Phosphorus-Nitrogen Compounds: Novel Spirocyclic Phosphazene Derivatives. Structure of 3,3″-Propane-1,3-diylbis[4′,4′,6′,6′-tetrachloro-3,4-dihydrospiro[1,3,2-benzoxazaphosphorine-2,2′λ^5-[4λ^5,6λ^5][1,3,5,2,4,6]triazatriphosphorine]][1])

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The reactions of N_2O_2-donor-type aminopodands **1**–**3** with trimer $N_3P_3Cl_6$ led to the novel spirocyclic phosphazene derivatives **4**–**10** (*Scheme*). Compounds **4**–**7** and **8**–**10** are the first examples of the substituted spiro-ansa-spiro and spiro-bino-spiro phosphazene derivatives, respectively. The pyrrolidinyl-substituted phosphazene derivatives **7** and **10** were synthesized from **5** and **9**, respectively, with an excess of pyrrolidine. The reaction of aminopodand **3** (R=$(CH_2)_4$) with $N_3P_3Cl_6$ in dry THF afforded only spiro-ansa-spiro phosphazene **6**. The molecular structure of compound **9** was determined by X-ray diffraction: it shows the novel spiro-bino-spiro phosphazene architecture.

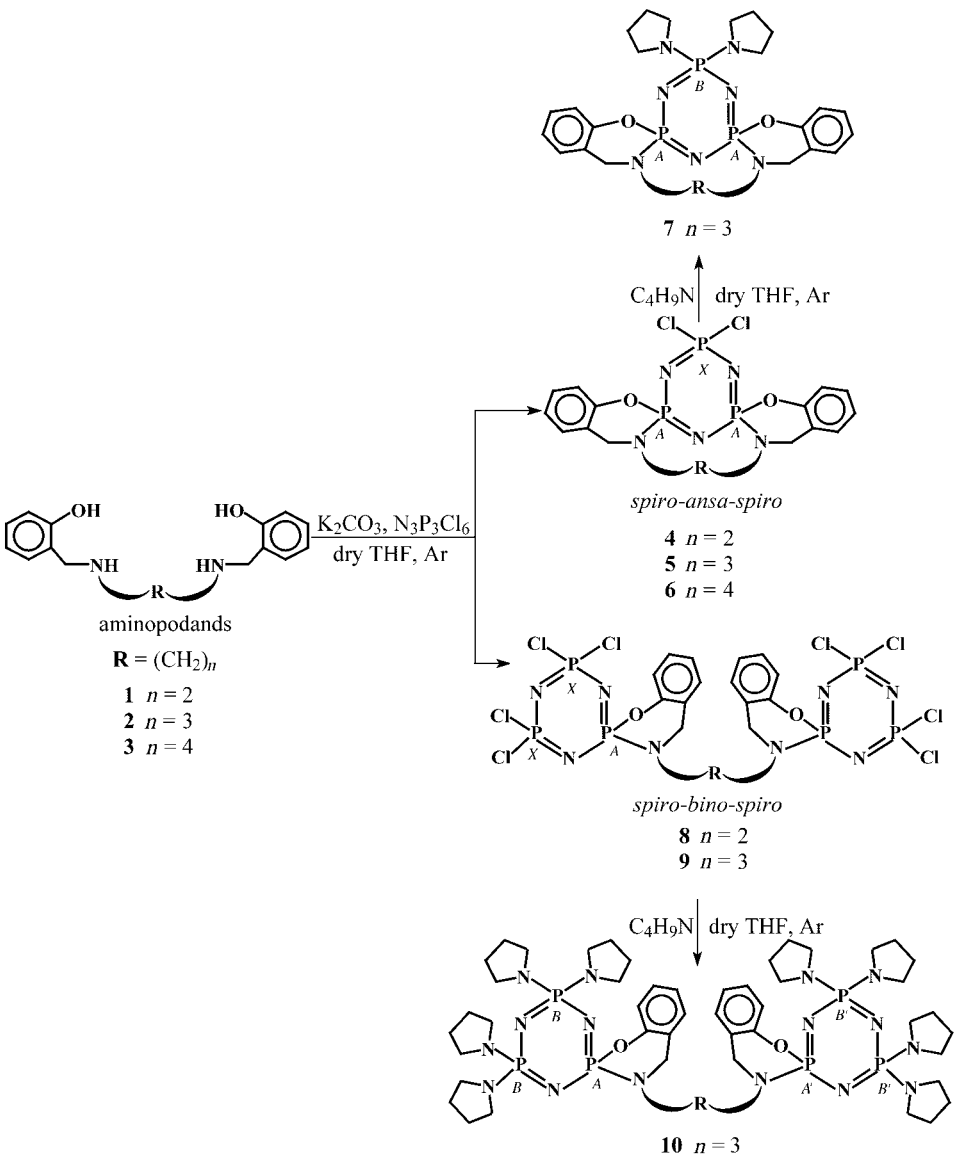
Introduction. – Cyclophosphazene derivatives and polyorganophosphazenes are in the borderline between inorganic, organic, and high polymer chemistry [2–4]. Numerous reactions of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, with primary and secondary amines [5–11], diamines [12–14], polyamines, *e.g.*, spermidine (a triamine) and spermine (a tetramine) [12][15–19], aryl oxides [20–27], hydroxylamines [28], and oligoethylene glycols [29][30] have been investigated and reviewed over the years [9–11][17][31–33]. There are four possible routes known for the reactions of $N_3P_3Cl_6$ with diamines and diols; *i*) replacement of two geminal Cl-atoms to give a spiro architecture, *ii*) replacement of two non-geminal Cl-atoms to give an ansa architecture, *iii*) intermolecular reactions between Cl-atoms of phosphazene rings to yield a bino architecture, or *iv*) intermolecular condensation reactions to yield cyclolinear or cyclomatrix polymers [34][35]. The interesting PNP-pivot lariat ethers have also been synthesized, and some of them are complexation agents for alkali, alkaline-earth, and transition-metal cations [36–42]. The reactions of $N_3P_3Cl_6$ with spermidine and spermine led to the formation of spiro, spiro-bino, and spiro-ansa derivatives [12][15][18][19]. Several structures of these types of architectures have been confirmed by X-ray crystallography [12][19][37][41][43]. The reactions of $N_3P_3Cl_6$ with N_xO_y-donor-type aminopodands (x, $y = 2, 3, \ldots$) such as compounds **1**–**3** have not yet been reported.

In this study, the reactions of $N_3P_3Cl_6$ with N_2O_2-donor-type aminopodands (tetradentate ligands) **1**–**3** leading to the novel spirocyclic phosphazene derivatives **4**–

[1]) Part VIII; for Part VII, see [1].

6, **8**, and **9** are described (*Scheme*). Compounds **7** and **10** were synthesized from the reaction of **5** and **9** respectively, with an excess of pyrrolidine. Compounds **4**–**7** and **8**–**10** are the first examples of spiro-ansa-spiro and spiro-bino-spiro phosphazene derivatives, respectively. The reactions of aminopodands **1** and **2** with $N_3P_3Cl_6$ in dry THF afford both spiro-ansa-spiro (**4** and **5**) and spiro-bino-spiro (**8** and **9**) architectures ($R=(CH_2)_2$, $(CH_2)_3$)). In contrast, only spiro-ansa-spiro compound **6** was obtained,

Scheme



when **3** was used for the same reaction (R=$(CH_2)_4$). The structures of all compounds **1**–**10** were determined by elemental analyses, ^{1}H-, ^{13}C-, and ^{31}P-NMR, HETCOR, FT-IR, and MS data. In addition, the molecular structure of spiro-bino-spiro phosphazene **9** was established by X-ray diffraction.

Results and Discussion. – *Synthesis.* All aminopodands **1**–**3** were prepared by reduction of bis-iminopodands with the $NaBH_4$/borax system [44–47]. The latter podands were formed from 2 equiv. of salicylaldehyde (=2-hydroxybenzaldehyde) and 1 equiv. of the appropriate alkanediamines in boiling MeOH for 1.5 h [48–50]. The spiro-ansa-spiro phosphazenes **4**–**6** and spiro-bino-spirophosphazenes **8** and **9** were obtained from the corresponding aminopodand and K_2CO_3 and $N_3P_3Cl_6$ in dry THF, and the pyrrolidinyl-substituted spiro-ansa-spiro- and spiro-bino-spiro phosphazenes **7** and **10** were synthesized from **5** and **9**, respectively, and an excess of pyrrolidine in dry THF. In the synthesis of **4**–**6**, **8**, and **9**, an excess of aminopodand with respect to $N_3P_3Cl_6$ (mol ratio 2:1) was used. The excess of aminopodand led to the formation of the aminopodand·HCl salt. The spiro-ansa-spiro-structure of compound **4** has previously been confirmed by crystallography and is reported elsewhere [51]. This compound is the first example of the ansa structure to have an ethane-1,2-diamine precursor. As far as we know, only spiro phosphazene derivatives have been obtained from the reaction of $N_3P_3Cl_6$ with ethane-1,2-diamine [18]. In compound **4**, the P–N bonds of the seven-membered ansa ring have '*cis*'-configuration according to the crystallographic data [51]. Analogously, compounds **5**–**7** are expected to be in the same configurations. Owing to the fact that the two P-atoms of the ansa ring (P_A) have four different substituents (*Scheme*), these P-centers are stereogenic, they have (*R*)- and (*S*)-configuration, *i.e.*, **4**–**7** are *meso* forms. Recently, several reports have been appeared concerning of stereoisomerism of phosphazene derivatives [13][19][34][40][41]. Elemental analyses and MS data (see *Exper. Part*) are in accordance with the proposed structures. The EI-MS of compounds **4**–**6** and FAB-MS of compounds **7**–**10** show the molecular-ion (M^+) and/or protonated-molecular-ion $[M+H]^+$ peaks. In the unimolecular decomposition of spiro-ansa-spiro phosphazenes **4**–**6**, the major fragmentation pathway involves initial cleavage of the C–N bonds in the N–R–N precursors, while, in the fully substituted phosphazenes **7** and **10**, the major fragmentation pathway involves the initial cleavage of an exocyclic P–N bond with the loss of pyrrolidinyl groups (C_4H_8N). In the EI-MS of the other phosphazene derivatives, protonated fragments have usually been detected [52].

IR and NMR Spectroscopy. Selected FT-IR data for compounds **1**–**10** are given in *Table 1*. The phosphazenes **4**–**10** show strong absorption bands ($\tilde{\nu}$(P=N)) at 1167–1201 cm^{-1}. The characteristic $\tilde{\nu}$(N–H) bands for aminopodands **1**–**3** at 3276, 3289, and 3287 cm^{-1}, respectively, are not present in the IR spectra of **4**–**6**, **8**, and **9**.

The ^{1}H-decoupled ^{31}P-NMR spectra of **4**–**6**, **7**, **8** and **9**, and **10** have an A_2X, A_2B, AX_2, and $AB_2A'B'_2$ spin system, respectively (*Table 2*). All ^{1}H- and ^{13}C-NMR data (*Tables 3* and *4*) are consistent with the structures.

Compounds **4**–**7** show a typical five-line resonance pattern consisting of a *d* and a *t* that are assigned to the two P_A atoms in the spiro-ansa-spiro ring and one P-atom (P_X for **4**–**6**; P_B for **7**), respectively. The $\delta(P_A)$ signal of **7** is downfield-shifted by 4.73 ppm with respect to $\delta(P_A)$ of **5**, while the signal of the dipyrrolidinyl-substituted

Table 1. *Selected FT-IR Absorptions* (KBr) *of* **1**–**10**. $\tilde{\nu}$ in cm^{-1}.

	$\tilde{\nu}$(P=N)	$\tilde{\nu}$(P–Cl)	$\tilde{\nu}$(O–H)	$\tilde{\nu}$(N–H)	$\tilde{\nu}$(C=C)	$\tilde{\nu}$(C–H(aliph.))	$\tilde{\nu}$(C–H (arom.))	
1	–	–	[a])	3276	1591	2912–2861	3058	
2	–	–	[a])	3289	1597	2930–2826	3031	
3	–	–	[a])	3287	1597	2932–2817	3037	
4	1167	546	–	–	1583	2936–2857	3065	
5	1182	583	–	–	1589	2959–2851	3050	
6	1170	550	–	–	1585	2952–2851	3067–3031	
7	1192	–	–	–	1587	2969–2826	3075–3044	
8	1186	575	–	–	1585	2963–2851	3058, 3025	
9	1174	595	–	–	1585	2951–2848	3078–3030	
10	1201	–	3481, 3437	–	1587	2963–2837	3055	

[a]) Not observed due to the zwitterion structure.

Table 2. *^{31}P-NMR Data* ($CDCl_3$) *of* **4**–**10**. δ in ppm, J in Hz.

	Spin system	$\delta(P_A)$	$\delta(P_B)$	$\delta(P_X)$	^2J(P,P)
4	A_2X	19.59		29.35	70.1
5		15.95	–	32.28	69.4
6		15.83		32.28	69.4
7	A_2B	20.68	23.42	–	55.7
8	AX_2	6.56		25.10	56.1
9		6.78		25.09	55.7
10	$AB_2A'B'_2$	18.89	20.38	–	44.6
		18.92	20.39	–	47.0

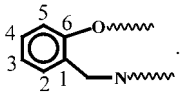
Table 3. *^{1}H-NMR Data* ($CDCl_3$) *of* **1**–**10**. δ in ppm, J in Hz.

	CH_2CH_2N	CH_2N	$ArCH_2N$	arom. H
1	–	2.71 (*s*, 4 H)	3.76 (*s*, 4 H)	6.74–6.94 (8 H)
2	1.81 (*m*, ^3J(H,H) = 7.0, 2 H)	2.77 (*t*, ^3J(H,H) = 7.0, 4 H)	4.02 (*s*, 4 H)	6.78–7.28 (8 H)
3	1.79 (*t*, ^3J(H,H) = 7.0, 4 H)	2.76 (*t*, ^3J(H,H) = 7.0, 4 H)	4.00 (*s*, 4 H)	6.76–7.27 (8 H)
4	–	3.30 (2*m*, 3.54, each 2 H)	3.94 (*m*, ^3J(P,H) = 15.0, 2 H), 4.56 (*m*, ^3J(P,H) = 15.1, 2 H)	7.08–7.29 (8 H)
5	1.88, 2.02 (2*m*, each 1 H)	3.41 (*m*, 4 H)	4.26 (*m*, 4 H)	6.98–7.28 (8 H)
6	2.18 (*m*, 4 H)	3.38 (*m*, 4 H)	4.27 (*m*, 4 H)	7.04–7.29 (8 H)
7[a])	1.83–1.89 (*m*, 8 H(pyrr.)), 1.91 (*m*, 2 H(ansa))	3.24–3.37 (*m*, 8 H(pyrr.)), 3.49 (*m*, 4 H(ansa))	4.15, 4.29 (2*m*, each 2 H)	6.94–7.17 (8 H)
8	–	3.34 (*d*, ^3J(P,H) = 14.0, 4 H)	4.38 (*d*, ^3J(P,H) = 15.5, 4 H)	6.90–7.30 (8 H)
9	2.02 (*m*, ^3J(P,H) = 7.1, 2 H)	3.17 (*m*, ^3J(P,H) = 12.4, ^3J(H,H) = 7.1, 4 H)	4.28 (*d*, ^3J(P,H) = 15.6, 4 H)	7.00–7.31 (8 H)
10[b])	1.74–1.80 (*m*, 32 H(pyrr.)), 1.88 (*m*, 2 H(bino))	3.02–3.16 (*m*, 32 H(pyrr.)), 3.25 (*m*, 4 H(bino))	4.21 (*m*, ^3J(P,H) = 14.1, 4 H)	6.85–7.14 (8 H)

[a]) ansa = $PNCH_2CH_2CH_2NP$ for **7**. [b]) bino = $PNCH_2CH_2CH_2NP$ for **10**.

Table 4. *^{13}C-NMR Data* (decoupled $CDCl_3$) *of* **1**–**10**. δ in ppm, J in Hz.

	CH_2CH_2N	CH_2N	ArCH_2N	C(1)[a])	C(2)[a])	C(3)[a])	C(4)[a])	C(5)[a])	C(6)[a])
1	–	46.8	53.0	118.5	125.2	122.6	128.7	116.7	158.4
2	30.1	46.7	53.2	118.5	125.2	122.7	128.8	116.8	158.5
3	30.1	46.7	53.1	118.5	125.1	122.8	128.7	116.8	158.8
4	–	52.0	53.7	124.1 (^3J(P,C) = 8.3)	129.4	124.5	127.0	119.6 (^3J(P,C) = 9.2)	150.5 (^2J(P,C) = 6.2)
5	26.8	49.1	50.2	123.7 (t, ^3J(P,C) = 7.8)	129.2	124.2	127.0	119.3 (t, ^3J(P,C) = 9.1)	150.9 (t, ^2J(P,C) = 6.2)
6	26.8	49.1	50.2	123.7 (t, ^3J(P,C) = 8.4)	129.2	124.1	127.0	119.4 (t, ^3J(P,C) = 9.2)	150.8 (t, ^2J(P,C) = 6.2)
7	26.8 (^3J(P,C) = 9.3, pyrr.) ansa[b])	46.6, 46.8 (pyrr.) 49.0 (ansa)	49.7	123.1	128.6	123.9	126.9	119.3 (t, ^3J(P,C) = 9.2)	151.7
8	–	47.3 (^2J(P,C) = 3.1)	50.2 (^2J(P,C) = 1.8)	124.5 (^3J(P,C) = 7.0)	129.5	124.9	127.0	119.0 (^3J(P,C) = 8.2)	150.2 (^2J(P,C) = 8.4)
9	26.4	46.0 (^2J(P,C) = 3.7)	48.9	123.8 (^3J(P,C) = 7.5)	129.5	124.8	127.0	119.1 (^3J(P,C) = 8.3)	150.2 (^2J(P,C) = 8.0)
10	26.8 (^3J(P,C) = 9.0, pyrr.) 28.3 (bino)	46.4, 46.6 (pyrr.) 47.1 (bino)	49.4	124.5 (^3J(P,C) = 8.4)	128.2	122.5	127.0	118.9 (^3J(P,C) = 7.3)	152.6 (^2J(P,C) = 7.2)

[a]) Arbitrary numbering: 

. [b]) Overlapped by pyrrolidine peaks.

P_B atom of **7** is upfield-shifted by 8.86 ppm with respect to the corresponding P_X atom of **5**, probably due to the lone electron pairs of the pyrrolidine N-atoms releasing to the P_B atom. The ^{31}P-NMR spectra of **8** and **9** consist of a *t* and a *d*, which are assigned to the two spiro atoms P_A and the four P_X atoms, respectively. The ^{31}P-NMR signals of **8** and **9** are upfield-shifted as compared to those of **4**–**6**. All the values of the two-bond coupling constants, ^2J(P,P) are between *ca.* 45 and 70 Hz (*Table 2*). Generally, the ^2J(P,P) values of the spiro-bino-spiro phosphazenes are smaller than those of the spiro-ansa-spiro phosphazenes. Consequently, according to the signal patterns (δ(P) and ^2J(P,P) in the ^{1}H-decoupled ^{31}P-NMR spectra of **4**–**10**, it can be easily deduced whether the phosphazenes obtained from aminopodands **1**–**3** and $N_3P_3Cl_6$ have the spiro-ansa-spiro or spiro-bino-spiro architecture (*Fig. 1*). The ^{31}P-NMR data have been reviewed for some spiro-, ansa-, and bino-phosphazene derivatives which have been obtained from the reaction of polyamines with $N_3P_3Cl_6$ [53].

The C*H*$_2$CH$_2$N and C*H*$_2$N protons of **1**–**10** give ^{1}H-NMR signals in the range δ(H) 1.74–2.18 and 2.71–3.54, respectively. The spectra of **7** and **10** indicate that all of the Cl-atoms of **5** and **9** are substituted by pyrrolidinyl residues. On the other hand, in the fully substituted pyrrolidinyl derivatives **7** and **10**, the C*H*$_2$CH$_2$N and CH$_2$N signals of the pyrrolidine rings are easily distinguished from those of the ansa- and bino rings in the HETCOR spectra (*Table 3*). The values of the three-bond coupling constants ^3J(P,H), for the CH$_2$N protons of **8** and **9** are 14.0 and 12.4 Hz. The protons of the benzylic moieties ArC*H*$_2$N, give rise to *m* for **4**–**7** and to *d* for **8**–**10**, probably due to the higher flexibility of the spiro-bino-spiro phosphazenes.

In the ^{13}C-NMR spectra of **2**, **3**, **5**–**7**, **9**, and **10**, all *C*H$_2$CH$_2$N signals are observed between δ(C) 26.4 and 30.1 (*Table 4*). The *C*H$_2$CH$_2$N and CH$_2$N signals of the ansa ring of **7** and bino ring of **10**, which are confirmed by HETCOR experiments, are distinguished from the *C*H$_2$CH$_2$N and CH$_2$N signals of the pyrrolidine rings, except for the ansa *C*H$_2$CH$_2$N signal of **7**. HETCOR Experiments with **7** and **10** are very useful for the assignments of the chemical shifts of all the *C*H$_2$CH$_2$N. The values of the three-bond coupling constants ^3J(P,C) are 9.3 Hz for **7** and 9.0 Hz for **10**, and they are in accordance with the corresponding reported values for pyrrolidinyl-substituted phosphazenes [54]. For CH$_2$N, the values of the two-bond coupling constants ^2J(P,C), are estimated at 3.1 and 3.7 Hz for **8** and **9**. In the spirocyclic phosphazenes **4**–**10**, expected couplings between aromatic C-atoms and P-atoms are observed for C(1), C(5) and C(6), except for C(1) and C(6) of **7** (arbitrary numbering, see *Table 4*). These couplings (^3J(P,C(1), ^3J(P,C(5)), and ^2J(P,C(6)) give rise to as *d* in the case of

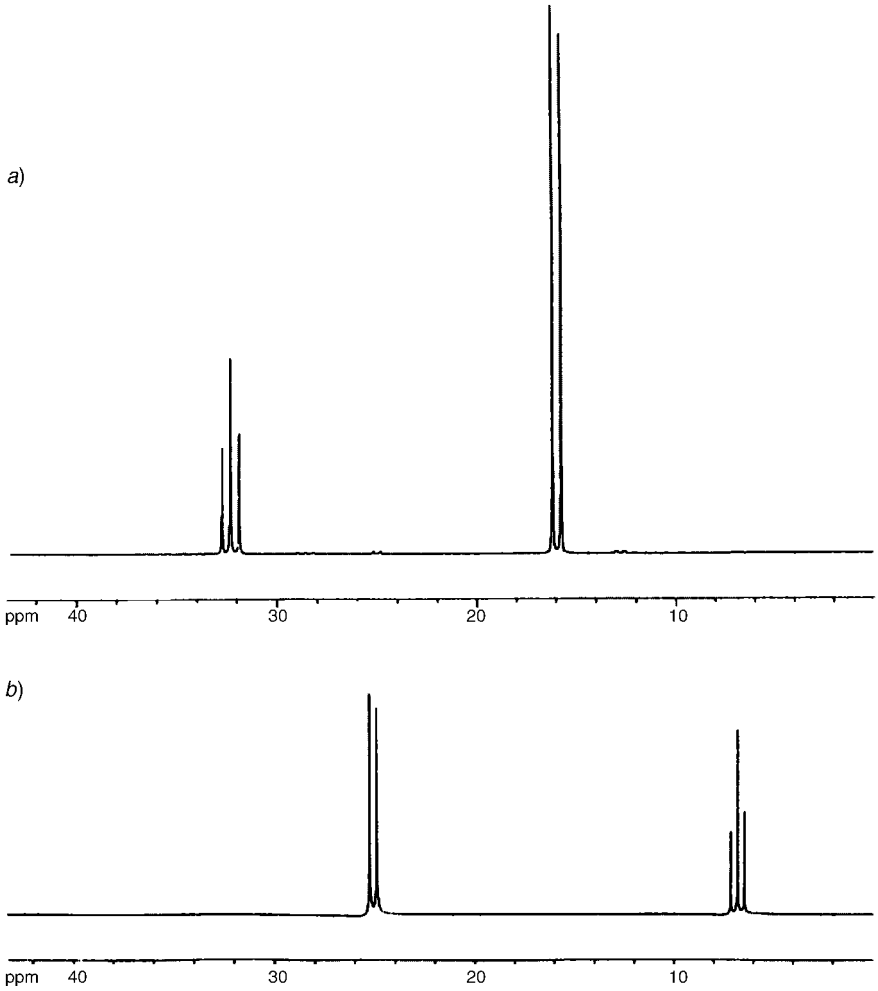


Fig. 1. ^{31}*P-NMR Spectra of* a) *compound* **5** *and* b) *compound* **9**

8–**10** and to *t*s in the case of **4**–**7**. The *t* observed for spiro-ansa-spiro phosphazenes may be due to the second-order effects, which have previously been observed [55][56]. A useful paper has appeared on this subject [57], which allows to estimate the *J*(P,C) coupling constants between the external transitions of the *t*.

Crystal-Structure Analysis. The crystal structure of compound **9** was established by X-ray crystallography[2]). The molecular structure with the atom numbering is shown in *Fig. 2*, and the experimental details are given in *Table 5*. As can be seen from the packing diagram (*Fig. 3*), the molecules are elongated approximately parallel to the

[2]) Supplementary crystallographic data have been deposited with the *Cambridge Crystallographic Data Centre* (CCDC deposition number 237641). These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 EZ, UK; fax: +44(1223)336033; e-mail: deposit@ccdc.cam.ac.uk).

Table 5. *Crystallographic Data of Compound* **9**

Crystallized from	CH_2Cl_2/heptane 1 : 1	Linear absorption coefficient [mm^{-1}]	1.014
Empirical formula	$C_{17}H_{18}Cl_8N_8O_2P_6$	Transmission factors (min; max)	0.745; 0.816
M_r	835.81	Scan type	*w*
Crystal color, habit	colorless, rod-shaped	$2\theta_{max}$ [°]	52.6
Crystal dimensions [mm]	$0.20 \times 0.25 \times 0.40$	Total reflections measured	6558
Temp. [K]	293	Symmetry-independent reflections	6525
Crystal system	monoclinic	Reflections with $I > 2\sigma(I)$	3964
Space group	$P2_1/c$	Reflections used in refinement	6325
Z	4	Parameters refined; restrains	370
Reflections for cell determination	25	Final $R(F_2)$ ($I > 2\sigma(I)$ reflections)	0.0570
2θ Range for cell determination [°]	11–22	$WR(F)$ (all data)	0.1558
Unit-cell parameters *a* [Å]	15.692(2)	Weighting parameters (a; b)[a]	0.0797; 2.1953
b [Å]	9.282(1)	Goodness-of-fit	1.010
c [Å]	22.649(2)	Secondary extinction coefficient	–
β [°]	96.04(1)	Final Δ_{max}/σ	0.000
V [Å^3]	3280.7(6)	$\Delta\rho$(max; min) [e Å^{-3}]	0.606; −0.532
D_x [g cm^{-3}]	1.692		

[a]) $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = (F_o^2 + 2F_c^2)/3$

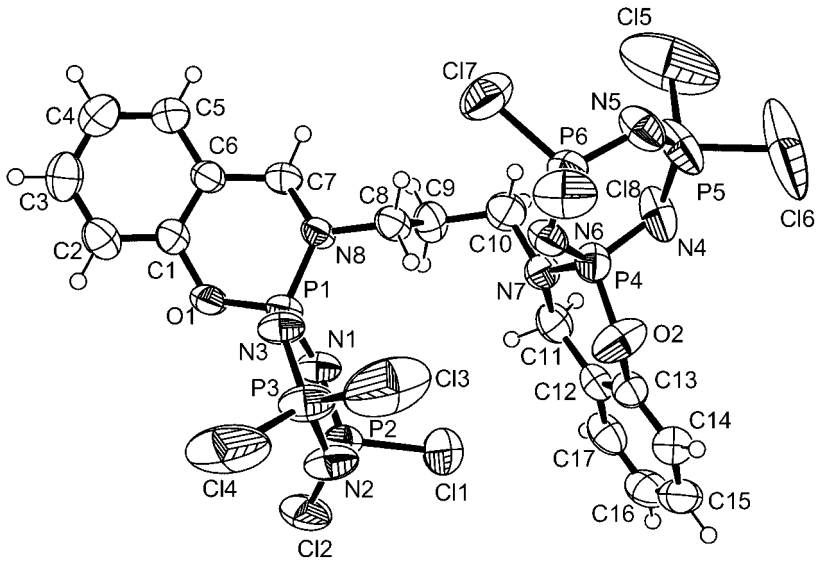


Fig. 2. *ORTEP-3 Drawing of compound* **9**. Arbitrary atom numbering. Displacement ellipsoids are drawn at the 50% probability level.

(101) plane when viewed down the *b*-axis. Dipole-dipole and *Van der Waals* interactions are also effective in the molecular packing.

The X-ray structure analysis shows that compound **9** has a spiro-bino-spiro architecture. The two phosphazene rings A(P(1)–N(1)–P(2)–N(2)–P(3)–N(3)) and B(P(4)–N(4)–P(5)–N(5)–P(6)–N(6)) and the two spirocyclic six-membered

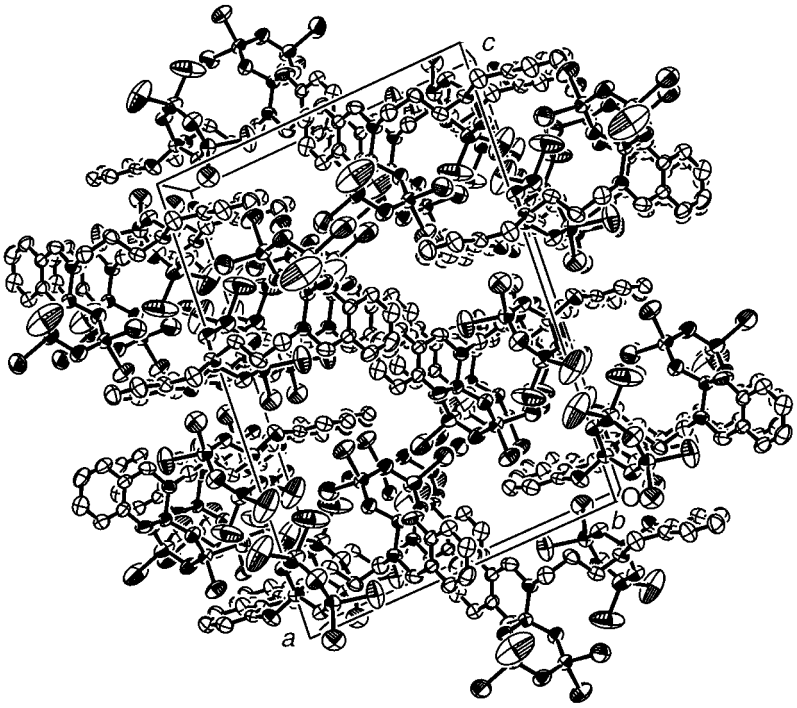


Fig. 3. *Packing diagram for* **9**, *viewed down the* b-*axis*

rings C(C(1)–O(1)–P(1)–N(8)–C(7)–C(6)) and D(C(13)–O(2)–P(4)–N(7)–C(11)–C(12)) are not planar, the *Cremer* and *Pople* [58] total puckering amplitudes being 0.150(3), 0.117(3), 1.560(4), and 0.529(4) Å, respectively. The dihedral angles between A, B, C, D, E(C(1)–C(6)), and F(C(12)–C(17)) are A/C 86.2(1), C/E 19.8(2), B/D 88.5(1), and D/F 8.0(2)°. The P–N–P bond angles range from 118.1(4) to 123.7(3)°. In addition, the variation in the endocyclic N–P–N bond angles ranging from 113.9(3) to 119.8(3)° is large. The exocyclic Cl–P–Cl angles are between 99.3(1)–102.8(2)°, and the values of the endocyclic angles N(1)–P(1)–N(3) (113.9(3)°) and N(4)–P(4)–N(6) (114.4(3)°) are decreased due to the variations in the electron supply and the conformations of the six-membered rings (C and D) with respect to the values in the standard $N_3P_3Cl_6$ compound (N–P–N 118.3(2)° and Cl–P–Cl 101.2(1)°) [59]. It has been found that, in trimeric phosphazenes, the endocyclic N–P–N angles about the P-atoms decrease, while the exocyclic R(1)–P–R(2) angles increase [20][60–62], which is different for those angles found in tetrameric phosphazenes containing bulky phenoxy groups [24][63][64]. In compound **9**, the N(1)–P(1)–N(3) and N(4)–P(4)–N(6) angles are nearly the same, and the exocyclic O(1)–P(1)–N(8) (102.5(3)°) and O(2)–P(4)–N(7) (103.8(3)°) angles are smaller than the corresponding ones in $N_3P_3Cl_5(NPPh_3)$ (114.4(1) and 107.2(1)°) [60], $N_3P_3Cl_4Ph(PPh_2)$ (114.5(2) and 106.7(1)°) [65], and $Cl_5N_3P_3(OC_6H_2$-2,6-^{t}Bu$_2$-4-Me) (115.8(1) and 104.5(6)°) [20], which implies increased electron donation

to the N_3P_3 ring. In contrast to the trimeric phosphazenes, in compound **9**, while the endocyclic N(1)–P(1)–N(3) and N(4)–P(4)–N(6) angles decrease, the exocyclic O(1)–P(1)–N(8) and O(2)–P(4)–N(7) angles remain nearly the same with respect to the values in the standard compound $N_3P_3Cl_6$ [59], possibly due to the conformations of rings C and D. The six-membered ring C has a boat conformation with the parameter $\theta = 91.5\ (7)^\circ$ [58] ($\theta = 0^\circ$ for a perfect chair and 90° for a perfect boat conformation. On the other hand, ring D has an irregular conformation with the parameter $\theta = 134.0(1.4)^\circ$. In the phosphazene rings A and B, the P–N bond distances are in the range 1.554(6)–1.594(5) Å (average 1.575(6) Å). The corresponding mean bond lengths are 1.576(3) Å in $Cl_4N_3P_3[(OC_6H_3)(NO)_2)CH_2(OC_6H_3)(NO)_2]$ [66], 1.573(3) Å in $Cl_5N_3P_3(OC_6H_2$-2,6-^{t}Bu$_2$-4-Me) [67], 1.58(1) Å in $Cl_5N_3P_3(OC_6H_2$-2,4,6-^{t}Bu$_3$) [20], 1.576(5) Å in $Cl_5N_3P_3$-$P_3N_3Cl_4(OC_6H_3$-2,6-^{t}Bu$_2$) [62], 1.572(3) Å in $N_3P_3Cl_4Ph(PPh_2)$ [65], and 1.581(3) Å in $N_3P_3Cl_6$ [59]. These values for P–N bonds are considerably smaller than the P–N single-bond length of 1.683(5) Å [68]. The short bonds in the rings have appreciable double-bond character; this is generally observed for phosphazene derivatives [69].

Conclusions. – Substitution of the Cl-atoms of $N_3P_3Cl_6$ by the N_2O_2-donor-type tetradentate aminopodands **1**–**3** afforded two kinds of phosphazene derivatives, namely spiro-ansa-spiro and spiro-bino-spiro phosphazenes **4**–**7** and **8**–**10**, respectively (*Scheme*). These compounds are the first examples with these architectures. It can easily be deduced whether the phosphazenes may have the spiro-ansa-spiro or spiro-bino-spiro architectures from the signal patterns of the proton decoupled ^{31}P-NMR spectra (*Fig. 1*). Compounds **7** and **10** are thought to be strong phosphazene bases and ligands for transition-metal cations. It was found that the phosphazene rings of **9** are not planar, in contrast to expectations.

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Experimental Part

General. Compounds **1**–**3** were synthesized according to [50]. CC = column chromatography. Melting point: *Gallenkamp* apparatus, capillary tube. ^{1}H-, ^{13}C-, and ^{31}P-NMR and HETCOR Spectra: *Bruker DPX-FT-NMR* (400 MHz) spectrometer; in $CDCl_3$ with $SiMe_4$ as internal standard and 85% H_3PO_4 soln. as external standard; δ in ppm, J in Hz. IR Spectra: KBr discs; *Mattson 1000-FTIR* spectrometer; in cm^{-1}. EI- and FAB-MS: *Platform-II-LC-MS* and *VG-Zapspec* spectrometers, resp.; in m/z (rel. %). Elemental analyses: *Leco-CHNS-932* analyzer.

2,2′-[Ethane-1,2-diylbis(iminomethylene)]bis[phenol] (**1**). M.p. 101°. Anal. calc. for $C_{16}H_{20}N_2O_2$: C 70.56, H 7.40, N 10.29; found: C 71.01, H 6.97, N 10.37.

2,2′-[Propane-1,3-diylbis(iminomethylene)]bis[phenol] (**2**). M.p. 107°. Anal. calc. for $C_{17}H_{22}N_2O_2$: C 71.30, H 7.74, N 9.78; found: C 71.33, H 7.88, N 10.03.

2,2′-[Butane-1,4-diylbis(iminomethylene)]bis[phenol] (**3**). M.p. 105°. Anal. calc. for $C_{18}H_{24}N_2O_2$: C 71.96, H 8.05, N 9.33; found: C 72.01, H 8.00, N 9.33.

*8,8-Dichloro-18,19-dihydro-6λ^5,8λ^5,10λ^5-6,10-nitrilo-16*H,*21*H-*[1,3,5,7,2,4,6]tetrazatriphosphonino[2,1-*b:*6,7-*b′*]bis[1,3,2]benzoxazaphosphorine* (**4**) *and 3,3″-Ethane-1,2-diylbis[4′,4′,6′,6′-tetrachloro-3,4-dihydrospiro[1,3,2-benzoxazaphosphorine-2,2′λ^5-[4λ^5,6λ^5][1,3,5,2,4,6]-triazatriphosphorine]]* (**8**). K_2CO_3 (3.00 g, 22.0 mmol) was added to a stirred soln. of **1** (3.00 g, 11.0 mmol) in dry THF (200 ml). The mixture was

refluxed for 2 h and then cooled. A soln. of $N_3P_3Cl_6$ (1.90 g, 5.50 mmol) in dry THF (100 ml) was added dropwise to the stirred mixture at $-10°$ within 1 h. After the mixture had been allowed to reach r.t., stirring was continued for 23 h, with Ar being passed over the mixture. The precipitated amine hydrochloride and excess of K_2CO_3 were filtered off, and the solvent was evaporated. The residue was dissolved in CH_2Cl_2/benzene 5:1 (50 ml) and subjected to CC (silica gel (30 g), CH_2Cl_2/benzene 5:1): **8** and **4**.

Data of **8**: R_f (CH_2Cl_2/benzene 5:1) 0.69. Crystallization from THF/benzene 1:1 gave 0.9 g (40%). M.p. 230°. FAB-MS (fragments based on ^{35}Cl): 819 (7, $[M+H]^+$). Anal. calc. for $C_{16}H_{16}Cl_8N_8O_2P_6$: C 23.38, H 1.96, N 13.63; found: C 23.25, H 1.98, N 13.40.

Data of **4**: R_f (CH_2Cl_2/benzene 5:1) 0.3. Crystallization from CH_2Cl_2/heptane 4:1 gave 0.55 g (21%). M.p. 280°. EI-MS (fragments based on ^{35}Cl): 473 (4, M^+), 474 (3, $[M+H]^+$), 446 (5, $[N_3P_3Cl_2(C_{14}H_{12}N_2O_2)+H]^+$). Anal. calc. for $C_{16}H_{16}Cl_2N5O_2P_3$: C 40.53, H 3.40, N 14.77; found: C 40.25, H 3.58, N 14.82.

*8,8-Dichloro-19,20-dihydro-6λ⁵,8λ⁵,10λ⁵-6,10-nitrilo-16*H,*18*H,*22*H-*[1,3,5,7,2,4,6]tetrazatriphosphecino[2,1-*b:*6,7-*b′*]bis[1,3,2]benzoxazaphosphorine* (**5**) *and 3,3″-Propane-1,3-diylbis[4′,4′,6′,6′-tetrachloro-3,4-dihydrospiro[1,3,2-benzoxazaphosphorine-2,2′λ⁵-[4λ⁵,6λ⁵][1,3,5,2,4,6]triazatriphosphorine]]* (**9**). As described for **4** and **8**, with K_2CO_3 (2.90 g, 21.0 mmol), **2** (3.00 g, 10.5 mmol), and $N_3P_3Cl_6$ (1.80 g, 5.30 mmol) (20 h). CC (silica gel: (38 g), dry benzene) gave **9** and **5**.

Data of **9**: R_f (benzene) 0.64. Crystallization from CH_2Cl_2/heptane 1:1 gave 1.00 g (43%). M.p. 164°. FAB-MS (fragments based on ^{35}Cl): 833 (43, $[M+H]^+$). Anal. calc. for $C_{17}H_{18}Cl_8N_8O_2P_6$: C 24.43, H 2.17, N 13.41; found: C 24.57, H 2.06, N 13.40.

Data of **5**: R_f (benzene) 0.33. Crystallization from CH_2Cl_2/heptane 1:1 gave 0.60 g (24%). M.p. 242°. EI-MS (fragments based on ^{35}Cl): 487 (6, M^+), 488 (4, $[M+H]^+$), 446 (2, $[N_3P_3Cl_2(C_{14}H_{12}N_2O_2)+H]^+$). Anal. calc. for $C_{17}H_{18}Cl_2N_5O_2P_3$.

*8,8-Dichloro-18,19,20,21-tetrahydro-6λ⁵,8λ⁵,10λ⁵-6,10-nitrilo-16*H,*23*H-*[1,3,5,7,2,4,6]tetraazatriphosphacycloundecino[2,1-*b:*6,7-*b′*]bis[1,3,2]benzoxazaphosphorine* (**6**). As described for **4** and **8**, with K_2CO_3 (2.80 g, 20.0 mmol), **3** (3.00 g, 10.0 mmol), and $N_3P_3Cl_6$ (1.70 g, 5.00 mmol) (24 h). CC (silica gel (35 g), dry benzene) gave **6**. R_f (benzene) 0.30. Crystallization from benzene yielded 1.40 g (56%). M.p. 189°. EI-MS (fragments based on ^{35}Cl): 501 (3, M^+), 502 (2, $[M+H]^+$), 446 (7, $[N_3P_3Cl_2(C_{14}H_{12}N_2O_2)+H]^+$). Anal. calc. for $C_{18}H_{20}Cl_2N_5O_2P_3$: C 43.05, H 4.01, N 13.95; found: C 42.85, H 3.82, N 13.94.

*19,20-Dihydro-8,8-dipyrrolidin-1-yl-6λ⁵,8λ⁵,10λ⁵-6,10-nitrilo-16*H,*18*H,*22*H-*[1,3,5,7,2,4,6]tetrazatriphosphecino[2,1-*b:*6,7-*b′*]bis[1,3,2]benzoxazaphosphorine* (**7**). A soln. of pyrrolidine (0.43 g, 6.00 mmol) in dry THF (30 ml) was slowly added to a soln. of **5** (0.50 g, 1.00 mmol) in dry THF (30 ml). The mixture was stirred for 48 h at r.t., with Ar being passed over the mixture. The precipitated amine hydrochloride was filtered off, and the solvent was evaporated. The residue was dissolved in benzene/THF 1:1 (20 ml) and then subjected to CC (silica gel (20 g), benzene/THF 1:1): **7**. R_f (benzene/THF 1:1) 0.67. Crystallization from CH_2Cl_2/heptane 1:1 gave 0.20 g (35%). M.p. 153°. FAB-MS: 557 (28, M^+), 558 (100, $[M+H]^+$), 487 (49, $[N_3P_3(C_{17}H_{18}N_2O_2)(C_4H_8N)]^+$), 418 (26, $[N_3P_3(C_{17}H_{18}N_2O_2)+H]^+$, 26). Anal. calc. for $C_{25}H_{34}N_7O_2P_3$: C 53.86, H 6.15, N 17.58; found: C 53.75, H 6.18, N 17.10.

3,3″-Propane-1,3-diylbis[3,4-dihydro-4′,4′,6′,6′-tetrapyrrolidin-1-yl(spiro[1,3,2-benzoxazaphosphorine-2,2′λ⁵-[4λ⁵,6λ⁵][1,3,5,2,4,6]triazatriphosphorine]] (**10**). As described for **7**, with **9** (0.50 g, 0.60 mmol) and pyrrolidine (1.02 g, 14.4 mmol) (54 h). CC (silica gel (20 g), benzene/THF 1:1) gave **9**. R_f (benzene/THF 1:1) 0.58. Crystallization from CH_2Cl_2/heptane 1:1 gave 0.20 g (37%). M.p. 193°. FAB-MS: 1112 (49, M^+), 1113 (100, $[M+H]^+$). Anal. calc. for $C_{49}H_{82}N_{16}O_2P_6 \cdot 2\,H_2O$: C 51.21, H 7.54, N 19.50; found: C 51.13, H 7.13, N 19.37.

X-Ray Crystal-Structure Analysis of **9**. All measurements were made on an *Enraf Nonius-CAD-4* diffractometer [70] with graphite monochromated MoK_α radiation (λ 0.71073 Å). For data collection and refinement parameters, see *Table 5*. Data reduction was performed with XCAD4 [71]. The intensities were corrected for *Lorentz* and polarization effects. Semiempirical (ψ-scan method [72]) absorption correction was applied. The structure was solved by direct methods [73], which revealed the positions of all non-H-atoms. All of the H-atoms were positioned geometrically at distances of 0.93 ($C(sp^2)$ – H) and 0.97 Å ($C(sp^3)$ – H) from the carrier atoms; a riding model was used during the refinement process. The $U_{iso}(H)$ values were constrained to be $1.2U_{eq}$ of the carrier atom. Refinement of structure [73] was carried out on F^2 by full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. For the ORTEP-3 [74] drawing and the packing diagram, see *Figs. 2* and *3*, resp.

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