

Synthesis and structures of oligothioarylenecyclophosphonites

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A new representative of phospho(III)crown ethers was obtained based on 4,4'-thiodiphenol and tetraethyldiamide of phenylphosphonous acid. Thiaphospho(III)crown ethers can be prepared by different methods depending on the ratio of the initial reactants and the reaction conditions. The structures of the compounds obtained were confirmed by spectroscopic data and X-ray structural analysis.

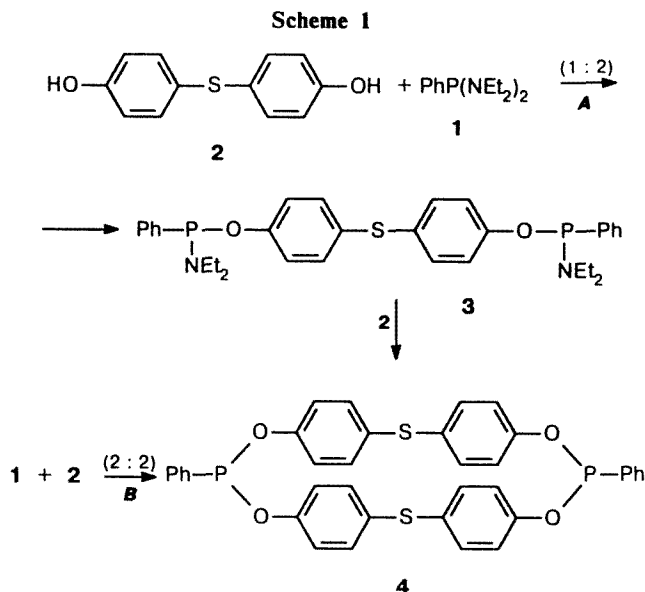
Key words: 4,4'-thiodiphenol, diamide of phenylphosphonous acid, crown ethers, synthesis; oligothioarylenecyclophosphonites, structure.

Previously,^{1,2} we performed the first synthesis of oligothioarylenecyclophosphonites based on 2,2-di(*p*-hydroxyphenyl)propane and tetraethyldiamide phenylphosphonous acid (**1**). As part of continuing studies, we replaced the alkyl fragment in the initial dihydric phenol with a heteroatom using 4,4'-thiodiphenol (**2**) as a phosphorylating agent.

Studies demonstrated (Scheme 1) that oligothioarylenecyclophosphonites can be obtained by two methods, *i.e.*, by stepwise synthesis (method **A**) or by direct synthesis (method **B**) depending on the ratio of the initial compounds and the reaction conditions (the amount of solvent).

The structure of macrocyclic phosphonite **4** was established by ³¹P NMR and IR spectroscopy and mass spectrometry and was confirmed by the data of elemental analysis (Table 1). In the IR spectrum of the product obtained by the stepwise method **A**, the P—N stretching band (900 cm⁻¹) typical of the intermediate bis(amido-ester) of phenylphosphonous acid **3** is absent, but the absorption band of the P—Ph group is observed. The ³¹P NMR spectrum shows a singlet, whose chemical shift is close to that of the ³¹P signal of macrocyclic phosphonite obtained previously from 2,2-di(*p*-hydroxyphenyl)propane. The value of *m/z* of the [M]⁺ molecular ion in the mass spectrum corresponds to the theoretical value.

We studied the structure of phospho(III)crown ether **4** by X-ray structural analysis (Fig. 1, Tables 2–4). The P atoms in the molecule are statistically disordered (0.75 : 0.25) relative to the O(1)O(2)O(13) plane. In the centrosymmetric molecule, the P atoms are in *trans* positions with respect to the mean plane of the



macrocycle, which agrees with the structural data on the oligoarylenecyclophosphonite studied previously.²

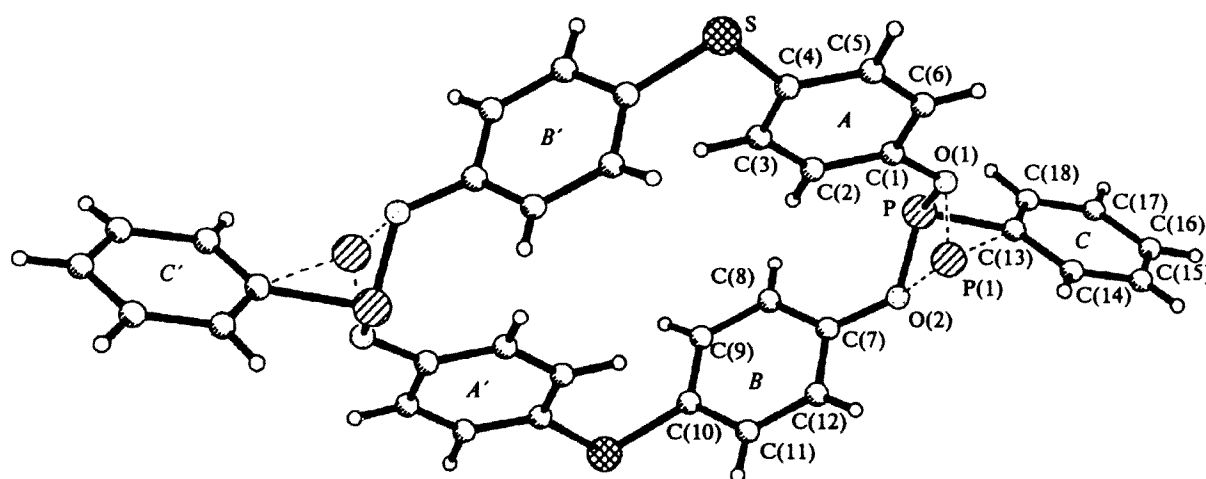
Experimental

The ³¹P NMR spectra were recorded on a Bruker WP-80 SY instrument (32.4 MHz) in benzene or dioxane solutions. Chemical shifts were measured relative to 85% H₃PO₄ (external standard). The mass spectra were obtained on an MKh-1321A instrument with direct introduction of the sample, and on an MSBK instrument (the Elektron Joint-Stock Company, Sumy, Ukraine) using ionization by the products of

Table 1. Characteristics of bis(amidophenylphosphonite) **3** and macrocyclic phosphonite **4**

Compound	Yield (%)	R_f (system)	Found ————— Calculated (%)			Molecular formula	^{31}P NMR, δ	MS, $[\text{M}]^+$	IR, ν/cm^{-1}
			C	H	P				
3	97	0.65 (benzene— dioxane, 4 : 1)	66.66	6.60	10.76	$\text{C}_{32}\text{H}_{38}\text{N}_2\text{O}_2\text{P}_2\text{S}$	131*	576	900 (P—N); 1200 (P—Ph)
			66.73	6.72	10.71				
4	67	0.88 (benzene— dioxane, 5 : 1)	66.66	4.01	9.57	$\text{C}_{36}\text{H}_{26}\text{O}_4\text{P}_2\text{S}_2$	164	648	1200 (P—Ph)
			66.62	4.08	9.52				

* Apparently, the product is a mixture of the *meso*- and (*R,S*)- diastereoisomers, whose signals in the ^{31}P NMR spectra are identical. Under the reaction conditions, these diastereoisomers can interconvert.

**Fig. 1.** Structure of oligothioarylenecyclophosphonite **4**.**Table 2.** Coordinates of nonhydrogen atoms ($\times 10^4$) and equivalent isotropic thermal parameters ($U_{\text{iso}}^{\text{eq}} \times 10^3$) in the structure of **4**

Atom	x	y	z	$U_{\text{iso}}^{\text{eq}}/\text{\AA}^2$	Atom	x	y	z	$U_{\text{iso}}^{\text{eq}}/\text{\AA}^2$
S	-268(1)	463(2)	3526(1)	62(1)	C(8)	2703(5)	5748(7)	6783(3)	61(2)
P*	4710(1)	3264(2)	6374(1)	44(1)	C(9)	1698(5)	6783(6)	6823(3)	55(1)
P(1)**	4997(5)	4149(7)	5825(3)	59(1)	C(10)	1478(4)	8136(5)	6388(2)	45(1)
O(1)	4564(3)	2517(4)	5554(2)	63(1)	C(11)	2271(5)	8420(7)	5905(3)	61(1)
O(2)	4522(3)	5149(4)	6251(2)	86(1)	C(12)	3260(5)	7407(7)	5867(3)	68(2)
C(1)	3386(4)	2111(5)	5104(2)	47(1)	C(13)	6461(4)	3324(6)	6590(3)	61(1)
C(2)	2236(4)	2714(6)	5199(3)	53(1)	C(14)	7242(7)	3978(8)	6179(4)	78(2)
C(3)	1095(4)	2240(6)	4722(2)	51(1)	C(15)	8563(7)	3944(8)	6418(4)	83(2)
C(4)	1112(4)	1178(5)	4155(2)	43(1)	C(16)	9095(6)	3260(7)	7083(4)	74(2)
C(5)	2284(4)	597(6)	4060(2)	49(1)	C(17)	8320(6)	2628(7)	7496(3)	75(2)
C(6)	3413(4)	1057(6)	4537(2)	50(1)	C(18)	7016(6)	2641(7)	7252(3)	69(2)
C(7)	3481(4)	6062(6)	6299(3)	51(1)					

* 75%. ** 25%.

the decomposition of ^{252}Cf . The IR spectra were recorded on a Specord 75 IR spectrometer in a thin layer (KBr).

TLC was carried out on Silufol UV-254 plates. The chromatograms were developed in an iodine chamber or were calcinated at 200–250 °C. X-ray diffraction analysis was car-

ried out on an automated CAD-4 diffractometer (Mo-K α radiation, graphite monochromator).

All syntheses involving compounds of trivalent phosphorus were carried out under an atmosphere of dry argon or nitrogen purified from oxygen.

Table 3. Bond lengths (*d*) and bond angles (ω) in molecule **4**

Bond	<i>d</i> /Å	Angle	ω /deg
S—C(4)	1.768(4)	C(4)—S—C(10)*	103.7(2)
S—C(10)*	1.769(4)	O(2)—P—O(1)	105.0(2)
P—O(2)	1.586(4)	O(2)—P—C(13)	95.5(2)
P—O(1)	1.619(3)	O(1)—P—C(13)	95.8(2)
P—C(13)	1.821(5)	C(1)—O(1)—P	123.1(3)
O(1)—C(1)	1.388(5)	C(7)—O(2)—P	128.1(4)
O(2)—C(7)	1.362(5)	C(2)—C(1)—C(6)	120.1(4)
C(1)—C(2)	1.370(6)	C(2)—C(1)—O(1)	123.4(4)
C(1)—C(6)	1.373(6)	C(6)—C(1)—O(1)	116.5(4)
C(2)—C(3)	1.395(6)	C(1)—C(2)—C(3)	119.7(4)
C(3)—C(4)	1.376(6)	C(4)—C(3)—C(2)	120.7(4)
C(4)—C(5)	1.386(6)	C(3)—C(4)—C(5)	118.9(4)
C(5)—C(6)	1.382(6)	C(3)—C(4)—S	124.9(3)
C(7)—C(12)	1.364(7)	C(5)—C(4)—S	116.3(3)
C(7)—C(8)	1.375(7)	C(6)—C(5)—C(4)	120.3(4)
C(8)—C(9)	1.387(7)	C(1)—C(6)—C(5)	120.4(4)
C(9)—C(10)	1.372(6)	O(2)—C(7)—C(12)	117.1(5)
C(10)—C(11)	1.381(6)	O(2)—C(7)—C(8)	123.7(5)
C(10)—S*	1.769(4)	C(12)—C(7)—C(8)	119.2(5)
C(11)—C(12)	1.362(7)	C(7)—C(8)—C(9)	120.1(5)
C(13)—C(14)	1.360(8)	C(10)—C(9)—C(8)	120.6(5)
C(13)—C(18)	1.365(7)	C(9)—C(10)—C(11)	118.1(4)
C(14)—C(15)	1.382(9)	C(9)—C(10)—S*	121.2(4)
C(15)—C(16)	1.364(9)	C(11)—C(10)—S*	120.6(4)
C(16)—C(17)	1.350(8)	C(12)—C(11)—C(10)	121.3(5)
C(17)—C(18)	1.364(7)	C(11)—C(12)—C(7)	120.7(5)
		C(14)—C(13)—C(18)	118.2(5)
		C(14)—C(13)—P	127.7(5)
		C(18)—C(13)—P	114.1(5)
		C(13)—C(14)—C(15)	121.2(6)
		C(16)—C(15)—C(14)	119.4(7)
		C(17)—C(16)—C(15)	119.4(6)
		C(16)—C(17)—C(18)	120.9(6)
		C(17)—C(18)—C(13)	120.7(6)

* The equivalent atoms are generated by the symmetry transformation $1 - x, 1 - y, 1 - z$.

***N,N,N',N'*-Tetraethyl-4,4'-thiodiphenylenebis(amidophenylphosphonite) (3).** A mixture of 4,4'-thiodiphenol **2** (2.18 g, 10 mmol) and tetraethyldiamide of phenylphosphonous acid **1** (5.05 g, 20 mmol) was heated at 120–125 °C for 2.5–3 h. The diethylamine that evolved in the course of the reaction was condensed in an ice-cooled receiver. Then the product was kept at the temperature mentioned for 1 h *in vacuo* (1 Torr). Viscous colorless compound **3** (see Table 1) was obtained.

2,18-Diphenyl-1,3,17,19-tetraoxa-10,26-dithia-2,18-diphospha[3,1,3,1]paracyclophane (4). A solution of bis(amidophenylphosphonite) **3** (1.06 g, 1.84 mmol) in *o*-xylene (5 mL) was added to a solution of 4,4'-thiodiphenol **2** (0.4 g,

Table 4. The principal crystallographic parameters of the structure of **4** and the results of the refinement

Parameter	X-ray structural data
Molecular formula	C ₃₆ H ₂₆ O ₄ P ₂ S ₂
Molecular weight	648.63
<i>a</i> /Å	10.660(2)
<i>b</i> /Å	8.2940(1)
<i>c</i> /Å	18.564(3)
β /deg	102.68(1)
<i>V</i> /Å ³	1601.3(4)
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>Z</i>	2
<i>d</i> _{calc} /g cm ⁻³	1.345
<i>F</i> (000)	672
θ /deg	2.03 < θ < 22.43
Indices <i>h, k, l</i>	0 < <i>h</i> < 10, 0 < <i>k</i> < 8, 0 < <i>l</i> < 19,
<i>N</i> *	1501
<i>N</i> '*	1422 [<i>R</i> _{int} = 0.0132]
<i>n</i> **	261
GOOF	1.116
<i>R</i> [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0411, <i>wR</i> ₂ = 0.0928

* *N* and *N'* are the numbers of measured and independent reflections, respectively; ** *n* is the number of parameters refined.

1.84 mmol) in anhydrous *o*-xylene (25 mL) (obtained by boiling the mixture under an atmosphere of inert gas) at 60–80 °C for 30 min. The mixture was boiled for 14–15 h, and then kept at –20 °C for 7 days. The crystals that formed were filtered off, washed with hexane, and dried. Macrocylic product **4** was obtained, m.p. 242–243 °C (see Table 1).

B. A mixture of 4,4'-thiodiphenol **2** (0.6 g, 2.75 mmol) and diamidophenylphosphonite **1** (0.7 g, 2.77 mmol) in *o*-xylene (20 mL) was boiled for 12 h under an atmosphere of inert gas and then kept at –20 °C for 7 days. The crystals that formed exhibit properties analogous to those of the product obtained by the two-step method **A**.

References

1. E. E. Nifant'ev, Yu. I. Blokhin, and M. Ya. Ergashev, *Dokl. Akad. Nauk*, 1992, 325 [*Dokl. Chem.*, 1992, 325 (Engl. Transl.)].
2. Yu. I. Blokhin, D. V. Gusev, V. K. Belsky, A. I. Stash, and E. E. Nifant'ev, *Phosphorus, Sulfur, Silicon, and Relat. Elem.*, 1995, 102, 143.

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