosphorous triamide (0.24 g; 0.96 mmol) in 0.5 mL of acetonitrile was added to a suspension of 0.1 g (0.48 mmol) of 2,6-dihydroxyanthracene in 0.5 mL of acetonitrile under stirring. According to ^{31}P NMR data, an equilibrium between compounds **3** (δ =132 ppm), **5** (δ =140 ppm), and **1b** (δ = 118 ppm) at a ratio of 1.3:1:1.3 was established in the reaction mixture after 3 days.

9,10-Bis(tetramethyldiamidothiophosphatoxy)anthracene (11a)

A solution of 0.11 g (0.68 mmol) of hexamethyl phosphorous triamide in 0.5 mL of pyridine was added to a suspension of 0.1 g (0.34 mmol) of 9,10-diacetoxyanthracene in 0.5 mL of pyridine, and the reaction mixture was stirred at room temperature. The mixture became homogeneous after 72 h. Sulfur (0.0218 g; 0.68 mmol) was added to the reaction solution, and the mixture was left to stand for 9 days. Compound **11a** was crystallized from the solution. It was filtered off and washed with 5 mL of acetonitrile. The product was dried in vacuo for 2 h (1 mm Hg, 70°C). Yield 0.0972 g (56%), m.p. (dec.) 232°C, R_f 0.63 (B); ^{1}H NMR ($CDCl_3$): δ 2.71 (d, $^3J_{PH}$ = 12.2 Hz, 24H, CH_3), 7.50 (m, 4H, 2,3,6,7-H), 8.41 (m, 4H, 1,4,5,8-H). ^{31}P NMR (CH_2Cl_2): δ 81.0; $C_{22}H_{32}N_4O_2P_2S_2$: calcd.: C 51.75, H 6.32, N 10.97, P 12.13 %; found: C 51.73, H 6.26, N 11.09, P 12.50%.

9,10-Bis(tetraethyldiamidothiophosphatoxy)anthracene (11b)

A solution of 0.255 g (1.02 mmol) of hexaethyl phosphorous triamide in 0.5 mL of pyridine was added to a suspension of 0.1 g (0.34 mmol) of 9,10-diacetoxyanthracene in 0.5 mL of pyridine, and the reaction mixture was heated to 100°C for 2 h. The solvent with an excess of hexaethyl phosphorous triamide was evaporated in vacuo; the residue was dissolved in 5 mL of hexane, and 0.0326 g (1.02 mmol) of sulfur was added to the reaction solution. The reaction mixture was stirred

for 30 min when compound **11b** crystallized from the solution. It was separated by filtration and subjected to column chromatography, using system (C) as an eluent. The isolated product was dried in vacuo for 2 h (1 mm Hg, 70°C). Yield 0.1186 g (56%), m.p. 164°C, R_f 0.71 (C); ^{1}H NMR ($CDCl_3$): δ 1.08 (q, $^3J_{HH} = 7.0$ Hz, 24H, CH_3), 3.33 (dd, $^3J_{PH} = 11.6$ Hz, $^3J_{PH} = 12.2$ Hz, 16H, CH_2), 7.45 (m, 4H, 2,3,6,7-H), 8.42 (m, 4H, 1,4,5,8-H); ^{31}P NMR (pyridine): δ 76.0. $C_{30}H_{48}N_4O_2P_2S_2$: Calcd.: C 57.85, H 7.77, N 9.00, P 9.95%; found: C 57.90, H 7.95, N 9.25, P 9.62%.

Cyclo[Bis(9,10-anthracenyldimethylamidophosphite)] (12)

(a) Molecular Assemblage

A solution of 0.11 g (0.68 mmol) of hexamethyl phosphorous triamide was added to a suspension of 0.1 g (0.34 mmol) of 9,10-diacetoxyanthracene in 0.5 mL of pyridine. After 24 h, a further 0.1 g (0.34 mmol) of 9,10-diacetoxyanthracene was added to the homogeneous mixture. The reaction was completed within 4 days. The solvent was evaporated in vacuo, and the residue was washed with dry acetonitrile. Yield 0.04 g (42%), m.p. 184°C, R_f0.73 (A); ^{1}H NMR: δ 2,87 (d, $^3J_{PH} = 7.7$ Hz, 12H, CH_3), 7.19 (m, 4H, 2,3,6,7-H), 7,19 (m, 2H, 5,8-H), 8.22 (m, 2H, 1,4-H); ^{31}P NMR (pyridine): δ 151.7; $C_{32}H_{28}N_2P_2O_4$: Calcd.: C 67.84, H 4.98, N 4.94, P 10.93%; found: C 69.55, H 5.91, N 4.43, P 9.87%.

(b) Direct Synthesis

A solution of 0.055 g (0.34 mmol) of hexamethyl phosphorous triamide in 0.5 mL of pyridine was added to a suspension of 0.1 g (0.34 mmol) of 9,10-diacetoxyanthracene in 0.5 mL of pyridine, and the mixture was kept at room temperature for 4 days. The solvent was removed in vacuo, and the residue was washed with acetonitrile. Yield 0.0607 g (63%).

(c) Dismutation

A solution of 0.11 g (0.68 mmol) of hexamethyl phosphorous triamide in 0.5 mL of pyridine was added to a suspension of 0.1 g (0.34 mmol) of 9,10-diacetoxyanthracene in 0.5 mL of pyridine. The mixture was kept at room temperature for 6 days. The solvent was removed in vacuo, and the residue was washed with acetonitrile. Yield 0.0385 g (40%).

Cyclo-[bis(2,6-anthracenyldiethylamidothiophosphate)] (6)

Sulfur (0.012 g, 0.36 mmol) was added to a solution of 0.112 g (0.18 mmol) of compound **(5)** in 1 mL of chloroform, and the mixture was kept at room temperature for 2.5 h under constant stirring. The

thiophosphate was isolated from the solution by reprecipitation with hexane. The solution was decanted, and the residue was dried in vacuo (1 mm Hg, 50°C). Yield 0.055 g (42%), m.p. (dec.) 260°C; ^{1}H NMR ($CDCl_3$): δ 1.21 (m, 12H, CH_3), 3.56 (d, $^3J_{PH}$ = 14.0 Hz, 8H, NCH_2), 7.84 (d, $^3J_{HH}$ = 9.2 Hz, 4H, 3,7-H), 7.92 (s, 4H, 1,5-H), 7.97 (m, 4H, 4,8-H), 8.34 (s, 4H, 9,10-H); ^{31}P NMR (CH_2Cl_2): δ 67.2.

Cyclo-[bis(2,6-anthracenyldiethylamidophosphate)] (7)

The complex of urea with hydrogen peroxide 0.068 g (0.72 mmol) was added to a solution of 0.112 g (0.18 mmol) of cyclophosphite 5 in 4 mL of chloroform, and the mixture was kept at room temperature for 24 h. The solution was filtered, and the solvent evaporated to a minimum volume; cyclophosphate **7** was recrystallized from hexane. Yield 0.096 g (81%), m.p. (dec.) 240°C; ^{1}H NMR: δ 1.09 (m, 12H, CH_3), 3.32 (d, $^3J_{PH}$ =11.3 Hz, 8H, NCH_2), 7.28 (d, $^3J_{HH}$ =9.2 Hz, 4H, 3,7-H), 7.39 (s, 4H, 1,5-H), 7.88 (m, 4H, 4,8-H), 8.32 (s, 4H, 9,10-H); ^{31}P NMR (CH_2Cl_2): δ 1.0.

REFERENCES

[1] (a) J. S. Meek and L. L. Koh, *J. Org. Chem.*, **33,** 2942 (1968); (b) F. Ramirez, S. B. Bhatia, A. V. Patwardhan, E. H. Chen, and C. P. Smith, *J. Org. Chem*., **33,** 20 (1968); (c) Y. Okada, K. Okeya, Y. Murata, N. Aoki, T. Aoki, M. Sugitani, et al., *Phosphorus, Sulfur, and Silicon*, **178,** 821 (2003).

[2] (a) E. N. Rasadkina, P. V. Slitikov, M. C. Mel'nik, A. I. Stach, V. K. Belsky, and E. E. Nifantiev, *Zh. Obshch. Khim.*, **74,** 1170 (2004); (b) E. N. Rasadkina,Yu. B. Evdokimenkova,A. I. Stach, V. K. Belsky, and E. E. Nifantiev, *Zh. Obshch. Khim*., **74,** 55 (2004); (c) E. E. Nifantiev,E. N. Rasadkina, and A. V. Petrov, *Zh. Obshch. Khim*., **74,** 698 (2005); (d) E. N. Rasadkina, P. V. Slitikov, M. C. Mel'nik, and E. E. Nifantiev, *Russ. Chem. Bull.*, **53,** 376 (2004).

[3] H. L. Allinger, *J. Am. Chem. Soc.*, **99,** 8127 (1977).

[4] E. E. Nifantiev, E. N. Rasadkina, Yu. B. Evdokimenkova, L. K. Vasianina, A. I. Stach, and V. K. Belsky, *Zh. Obshch. Khim*., **71,** 203 (2001).

[5] J. H. Hargis and G. A. Mattson, *J. Org. Chem*., **46,** 1597 (1981).

[6] H. Nöth and H. J. Vetter, *Chem. Ber.*, **98,** 1981 (1965).

[7] A. Zwierzak, *Bull. Acad. Polon. Sci. Ser. Sci. Chim.*, **13,** 609 (1965).

[8] V. L. Foss, N. V. Lukachev, and I. F. Luzenko, *A.P*., 827491 (1979).

[9] E. de B. Barnett, *J. Chem. Soc*., **8,** 1227 (1934).