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Synthesis and Crystal and Molecular Structures of 2-Diethylaminomethyl- and 2-Chloromethyl-2,2'-spirobi[benzo-1,3,2-oxazaphospholines]

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Abstract — Chloromethylphosphonic dichloride reacts with *o*-aminophenol in the presence of triethylamine to form 2-chloromethyl-1,3,2-benzoxazaphospholine 2-oxide and 2-chloromethyl-2,2'-spirodi[1,3,2-benzoxazaphospholine] in a 1 : 1 ratio. 3-Diethylaminomethyl-2-ethoxy-1,3,2-benzoxazaphospholine reacts with o-aminophenol to form 2-diethylaminomethyl-2,2'-spirodi[benzo-1,3,2-oxazaphospholine]. The crystal and molecular structures of the synthesized spirophosphoranes were determined by single crystal X-ray diffraction.

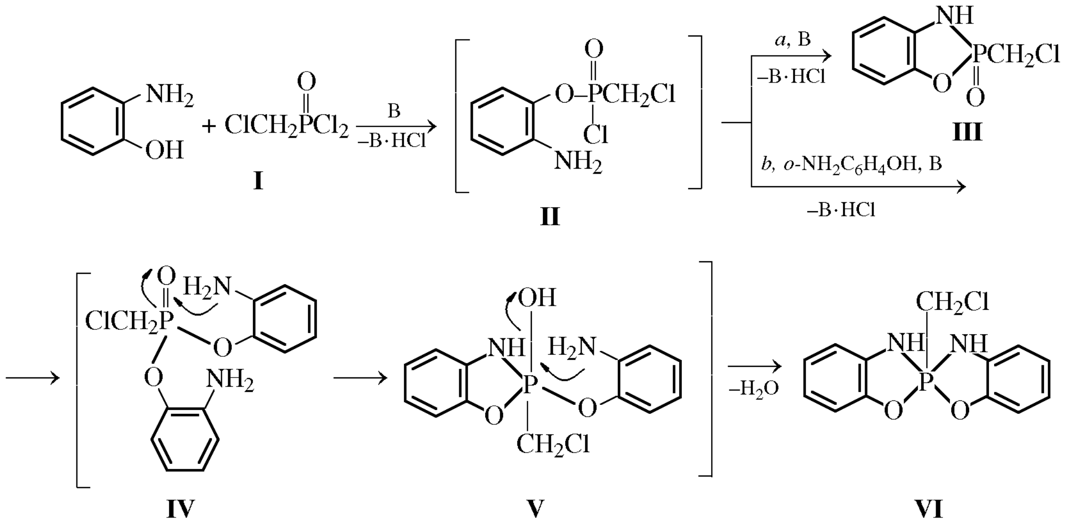
o-Aminophenol is phosphorylated with aryl (alkyl) phosphorodichloridothioates, aryl(alkyl-)phosphonothioic dichlorides, and aryl phosphorodichloridates at room temperature or on heating in the presence of a base to form the corresponding 2-substituted 1,3,2-benzoxazaphospholine 2-oxides or 2-sulfides [1–3]. Ethylphosphonic dichloride reacts with o-aminophenol in the presence of a base to give 2-ethyl-1,3,2-benzoxazaphospholine 2-oxide [4]. Recently we prepared various types of polyheterophosphacyclanes starting from polyfunctional chloromethyl derivatives of four-coordinate phosphorus [5–8].

Proceeding with these studies, with the aim to prepare 2-chloromethyl-1,3,2-benzoxazaphospholine 2-oxide **III** and its new cyclic derivatives, we performed a reaction of chloromethylphosphonic dichloride **I** with *o*-aminophenol in the presence of triethylamine. We found that the reaction of equimolar amounts of *o*-aminophenol and dichloride **I** at room temperature yields two products, oxazaphospholine **III** (δ_P 36 ppm) and spirophosphorane **VI** (δ_P –35 ppm) in a 1 : 1 ratio (from the ^{31}P NMR spectrum of the reaction mixture).

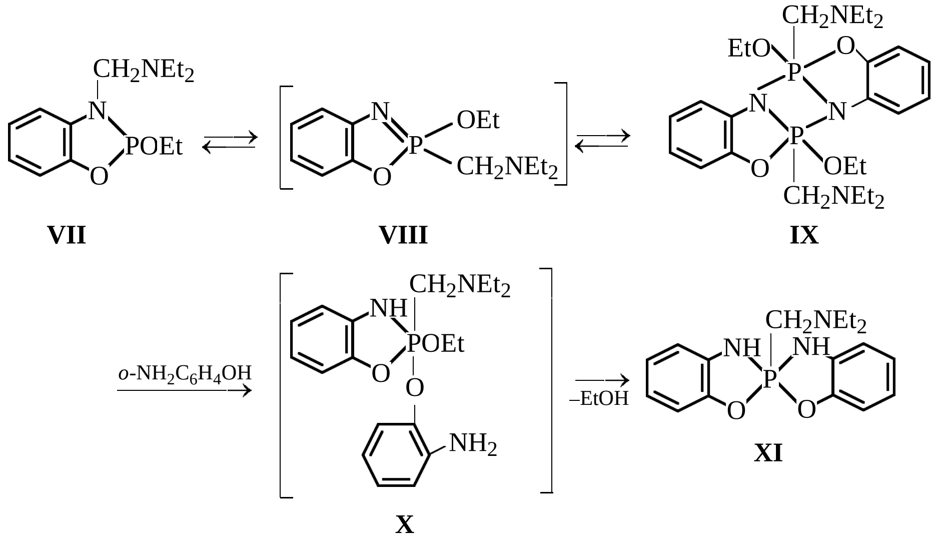
The IR spectrum of phospholine **III** contains strong absorption bands at 1230 (P=O) and 3260 cm^{-1} (NH). The secondary amino groups in spirophosphorane **VI** give a band at 3330 cm^{-1}. The ^{1}H NMR spectrum of **VI** contains two doublets from the methylene group (3.45 ppm, $^2J_{HP}$ 9 Hz) and spectroscopically equivalent secondary amino groups (4.33 ppm, $^2J_{HP}$ 18 Hz).

The presumable pathways of product formation are as follows. Phosphorylation of the hydroxy group of *o*-aminophenol with chloride I [9] initially yields *o*-aminophenyl chloromethylphosphonochloridate **II**, which undergoes intramolecular cyclization to give oxazaphospholine **III** (pathway *a*). Since dichloride **I** is highly reactive, another pathway is also realized. Phosphonochloridate **II** reacts with the second molecule of *o*-aminophenol to give bis(*o*-aminophenyl) chloromethylphosphonate IV, which undergoes cyclization involving the phosphoryl group with intermediate formation of unstable 2-chloromethyl-1,3,2-benzoxazaphospholine 2-hydroxyde 2-*o*-aminophenolate **V**. The intramolecular nucleophilic attack of the amino group at the electrophilic phosphorus atom results in formation of spirophosphorane **VI** with elimination of a water molecule (pathway *b*). Formation of spirophosphorane in reaction of phenyl phosphorodichloridate with *o*-aminophenol was described in [10]. However, in that work *o*-aminophenol and phosphorodichloridate were taken in a 2 : 1 ratio, and the reaction was performed under relatively rigorous conditions (refluxing in toluene for 4 h). Chekhlov *et al*. [11] studied spirophosphorane **VI** by single crystal X-ray diffraction, but they have not reported the synthesis procedure. We have performed the reaction of *o*-aminophenol with chloride **I** in benzene in a 2 : 1 ratio with heating and detected formation of **VI** by ^{31}P NMR spectroscopy; however, we failed to isolate this compound pure because of extensive tarring.

As phosphorylating agent for *o*-aminophenol, we also used 3-diethylaminomethyl-2-ethoxy-1,3,2-benz-



oxazaphospholine **VII**. Our previous studies showed that 2-alkoxy-1,3,2-benzoxazaphospholines are readily aminoalkylated with bis(dialkylamino)methanes at room temperature to form polycyclic phosphoranes, e.g., compound **IX** (δ_P –40 ppm). However, vacuum distillation of **IX** gave only oxazaphospholine **VII** (δ_P 130 ppm), which is probably due to decomposition of the phosphorane into cyclic phosphonimidate **VIII** followed by P→N 1,2-migration of the diethylaminomethyl group [12]. The reverse transformation of phospholine **VII** into phosphorane **IX** occurs in 30 days at 20°C. We found that reaction of both oxazaphospholine **VII** and phosphorane **IX** with *o*-aminophenol finally yields spirophosphorane **XI**.



Apparently, in this reaction the *o*-aminophenol molecule adds to phosphonimidate **VIII** to form phosphorane **X** which cyclizes with release of the ethanol molecule. The crystal and molecular structure of spirophosphoranes **VI** and **XI** was determined by single crystal X-ray diffraction.

It should be noted that the crystal structure of **VI** was studied previously in [11]. However, we obtained a more complete set of experimental data (the larger number of reflections were measured) than in [11] and, despite somewhat greater divergence factors, determined the geometric parameters more accurately.

Table 1. Atomic coordinates in the structure of **VI**; equivalent isotropic thermal parameters for nonhydrogen atoms $B = 4/3\sum_{i=1}^{3}\sum_{j=1}^{3}(a_i a_j)B(i, j)$ (Å^2) and isotropic thermal parameters of H atoms (Å^2)

Atom	*x*	*y*	*z*	*B*
Cl^{1}	0.9482(1)	0.1462(1)	0.2432(1)	11.16(6)
Cl^{2}	0.9387(3)	0.1727(3)	0.1722(4)	16.9(2)
P^{5}	0.83023(5)	0.03922(6)	0.18028(4)	3.95(2)
O^{1}	0.8090(1)	0.0680(1)	0.0945(1)	4.59(5)
O^{6}	0.8444(1)	0.0078(1)	0.2658(1)	4.45(5)
N^{4}	0.7587(2)	0.0946(2)	0.2076(1)	4.99(7)
N^{9}	0.8272(2)	–0.0523(2)	0.1557(1)	4.49(7)
C^{2}	0.7482(2)	0.1185(2)	0.0908(2)	4.25(8)
C^{3}	0.7170(2)	0.1349(2)	0.1559(2)	4.54(8)
C^{7}	0.8469(2)	–0.0716(2)	0.2719(2)	4.04(7)
C^{8}	0.8369(2)	–0.1084(2)	0.2078(2)	4.03(7)
C^{10}	0.7178(2)	0.1514(2)	0.0304(2)	5.52(9)
C^{11}	0.6561(3)	0.2023(2)	0.0390(2)	6.7(1)
C^{12}	0.6254(3)	0.2185(3)	0.1034(2)	7.1(1)
C^{13}	0.6552(2)	0.1846(2)	0.1634(2)	6.1(1)
C^{14}	0.8581(2)	–0.1129(2)	0.3325(2)	5.20(9)
C^{15}	0.8603(3)	–0.1920(2)	0.3279(2)	6.5(1)
C^{16}	0.8500(3)	–0.2291(2)	0.2646(2)	6.5(1)
C^{17}	0.8383(2)	–0.1876(2)	0.2033(2)	5.37(9)
C^{18}	0.9258(2)	0.0836(2)	0.1758(2)	5.7(1)
H^{4}	0.742(2)	0.095(2)	0.245(2)	6.1(8)
H^{9}	0.819(1)	–0.061(1)	0.119(1)	2.7(6)
H^{10}	0.744(2)	0.143(2)	–0.009(2)	6.6(8)
H^{11}	0.643(2)	0.224(2)	0.000(1)	7.0(8)
H^{12}	0.587(2)	0.247(2)	0.109(2)	9(1)
H^{13}	0.634(2)	0.190(2)	0.205(1)	6.3(8)
H^{14}	0.866(2)	–0.085(2)	0.376(2)	6.5(8)
H^{15}	0.875(2)	–0.220(2)	0.365(2)	8.0(9)
H^{16}	0.854(2)	–0.278(2)	0.261(1)	6.1(8)
H^{17}	0.831(1)	–0.211(1)	0.162(1)	3.9(6)
H^{181}	0.9643	0.0452	0.1938	4
H^{182}	0.9209	0.0687	0.1265	7

On the whole, the geometric parameters of **VI** determined in this work and in [11] coincide within experimental error. Therefore we use our data (Tables 1–3) for **VI** when comparing the geometric parameters.

The computer search using the Cambridge Crystallographic Database [13] showed that the structures of only three 2-R-2λ^5-2,2'(3*H*,3'*H*)-spirobi[benz*o*-1,3,2-oxazaphospholines] have been determined: with R = H (**XII**) [14], CH_2Cl (**VI**) [11], and OPh (**XIII**) [15].

The phosphorus atom in all the studied structures has a trigonal bipyramidal coordination with axial

Table 2. Atomic coordinates in the structure of **XI**; equivalent isotropic thermal parameters for nonhydrogen atoms $B = 4/3\sum_{i=1}^{3}\sum_{j=1}^{3}(a_i a_j)B(i, j)$ (Å^2) and isotropic thermal parameters of H atoms (Å^2)

Atom	*x*	*y*	*z*	*B*
P^{5}	0.1089(1)	0.3634(1)	0.5203(1)	5.95(3)
O^{1}	0.0018(3)	0.3623(3)	0.4719(2)	6.64(9)
æ^{6}	0.2109(2)	0.3572(3)	0.5770(3)	6.1(1)
N^{4}	0.1065(3)	0.2451(3)	0.5184(3)	6.4(1)
N^{9}	0.0647(3)	0.4370(3)	0.5837(3)	5.6(1)
N^{19}	0.1501(3)	0.4874(3)	0.3993(3)	5.0(1)
C^{2}	–0.0251(4)	0.2749(5)	0.4474(4)	6.5(2)
C^{3}	0.0367(4)	0.2062(4)	0.4729(4)	6.3(2)
C^{7}	0.2051(4)	0.4138(3)	0.6428(4)	5.5(1)
C^{8}	0.1211(4)	0.4622(3)	0.6470(4)	5.3(1)
C^{10}	–0.1017(4)	0.2529(5)	0.4022(4)	7.9(2)
C^{11}	–0.1181(5)	0.1586(5)	0.3831(5)	9.1(2)
C^{12}	–0.0559(5)	0.0926(6)	0.4073(5)	9.3(2)
C^{13}	0.0202(5)	0.1123(5)	0.4538(5)	8.7(2)
C^{14}	0.2750(4)	0.4233(4)	0.7006(4)	6.7(2)
C^{15}	0.2552(4)	0.4801(4)	0.7618(5)	7.2(2)
C^{16}	0.1734(5)	0.5303(5)	0.7659(5)	8.3(2)
C^{17}	0.1044(4)	0.5201(4)	0.7074(5)	7.1(2)
C^{18}	0.1697(5)	0.4033(6)	0.4324(5)	15.9(2)
C^{20}	0.1631(6)	0.4836(9)	0.3192(6)	13.8(3)
C^{21}	0.2544(7)	0.466(1)	0.2800(7)	14.6(4)
C^{22}	0.2106(7)	0.5503(7)	0.4456(6)	11.7(3)
C^{23}	0.2095(8)	0.6465(8)	0.4200(8)	17.5(4)
H^{4}	0.1636	0.2033	0.5499	6
H^{9}	0.0159	0.4747	0.5658	6
H^{10}	–0.1455	0.3030	0.3860	9
H^{11}	–0.1751	0.1428	0.3529	12
H^{12}	–0.0686	0.0213	0.3948	12
H^{13}	0.0623	0.0622	0.4743	10
H^{14}	0.3340	0.3912	0.6935	7
H^{15}	0.3014	0.4838	0.8030	10
H^{16}	0.1639	0.5742	0.8096	11
H^{17}	0.0444	0.5538	0.7093	9
H^{181}	0.1515	0.3526	0.3914	17
H^{182}	0.2343	0.3938	0.4401	17
H^{201}	0.1495	0.5506	0.2997	17
H^{202}	0.1162	0.4464	0.2960	17
H^{211}	0.2512	0.4646	0.2256	18
H^{212}	0.3044	0.5026	0.2986	18
H^{213}	0.2730	0.3978	0.2954	18
H^{221}	0.2733	0.5238	0.4476	22
H^{222}	0.1873	0.5453	0.5009	22
H^{231}	0.2510	0.6846	0.4499	20
H^{232}	0.2296	0.6523	0.3648	20
H^{233}	0.1474	0.6732	0.4222	20

Table 3. Selected bond lengths (*d*, Å) and bond angles (ω, deg) in molecules of **VI** and **XI**

Bond	*d*		Bond	*d*	
	VI	**XI**		**VI**	**XI**
$\mathrm{P^5{-}O^1}$	1.740(2)	1.728(4)	$\mathrm{O^1{-}C^2}$	1.361(4)	1.362(7)
$\mathrm{P^5{-}O^6}$	1.727(2)	1.740(4)	$\mathrm{O^6{-}C^7}$	1.371(4)	1.381(7)
$\mathrm{P^5{-}N^4}$	1.639(3)	1.676(5)	$\mathrm{N^4{-}C^3}$	1.398(4)	1.371(8)
$\mathrm{P^5{-}N^9}$	1.642(3)	1.628(5)	$\mathrm{N^9{-}C^8}$	1.392(4)	1.389(8)
$\mathrm{P^5{-}C^{18}}$	1.814(4)	1.818(9)	$\mathrm{C^2{-}C^3}$	1.375(5)	1.380(9)
			$\mathrm{C^7{-}C^8}$	1.380(4)	1.375(7)
Angle	ω		Angle	ω	
$\mathrm{O^1P^5O^6}$	175.7(1)	173.8(2)	$\mathrm{P^5N^9C^8}$	117.3(2)	117.2(3)
$\mathrm{O^1P^5N^4}$	88.4(1)	87.9(2)	$\mathrm{P^5N^9H^9}$	119(2)	116.1(4)
$\mathrm{O^1P^5N^9}$	90.0(1)	89.1(2)	$\mathrm{C^8N^9H^9}$	124(2)	122.5(4)
$\mathrm{O^1P^5C^{18}}$	91.5(1)	91.5(3)	$\mathrm{O^1C^2C^3}$	112.7(3)	111.5(5)
$\mathrm{O^6P^5N^4}$	89.5(1)	88.8(2)	$\mathrm{O^1C^2C^{10}}$	126.5(3)	127.1(6)
$\mathrm{O^6P^5N^9}$	88.4(1)	89.1(2)	$\mathrm{C^3C^2C^{10}}$	120.8(3)	121.4(6)
$\mathrm{O^6P^5C^{18}}$	92.8(1)	94.6(3)	$\mathrm{N^4C^3C^2}$	109.0(3)	110.6(5)
$\mathrm{N^4P^5N^9}$	128.5(2)	130.2(3)	$\mathrm{N^4}$Cé$\mathrm{C^{13}}$	129.4(3)	129.8(6)
$\mathrm{N^4P^5C^{18}}$	116.8(2)	107.8(3)	$\mathrm{C^2C^3C^{13}}$	121.6(3)	119.6(6)
$\mathrm{N^9P^5C^{18}}$	114.7(2)	122.0(3)	$\mathrm{O^6C^7C^8}$	112.3(3)	112.5(5)
$\mathrm{P^5O^1C^2}$	112.9(2)	113.6(3)	$\mathrm{O^6C^7C^{14}}$	126.4(3)	125.7(5)
$\mathrm{P^5O^6C^7}$	113.2(2)	111.8(3)	$\mathrm{C^8C^7C^{14}}$	121.4(3)	121.7(5)
$\mathrm{P^5N^4C^3}$	116.9(2)	115.4(4)	$\mathrm{N^9C^8C^7}$	108.8(3)	109.3(5)
$\mathrm{P^5N^4H^4}$	126(2)	119.7(4)	$\mathrm{N^9C^8C^{17}}$	130.5(3)	130.7(5)
$\mathrm{C^3N^4H^4}$	117(2)	124.8(4)	$\mathrm{C^7C^8C^{17}}$	120.7(3)	120.0(6)

endocyclic P–O bonds. The OPO bond angles in **VI** and **XI** are 175.7(1)° and 173.8(2)°, respectively; the sum of the bond angles in the equatorial plane is 360° in **VI** and 359.92(8)° in **XI**. It should be noted that the distortion of the trigonal-bipyramidal coordination of the phosphorus atom in **XI** toward the square-pyramidal structure, evaluated by the formula in [15] (25.9%), is appreciably larger than in **VI** (21.6%) but smaller than in **XIII** (27.8%). This is consistent with the assumption [15] that distortions of the coordination in these molecules increase with increasing volume and electronegativity of substituents at the phosphorus atom.

The length of the respective bonds in **VI** and **IX** coincide within experimental error and agree with those found in **XII** and **XIII**, except that the axial P–O bonds in **XIII** are appreciably shorter than in the other three molecules. The five-membered heterocycles in **VI** are planar within 0.004(3) Å and together with the annelated benzene rings form planar nonaatomic fragments. The dihedral angles between these fragments are 51.1(1)°. In the molecule of **XI** one five-membered heterocycle $\mathrm{P^5O^6C^7C^8N^9}$ is planar within 0.014(6) Å, and the other, $\mathrm{P^5O^1C^2C^3N^4}$, has the flattened envelope conformation with deviation of $\mathrm{P^5}$ from the plane of the other four atoms by 0.173(2) Å (Fig. 1). In molecules of **XII** and **XIII** both heterocycles have the P-envelope conformation. Probably, the conformation of the heterocycles in **XI** is determined by the asymmetrical environment of the molecule in the crystal.

In the crystal of **VI**, the molecules are linked by N–H···O hydrogen bonds in infinite helices around the 4_1 screw axis; the system of hydrogen bonds in this crystal is described in detail in [11]. The hydrogen bonds in **VI** are equivalent. At the same time, in the crystal of **XI** another type of hydrogen bonds is realized, $\mathrm{N^4{-}H^4{\cdots}O^{6'}}$ (1/2 – –, 1/2 – *y*, *z*), $\mathrm{N^4{-}H^4}$ 1.14, $\mathrm{H^4{\cdots}O^{6'}}$ 2.02, $\mathrm{N^4{\cdots}O^{6'}}$ 3.121(5) Å, $\angle\mathrm{N^4H^4O^{6'}}$ 162°; bifurcate hydrogen bonds $\mathrm{N^9{-}H^9{\cdots}O^{1''}}$ (–*X*, –*y*, –*z*), $\mathrm{N^4{-}H^4}$ 0.93, $\mathrm{H^4{\cdots}O^{1''}}$ 2.41, $\mathrm{N^4{\cdots}O^{1''}}$ 3.145(6) Å, $\angle\mathrm{N^9H^9O^{1''}}$ 136°; $\mathrm{N^9H^9N^{19''}}$, $\mathrm{H^9{\cdots}N^{19''}}$ 2.49, $\mathrm{N^9{\cdots}N^{1''}}$ 3.244(6) Å, $\angle\mathrm{N^9H^9N^{19''}}$ 139° (Fig. 2).

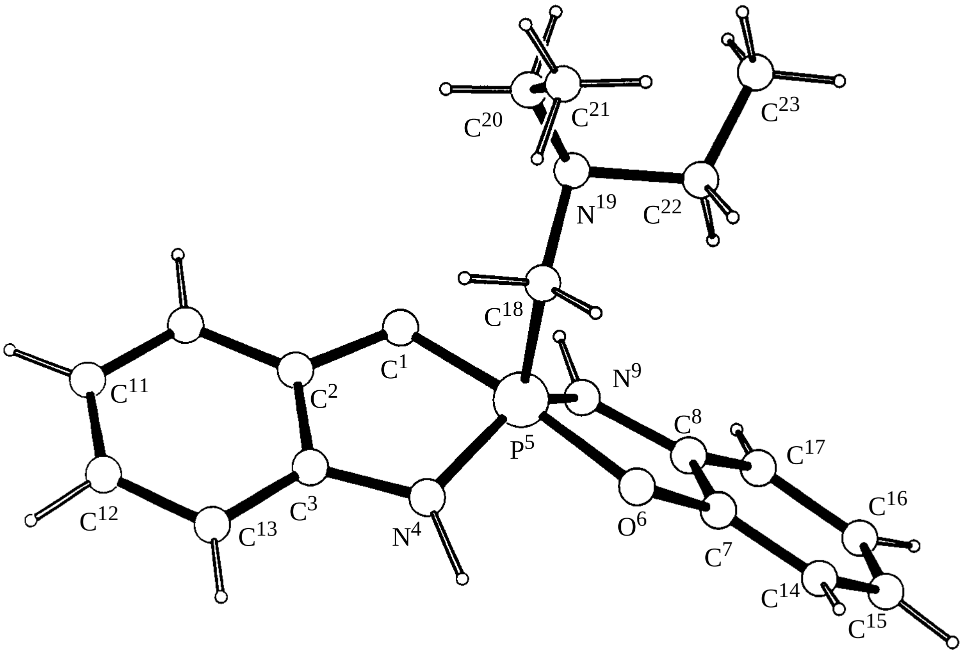


Fig. 1. Steric structure of the molecule of 2-diethylaminomethyl-2,2'-spirobi[benzo-1,3,2-oxazaphospholine] **XI**.

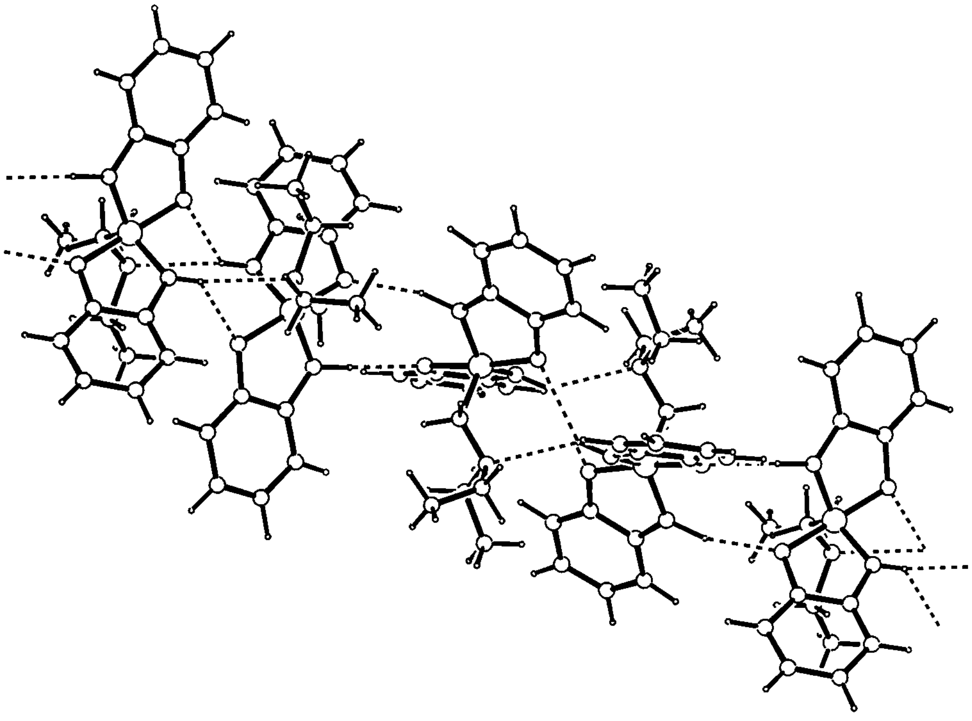


Fig. 2. Fragment of molecular packing in the crystal of 2-diethylaminomethyl-2,2'-spirobi[benzo-1,3,2-oxazaphospholine] **XI**.

The substituents at phosphorus in **VI** and **XI** and the annelated benzene ring have the usual geometry.

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrometer in the range 400–3600 cm^{-1} from mulls in mineral oil. The ^{1}H NMR spectra were taken on a Varian T-60 spectrometer (internal reference TMS), and the ^{31}P NMR spectra, on a KGU-4 NMR spectrometer (10.2 MHz, external reference 85% H_3PO_4).

Single crystal X-ray diffraction study. Compounds **VI** and **XI** crystallize in the tetragonal system; the unit cell parameters and reflection intensities were measured with Enraf-Nonius CAD-4 automated four-circle diffractometers at 20°C. The unit cell parameters of VI are as follows: a 17.199(7), c 18.960(5) Å; V 5608(2) Å^3, Z 16, d_{calc} 1.4 g cm^{-3}, space group $I4_1/a$, and those of XI, a 14.172(3), c 17.046(4) Å; V 3424(2) Å^3, Z 4, space group $P4_2/n$. The unit cell parameters of VI and the intensities of 2984 reflections, 1585 of which had $I \geq 3\sigma$, were measured with MoK_α radiation (λMoK_α 0.71073 Å, graphite monochromator, $\omega/2\theta$ scanning, $\theta \leq 26.3°$). The unit cell parameters of **XI** and the intensities of 3905 reflections, 2033 of which had $I \geq 3\sigma$, were measured with CuK_α radiation (λCuK_α 1.54184 Å, graphite monochromator, $\omega/2\theta$ scanning, $2\theta \leq 76.3°$). In the course of the experiment the intensities of check reflections did not decrease. The absorption was neglected for **VI** (μMo 3.81 cm^{-1}) and was taken into account empirically for **XI** (μCu 26.82 cm^{-1}). The structures were solved by the direct method using the SIR program [16] and refined first in the isotropic and then in the anisotropic approximation. In the structure of **VI** the chlorine atom of the chloromethyl group is disordered over two positions with the occupancies of 0.7 and 0.3. All hydrogen atoms were revealed from the differential electron density series. In the structure of **XI** all hydrogen atoms, except those of the disordered chloromethyl group, were refined in the isotropic approximation; their contribution to structural amplitudes in **XI** was taken into account with fixed positional and isotropic thermal parameters. The final divergence factors were as follows: for **VI**, R 0.047, R_W 0.060 from 1582 unique reflections with $F^2 \geq 3\sigma$; for XI, R 0.078, R_W 0.071 from 1318 unique reflections with $F^2 \geq 3\sigma$. All calculations were performed with a DEC Alpha Station-200 computer using MolEN program package [17].

The atomic coordinates are listed in Tables 1 and 2; the molecular geometry and the system of H bonds in the crystal of **XI** are shown in Figs. 1 and 2, respectively. The main geometric parameters of the molecules are shown in Table 3. The molecules and systems of hydrogen bonds in the crystals were drawn and the intermolecular interactions were analyzed using the PLATON 98 program [18].

2-Chloromethyl-2,2'-spirobi[benzo-1,3,2-oxazaphospholine] VI. To a solution of 2.18 g of *o*-aminophenol and 5 g of triethylamine in 50 ml of benzene, we added with stirring 3.35 g of chloride **I**. The mixture was allowed to stand for 12 h at 20°C. After removal of the solvent, 0.25 g (6%) of phospholine **III** was separated, mp 128–130°C. Found, %: C 40.69; H 3.01; N 6.53. $C_7H_7ClNO_2P$. Calculated, %: C 41.27; H 3.43; N 6.87.

By chromatography of the remaining black mixture on alumina (eluent chloroform) we isolated 0.7 g (24%) of crystalline product **VI**, mp 155°C (from hexane). Found, %: P 10.66. $C_{13}H_{12}ClN_2O_2P$. Calculated, %: P 10.52.

2-Diethylaminomethyl-2,2'-spirobi[benzo-1,3,2-oxazaphospholine] XI. *a*. A solution of 2.68 g of phospholine **VII** and 1.09 g of *o*-aminophenol in 30 ml of anhydrous diethyl ether was refluxed for 3 h. After cooling, 1.09 g (33%) of **XI** was filtered off; mp 157–159°C. ^{31}P NMR spectrum: δ_P –26 ppm [14]. Found, %: P 9.41. $C_{14Æ22}N_3O_2P$. Calculated, %: P 9.39.

b. A mixture of 2.68 g of **IX** and 1.09 g of *o*-aminophenol in 30 ml of chloroform was refluxed for 3 h. From the reaction mixture 0.63 g (19%) of spirophosphorane **XI** was isolated; mp 157–159°C. ^{31}P NMR spectrum: δ_P –26 ppm.

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