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Higher 1,3,2-Diazaphosphacyclanes: V.[1] Synthesis, Structure, and Chemical Features of 4,5;7,8-Dibenzo-1,3,2-diazaphosphocanes

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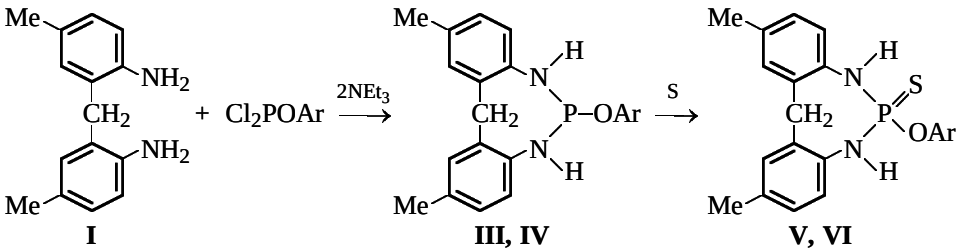
Abstract—A procedure was developed for preparing 4,5;7,8-dibenzo-1,3,2-diazaphosphocanes containing trivalent and pentavalent phosphorus atoms. The structure of the compounds was determined by NMR spectroscopy and single crystal X-ray diffraction. The conformational transitions of the diazaphosphocanes in solution were analyzed. First data were obtained on transformations of the obtained eight-membered heterocycles.

1,3,2-Diazaphosphacyclanes with five- [2], six- [3–5], and seven-membered [1] rings have been subject to comprehensive synthetic and structural studies, as well as to applied research [6]. At the same time, much less attention was given to the corresponding eight-membered cyclic systems. Data are available [7–10] only on the reaction of *N*,*N*-dimethyl-*p*-toluidine with phosphorus oxychloride and thiochloride, affording 4,5;7,8-dibenzo-1,3,2-diazaphosphocanes in moderate yields. These compounds contain in their structure the phosphoryl and thiophosphoryl groups. The reaction in question is unusual. Shaw *et al.* [7–10] discussed its mechanism and elucidated the chemical and steric structure of the obtained compounds by X-ray diffraction and independent synthesis.

The aim of this work is to develop of a general route to 1,3,2-diazaphosphocanes containing trivalent phosphorus atoms. If necessary, these compounds can be converted by oxidative methods to various pentavalent phosphorus derivatives.

2,2'-Methylenebis-*p*-toluidine **I** and *N*,*N*'-diisopropyl-2,2'-methylenebis-*p*-toluidine **II** were chosen as starting compounds. First we studied the reaction of diamine **I** with phenyl- and *p*-cresyl phosphorodichloridites in the presence of triethylamine.



Ar = Ph (**III, V**), $C_6H_4CH_3$ (**IV, VI**).

The reaction proceeds easily. The ^{31}P NMR spectrum of the reaction mixture contains only one singlet with δ_P 107.61 or 107.88 ppm, belonging to phosphorodiamidites **III** and **IV**, respectively. Unfortunately, we failed to isolate these compounds pure. They polymerize during vacuum distillation and are hydrolyzed during chromatographic purification. Therefore, for determining the structure, these compounds were isolated and characterized as the corresponding thiophosphates **V** and **VI**.

[1] For communication IV, see [1].

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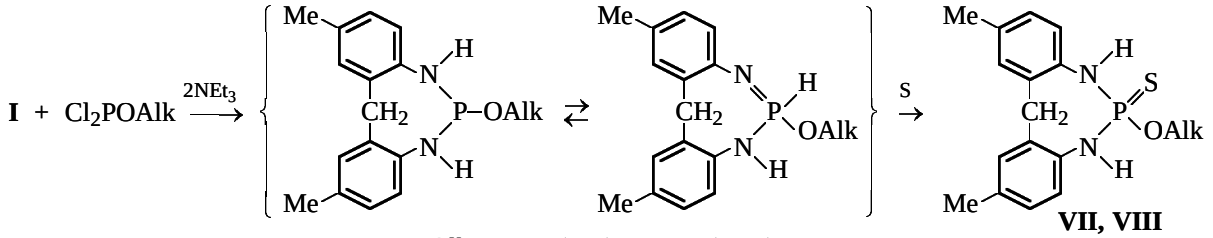
The reaction of diamine **I** with aliphatic acid chlorides is more complex. The ^{31}P NMR spectrum of the reaction products contains two signals with δ_P 113 and 6 ppm. In the spectrum recorded without proton decoupling, the latter signal is a doublet with J_{PH} 614 Hz. Such a spectrum suggests the presence of two tautomers: phosphite and iminohydrophosphoryl species.

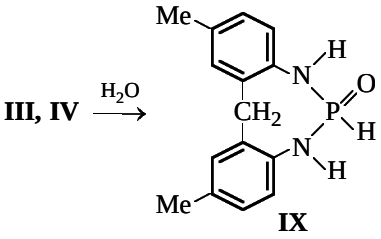


Alk = Et (**VII**), *n*-Bu (**VIII**).

Treatment of the reaction mixture with sulfur yields thiophosphates **VII** and **VIII**, with disappearance of the signals with δ_P 113 and 6 ppm. This fact confirms our suggestion about the prototropism of the primary phosphorylation products.

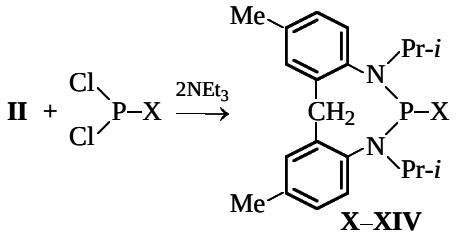
The different results of cyclophosphorylation with aliphatic and aromatic phosphorochloridites are evidently due to different electron-accepting powers of alkoxy and aroxy groups.

The electron-accepting power of aroxy groups in phosphocanes **III** and **IV** is manifested in the extremely easy hydrolysis of these compounds, yielding hydrophosphoryl compounds **IX**.



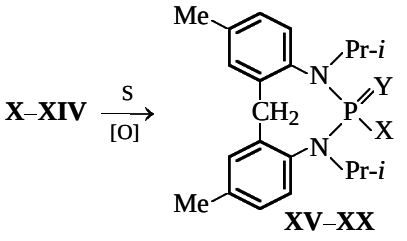
Note that the hydrolytic cleavage of the phosphite bond with the preservation of the phosphoroamidite group under the same conditions is an unusual fact.

Further experiments on synthesis of 1,3,2-diazaphosphocanes were performed with *N*,*N*'-diisopropyl-2,2'-methylenebis-*p*-toluidine **II**. It was shown that diamine **II** is readily phosphorylated with phosphorus trichloride, alkyl and aryl phosphorodichloridites, and diethylphosphorodichloridous amide.



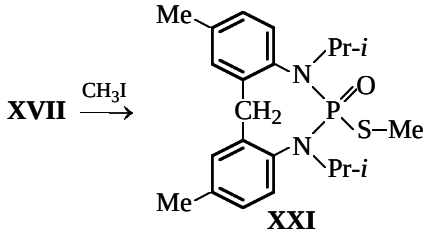
X = Cl (**X**), OMe (**XI**), OEt (**XII**), OPh (**XIII**), NEt_2 (**XIV**).

In the spectra of the reaction mixtures we detected the signals related to the target products. Because of their lability, we failed to isolate these compounds pure, but crude products can be used in synthetic practice without special purification. For example, we showed that 1,3-diisopropyl-1,3,2-diazaphosphocanes easily take up sulfur and oxygen with the formation of stable compounds.

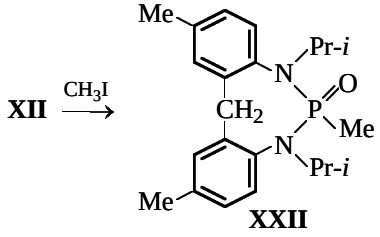


Y = S, X = Cl (**XV**), OMe (**XVI**), OEt (**XVII**), OPh (**XVIII**), NEt_2 (**XIX**); Y = O, X = OEt (**XX**).

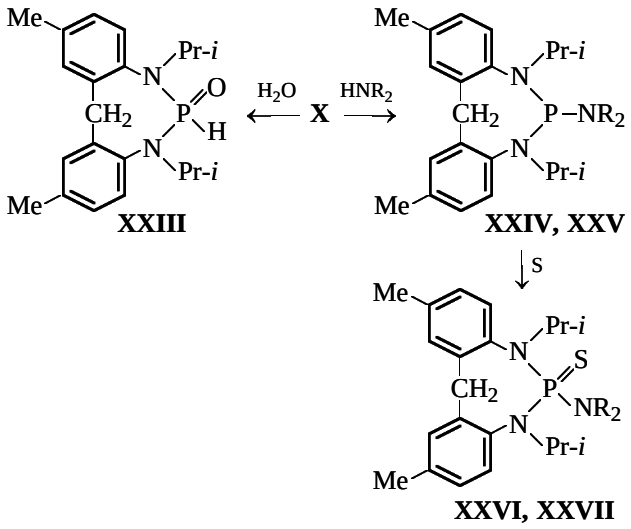
O-Ethyl phosphoramidothioate **XVII**, when treated with excess methyl iodide, is converted to *S*-methyl phosphoramidothioate **XXI**.



Diamido ester **XII** was subjected to alkylation with excess methyl iodide (Arbuzov reaction).



Phosphorochloridite **X** was studied in nucleophilic substitutions of chlorine.



R = Me (**XXIV, XXVI**), R_2 = CH_2–CH_2 (**XXV, XXVII**).

The obtained derivatives of three-coordinate phosphorus **XXIV** and **XXV** were stabilized as thiophosphoryl compounds **XXVI** and **XXVII**.

Thus, using a procedure based on cyclophosphorylation of diamines **I** and **II**, we obtained a series of 1,3,2-diazaphosphocanes with phosphorus-containing functional groups. All the obtained P(V) derivatives of 4,5;7,8-dibenzo-1,3,2-diazaphosphocanes are crystalline compounds, which were purified either by crystallization from appropriate solvents or by column chromatography on silica gel. The composition, structure, and purity of the compounds obtained were confirmed by elemental analysis, TLC, ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, and mass spectrometry. Thiophosphates **VI**, **XVIII**, and **XXVI** were also studied by single crystal X-ray diffraction.

Major attention was given to determining the steric structure of the products in the crystalline state and in solutions. The H–N–P and *i*-Pr–N–P systems strongly differ in their structural features, and it is appropriate to consider them separately.

The ^{1}H NMR spectrum of 1,3-dihydro-1,3,2-diazaphosphocanes at room temperature is presented by one set of signals of all groups of protons, characterizing a certain averaged configuration. The integral intensities of the signals are consistent with this assignment. In the cyclic system, the signals of the methylene protons in the 6-position of the heteroring become magnetically nonequivalent; the difference Δδ in the chemical shifts of these two protons allows certain conclusions about the presence or absence of one or another conformer or the conformational balance. The value Δδ 0.21 ppm for 2-(4-methylphenoxy)-1,3-dihydro-4,5;7,8-dibenzo-11,11'-dimethyl-1,3,2-diazaphosphocane 2-sulfides **VI** shows that the protons of the methylene ring do not preferably occupy the axial or equatorial position. It is important that the downfield signal has the coupling constant $^5J_{PH}$ 2.1 Hz. This fact suggests that in solution 1,3-dihydro-1,3,2-diazaphosphocane 2-sulfides **V** and **VI** behave as a two-component system containing the axial and equatorial *boat–chair* forms (*a-BC* ⇄ *e-BC*). According to [11], such a form is characterized by the low Δδ value (0.2–0.5 ppm) and $^5J_{HP}$ ~2 Hz. To determine the steric structure of such compounds in more detail, we performed single crystal X-ray diffraction study of 1,3,2-diazaphosphocane **VI**. The general view of the molecule of **VI** is shown in Fig. 1. The atomic coordinates, interatomic distances, and bond angles are given in Tables 1–3. The eight-membered heteroring has the *distorted boat–chair* conformation (Fig. 2).

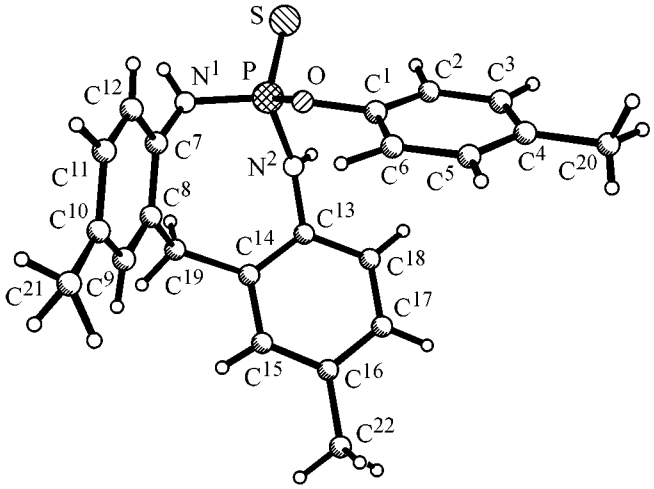


Fig. 1. General view of the molecule of **VI**.

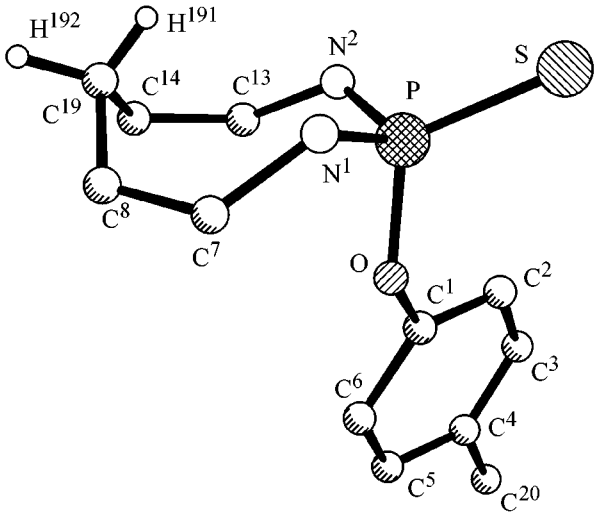


Fig. 2. Conformation of the heteroring in the molecule of **VI**.

Table 1. Atomic coordinates ($\times 10^4$) and their equivalent isotropic temperature factors ($Å^2 \times 10^3$) of **VI**

Atom	*x*	*y*	*z*	U_{eq}	Atom	*x*	*y*	*z*	U_{eq}
P	1510(1)	3367(1)	2460(1)	54(1)	C^{10}	3102(6)	5638(3)	–544(5)	78(2)
S	1005(1)	2310(1)	2582(2)	73(1)	C^{11}	3370(6)	4892(4)	–926(7)	84(2)
O	2812(2)	3551(2)	2635(3)	57(1)	C^{12}	2765(5)	4272(4)	–486(6)	76(2)
N^1	1317(4)	3712(2)	927(5)	63(1)	C^{13}	1220(3)	4665(2)	4077(5)	53(1)
N^2	928(3)	3901(2)	3609(5)	60(1)	C^{14}	1079(3)	5304(3)	3240(5)	56(1)
C^1	3464(3)	3514(2)	3827(5)	50(1)	C^{15}	1317(4)	6027(3)	3775(6)	58(1)
C^2	3281(5)	3032(3)	4897(6)	76(2)	C^{16}	1678(4)	6137(3)	5098(6)	67(1)
C^3	4016(5)	3025(4)	6003(7)	84(2)	C^{17}	1813(4)	5492(3)	5933(6)	70(1)
C^4	4925(4)	3481(3)	6080(6)	71(1)	C^{18}	1601(4)	4755(3)	5419(6)	63(1)
C^5	5093(5)	3974(4)	5001(7)	84(2)	C^{19}	659(4)	5233(3)	1771(6)	64(1)
C^6	4362(4)	4004(3)	3871(6)	71(1)	C^{20}	5723(7)	3462(8)	7293(9)	105(3)
C^7	1908(4)	4368(3)	405(5)	59(1)	C^{21}	3796(10)	6314(5)	–991(10)	113(3)
C^8	1590(4)	5103(3)	799(5)	58(1)	C^{22}	1908(8)	6933(4)	5651(10)	99(2)
C^9	2217(5)	5718(3)	323(6)	70(2)					

Table 2. Selected interatomic distances (*d*, Å) in the molecule of **VI**

Bond	*d*	Bond	*d*	Bond	*d*	Bond	*d*	Bond	*d*
P–O	1.601(3)	N^2–C^{13}	1.440(6)	C^4–C^{20}	1.503(9)	C^9–C^{10}	1.385(8)	C^{14}–C^{15}	1.385(7)
P–N^1	1.623(5)	C^1–C^2	1.360(7)	C^5–C^6	1.392(8)	C^{10}–C^{11}	1.385(8)	C^{14}–C^{19}	1.513(7)
P–N^2	1.628(4)	C^1–C^6	1.373(7)	C^7–C^{12}	1.377(8)	C^{10}–C^{21}	1.510(9)	C^{15}–C^{16}	1.365(7)
P–S	1.9349(16)	C^2–C^3	1.377(8)	C^7–C^8	1.388(6)	C^{11}–C^{12}	1.373(9)	C^{16}–C^{17}	1.391(8)
O–C^1	1.387(5)	C^3–C^4	1.349(8)	C^8–C^9	1.392(7)	C^{13}–C^{14}	1.385(7)	C^{16}–C^{22}	1.505(8)
N^1–C^7	1.441(6)	C^4–C^5	1.376(9)	C^8–C^{19}	1.504(7)	C^{13}–C^{18}	1.387(7)	C^{17}–C^{18}	1.394(7)

Table 3. Selected bond angles (ω, deg) in the molecule of **VI**

Angle	ω	Angle	ω	Angle	ω	Angle	ω	Angle	ω
OPN^1	98.0(2)	$C^2C^1C^6$	119.9(5)	$C^1C^6C^5$	118.6(5)	$C^9C^{10}C^{21}$	122.6(6)	$C^{13}C^{14}C^{19}$	121.7(4)
OPN^2	104.46(19)	C^2C^1O	125.0(4)	$C^{12}C^7C^8$	120.2(5)	$C^{11}C^{10}C^{21}$	120.8(7)	$C^{16}C^{15}C^{14}$	122.7(5)
N^1PN^2	111.9(2)	C^6C^1O	115.0(4)	$C^{12}C^7N^1$	120.8(4)	$C^{12}C^{11}C^{10}$	121.2(6)	$C^{15}C^{16}C^{17}$	118.2(5)
OPS	119.27(14)	$C^1C^2C^3$	119.7(5)	$C^8C^7N^1$	119.0(5)	$C^{11}C^{12}C^7$	121.0(6)	$C^{15}C^{16}C^{22}$	121.2(6)
N^1PS	111.67(16)	$C^4C^3C^2$	122.6(6)	$C^7C^8C^9$	117.0(5)	$C^{14}C^{13}C^{18}$	120.0(4)	$C^{17}C^{16}C^{22}$	120.6(6)
N^2PS	110.81(17)	$C^3C^4C^5$	117.1(5)	$C^7C^8C^{19}$	121.8(5)	$C^{14}C^{13}N^2$	121.6(4)	$C^{16}C^{17}C^{18}$	120.6(6)
C^1OP	127.5(3)	$C^3C^4C^{20}$	121.9(7)	$C^9C^8C^{19}$	121.0(5)	$C^{18}C^{13}N^2$	118.4(4)	$C^{13}C^{18}C^{17}$	119.7(5)
C^7N^1P	123.9(3)	$C^5C^4C^{20}$	120.9(7)	$C^{10}C^9C^8$	124.0(5)	$C^{15}C^{14}C^{13}$	118.7(5)	$C^8C^{19}C^{14}$	112.1(4)
$C^{13}N^2P$	129.5(3)	$C^4C^5C^6$	121.9(6)	$C^9C^{10}C^{11}$	116.5(5)	$C^{15}C^{14}C^{19}$	119.5(5)		

The atomic fragments $N^1N^2C^7C^8C^{13}C^{14}$ are planar within 0.1816 Å. The deviations (Å) are –0.1880 for N^1, –0.0730 for N^2, 0.2864 for C^7, –0.1015 for C^8, 0.2583 for C^{13}, and –0.1822 for C^{14}. The P and C^{19} atoms deviate from this plane by 0.4241 and –0.9833 Å, respectively. The conformation of the ring is distorted, because the N^1 and N^2 atoms deviate from the mean plane by different distances (–0.188 and –0.073 Å, respectively). The bond angles at nitrogen atoms C^7N^1P (123.9°) and $C^{13}N^2P$ (129.5°) differ. These values show that both nitrogen atoms have the hybridization close to sp^2.

The deviations of the S and O atoms from the mean plane of the heterocycle are 0.02 and 1.94 Å, respectively, which is indicative of their equatorial (P=S) and axial ($OPhCH_3$) location. The protons of the methylene group (at the C^{19} atom) are located at almost equal distances from the central plane (H^{191} at –1.57 Å and H^{192} at –1.48 Å). Therefore, their location cannot be considered as preferably axial or equatorial. The distance between the oxygen atom and the nearest proton of the amido group is 3 Å, which rules out hydrogen bonding in this part of the molecule. The four-coordinate phosphorus atom in **VI** has

the usual distorted tetrahedral surrounding. The interatomic distances P–N^1 [1.623(5) Å] and P–N^2 [1.628(4) Å] are practically equal, and all the bonds of phosphorus are somewhat longer compared to the usual values [P=S 1.9349(16), P–O 1.601(3) Å] [12]. The angles at phosphorus (N^1PN^2 111.9°, SPO 119.27°) are considerably larger than the endocyclic OPO and NPN angles in six- and seven-membered heterorings [13, 14], as well as in eight-membered dioxa derivatives [15]. This fact is indicative of considerable flattening of the phosphamide fragment. The distance between the two benzene rings in the exocyclic groups of the neighboring molecules is 5.54 Å, which rules out intermolecular interactions. The diameter of the cavity (the distance between C^{19} and P) is 3.453 Å. The distances between the methylene protons and the phosphorus atom are the following: H^{191}–P 3.165 Å and H^{192}–P 4.384 Å.

Thus, in the crystalline state 1,3-dihydro-1,3,2-diazaphosphocane 2-sulfide **VI** is in *e-BC* conformation, whereas in solutions of thiophosphates **V** and **VI** the *e-BC* $\rightleftarrows$ *a-BC* equilibrium probably takes place. As the transfer from one conformation to another is fast, the ^{1}H NMR spectrum corresponds to the averaged form.

Introduction of two isopropyl groups to the nitrogen atoms of 1,3,2-diazaphosphocanes considerably alters the steric arrangement of the eight-membered heterocycles under study. The ^{1}H and ^{31}P NMR spectra show that these systems are conformationally heterogeneous in solution at room temperature. The bulky isopropyl substituents inhibit the conformational transitions, so that it becomes possible to observe them in the NMR time scale. Note that the solvent does not significantly influence these conformational transitions. The NMR spectra were recorded in $CDCl_3$ and DMSO-d_6.

The conformational pattern of 1,3-diisopropyl-1,3,2-diazaphosphocanes in solution depends on substituent **X** at phosphorus.

The ^{1}H NMR spectrum of solution of 2-phenoxy-1,3-diisopropyl-4,5;7,8-dibenzo-11,11'-dimethyl-1,3,2-diazaphosphocane 2-sulfide **XVIII**, taken immediately after the dissolution, contains a double set of signals corresponding to the presence of two forms in the 1 : 1 ratio. For one of them (form **A**) the isopropyl groups are located symmetrically relative to the heteroring plane. The CH_2 protons in the 6-position of the ring give two doublets. One of them has the coupling constant $^5J_{HP}$ 3.4 Hz, Δδ 1.15 ppm. In the other form (**B**), all four methyl groups of the isopropyl substituents are nonequivalent, which suggests their asymmetric location relative to the heteroring plane. In this case the CH_2 protons give a doublet of doublets, Δδ 0.15 ppm. It is interesting that 10–15 min after the dissolution the proton signals of the symmetric form practically disappear.

The same dynamics is observed in the ^{1}H NMR spectra of the other esters of the 1,3-diisopropyl-1,3,2-diazaphosphocane series (**XVI**, **XVII**, **XX**).

If the alkoxy or aroxy group at phosphorus is substituted by methyl radical, an equilibrium is established in solution between forms **A** and **B** of 2-methyl-1,3-diisopropyl-4,5;7,8-dibenzo-11,11'-dimethyl-1,3,2-diazaphosphocane 2-oxide **XXII**. According to the ^{1}H NMR spectra, the ratio of these forms immediately after the dissolution is 85 : 15. With time, the equilibrium ratio of 68 : 32 is attained. Further heating or increasing the acidity of the medium by adding trifluoroacetic acid does not alter this ratio even in the course of 1 month. This means that the system exists in the stable equilibrium. These two forms considerably differ in characteristics of isopropyl radicals and methylene groups. In the major form **A** the two isopropyl groups are magnetically equivalent, which suggests their symmetric location relative to the heteroring plane. One of the methylene protons has the coupling constant $^5J_{HP}$ 3.4 Hz, Δδ 1.08 ppm. In the minor form **B** all four methyl groups of the isopropyl substituent are nonequivalent, which proves their asymmetric location relative to the heteroring plane. Both protons of the methylene ring give a doublet of doublets. No coupling constant J_{PH} is revealed, Δδ 0.16 ppm. Using saturation transfer, we found that in a solution of phosphonate **XXII** isopropyl substituents of both symmetric and asymmetric forms are simultaneously involved in the exchange. For example, at 360 K in DMSO solution irradiation of the methyl signal with δ 0.95 ppm causes the integral intensity of the signals with δ 0.45 and δ 1.34 ppm to considerably decrease. At the excitation of the CH signals of the isopropyl group in the symmetric form, the response of both CH proton signals is observed in the asymmetric form.

Thus, for form **A** in the cases under study $^2J_{HH}$ 11.9–12.1 Hz, $^5J_{PH}$ 3.4–3.48 Hz, and the methylene protons show a considerable magnetic nonequivalence (Δδ 1.08–1.15 ppm). These facts allow us to identify this form as symmetric *boat–chair* conformation. The synchronous inversion of two nonplanar nitrogen atoms takes place in solution, resulting in interconversion of the symmetric and asymmetric forms. In the process, the heteroring conformation is altered. This fact is confirmed by changes in Δδ and

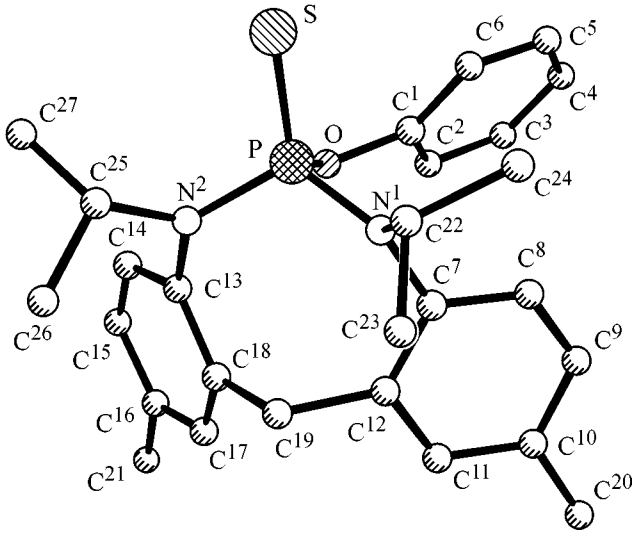


Fig. 3. General view of the molecule of thiophosphate **XVIII**.

the coupling constant of the methylene protons. For the asymmetric form **B** $^2J_{HH}$ 14.9 Hz, $\Delta\delta$ 0.15–0.16 ppm. These values evidently correspond to the equilibrium *e-B* ⇄ *a-B*.

To conclude, phosphonate **XXII** presumably exists in the conformation equilibrium *a-B* ⇄ *BC* ⇄ *e-B*. Evidently, the methyl group at the phosphorus atom has such steric orientation that all the three conformations appear to be relatively favorable, and the transition of one form into another can be monitored by ^{1}H NMR spectroscopy at room temperature.

We believe that for phosphorodiamidites the equilibrium *a-B* ⇄ *e-B* is attained in solutions. The transition of one form to another occurs through the *BC* conformation at such a rate (this conformation is unfavorable for such systems in solution) that it cannot be detected in the NMR time scale.

As form **A** in phosphorodiamidites is observed only at the initial moment after dissolution, the corresponding conformation is presumably stable in the crystalline state. To confirm this hypothesis, we studied by X-ray diffraction 2-phenoxy-1,3-diisopropyl-4,5;7,8-dibenzo-11,11'-dimethyl-1,3,2-diazaphosphocane 2-sulfide **XVIII**. The general view of the molecule is shown in Fig. 3. The atomic coordinates, interatomic distances, and bond angles are listed in Tables 4–6.

Table 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors (Å$^2 \times 10^3$) of **XVIII**

Atom	*x*	*y*	*z*	U_{eq}	Atom	*x*	*y*	*z*	U_{eq}
S	2865(1)	9936(2)	1504(1)	74(1)	C^{12}	4147(3)	4732(8)	1679(1)	43(2)
P	2922(1)	7972(2)	1399(1)	54(1)	C^{13}	1027(3)	5950(7)	1207(1)	49(2)
O	3072(2)	7433(2)	842(1)	61(1)	C^{14}	–4(3)	5917(7)	784(2)	58(3)
N^1	4253(2)	7251(4)	1757(1)	44(2)	C^{15}	–456(4)	4716(9)	553(1)	57(3)
N^2	1441(2)	7226(4)	1449(1)	47(2)	C^{16}	118(4)	3474(8)	713(1)	50(3)
C^1	4175(3)	7663(5)	575(1)	58(1)	C^{17}	1159(3)	3502(7)	1137(2)	49(2)
C^2	4255(3)	6777(6)	184(1)	80(2)	C^{18}	1603(3)	4706(8)	1383(1)	52(2)
C^3	5304(4)	6942(7)	–105(1)	103(2)	C^{19}	2732(2)	4641(5)	1838(1)	52(2)
C^4	6245(4)	7968(6)	4(2)	91(2)	C^{20}	6695(5)	2097(8)	1323(2)	83(3)
C^5	6140(4)	8828(6)	394(2)	88(2)	C^{21}	–325(6)	2128(9)	460(3)	87(3)
C^6	5112(3)	8703(5)	685(1)	79(2)	C^{22}	4823(3)	7857(4)	2264(1)	55(1)
C^7	4816(3)	5965(7)	1629(1)	48(2)	C^{23}	4873(5)	6805(6)	2690(1)	88(2)
C^8	6086(4)	5896(8)	1467(1)	53(3)	C^{24}	6219(4)	8529(7)	2256(2)	82(2)
C^9	6695(4)	4706(10)	1368(1)	52(3)	C^{25}	507(3)	7862(4)	1781(1)	63(1)
C^{10}	6075(4)	3455(9)	1422(1)	43(3)	C^{26}	–9(4)	6832(6)	2128(1)	73(2)
C^{11}	4775(4)	3498(8)	1579(1)	49(3)	C^{27}	–681(3)	8637(6)	1463(2)	84(2)

Table 5. Selected interatomic distances (*d*, Å) in the molecule of **XVIII**

Bond	*d*	Bond	*d*	Bond	*d*	Bond	*d*
S–P	1.9283(17)	C^1–C^2	1.361(5)	C^9–C^{10}	1.378(8)	C^{16}–C^{17}	1.407(6)
P–O	1.5982(18)	C^1–C^6	1.371(4)	C^{10}–C^{11}	1.409(6)	C^{16}–C^{21}	1.504(8)
P–N^2	1.655(3)	C^2–C^3	1.388(5)	C^{10}–C^{20}	1.493(8)	C^{17}–C^{18}	1.379(7)
P–N^1	1.658(3)	C^3–C^4	1.363(6)	C^{11}–C^{12}	1.393(7)	C^{18}–C^{19}	1.517(5)
O–C^1	1.403(3)	C^4–C^5	1.346(6)	C^{12}–C^{19}	1.521(4)	C^{22}–C^{23}	1.519(5)
N^1–C^7	1.429(6)	C^5–C^6	1.371(4)	C^{13}–C^{18}	1.387(7)	C^{22}–C^{24}	1.528(4)
N^1–C^{22}	1.499(4)	C^7–C^8	1.387(5)	C^{13}–C^{14}	1.399(5)	C^{25}–C^{26}	1.499(5)
N^2–C^{13}	1.427(6)	C^7–C^{12}	1.383(7)	C^{14}–C^{15}	1.361(7)	C^{25}–C^{27}	1.536(5)
N^2–C^{25}	1.501(4)	C^8–C^9	1.347(7)	C^{15}–C^{16}	1.373(8)		

Table 6. Selected bond angles (ω, deg) in the molecule of **XVIII**

Angle	ω	Angle	ω	Angle	ω	Angle	ω
OPN^2	97.74(13)	$C^9C^{10}C^{11}$	116.3(7)	$C^2C^1C^6$	121.0(3)	$C^{15}C^{16}C^{21}$	123.1(6)
OPN^1	102.55(13)	$C^9C^{10}C^{20}$	124.1(5)	C^2C^1O	115.0(3)	$C^{17}C^{16}C^{21}$	120.2(7)
N^2PN^1	113.82(16)	$C^{11}C^{10}C^{20}$	119.6(7)	C^6C^1O	124.0(3)	$C^{18}C^{17}C^{16}$	122.6(6)
OPS	117.76(9)	$C^{12}C^{11}C^{10}$	122.2(7)	$C^1C^2C^3$	118.9(5)	$C^{17}C^{18}C^{13}$	119.5(5)
N^2PS	112.12(13)	$C^7C^{12}C^{11}$	119.6(4)	$C^4C^3C^2$	120.6(5)	$C^{17}C^{18}C^{19}$	119.1(6)
N^1PS	111.93(14)	$C^7C^{12}C^{19}$	123.2(6)	$C^5C^4C^3$	119.2(4)	$C^{13}C^{18}C^{19}$	121.4(6)
C^1OP	126.96(19)	$C^{11}C^{12}C^{19}$	117.1(6)	$C^4C^5C^6$	121.9(5)	$C^{18}C^{19}C^{12}$	111.9(2)
$C^7N^1C^{22}$	116.7(2)	$C^{18}C^{13}C^{14}$	117.6(6)	$C^5C^6C^1$	118.5(4)	$N^1C^{22}C^{23}$	111.7(3)
C^7N^1P	122.45(19)	$C^{18}C^{13}N^2$	121.9(4)	$C^8C^7C^{12}$	117.1(6)	$N^1C^{22}C^{24}$	111.9(3)
$C^{22}N^1P$	120.5(3)	$C^{14}C^{13}N^2$	120.5(6)	$C^8C^7N^1$	121.2(6)	$C^{23}C^{22}C^{24}$	111.6(3)
$C^{13}N^2C^{25}$	117.5(2)	$C^{15}C^{14}C^{13}$	122.1(6)	$C^{12}C^7N^1$	121.7(4)	$C^{26}C^{25}N^2$	112.4(4)
$C^{13}N^2P$	122.8(2)	$C^{14}C^{15}C^{16}$	121.4(5)	$C^9C^8C^7$	123.6(6)	$C^{26}C^{25}C^{27}$	111.3(3)
$C^{25}N^2P$	119.6(3)	$C^{15}C^{16}C^{17}$	116.7(7)	$C^8C^9C^{10}$	121.2(5)	$N^2C^{25}C^{27}$	111.3(3)

In the eight-membered heterocycle the atomic fragments $N^1N^2C^7C^{12}C^{13}C^{18}$ are planar within 0.1805 Å. The P and C^{19} atoms deviate from this plane by –0.4858 and 0.9919 Å, respectively. The heteroring has a symmetric *boat–chair* conformation (Fig. 4). This is confirmed by the fact that the angles C^7N^1P and $C^{13}N^2P$ are practically equal and have the values of 122.45° and 122.8°, respectively. The deviation of sulfur from the mean plane of the ring is –0.36 Å, which suggests its pseudoequatorial orientation. The deviation of the phenoxyl oxygen is 1.94 Å. Thus, the exocyclic substituent has axial orientation relative to the ring plane. The methylene protons H^{191} and H^{192} deviate from the central plane by 1.56 and 1.60 Å. Therefore, it cannot be considered that the axial or equatorial location of these atoms is preferred. The angles at nitrogen atoms are close to those typical of the trigonal planar configuration (the sum of bond angles is 359.7° at N^1 and 359.92° at N^2). The four-coordinate phosphorus atom has the distorted tetrahedral surrounding. The interatomic distances $P–N^1$ (1.658 Å) and $P–N^2$ (1.655 Å) are practically equal. All the bonds at the phosphorus atom are longer than the standard values [P=S 1.9283(17) Å, P–O 1.5982(18) Å]. The angles at the phosphorus atom, N^1PN^2 (113.82°) and SPO (117.76°), demonstrate strong flattening of the phosphamide part of the ring as compared to the corresponding 1,3,2-diazaphosphepanes [16].

The distances through the space between the methylene protons and phosphorus atom (Å) are as follows: $P–H^{191}$ 4.43 and $P–H^{192}$ 3.10. The distance between the P and C^{19} atoms is 3.453 Å.

In the crystalline state, the two isopropyl groups are located symmetrically relative to the ring plane. Thus, the conformation of the heteroring in the crystalline state corresponds to the conformation of form **A** in solution.

Quite a different pattern is observed in the ^1H NMR spectra of cyclic triamides **XIX** and **XXVI**. Immediately after the dissolution of crystalline 2-dimethylamino-1,3-diisopropyl-4,5;7,8-dibenzo-11,11'-dimethyl-1,3,2-diazaphosphocane 2-sulfide **XXVI** in DMSO-d_6, only one form is observed at room temperature. The character of splitting and the number of

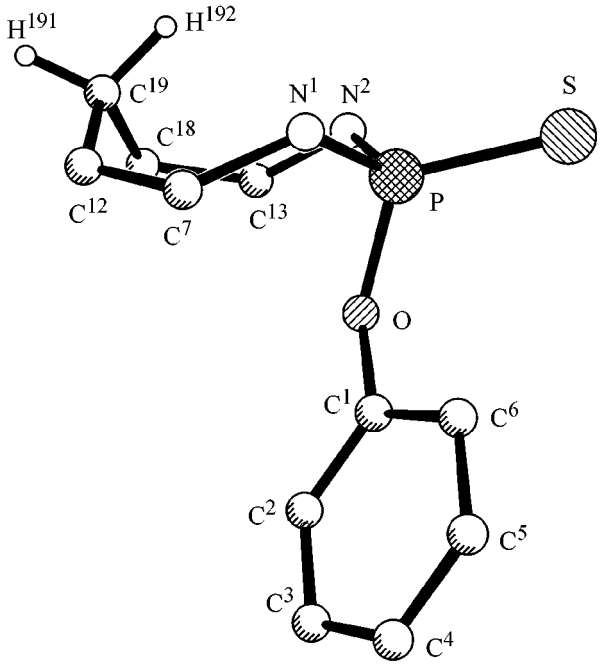


Fig. 4. Conformation of the heteroring in the molecule of **XVIII**.

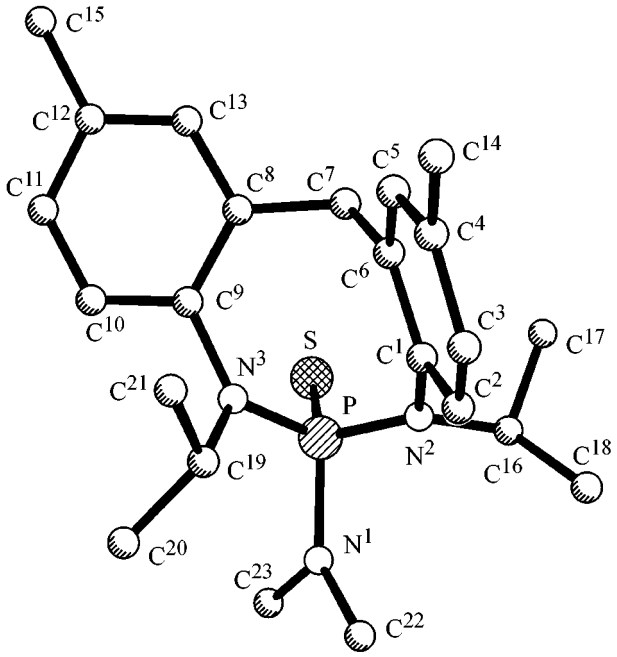


Fig. 5. General view of the molecule of phosphorothioic amide **XXVI.**

methyl signals suggest asymmetric location of the isopropyl groups relative to the ring plane. Using saturation transfer at 340 K for the CH and CH_3 protons of the isopropyl group, we revealed slow (in the NMR time scale) exchange between the two isopropyl groups. We found that the methyl signal with δ –0.35 ppm is coupled with the methyl signal with δ 0.79 ppm. Heating of solution to 380 K does not noticeably alter the spectrum, which suggests that the exchange remains slow. Study of the solution of cyclic triamide **XXVI** in the temperature range 290–380°C in the presence of a tenfold excess of trifluoroacetic acid revealed no apparent changes as compared to the spectra taken in the absence of the acid. This form is characterized by strong nonequivalence of the methylene protons, Δδ 1 ppm, and the presence of the geminal constant $^2J_{HH}$ 14.7 Hz. These data show that the conformation of the cycle in solution is *e-B*, and it is fairly rigid [17]. This hypothesis was confirmed by X-ray diffraction study of cyclic phosphorothioic triamide **XXVI**. The general view of the molecule is shown in Fig. 5. The atomic coordinates, interatomic distances, and bond angles are listed in Tables 7–9.

Table 7. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($Å^2 \times 10^3$) for **XXVI**

Atom	*x*	*y*	*z*	U_{eq}	Atom	*x*	*y*	*z*	U_{eq}
S	6333(1)	4160(1)	6990(1)	54(1)	C^{10}	6565(2)	1728(2)	7099(2)	50(1)
P	5204(1)	3644(1)	7242(1)	40(1)	C^{11}	7159(2)	1276(2)	6705(2)	54(1)
N^1	4856(2)	3944(1)	8024(1)	53(1)	C^{12}	7165(2)	1332(2)	5980(2)	50(1)
N^2	4323(1)	3835(1)	6727(1)	38(1)	C^{13}	6568(2)	1863(2)	5674(2)	46(1)
N^3	5297(1)	2643(1)	7220(1)	41(1)	C^{14}	2582(3)	1370(2)	5076(2)	65(1)
C^1	3903(2)	3215(1)	6307(1)	36(1)	C^{15}	7808(3)	850(3)	5537(2)	72(1)
C^2	3008(2)	3017(2)	6430(1)	43(1)	C^{16}	4125(2)	4701(2)	6550(1)	44(1)
C^3	2585(2)	2430(2)	6032(1)	48(1)	C^{17}	4503(2)	4924(2)	5838(2)	51(1)
C^4	3029(2)	2014(1)	5510(1)	46(1)	C^{18}	3139(2)	4911(2)	6604(2)	57(1)
C^5	3923(2)	2206(2)	5405(1)	43(1)	C^{19}	4620(2)	2131(2)	7597(1)	50(1)
C^6	4373(2)	2791(1)	5791(1)	37(1)	C^{20}	4902(3)	1947(3)	8352(2)	69(1)
C^7	5361(2)	2913(2)	5663(1)	40(1)	C^{21}	4394(2)	1370(2)	7200(2)	62(1)
C^8	5957(2)	2325(1)	6052(1)	39(1)	C^{22}	3929(2)	3952(3)	8262(2)	72(1)
C^9	5952(2)	2244(1)	6786(1)	40(1)	C^{23}	5501(3)	4166(3)	8575(2)	78(1)

Table 8. Selected interatomic distances (*d*, Å) in the molecule of **XXVI**

Bond	*d*	Bond	*d*	Bond	*d*	Bond	*d*
S–P	1.9474(14)	N^3–C^9	1.439(5)	C^5–C^6	1.389(5)	C^{12}–C^{13}	1.380(6)
P–N^1	1.648(4)	N^3–C^{19}	1.500(5)	C^6–C^7	1.506(5)	C^{12}–C^{15}	1.504(7)
P–N^3	1.663(3)	C^1–C^2	1.393(6)	C^7–C^8	1.512(5)	C^{16}–C^{17}	1.510(6)
P–N^2	1.667(3)	C^1–C^6	1.394(5)	C^8–C^{13}	1.387(6)	C^{16}–C^{18}	1.514(6)
N^1–C^{22}	1.455(6)	C^2–C^3	1.384(6)	C^8–C^9	1.400(5)	C^{19}–C^{21}	1.507(7)
N^1–C^{23}	1.468(6)	C^3–C^4	1.376(6)	C^9–C^{10}	1.384(6)	C^{19}–C^{20}	1.525(7)
N^2–C^1	1.442(5)	C^4–C^5	1.384(6)	C^{10}–C^{11}	1.380(6)		
N^2–C^{16}	1.501(5)	C^4–C^{14}	1.503(7)	C^{11}–C^{12}	1.380(6)		

Table 9. Selected bond angles (ω, deg) in the molecule of **XXVI**

Angle	ω	Angle	ω	Angle	ω	Angle	ω
N^1PN^3	110.37(17)	$C^4C^5C^6$	123.2(4)	$C^9N^3C^{19}$	118.1(3)	$C^{10}C^{11}C^{12}$	120.5(4)
N^1PN^2	102.95(17)	$C^5C^6C^1$	118.7(4)	C^9N^3P	121.9(2)	$C^{13}C^{12}C^{11}$	117.3(4)
N^3PN^2	103.92(16)	$C^5C^6C^7$	118.7(4)	$C^{19}N^3P$	119.6(3)	$C^{13}C^{12}C^{15}$	120.9(5)
N^1PS	111.15(15)	$C^1C^6C^7$	122.6(4)	$C^2C^1C^6$	118.8(4)	$C^{11}C^{12}C^{15}$	121.7(5)
N^3PS	110.97(12)	$C^6C^7C^8$	114.2(3)	$C^2C^1N^2$	119.3(3)	$C^{12}C^{13}C^8$	123.8(4)
N^2PS	116.98(12)	$C^{13}C^8C^9$	117.7(4)	$C^6C^1N^2$	121.8(3)	$N^2C^{16}C^{17}$	111.1(3)
$C^{22}N^1C^{23}$	113.4(5)	$C^{13}C^8C^7$	119.2(4)	$C^3C^2C^1$	120.6(4)	$N^2C^{16}C^{18}$	113.3(4)
$C^{22}N^1P$	125.6(4)	$C^9C^8C^7$	123.1(4)	$C^4C^3C^2$	121.7(4)	$C^{17}C^{16}C^{18}$	111.4(4)
$C^{23}N^1P$	120.8(4)	$C^{10}C^9C^8$	118.9(4)	$C^3C^4C^5$	116.9(4)	$N^3C^{19}C^{21}$	112.6(4)
$C^1N^2C^{16}$	118.0(3)	$C^{10}C^9N^3$	119.0(4)	$C^3C^4C^{14}$	122.4(4)	$N^3C^{19}C^{20}$	112.0(4)
C^1N^2P	122.1(2)	$C^8C^9N^3$	122.0(3)	$C^5C^4C^{14}$	120.7(4)	$C^{21}C^{19}C^{20}$	111.5(4)
$C^{16}N^2P$	117.8(3)	$C^{11}C^{10}C^9$	121.7(5)				

Two phenyl rings in the molecule are planar, ring **A** within 0.0064 Å, and ring **B** within 0.0074 Å. The angle between the planar fragments is 73.4°. The eight-membered heteroring has the *distorted boat* conformation (Fig. 6). The $N^3C^1C^6C^8C^9$ atomic fragment is planar within 0.0985 Å. The P, N^2, and C^7 atoms deviate to one side of this plane by 1.43, 1.2286, and 0.69 Å, respectively. The deviation of the sulfur atom from the mean plane is 2.96 Å, which suggests its axial location. The nitrogen atom of the exocyclic substituent deviates from the mean plane by 1.53 Å (it lies almost in the same plane with the phosphorus atom). Thus, the dimethylamino group has the equatorial location. The methylene protons H^{71} and H^{72} deviate from the central plane by 1.59 and 0.76 Å, respectively. Hence, the H^{71} proton is axial, and the H^{72} proton is equatorial relative to the mean plane. Two isopropyl groups are located asymmetrically relative to the heteroring plane. The bond angles at the ring nitrogen atoms are close to those typical of sp^2 hybridization; these atoms have trigonal planar coordination. The sum of the bond angles is 357.8° at N^2 and 359.6° at N^3. The nitrogen atom of the exocyclic P–N bond also has the trigonal planar coordination (the sum of bond angles is 359.8°). The four-coordinate phosphorus atom has the distorted tetragonal coordination. The interatomic distances P–N^2 and P–N^3 are practically equal. All the bonds of the phosphorus atom [P=S 1.9474(14), P–N^1 1.648(4) Å] are somewhat longer compared to the standard values. The angles at the phosphorus atom N^2PN^3 [103.92(16)°] and N^1PS [111.15(15)°] are close to those in some 1,3,2-diazaphosphorinanes [18, 19] and phosphepanes [16], but are somewhat larger than in the corresponding dioxa derivatives [20]. The distances between the methylene protons and the phosphorus atom (Å) are H^{71}–P 2.81 and H^{72}–P 4.2.

The diameter of the cavity conventionally characterized by the distance between phosphorus and C^7 is 3.24 Å.

Thus, 2-dimethylamido-1,3-diisopropyl-4,5;7,8-dibenzo-11,11'-dimethyl-1,3,2-diazaphosphocane 2-sulfide **XXVI** in solution preserves the distorted *e-B* conformation characteristic of the crystalline state. The exchange between two isopropyl groups occurring in solution suggests formation of the equilibrium mixture of the two conformers. However, the content of the second conformer *a-B* is so small that it practically does not affect the purity of the *e-B* form. This fact is also proved by the low rate of exchange processes.

EXPERIMENTAL

The ^1H NMR spectra were measured on Bruker WM-250 (250.13 MHz) and Bruker WM-400 (400.13 MHz) spectrometers against internal TMS and the residual signals of solvents (DMSO 2.5 ppm, $CDCl_3$ 7.27 ppm). The signals were assigned using

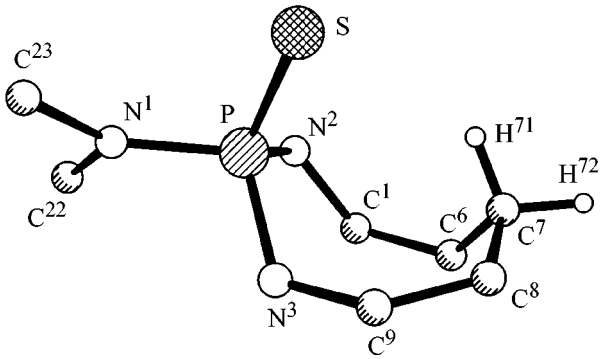


Fig. 6. Conformation of the heteroring in the molecule of **XXVI**.

double homonuclear resonance. The ^{13}C NMR spectra were recorded on a Bruker AC-200P (50.32 MHz) spectrometer. The ^{31}P NMR spectra were obtained on a Bruker WP-80 SY spectrometer (32.4 MHz) against external 85% orthophosphoric acid.

Column chromatography was carried out on a column 15 mm in diameter, packed with silica gel C-300 L 45/75 μm. The R_f values were determined by TLC on Silufol UV-254 plates in the systems 5 : 1 benzene–dioxane (A), 3 : 1 hexane–dioxane (B), and 1 : 3 benzene–methylene chloride (C). The chromatograms were developed with iodine vapor or by calcination at 250–300°C.

All X-ray studies were carried out on a Syntex P-1 four-circle diffractometer (CuK_α radiation, θ/2θ scanning).

A $0.40 \times 0.33 \times 0.16$-mm colorless transparent well-faced crystal of thiophosphate **VI**, $C_{22}H_{23}N_2OPS$, has the following cell parameters: *a* 12.012(2), *b* 17.334(3), *c* 9.770(2) Å; β 91.57(3)°: *M* 394.45, *Z* 4, d_{calc} 1.288 g/cm^3, *V* 2033.5(6) Å^3, space group $P2_1/c$. For the calculation and refinement, 2232 unique reflections with $I > 2\sigma(I)$ were used; *R* 0.0678. The structure was solved by the direct method using the SHELX 97 program.

The $0.36 \times 0.22 \times 0.16$-mm crystal of **XVIII**, $C_{27}H_{33}N_2OPS$, is monoclinic with the following cell parameters: *a* 9.874(2), *b* 9.711(2), *c* 26.554(5) Å; β 98.59(3)°, *M* 464.58, *Z* 4, d_{calc} 1.226 g/cm^3, *V* 2517.6(9) Å, space group $P2_1/n$. For the calculation and refinement, 2306 unique reflections with $I > 2\sigma(I)$ were used; *R* 0.0894. The structure was solved by the direct method using the SHELX 97 program.

The $0.45 \times 0.34 \times 0.28$-mm crystal of phosphorothioic amide **XXVI**, $C_{23}H_{34}N_3PS$, is rhombic with the following cell parameters: *a* 14.908(3), *b* 16.547(3), *c* 18.988(3) Å; *M* 415.56, *Z* 8, d_{calc} 1.179 g/cm^3, *V* 4684.0(15) Å^3, space group *Pbca*. For the calculation and refinement, 2148 unique reflections with $I > 2\sigma(I)$ were used; *R* 0.029. The structure was solved by the direct method using the SHELX 97 prorgam.

2,2'-Methylenebis-*p*-toluidine **I** was prepared as described in [21].

***N,N'*-Diisopropyl-2,2'-methylenebis-*p*-toluidine II.** Isopropyl iodide, 0.374 mol, was added with stirring to a solution of 0.017 mol of diamine **I** in 12 ml of ethanol, and the resulting mixture was refluxed for 24 h. Then the reaction mixture was neutralized with a concentrated ammonia solution at cooling with ice. Organic substances were exracted with benzene, the extract was dried over anhydrous calcium chloride, the solvent was removed, and the final product was isolated by column chromatography on silica gel. Yield 65%, mp 78–79°C, R_f 0.91 (A). ^1H NMR spectrum, δ, ppm: 1.00 d [12H, $(CH_3)_2CH$], 2.12 s (6H, CH_3–Ar), 3.48 q [2H, $(CH_2)_2CH$], 3.59 s (2H, CH_2), 6.50 d (2H^b, Ar), 6.76 s (2H^a, Ar), 6.90 d (2H^c, Ar).

2-X-1,3-Dihydro(-diisopropyl)-4,5;7,8-dibenzo-11,11'-dimethyl-1,3,2-diazaphosphocane 2-sulfide V, VI, and XV–XIX (general procedure). To a solution of 0.01 mol of diamine **I** or **II** and 0.02 mol of triethylamine in dry benzene, 0.01 mol of phosphorus trichloride, alkyl or aryl phosphorodichloridite, or phosphorodichloridous amide was slowly added with stirring at 5–10°C. After that the reaction mixture was stirred at room temperature for 2–3 h, and triethylamine hydrochloride was filtered off. To the resulting solution, sulfur was added, the reaction mixture was stirred for 2 h, and the solvent was removed. The target product was isolated by recrystallization from benzene (**V, VI, XVII**) or by column chromatography (**XV, XVI, XVIII, XIX**).

2-Phenoxy-1,3-dihydro-4,5;7,8-dibenzo-11,11'-dimethyl-1,3,2-diazaphosphocane 2-sulfide V. Yield 90%, mp 211–212°C, R_f 0.74 (A), 0.55 (B). *m/z* 380. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.29 s (6H, $CH_3^{11,11'}$), 3.98 d (1H, CH_2, $^2J_{HH}$ 13.2 Hz), 4.30 d.d (1H, CH_2, $^2J_{HH}$ 13.2, $^5J_{HP}$ 2.6 Hz), 5.23 d (2H, $NH^{1,3}$, $^2J_{HNP}$ 11.3 Hz), 6.68–7.14 m (11H, Ar). δ_P ($CHCl_3$) 58.43 ppm. Found, %: C 66.14; H 5.67; P 8.01. $C_{21}H_{21}N_2OPS$. Calculated, %: C 66.2; H 5.5; P 8.1.

2(4-Methyl)-1,3-dihydro-4,5;7,8-dibenzo-11,11'-dimethyl-1,3,2-diazaphosphocane 2-sulfide VI. Yield 92%, mp 213–214°C, R_f 0.89 (A), 0.77 (B). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.28 s (3H, CH_3–C_6H_4–O), 2.27 s (3H, CH_3^{11}), 2.3 s (3H, $CH_3^{11'}$), 4.05 d (1H, CH_2, $^2J_{HH}$ 13.6 Hz), 4.26 d.d (1H, CH_2, $^2J_{HH}$ 13.6, $^5J_{HP}$ 2.1 Hz), 5.19 d (2H, $NH^{1,3}$, $^2J_{PNH}$ 13.5 Hz), 6.72–7.15 (10H, Ar). δ_P ($CHCl_3$) 59.14 ppm. Found, %: C 66.61; H 5.95; P 7.39. $C_{22}H_{23}N_2OPS$. Calculated, %: C 67; H 5.84; P 7.86.

2-Chloro-1,3-diisopropyl-4,5;7,8-dibenzo-11,11'-dimethyl-1,3,2-diazaphosphocane 2-sulfide XV. Yield 78%, mp 225–228°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: –0.20 d (3H, $CH_3^{a,2}$ $^3J_{HH}$ 6.6 Hz),

[2] Two methyl groups of isopropyl radical in position 1 of the ring are marked by a and b, and in position 3, by a' and b'.

0.79 d (3H, $CH_3^{a'}$, $^3J_{HH}$ 6.6 Hz), 1.43 d (3H, CH_3^{b}, $^3J_{HH}$ 6.6 Hz), 1.48 d (3H, $CH_3^{b'}$, $^3J_{HH}$ 6.6 Hz), 2.29 s (3H, CH_3^{11}), 2.34 s (3H, $CH_3^{11'}$), 3.68 m (1H, $CH^{i\text{-Pr},a,b}$, $^3J_{HH}$ 6.6 Hz), 3.74 d (1H, CH_2, $^2J_{HH}$ 13.8 Hz), 4.43 d (1H, CH_2, $^2J_{HH}$ 13.8 Hz), 4.56 m (1H, $CH^{i\text{-Pr},a',b'}$, $^3J_{HH}$ 6.6 Hz), 7.03–7.20 m (6H, Ar). δ_P ($CHCl_3$) 68.95 ppm.

2-Methoxy-1,3-diisopropyl-4,5;7,8-dibenzo-11,11'-dimethyl-1,3,2-diazaphosphocane 2-sulfide XVI. Yield 50%, mp 174–176°C, R_f 0.62 (A), 0.58 (B), 0.56 (C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.09 d (3H, CH_3–O), 0.34 d (3H, CH_3^{a}, $^3J_{HH}$ 6.4 Hz), 0.35 d (3H, $CH_3^{a'}$, $^3J_{HH}$ 6.4 Hz), 1.34 d (3H, CH_3^{b}, $^3J_{HH}$ 6.8 Hz), 1.48 d (3H, $CH_3^{b'}$, $^3J_{HH}$ 6.8 Hz), 2.16 s (6H, $CH_3^{11,11'}$), 3.50 d (1H, CH_2, $^2J_{HH}$ 14.5 Hz), 3.96 m (1H, $CH^{i\text{-Pr},a,b}$, $^3J_{HH}$ 6.4, $^3J_{HH}$ 6.8 Hz), 4.12 m (1H, $CH^{i\text{-Pr},a',b'}$, $^3J_{HH}$ 6.4 Hz, $^3J_{HH}$ 6.8 Hz), 4.17 d (1H, CH_2, $^2J_{HH}$ 14.5 Hz), 6.56–7.06 m (6H, Ar). δ_P (C_6H_6) 73.92 ppm.

2-Ethoxy-1,3-diisopropyl-4,5;7,8-dibenzo-11,11'-dimethyl-1,3,2-diazaphosphocane 2-sulfide XVII. Yield 45%, mp 164–166°C, R_f 0.93 (A), 0.96 (B), 0.66 (C), *m*/*z* 416. Form **A**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.75 t (3H, $OCH_2C\mathit{H}_3$, $^3J_{HH}$ 7.2 Hz), 0.99 d (6H, $CH_3^{a,a'}$, $^3J_{HH}$ 6.4 Hz), 1.28 d (6H, $CH_3^{b,b'}$, $^3J_{HH}$ 6.4 Hz), 2.31 s (6H, $CH_3^{11,11'}$), 3.45 d (1H, CH_2, $^2J_{HH}$ 11.9 Hz), 3.72 m (2H, $CH_3C\mathit{H}_2O$, $^3J_{HP}$ 9.4 Hz, $^3J_{HH}$ 7.2 Hz), 4.31 d.d (1H, CH_2, $^2J_{HH}$ 11.9, $^5J_{HP}$ 3.4 Hz), 4.89 m (2H, $CH^{2i\text{-Pr}}$, $^3J_{HP}$ 13.2 Hz, $^3J_{HH}$ 6.4 Hz), 6.94–7.11 m (6H, Ar). δ_P ($CHCl_3$) 71.14 ppm. Form **B**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.25 d (3H, CH_3^{a}, $^3J_{HH}$ 6.8 Hz), 0.28 d (3H, $CH_3^{a'}$, $^3J_{HH}$ 6.8 Hz), 1.11 t (3H, $C\mathit{H}_3CH_2O$ $^3J_{HH}$ 6.8 Hz), 1.35 d (3H, CH_3^{b}, $^3J_{HH}$ 6.8 Hz), 1.44 d (3H, $CH_3^{b'}$, $^3J_{HH}$ 6.8 Hz), 2.28 s (6H, $CH_3^{11,11'}$), 3.77 m (1H, $CH^{i\text{-Pr},a,b}$, $^3J_{HP}$ 15.3, $^3J_{HH}$ 6.8 Hz, 6.8 Hz), 3.90 m (1H, $CH^{i\text{-Pr},a',b'}$, $^3J_{PH}$ 15.3, $^3J_{HH}$ 6.8, 6.8 Hz), 3.95 m (2H, $CH_3C\mathit{H}_2O$, $^3J_{HP}$ 8.5, $^3J_{HH}$ 6.8 Hz), 4.04 d (1H, CH_2, $^2J_{HH}$ 14.5 Hz), 4.17 d (1H, CH_2, $^2J_{HH}$ 14.5 Hz), 6.94–7.11 m (6H, Ar), δ_P ($CHCl_3$) 71.51 ppm. Found, %: C 65.90; H 8.26; P 6.26. $C_{23}H_{33}N_2OPS$. Calculated, %: C 66.3; H 7.9; P 7.4.

2-Phenoxy-1,3-diisopropyl-4,5;7,8-dibenzo-11,11'-dimethyl-1,3,2-diazaphosphocane 2-sulfide XVIII. Yield 30%, mp 148–150°C, R_f 0.83 (A), 0.76 (B). Form **A**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.01 d (3H, $CH_3^{a,a'}$, $^3J_{HH}$ 6.7 Hz), 1.28 d (3H, $CH_3^{b,b'}$, $^3J_{HH}$ 6.8 Hz), 2.28 s (6H, $CH_3^{11,11'}$), 3.48 d (1H, CH_2, $^2J_{HH}$ 11.9 Hz), 4.63 d.d (1H, CH_2, $^2J_{HH}$ 11.9, $^5J_{HP}$ 3.4 Hz), 5.02 m (2H, $CH^{2i\text{-Pr}}$, $^3J_{HH}$ 6.7, 6.8 Hz), 6.58–7.17 m (11H, Ar). δ_P (C_6H_6) 62.28 ppm. Form **B**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.36 d (3H, CH_3^{a}, $^3J_{HH}$ 6.8 Hz), 0.40 d (3H, $CH_3^{a'}$, $^3J_{HH}$ 6.8 Hz), 1.39 d (3H, CH_3^{b}, $^3J_{HH}$ 6.4 Hz), 1.47 d (3H, CH_3^{b}, $^3J_{HH}$ 6.8 Hz), 2.06 s (3H, CH_3^{11}), 2.10 s (3H, $CH_3^{11'}$), 4.10 m (1H, $CH^{i\text{-Pr},a,b}$, $^3J_{HP}$ 15, $^3J_{HH}$ 6.8, 6.4 Hz), 4.12 d (1H, CH_2, $^2J_{HH}$ 14.5 Hz), 4.27 d (1H, CH_2, $^2J_{HH}$ 14.5 Hz), 4.64 m (1H, $CH^{i\text{-Pr},a',b'}$, $^3J_{HP}$ 15, $^3J_{HH}$ 6.8 Hz), 6.78–7.34 m (11H, Ar). δ_P (C_6H_6) 67.39 ppm.

2-Diethylamino-1,3-diisopropyl-4,5;7,8-dibenzo-11,11'-dimethyl-1,3,2-diazaphosphocane 2-sulfide XIX. Yield 42%, mp 170–171°C, R_f 0.73 (A), *m*/*z* 443. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: –0.15 d (3H, CH_3^{a}, $^3J_{HH}$ 6.4 Hz), 0.80 d (3H, $CH_3^{a'}$, $^3J_{HH}$ 5.9 Hz), 1.23 t (6H, $C\mathit{H}_3CH_2$, $^3J_{HH}$ 7.2 Hz), 1.27 m (6H, $CH_3^{i\text{-Pr},b,b'}$, $^3J_{HH}$ 6.4 Hz), 2.28 s (3H, CH_3^{11}), 2.23 s (3H, $CH_3^{11'}$), 3.16 m (1H, $CH^{i\text{-Pr},a,b}$, $^3J_{HH}$ 6.4 Hz), 3.25 m (2H, $C\mathit{H}_2CH_3$, $^3J_{HH}$ 7.2, $^3J_{HP}$ 12.8 Hz), 3.48 m (2H, $C\mathit{H}_2CH_3$, $^3J_{HH}$ 7.2, $^3J_{HP}$ 13.2 Hz), 3.79 d (1H, CH_2, $^2J_{HH}$ 14.7 Hz), 4.03 m (1H, $CH^{i\text{-Pr},a',b'}$, $^3J_{HH}$ 6.4 Hz), 4.64 d (1H, CH_2, $^2J_{HH}$ 14.7 Hz), 6.97–7.12 m (6H, Ar). δ_P ($CHCl_3$) 70.97 ppm.

2-Ethoxy-1,3-diisopropyl-4,5;7,8-dibenzo-11,11'-dimethyl-1,3,2-diazaphosphocane 2-oxide XX. *a*. Through a solution of 0.01 mol of diazaphosphocane **XII** in 20 ml of anhydrous benzene, dry NO was passed for 15 min. The solvent was removed, and the residue purified chromatographically on a silica gel column, elution with 1 : 1 benzene–dioxane. Yield 57%, mp 182–183°C, R_f 0.55 (A). δ_P (C_6H_6) 10.83 ppm.

b. To a solution of 0.01 mol of diazaphosphocane **XII** in 20 ml of anhydrous benzene, 0.01 mol of a complex of hydrogen peroxide with urea was added, and the resulting mixture was stirred for 2 h. The unchanged complex was filtered off, and the filtrate was evaporated. The residue was purified on a silica gel column, elution with 1 : 1 benzene–dioxane. Yield 52%, mp 182–183°C. Form **A**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.86 t (3H, $OCH_2C\mathit{H}_3$, $^3J_{HH}$ 6.8 Hz), 1.02 d (6H, $CH_3^{a,a'}$, $^3J_{HH}$ 6.8 Hz), 1.36 d (6H, $CH_3^{b,b'}$, $^3J_{HH}$ 6.8 Hz), 2.3 s (6H, $CH_3^{11,11'}$), 3.45 d (1H, CH_2, $^2J_{HH}$ 11.9 Hz), 3.71 m (2H, $CH_3C\mathit{H}_2O$, $^3J_{HH}$ 6.8 Hz), 4.37 d.d (1H, CH_2, $^2J_{HH}$ 11.9, $^5J_{HP}$ 3.4 Hz), 4.91 m

(2H, $CH^{2i\text{-}Pr}$, $^3J_{HH}$ 6.8 Hz), 6.94–7.11 m (6H, Ar). δ_P ($CHCl_3$) 10.83 ppm. Form **B**. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.21 d (3H, CH_3^a, $^3J_{HH}$ 6.8 Hz), 0.56 d (3H, $CH_3^{a'}$, $^3J_{HH}$ 6.8 Hz), 1.03 t (3H, CH_3CH_2O, $^3J_{HH}$ 6.8 Hz), 1.37 d (3H, CH_3^b, $^3J_{HH}$ 6.8 Hz), 1.41 d (3H, $CH_3^{b'}$, $^3J_{HH}$ 6.4 Hz), 2.25 s (3H, CH_3^{11}), 2.28 s (3H, $CH_3^{11'}$), 3.57 m (1H, $CH^{i\text{-}Pr,a,b}$, $^3J_{HH}$ 6.8, 6.8 Hz), 3.81 m (1H, $CH^{i\text{-}Pr,a',b'}$, $^3J_{HH}$ 6.8, 6.4 Hz), 3.92 d (1H, CH_2, $^2J_{HH}$ 14.6 Hz), 4.02 m (2H, CH_3CH_2O, $^3J_{HH}$ 6.8 Hz), 4.14 d (1H, CH_2, $^2J_{HH}$ 14.6 Hz), 6.94–7.11 m (6H, Ar). δ_P ($CHCl_3$) 11.71 ppm.

2-Methylthio-1,3-diisopropyl-4,5;7,8-dibenzo-11,11'-dimethyl-1,3,2-diazaphosphocane 2-oxide XXI. A mixture of 0.01 mol of thiophosphate **XVII** and 0.015 mol of methyl iodide was refluxed in 30 ml of benzene for 8 h. After that the solvent was distilled off. The residue was recrystallized from benzene. Yield 89%, mp 192–193°C, R_f 0.49 (A), 0.44 (B). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.04 d (6H, $CH_3^{a,a'}$, $^3J_{HH}$ 6.8 Hz), 0.56 d (6H, $CH_3^{b,b'}$, $^3J_{HH}$ 6.4 Hz), 1.39 d (3H, CH_3S, $^3J_{HP}$ 6.8 Hz), 2.28 s (6H, $CH_3^{11,11'}$), 3.63 m (1H, $CH^{i\text{-}Pr,a,b}$ $^3J_{HH}$ 6.8 Hz), 3.81 d (1H, CH_2, $^2J_{HH}$ 14.9 Hz), 4.04 m (1H, $CH^{i\text{-}Pr,a',b'}$, $^3J_{HH}$ 6.4 Hz), 4.31 d (1H, CH_2, $^2J_{HH}$ 14.9 Hz), 6.93–7.22 m (6H, Ar). δ_P (C_6H_6) 33.58 ppm.

2-Methyl-1,3-diisopropyl-4,5;7,8-dibenzo-11,11'-dimethyl-1,3,2-diazaphosphocane 2-oxide XXII. A mixture of 0.01 mol of diamido ester **XII** and 0.015 mol of methyl iodide was refluxed in 30 ml of dry benzene for 2 h. After that the solvent was distilled off, and the residue was recrystallized from benzene. Yield 80%, mp 206–208°C, R_f 0.068 (A), 0.12 (B). Form **A**. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.76 d (3H, PCH_3, $^2J_{HP}$ 15.3 Hz), 1.02 d (6H, $CH_3^{a,a'}$, $^3J_{HH}$ 6.8 Hz), 1.32 d (6H, $CH_3^{b,b'}$, $^3J_{HH}$ 6.4 Hz), 2.32 s (6H, $CH_3^{11,11'}$), 3.48 d (1H, CH_2, $^2J_{HH}$ 11.9 Hz), 4.40 d.d (1H, CH_2, $^2J_{HH}$ 11.9, $^5J_{HP}$ 3.4 Hz), 4.63 m (2H, $CH^{2i\text{-}Pr}$, $^3J_{HH}$ 6.8, 6.4 Hz), 6.92–7.20 m (6H, Ar). δ_P ($CHCl_3$) 26.43 ppm. Form **B**. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.22 d (3H, CH_3^a, $^3J_{HH}$ 6.8 Hz), 0.45 d (3H, $CH_3^{a'}$, $^3J_{HH}$ 6.8 Hz), 1.37 d (3H, CH_3^b, $^3J_{HH}$ 6.4 Hz), 1.42 d (3H, $CH_3^{b'}$, $^2J_{HH}$ 6.8 Hz), 1.61 d (3H, PCH_3, $^2J_{PH}$ 14.5 Hz), 2.27 s (3H, CH_3^{11}), 2.3 s (3H, $CH_3^{11'}$), 3.57 m (1H, $CH^{i\text{-}Pr,a',b'}$, $^3J_{HH}$ 6.8, 6.8 Hz), 3.71 m (1H, $CH^{i\text{-}Pr,a,b}$, $^3J_{HH}$ 6.8, 6.4 Hz), 3.9 d (1H, CH_2, $^2J_{HH}$ 14.9 Hz), 4.06 d (1H, CH_2, $^2J_{HH}$ 14.9 Hz), 6.92–7.21 m (6H, Ar). δ_P ($CHCl_3$) 29.65 ppm.

Form **A**. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 0.60 d (3H, PCH_3, $^2J_{HP}$ 15.3 Hz), 0.95 d (6H, $CH_3^{a,a'}$, $^3J_{HH}$ 6.9 Hz), 1.23 d (6H, $CH_3^{b,b'}$, $^3J_{HH}$ 6.5 Hz), 2.27 s (6H, $CH_3^{11,11'}$), 3.56 d (1H, CH_2, $^2J_{HH}$ 11.8 Hz), 4.26 d.d (1H, CH_2, $^2J_{HH}$ 11.8, $^5J_{HP}$ 3.4 Hz), 4.40–4.53 m (2H, $CH^{2i\text{-}Pr}$, $^3J_{HH}$ 6.9, 6.5 Hz), 6.96 br.s (4H, Ar), 7.35 br.s (2H, Ar). Form **B**. ^1H NMR spectrum (DMSO-d_6), δ, ppm: –0.1 d (3H, CH_3^a, $^3J_{HH}$ 6.5 Hz), 0.45 d (3H, $CH_3^{a'}$, $^3J_{HH}$ 6.5 Hz), 1.25 d (3H, CH_3^b), 1.33 d (3H, $CH_3^{b'}$), 1.60 d (3H, PCH_3, $^2J_{HP}$ 14.9 Hz), 2.23 s (3H, CH_3^{11}), 2.25 s (3H, $CH_3^{11'}$), 3.40–3.55 m (1H, $CH^{i\text{-}Pr,a',b'}$, $^3J_{HH}$ 6.5 Hz), 3.58–3.70 m (1H, $CH^{i\text{-}Pr,a,b}$, $^3J_{HH}$ 6.5 Hz), 3.81 d (1H, CH_2, $^2J_{HH}$ 14.1 Hz), 4.19 d (1H, CH_2, $^2J_{HH}$ 14.1 Hz), 6.90–7.15 m (6H, Ar). Found, %: C 70.95; H 8.7; P 8.57. $C_{22}H_{31}N_2OP$. Calculated, %: C 71.35; H 8.37; P 8.37.

1,3-Diisopropyl-4,5;7,8-dibenzo-11,11'-dimethyl-1,3,2-diazaphosphocane 2-oxide XXIII. To a solution of 0.005 mol of crude acid chloride **X** in 8 ml of benzene, a mixture consisting of 0.005 mol of water, 0.005 mol of triethylamine, and 4 ml of dioxane was gradually added at 5–10°C. The resulting mixture was stirred at room temperature, triethylamine hydrochloride was filtered off, and the solvent was removed. The substance was purified by column chromatography on a silica gel column, elution with 1 : 1 benzene–dioxane. Yield 24%, mp 113–114°C, R_f 0.573 (A), 0.18 (B). Form **A**. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.11 d (6H, $CH_3^{a,a'}$, $^3J_{HH}$ 6.8 Hz), 1.37 d (6H, $CH_3^{b,b'}$, $^3J_{HH}$ 6.4 Hz), 2.27 s (6H, $CH_3^{11,11'}$), 3.48 d (1H, CH_2, $^2J_{HH}$ 11.9 Hz), 4.36 d.d (1H, CH_2, $^2J_{HH}$ 11.9, $^5J_{HP}$ 3.8 Hz), 4.47 m (2H, $CH^{2i\text{-}Pr}$, $^3J_{HH}$ 6.8, 6.4 Hz), 6.98–7.21 m (6H, Ar), 7.4 d (1H, PH, $^2J_{HP}$ 599.2 Hz). δ_P ($CHCl_3$) 11.16 ppm. Form **B**. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.45 d (3H, CH_3^a, $^3J_{HH}$ 6.8 Hz), 0.70 d (3H, $CH_3^{a'}$, $^3J_{HH}$ 6.8 Hz), 1.35 d (3H, CH_3^b, $^3J_{HH}$ 6.4 Hz), 1.40 d (3H, $CH_3^{b'}$, $^3J_{HH}$ 6.8 Hz), 2.30 s (3H, CH_3^{11}), 2.31 s (3H, $CH_3^{11'}$), 3.66 m (1H, $CH^{i\text{-}Pr,a,b}$, $^3J_{HH}$ 6.8, 6.4 Hz), 3.80 m (1H, $CH^{i\text{-}Pr,a',b'}$, $^3J_{HH}$ 6.8 Hz), 3.87 d (1H, CH_2, $^2J_{HH}$ 15.3 Hz), 4.02 d (1H, CH_2, $^2J_{HH}$ 15.3 Hz), 6.98–7.21 m (6H, Ar), 6.27 d (1H, PH, $^2J_{HP}$ 613.7 Hz). δ_P ($CHCl_3$) 17.05 ppm.

2-Dimethylamino-1,3-diisopropyl-4,5;7,8-dibenzo-11,11'-dimethyl-1,3,2-diazaphosphocane 2-sul-

fide XXVI. To a solution of 0.01 mol of dimethylamine in dry hexane, a solution of crude phosphorochloridite **X** (0.005 mol) in dry benzene was slowly added with stirring at 5–10°C. The resulting mixture was stirred at room temperature for 1.5 h, and dimethylamine hydrochloride was filtered off. To a solution of crude triamide **XXIV**, sulfur was added, and the reaction mixture was stirred for 2 h. The solvent was removed, and the phosphorothioic triamide was isolated by column chromatography on silica gel, elution with 10 : 1 benzene–dioxane. Yield 45%, mp 141–142°C, R_f 0.57 (A), 0.56 (B), 0.59 (C), *m*/*z* 415. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: –0.32 d (3H, CH_3^a, $^3J_{HH}$ 6.6 Hz), 0.78 d (3H, $CH_3^{a'}$, $^3J_{HH}$ 6.6 Hz), 1.18 d (3H, CH_3^b, $^3J_{HH}$ 6.6 Hz), 1.25 d (3H, $CH_3^{b'}$, $^3J_{HH}$ 6.6 Hz), 2.23 s (3H, CH_3^{11}), 2.27 s (3H, $CH_3^{11'}$), 2.86 s (3H, NCH_3), 2.89 s (3H, NCH_3), 3.04 m (1H, $CH^{i\text{-Pr,a,b}}$), 3.71 d (1H, CH_2, $^2J_{HH}$ 13.5 Hz), 3.85–4.00 m (1H, $CH^{i\text{-Pr,a',b'}}$), 4.60 d (1H, CH_2, $^3J_{HH}$ 13.5 Hz), 6.90–7.22 m (6H, Ar). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: –0.19 d (3H, CH_3^a, $^3J_{HH}$ 6.8 Hz), 0.85 d (3H, $CH_3^{a'}$, $^3J_{HH}$ 6.4 Hz), 1.26 d (3H, CH_3^b, $^3J_{HH}$ 6.4 Hz), 1.3 d (3H, $CH_3^{b'}$, $^3J_{HH}$ 7.8 Hz), 2.27 s (3H, CH_3^{11}), 2.32 s (3H, $CH_3^{11'}$), 2.78 d (3H, NCH_3, $^3J_{HP}$ 10.9 Hz), 3.00 d (3H, NCH_3, $^3J_{HP}$ 10.9 Hz), 3.09 m (1H, $CH^{i\text{-Pr,a,b}}$, $^3J_{HP}$ 15.3, $^3J_{HH}$ 6.8, 6.4 Hz), 3.74 d (1H, CH_2, $^2J_{HH}$ 14.7 Hz), 4.06 m (1H, $CH^{i\text{-Pr,a',b'}}$, $^3J_{HP}$ 15.3, $^3J_{HH}$ 7.8, 6.4 Hz), 4.7 d (1H, CH_2, $^2J_{HH}$ 14.7 Hz), 6.56–7.09 m (6H, Ar). δ_P ($CHCl_3$) 69.80 ppm. Found, %: C 66.3; H 8.39; P 7.07. $C_{23}H_{34}N_3PS$. Calculated, %: C 66.5; H 8.19; P 7.14.

2-Ethylenimino-1,3-diisopropyl-4,5;7.8-dibenzo-11,11'-dimethyl-1,3,2-diazaphosphocane 2-sulfide XXVII. To a solution of 0.005 mol of ethylenimine and 0.005 mol of triethylamine in dry hexane, a solution of crude phosphorochloridous diamide **X** in dry benzene was slowly added with stirring at 5–10°C. The reaction mixture was stirred at room temperature for 1.5–2 h, and triethylamine hydrochloride was filtered off. To a solution of crude triamide **XXV**, sulfur was added, the reaction mixture was stirred for 2 h, the solvent was removed, and the residue was recrystallized from benzene. Yield 41%, mp 234–235°C (with decomposition). Form **A**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.00 d (6H, $CH_3^{a,a'}$, $^3J_{HH}$ 6.8 Hz), 1.22 d (6H, $CH_3^{b,b'}$, $^3J_{HH}$ 6.8 Hz), 1.77 d (4H, CH_2CH_2, $^2J_{HP}$ 17.9 Hz), 2.29 s (6H, $CH_3^{11,11'}$), 3.52 d (1H, CH_2, $^2J_{HH}$ 11.9 Hz), 4.37 d.d (1H, CH_2, $^2J_{HH}$ 11.9 Hz, $^5J_{HP}$ 3.4 Hz), 4.92 m (2H, $CH^{2i\text{-Pr}}$, $^3J_{HH}$ 6.8 Hz), 6.85–7.20 m (6H, Ar). δ_P ($CHCl_3$) 81.67 ppm. Form **B**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: –0.13 d (3H, CH_3^a, $^3J_{HH}$ 6.4 Hz), 0.62 d (3H, $CH_3^{a'}$, $^3J_{HH}$ 6.4 Hz), 1.31 d (3H, CH_3^b, $^3J_{HH}$ 6.4 Hz), 1.41 d (3H, $CH_3^{b'}$, $^3J_{HH}$ 6.8 Hz), 1.55 d (4H, CH_2CH_2), 2.29 s (3H, $CH_3^{11,11'}$), 3.34 m (1H, $CH^{i\text{-Pr,a,b}}$, $^3J_{HH}$ 6.4 Hz), 3.81 d (1H, CH_2, $^2J_{HH}$ 14.5 Hz), 4.15 m (1H, $CH^{i\text{-Pr,a',b'}}$, $^3J_{HH}$ 6.8, 6.4 Hz), 4.52 d (1H, CH_2, $^2J_{HH}$ 14.5 Hz), 6.85–7.20 m (6H, Ar). δ_P ($CHCl_3$) 82.57 ppm. Found, %: C 67.10; H 7.68; P 7.31. $C_{22}H_{32}N_3PS$. Calculated, %: C 66.82; H 7.74; P 7.50.

4,5;7,8-Dibenzo-11,11'-dimethyl-1,3,2-diazaphosphocane 2-oxide IX. Yield 35%, mp 172–173°C, R_f 0.6 (A), *m*/*z* 272. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.29 s (6H, $CH_3^{11,11'}$), 3.93 d (1H, CH_2, $^2J_{HH}$ 14.2 Hz), 4.03 d (1H, CH_2, $^2J_{HH}$ 14.2 Hz), 4.97 s (2H, $NH^{1,3}$, $^3J_{HH}$ 2.2 Hz), 7.68 d (1H, J_{HP} 614, $^3J_{HH}$ 2.2 Hz), 6.86–7.11 (6H, Ar). δ_P ($CHCl_3$) 10.31 ppm.

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