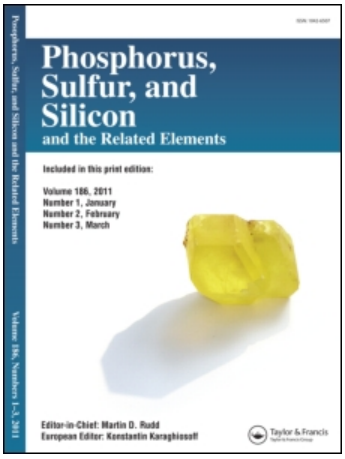

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

THE SYNTHESIS AND STRUCTURE OF THE FIRST REPRESENTATIVES OF OLIGOARYLENEPHOSPHOCYCLANES

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To cite this Article Blokhin, Yu. I. , Gusev, D. V. , Belsky, V. K. , Stash, A. I. and Nifantyev, E. I.(1995) 'THE SYNTHESIS AND STRUCTURE OF THE FIRST REPRESENTATIVES OF OLIGOARYLENEPHOSPHOCYCLANES', Phosphorus, Sulfur, and Silicon and the Related Elements, 102: 1, 143 — 154
To link to this Article: DOI: 10.1080/10426509508042552
URL: http://dx.doi.org/10.1080/10426509508042552

Phosphorus, Sulfur, and Silicon, 1995, Vol. 102, pp. 143–154
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THE SYNTHESIS AND STRUCTURE OF THE FIRST REPRESENTATIVES OF OLIGOARYLENEPHOSPHOCYCLANES

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(Received December 6, 1994)

Based on phenylphosphonous acid tetraethyldiamide and 2,2-di(*p*-oxyphenyl)propane diarylenecyclophenylphosphonite is synthesized. Its oxidation and sulfurization is investigated. It is shown that these reactions are stereospecific and lead to *cis*-isomers. The compounds obtained are the first representatives of oligoarylenephosphocyclanes. The structure of these compounds is confirmed by an X-ray structure analysis.

Key words: Diamide, diol, oligoarylenecyclophosphonite, crown-ethers, phosphorus(3+), cyclization, phosphorylation, NMR, X-ray analysis.

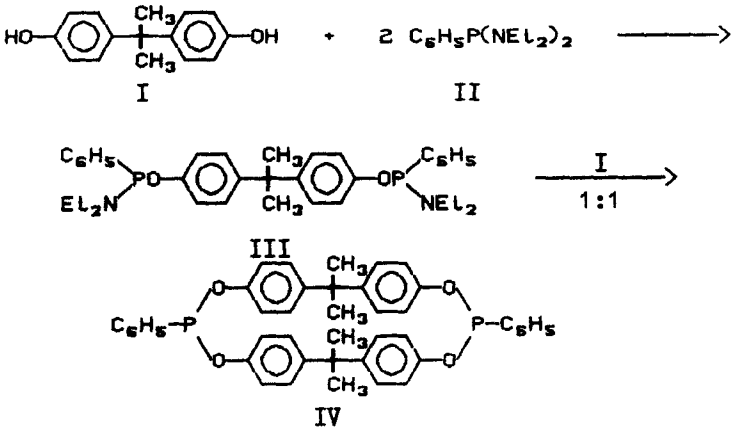
INTRODUCTION

After Pedersen's discovery of crown-ethers and their unique complexing properties[1] a lot of macrocyclic etheric systems including carbon-heteroatomic etheric fragments are under intensive research.[2,3] So far some specific kinds of macroheterocycles did not yet attact an appropriate attention. Thus oligoalkylencyclophosphites and -phosphonites are investigated only fragmentally[4,5] but corresponding arylene derivatives still were not studied.§ Meanwhile oligoarylene phosphite and phosphonite macrocycles are of great interest because they exhibit special perspectives for creating of metal complexes and other original systems of host-guest type. Actually in this case both phosphorus(III) atoms and arylene rings may take part in complex formation.

RESULTS AND DISCUSSION

To obtain oligoarylenecyclophosphonites we studied two approaches using as original reagents 2,2-di(*p*-oxyphenyl)propane (**I**) and phenylphosphonous acid tetraethyldiamide (**II**). The first approach ("assembly method") includes subsequent stages of the diol (**I**) phosphorylation by double molar amount of diamide (**II**) and cyclization of bisamidophosphite obtained by the diol (**I**):

§Recently we reported[6] the obtaining of the first representatives of this class of crown-ethers.



SCHEME I

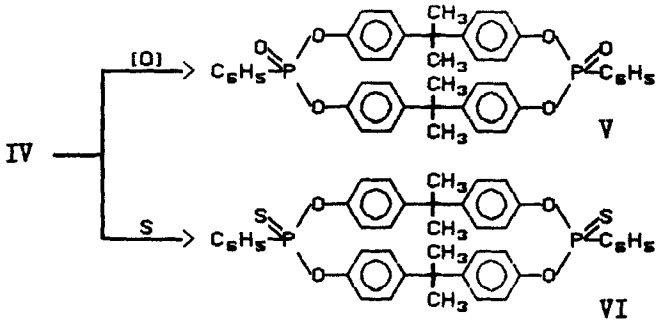
The fact of cyclization is confirmed by the absence in ^1H NMR spectra of signals corresponding to ethylamide protons. The individuality of the product is confirmed also by the data of ^{31}P NMR and TLC methods. The proving of two phosphonite residues presence in the cyclic systems is testified by mass spectrometry—maximal peak corresponds to this dimer.

The second approach ("direct phosphorylation method") consists in the interaction of diol (**I**) and diamide (**II**) in equimolar quantities in the presence of large amounts of solvents (toluene, *p*-xylene).

$$\mathbf{I} + \mathbf{II} \xrightarrow[\text{great excess of solvent}]{2:2} \mathbf{IV}$$

In this case the factor of the reagents small concentration blocks the polycondensation and provides of the dimer formation. Apparently the dimeric product among other oligomeres under these conditions is the most stable one. This fact determines the direction of the synthesis. The properties of the products obtained by both methods turned out to be identical.

We started the investigation of chemical peculiarities of the synthesized crown-systems. It is shown that oligoarylenecyclophosphonite (**IV**) is easily oxidized (**V**) by nitrogen oxides in solution of carbon tetrachloride and also sulfurized (**VI**) in dioxane.



SCHEME II

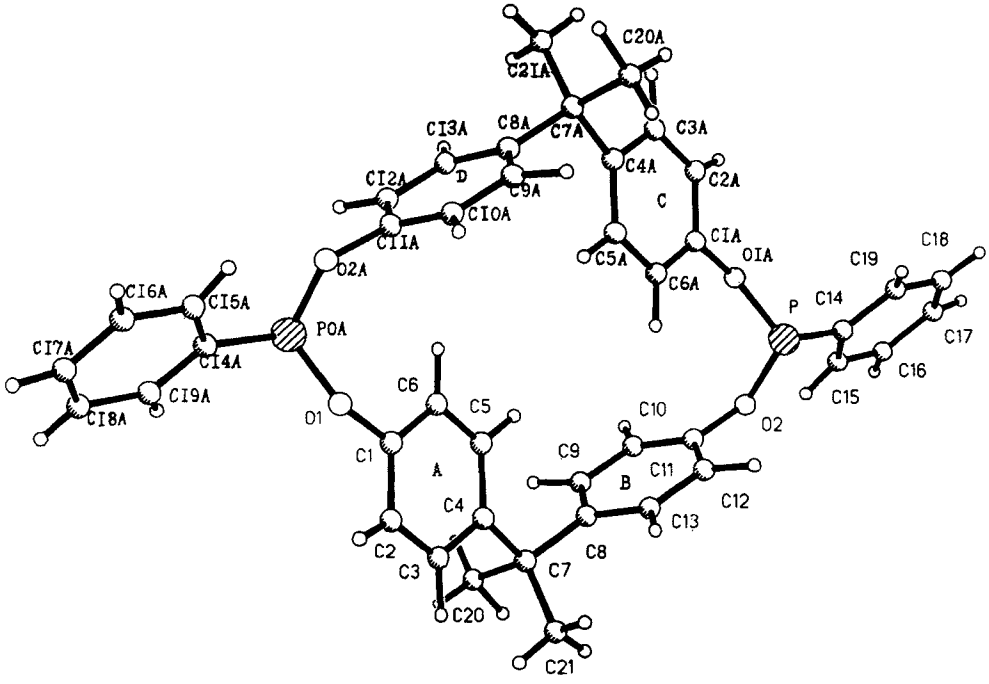


FIGURE 1 Molecular structure of oligoarylenecyclophosphonite (**IV**).

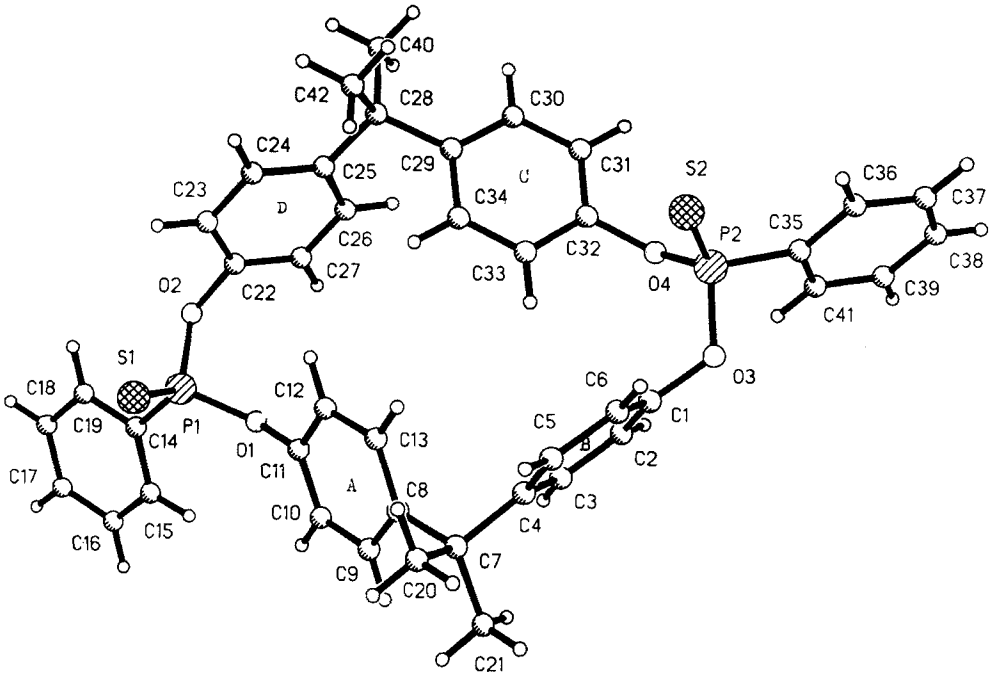


FIGURE 2 Molecular structure of oligoarylenecyclodithiophosphonate (**IV**).

At strict following of the conditions found the mentioned processes occur in a directed way yielding one product of reaction. Its individuality is confirmed by ^{31}P NMR spectroscopy. The values of the ^{31}P-chemical shifts of **V** and **VI** are 12.2 and 81.2 ppm respectively, and they differ substantially from that of original cycloarylenephosphonite (**IV**) 164.5 ppm. This fact along with the data of TLC gives evidence of the completion of the reactions mentioned.

The uncompromising justification of the structure of obtained products **IV** and **VI** is given by an X-ray structure analysis. Figures 1 and 2 show the molecular conformation and atomic numbering for **IV** and **VI** respectively.

In **IV** the phosphorus atoms P1 and P2 are in *trans*-position in respect to the mean plane of the macrocycle (it is required by an inversion center). In **VI** these atoms are in *cis*-position; also in **VI** the sulfur atoms S1 and S2 are *cis* with respect to P1···P2 line ("torsion" angle S1—P1—P2—S2 30.7). The geometric features of separate fragments of the macrocycles (interatomic bonds and bond angles) are usual. The only fact to be mentioned is the increasing of phenolic C—O bonds

TABLE I

Rings	Angle (deg)		
	IV	**VI**	**I**
AB	91.9	94.3	93.3 - 100.4
AC	180	113.4	-
AD	91.9	109.9	-
BC	91.9	90.7	-
BD	180	151.1	-
CD	91.9	109.2	-

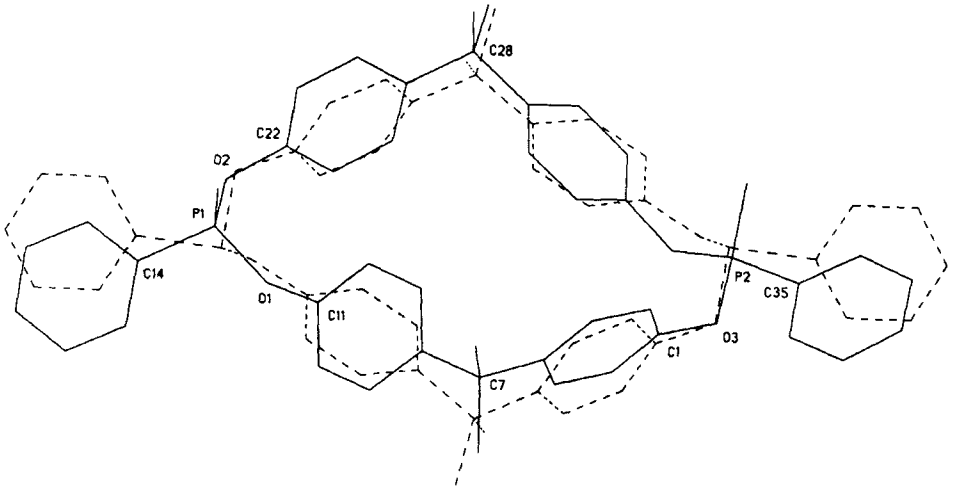


FIGURE 3 Comparison of molecular conformations in **IV** and **VI**.

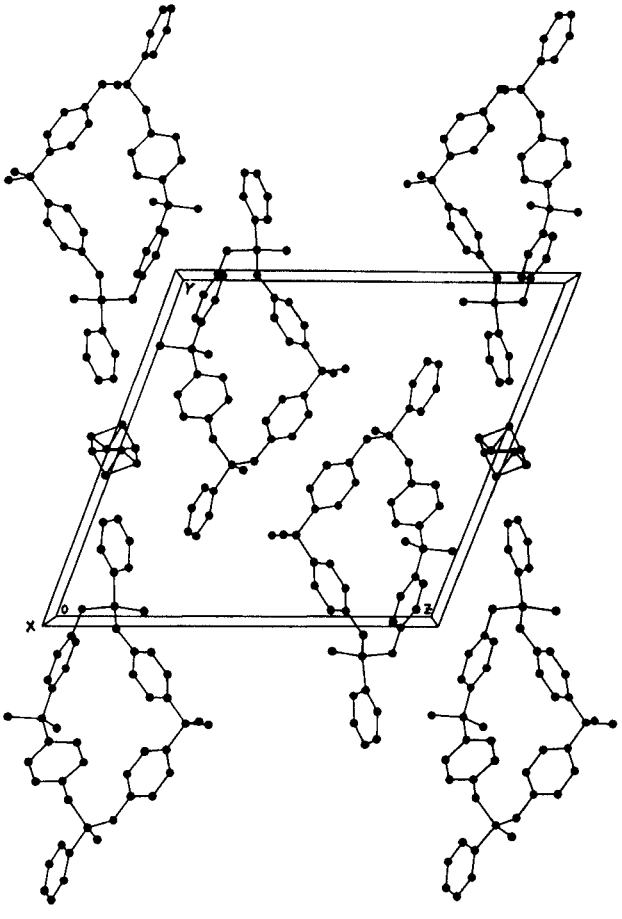


FIGURE 4 Molecular packing of **IV** onto plane (011).

with respect to the original diol **I**: 1.384 Å (mean for **I**),[7] 1.395 Å (**IV**), and 1.412 Å (**VI**). The sulfurization of **IV** results sterically in three ways. Firstly the whole conformation of the macrocycle changes from *trans* to *cis*, secondly it affects the interplanar angles between benzene rings planes (Table I) and thirdly it increases the size of cycle cavity: P···P distance in **IV** is 10.344 Å and in **VI** 10.584 Å, distances between the ring centers A and C 5.370 Å (**IV**), 6.329 Å (**VI**), B and D 5.370 Å (**IV**), 7.673 Å (**VI**). The more detailed picture comparing the two molecules at their best fitting is shown in Figure 3 (**IV**—dashed lines, **VI**—solid lines).

In both structures the molecular packing is determined by usual Van-der-Waals interactions only (there are no abnormal non-bonded interatomic contacts). In **VI** there are cylindric channels along [100], partly filled with solvent molecules (Figure 4), in **IV** such channels or other cavities are absent (Figure 5).

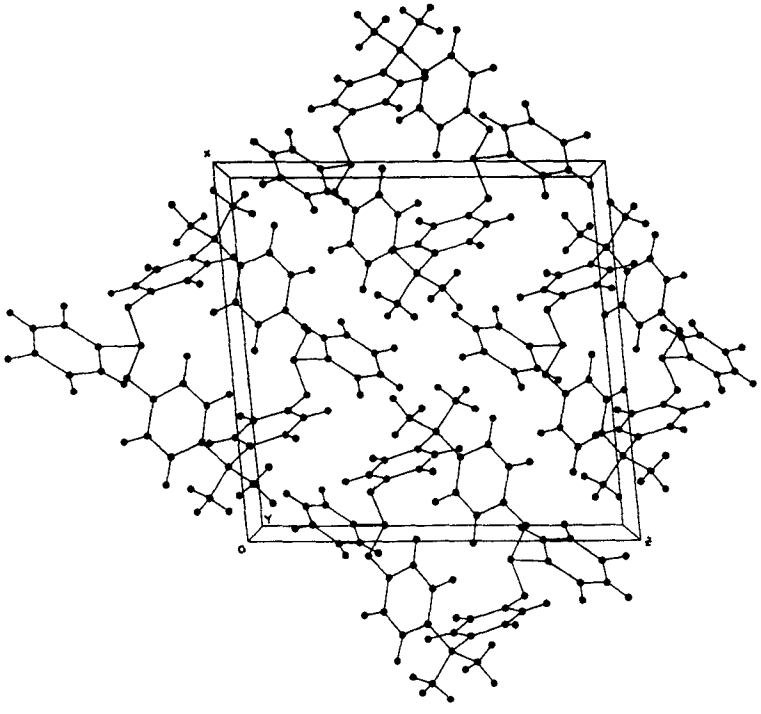


FIGURE 5 Molecular packing of **VI** onto plane (101).

EXPERIMENTAL

The ^{31}P NMR spectra were taken using Bruker Wp-80 SY spectrometer with working frequency 32.4 MHz in benzene or toluene solutions. The chemical shifts were mesured using 85% H_3PO_4 (external standard) as reference. ^1H NMR spectra were taken using Bruker AM-400 spectrometer (400 MHz) in CD_2Cl_2 solution. The mass spectra were measured on an MX-1321 apparatus with a direct inlet of a sample. TLC control was made by standard methods on "Silufol UV-254" plates. All syntheses were done in purified argon atmosphere.

Cyclodiphosphonite (**IV**): To the solution of 2.28 g (10^{-2} mole) of diol (**I**) in 75 mL of absolute xylene, 2.52 g (10^{-2} mole) of amide (**II**) was added with stirring. The mixture was boiled for 14 hours under refluxing. After cooling to room temperature the product slowly precipitates as a colorless amorphous substance. After recrystallization from *o*-xylene in a sealed ampule the product crystallizes as transparent needle-like crystals with m.p. 194–195°C. Yield 85%, R_f 0.57 (hexane-dioxane, 3:1). ^{31}P NMR (benzene) δ 164.5 ppm. Found, %: C 75.40, H 5.68, P 9.21. $C_{42}H_{38}O_4P_2$. Calcd., %: C 75.44, H 5.73, P 9.26.

Cyclodiphosphonate (**V**): To 0.5 g ($7.5 \cdot 10^{-4}$ mole) of **IV**, 2 mL of N_2O_4 solution in CCl_4 (10 g of N_2O_4 in 50 mL of CCl_4) was added, and the mixture let stand for 12 hours. The precipitate was filtered and after the dissolving in boiling toluene it was again precipitated by heptane vapor. Yield 82%, m.p. 265–267°C, R_f 0.48 (hexane-dioxane, 3:1). ^{31}P NMR (toluene) δ 12.2 ppm. Found, %: C 70.68, H 5.34, P 8.85. $C_{42}H_{38}O_6P_2$. Calcd., %: C 71.90, H 5.42, P 8.84.

Cyclodithiophosphonate (**VI**): 0.5 g ($7.5 \cdot 10^{-4}$ mole) of **IV** treated with 0.05 g ($1.5 \cdot 10^{-3}$ mole) of elemental sulfur in 15 mL of absolute dioxane. The mixture was boiled 1 hour. The filtered precipitate was dissolved in boiling benzene and it was again precipitated by heptane vapor. Yield 71%, m.p. 258–259°C, R_f 0.42 (hexane-dioxane, 3:1). ^{31}P NMR (benzene) δ 83.2 ppm. Found, %: C 60.79, H 5.16, S 8.69, P 8.40. $C_{42}H_{38}O_4S_2P_2$. Calcd., %: C 68.84, H 5.23, S 8.75, P 8.45.

TABLE II

X-ray analysis data for oligoarylenecyclophosphonite (IV)

A. Atom coordinates ($x10^4$) and temperature factors (A^2x10^3)

Atom	x	y	z	U
P	194(1)	5913(2)	3439(1)	51(1)*
O(1)	600(2)	-4728(4)	7033(2)	82(1)*
O(2)	1129(2)	5020(5)	3160(2)	89(1)*
C(1)	1125(3)	-3662(6)	6535(3)	58(2)*
C(2)	2039(3)	-3655(7)	6754(3)	75(2)*
C(3)	2589(3)	-2596(6)	6308(3)	65(2)*
C(4)	2240(3)	-1546(5)	5606(2)	43(1)*
C(5)	1316(3)	-1585(5)	5404(3)	48(1)*
C(6)	756(3)	-2639(6)	5859(3)	58(2)*
C(7)	2892(3)	-559(5)	5060(3)	50(1)*
C(8)	2400(2)	918(5)	4547(3)	41(1)*
C(9)	2110(3)	810(6)	3662(3)	56(2)*
C(10)	1688(3)	2159(7)	3209(3)	62(2)*
C(11)	1526(3)	3653(6)	3643(3)	59(2)*
C(12)	1786(3)	3814(6)	4531(3)	61(2)*
C(13)	2211(3)	2442(6)	4970(3)	54(2)*
C(14)	158(3)	7564(5)	2577(3)	50(2)*
C(15)	682(3)	7618(6)	1859(3)	64(2)*
C(16)	602(3)	8959(7)	1274(3)	72(2)*
C(17)	14(3)	10276(6)	1383(3)	70(2)*
C(18)	-498(3)	10252(6)	2081(4)	68(2)*
C(19)	-418(3)	8904(6)	2675(3)	60(2)*
C(20)	3276(4)	-1864(6)	4432(4)	85(2)*
C(21)	3696(3)	178(7)	5623(3)	79(2)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U(i,j) tensor

B. Bond lengths (A)

P-O(2)	1.636(4)	P-C(14)	1.827(4)
		P-O(1)a	1.611(4)

TABLE II (*Continued*)

O(1)-C(1)	1.400(6)	O(1)-Pa	1.611(4)
O(2)-C(11)	1.390(6)		
C(1)-C(2)	1.368(7)	C(1)-C(6)	1.374(6)
C(2)-C(3)	1.374(7)	C(3)-C(4)	1.404(6)
C(4)-C(5)	1.378(5)	C(4)-C(7)	1.530(6)
C(5)-C(6)	1.389(6)	C(7)-C(8)	1.533(5)
C(7)-C(20)	1.531(7)	C(7)-C(21)	1.518(6)
C(8)-C(9)	1.381(6)	C(8)-C(13)	1.383(6)
C(9)-C(10)	1.371(6)	C(10)-C(11)	1.362(7)
C(11)-C(12)	1.378(7)	C(12)-C(13)	1.377(6)
C(14)-C(15)	1.392(6)	C(14)-C(19)	1.360(6)
		C(15)-C(16)	1.365(7)
C(16)-C(17)	1.354(7)	C(17)-C(18)	1.357(7)
C(18)-C(19)	1.378(7)		

C. Bond angles (deg)

O(2)-P-C(14)	94.7(2)		
O(2)-P-O(1)a	104.3(2)		
C(14)-P-O(1)a	95.9(2)		
C(1)-O(1)-Pa	120.8(4)	P-O(2)-C(11)	120.9(3)
O(1)-C(1)-C(2)	117.1(4)	O(1)-C(1)-C(6)	122.7(4)
C(2)-C(1)-C(6)	120.2(4)	C(1)-C(2)-C(3)	120.0(4)
C(2)-C(3)-C(4)	121.6(4)	C(3)-C(4)-C(5)	116.9(4)
C(3)-C(4)-C(7)	119.4(3)	C(5)-C(4)-C(7)	123.4(3)
C(4)-C(5)-C(6)	121.7(4)	C(1)-C(6)-C(5)	119.6(4)
C(4)-C(7)-C(8)	110.6(3)	C(4)-C(7)-C(20)	107.1(3)
C(8)-C(7)-C(20)	111.1(3)	C(4)-C(7)-C(21)	112.5(3)
C(8)-C(7)-C(21)	108.9(3)	C(20)-C(7)-C(21)	106.5(3)
C(7)-C(8)-C(9)	123.2(4)	C(7)-C(8)-C(13)	120.4(3)
C(9)-C(8)-C(13)	116.5(4)	C(8)-C(9)-C(10)	122.3(4)
C(9)-C(10)-C(11)	119.7(4)	O(2)-C(11)-C(10)	118.3(4)
C(2)-C(11)-C(12)	121.3(4)	C(10)-C(11)-C(12)	120.3(4)
C(11)-C(12)-C(13)	118.9(4)	C(8)-C(13)-C(12)	122.3(4)
P-C(14)-C(15)	126.8(3)	P-C(14)-C(19)	115.8(3)
C(15)-C(14)-C(19)	117.4(4)		
C(14)-C(15)-C(16)	120.7(4)	C(15)-C(16)-C(17)	120.6(5)
C(16)-C(17)-C(18)	119.8(5)	C(17)-C(18)-C(19)	119.8(4)
C(14)-C(19)-C(18)	121.7(4)		

TABLE III

X-ray analysis data for oligoarylenecyclodithiophosphonate (VI)

A. Atom coordinates ($x10^4$) and temperature factors (A^2x10^3)

Atom	x	y	z	U
P(1)	4830(2)	-702(1)	1727(1)	40(1)*
P(2)	2477(2)	5428(1)	3169(1)	44(1)*
S(1)	2843(2)	-629(1)	2504(1)	56(1)*
S(2)	-327(3)	5575(1)	3534(1)	66(1)*
O(1)	6239(6)	-56(2)	1938(2)	50(2)*
O(2)	4008(6)	-650(2)	989(2)	49(2)*
O(3)	4141(6)	5324(2)	3697(2)	51(2)*
O(4)	3202(7)	4678(2)	2434(2)	56(2)*
C(1)	4511(9)	4666(3)	3902(3)	42(2)*
C(2)	6215(9)	4120(4)	3577(4)	50(3)*
C(3)	6620(9)	3481(3)	3786(3)	50(2)*
C(4)	5357(9)	3375(3)	4311(3)	43(2)*
C(5)	3617(10)	3939(3)	4628(3)	49(2)*
C(6)	3208(10)	4589(3)	4428(3)	52(2)*
C(7)	5930(10)	2660(3)	4528(3)	51(2)*
C(8)	6001(9)	1918(3)	3836(3)	43(2)*
C(9)	7661(10)	1321(4)	3608(4)	59(3)*
C(10)	7692(10)	665(4)	2992(4)	65(3)*
C(11)	6045(9)	597(3)	2594(3)	42(2)*
C(12)	4402(9)	1181(3)	2791(3)	52(3)*
C(13)	4405(9)	1845(3)	3412(3)	50(2)*
C(14)	6591(9)	-1600(3)	1358(3)	46(2)*
C(15)	8460(10)	-1682(4)	1642(4)	58(3)*
C(16)	9737(11)	-2398(5)	1391(5)	75(3)*
C(17)	9143(14)	-3030(4)	899(5)	79(4)*
C(18)	7311(13)	-2965(4)	619(4)	75(3)*
C(19)	6022(10)	-2240(3)	849(4)	62(3)*
C(20)	4353(12)	2625(4)	5112(4)	68(3)*
C(21)	7992(12)	2697(4)	4837(4)	71(3)*
C(22)	2710(8)	41(3)	1007(3)	39(2)*
C(23)	650(10)	140(4)	1206(4)	54(3)*
C(24)	-569(9)	833(4)	1247(4)	53(3)*
C(25)	240(8)	1407(3)	1080(3)	40(2)*
C(26)	2305(9)	1256(3)	854(3)	44(2)*
C(27)	3551(8)	578(3)	816(3)	43(2)*
C(28)	-1072(9)	2171(3)	1136(3)	46(2)*
C(29)	41(8)	2858(3)	1481(3)	42(2)*
C(30)	177(12)	3425(4)	1189(4)	67(3)*
C(31)	1202(12)	4034(4)	1518(4)	62(3)*
C(32)	2056(9)	4082(3)	2139(3)	45(2)*
C(33)	1901(9)	3539(3)	2461(3)	47(2)*

TABLE III (*Continued*)

A. Atom coordinates ($\times 10^4$) and temperature factors ($A^2 \times 10^3$)

Atom	x	y	z	U
C(34)	906(9)	2933(3)	2132(3)	44(2)*
C(35)	3310(11)	6194(4)	2951(3)	54(3)*
C(36)	2020(14)	6894(4)	3089(4)	79(3)*
C(37)	2751(24)	7503(5)	2953(6)	96(5)*
C(38)	4706(28)	7395(7)	2679(7)	114(6)*
C(39)	6036(16)	6718(7)	2525(6)	96(5)*
C(40)	-1538(13)	2094(4)	346(4)	80(3)*
C(41)	5345(12)	6101(5)	2664(4)	70(3)*
C(42)	-3101(10)	2351(4)	1630(5)	77(3)*
O(4)	7040(15)	4986(6)	-251(5)	114(3)*
C(43)	6284(21)	4954(8)	493(7)	133(4)*
C(44)	5766(21)	4602(8)	-726(7)	130(4)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U(i,j) tensor

B. Bond lengths (A)

P(1)-S(1)	1.912(2)	P(1)-O(1)	1.584(4)
P(1)-O(2)	1.596(5)	P(1)-C(14)	1.781(5)
P(2)-S(2)	1.904(2)	P(2)-O(3)	1.585(5)
P(2)-O(4)	1.602(4)	P(2)-C(35)	1.773(8)
O(1)-C(11)	1.406(6)	O(2)-C(22)	1.425(7)
O(3)-C(1)	1.408(8)	O(4)-C(32)	1.409(7)
C(1)-C(2)	1.361(7)	C(1)-C(6)	1.365(9)
C(2)-C(3)	1.38(1)	C(3)-C(4)	1.376(9)
C(4)-C(5)	1.390(7)	C(4)-C(7)	1.533(9)
C(5)-C(6)	1.39(1)	C(7)-C(8)	1.548(7)
C(7)-C(20)	1.53(1)	C(7)-C(21)	1.52(1)
C(8)-C(9)	1.375(8)	C(8)-C(13)	1.372(9)
C(9)-C(10)	1.377(8)	C(10)-C(11)	1.369(9)
C(11)-C(12)	1.354(8)	C(12)-C(13)	1.394(8)
C(14)-C(15)	1.394(9)	C(14)-C(19)	1.376(8)
C(15)-C(16)	1.38(1)	C(16)-C(17)	1.36(1)
C(17)-C(18)	1.37(1)	C(18)-C(19)	1.394(9)
C(22)-C(23)	1.369(8)	C(22)-C(27)	1.360(9)
C(23)-C(24)	1.390(9)	C(24)-C(25)	1.39(1)
C(25)-C(26)	1.375(8)	C(25)-C(28)	1.518(8)
C(26)-C(27)	1.378(8)	C(28)-C(29)	1.535(8)
C(28)-C(40)	1.55(1)	C(28)-C(42)	1.538(9)
C(29)-C(30)	1.37(1)	C(29)-C(34)	1.392(9)
C(30)-C(31)	1.38(1)	C(31)-C(32)	1.34(1)
C(32)-C(33)	1.37(1)	C(33)-C(34)	1.369(8)

TABLE III (*Continued*)

A. Atom coordinates ($\times 10^4$) and temperature factors ($A^2 \times 10^3$)

Atom	x	y	z	U
C(35)-C(36)	1.38(1)		C(35)-C(41)	1.40(1)
C(36)-C(37)	1.39(2)		C(37)-C(38)	1.34(2)
C(38)-C(39)	1.35(2)		C(39)-C(41)	1.40(2)
O(5)-C(43)	1.53(2)		O(5)-C(44)	1.37(2)
C(43)-O(5)a	1.40(3)		C(43)-C(44)a	1.44(2)
C(44)-C(43)a	1.44(2)			

C. Bond angles (deg)

S(1)-P(1)-O(1)	114.9(2)	S(1)-P(1)-O(2)	117.5(2)
O(1)-P(1)-O(2)	102.8(2)	S(1)-P(1)-C(14)	115.3(2)
O(1)-P(1)-C(14)	104.3(2)	O(2)-P(1)-C(14)	100.0(2)
S(2)-P(2)-O(3)	117.4(2)	S(2)-P(2)-O(4)	114.4(2)
O(3)-P(2)-O(4)	102.9(2)	S(2)-P(2)-C(35)	117.6(2)
O(3)-P(2)-C(35)	98.7(3)	O(4)-P(2)-C(35)	103.5(3)
P(1)-O(1)-C(11)	127.4(4)	P(1)-O(2)-C(22)	119.9(3)
P(2)-O(3)-C(1)	123.0(4)	P(2)-O(4)-C(32)	124.7(4)
O(3)-C(1)-C(2)	118.4(6)	O(3)-C(1)-C(6)	120.5(5)
C(2)-C(1)-C(6)	121.2(6)	C(1)-C(2)-C(3)	118.9(6)
C(2)-C(3)-C(4)	122.3(5)	C(3)-C(4)-C(5)	117.4(6)
C(3)-C(4)-C(7)	119.3(5)	C(5)-C(4)-C(7)	123.2(6)
C(4)-C(5)-C(6)	120.7(6)	C(1)-C(6)-C(5)	119.5(5)
C(4)-C(7)-C(8)	108.3(5)	C(4)-C(7)-C(20)	112.8(5)
C(8)-C(7)-C(20)	107.0(5)	C(4)-C(7)-C(21)	108.3(6)
C(8)-C(7)-C(21)	112.2(5)	C(20)-C(7)-C(21)	108.4(6)
C(7)-C(8)-C(9)	122.2(6)	C(7)-C(8)-C(13)	120.5(5)
C(9)-C(8)-C(13)	117.2(5)	C(8)-C(9)-C(10)	121.3(6)
C(9)-C(10)-C(11)	120.1(6)	O(1)-C(11)-C(10)	117.2(5)
O(1)-C(11)-C(12)	122.1(5)	C(10)-C(11)-C(12)	120.3(5)
C(11)-C(12)-C(13)	118.9(6)	C(8)-C(13)-C(12)	122.1(5)
P-C(14)-C(15)	120.2(4)	P-C(14)-C(19)	120.0(5)
C(15)-C(14)-C(19)	119.4(5)	C(14)-C(15)-C(16)	119.5(6)
C(15)-C(16)-C(17)	120.5(7)	C(16)-C(17)-C(18)	120.9(7)
C(17)-C(18)-C(19)	119.5(7)	C(14)-C(19)-C(18)	120.1(7)
O(2)-C(22)-C(23)	119.2(6)	O(2)-C(22)-C(27)	118.9(5)
C(23)-C(22)-C(27)	121.9(6)	C(22)-C(23)-C(24)	118.0(7)
C(23)-C(24)-C(25)	121.9(5)	C(24)-C(25)-C(26)	117.1(5)
C(24)-C(25)-C(28)	122.2(5)	C(26)-C(25)-C(28)	120.6(6)
C(25)-C(26)-C(27)	122.1(6)	C(22)-C(27)-C(26)	118.9(5)
C(25)-C(28)-C(29)	110.8(5)	C(25)-C(28)-C(40)	107.0(4)
C(29)-C(28)-C(40)	111.4(6)	C(25)-C(28)-C(42)	112.4(6)
C(29)-C(28)-C(42)	106.1(4)	C(40)-C(28)-C(42)	109.2(6)
C(28)-C(29)-C(30)	123.0(6)	C(28)-C(29)-C(34)	119.4(6)

TABLE III (*Continued*)

A. Atom coordinates ($\times 10^4$) and temperature factors ($A^2 \times 10^3$)

Atom	x	y	z	U
C(30)-C(29)-C(34)	117.5(6)	C(29)-C(30)-C(31)		121.0(7)
C(30)-C(31)-C(32)	120.0(7)	O(4)-C(32)-C(31)		118.6(6)
O(4)-C(32)-C(33)	120.5(5)	C(31)-C(32)-C(33)		120.8(6)
C(32)-C(33)-C(34)	119.1(6)	C(29)-C(34)-C(33)		121.5(6)
P(2)-C(35)-C(36)	121.5(6)	P(2)-C(35)-C(41)		119.4(5)
C(36)-C(35)-C(41)	119.0(8)	C(35)-C(36)-C(37)		120.2(9)
C(36)-C(37)-C(38)	119.1(10)	C(37)-C(38)-C(39)		123.3(13)
C(38)-C(39)-C(41)	118.6(11)	C(35)-C(41)-C(39)		119.6(7)
C(43)-O(5)a-C(44)	104.2(11)			
O(5)a-C(43)-C(44)a	109.1(12)	O(5)b-C(43)-C(44)a		105.2(15)
O(5)a-C(44)-C(43)a	107.8(10)			

X-ray crystallography: Intensity data for **IV** and **VI** were collected using crystals of approximate dimensions 0.25 × 0.25 × 0.40 mm³ on Syntex $P\bar{1}$ four-circle diffractometer using Nb-filtered Mo-K_α radiation (λ = 0.71069 Å). Crystal data are as follows: **IV**, $C_{42}H_{38}O_4P_2$, monoclinic, a = 14.818(4), b = 7.735(1), c = 15.203(4) Å, β = 94.83(2) Å, space group $P2_1/n$, Z = 2, D_x = 1.279 g/cm³, V = 1736(1) Å³, T = 298 K, μ(Mo-K_α) = 1.62 cm^{-1}; **VI**, $C_{42}H_{38}O_4S_2P_2 \cdot 1/2\ C_4H_8O_2$, triclinic, a = 6.640(2), b = 18.582(6), c = 19.512(7) Å, α = 110.45(3), β = 87.06(3), γ = 81.55(3)°, space group $P\bar{1}$, Z = 2, D_x = 1.19 g/cm³, V = 2217(2) Å³, T = 298 K, μ(Mo-K_α) = 2.25 cm^{-1}.

Lattice parameters were determined by the least-squares method from 12 reflections for each crystal ($20 \le 2\theta \le 25°$). For the calculations 1701 and 3694 reflections with $I \ge 3\sigma(I)$ were used for **IV** and **VI** correspondingly ($\theta/2\theta$ scan mode up to θ = 25°). Both structures were solved by the direct method and refined with the anisotropic approximation for non-hydrogen atoms.

Weights of each reflection in the refinement (on F) were calculated from $w = 1/[\gamma^2(F_0) + 0.000192F_0^2]$ (**IV**) and $w = 1/[\gamma^2(F_0) + 0.000845F_0^2]$ (**VI**), $\sigma(F_0)$ being the esd, based on counting statistics of the observed structure factor. Scattering factors were taken from the International Tables for X-ray crystallography.[8] All H atoms included in the refinement were found from difference syntheses and were refined isotropically.

The refinements resulted in final values: (**IV**) R = 0.053, R_w = 0.058, S = 2.41; (**VI**) R = 0.065, R_w = 0.074, S = 2.14. The rather big values of R-factors are due to statistic disorder found in both structures. In **IV** phosphorus atom is 85:15 up/down according the plane of its 3 neighbors, in **IV** solvated 1,4-dioxane molecules are also statistically disordered around the symmetry center. Atomic coordinates for non-hydrogen atoms are given in Tables II and III.

All calculations were performed on NOVA-3 computer using SHELXTL crystallographic computing system.[9] The interatomic bonds and valence angles are given in Tables II and III.

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