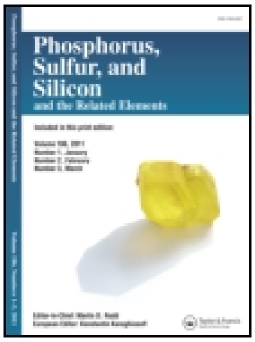

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Synthesis and characterization of spiro-, ansa-, and spiro-ansa-cyclic derivatives of cyclotetraphosphazene with the reactions of pentane-1,5-diol

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ABSTRACT

The reactions of octachlorocyclotetraphosphazatetraene, $N_4P_4Cl_8$ (**1**) with difunctional aliphatic reagent, HO-$(CH_2)_5$-OH (**3**) have aroused a good deal of attention, and four types of products have been realized: one 2-open chain-(1′-oxy-5′-hidroxy-pentane)-2,4,4,6,6,8,8-heptachlorocylotetraphosphazatetraene, $N_4P_4Cl_7[O(CH_2)_5OH]$ (**4**); one 2,2-mono-spiro-(1′,5′-pentanedioxy)-4,4,6,6,8,8-hexachlorocyclotetraphosphazatetraene, $N_4P_4Cl_6[O(CH_2)_5O]$ (**5**); its isomers 2,4-mono-ansa-((1′,5′-pentanedioxy)-2,4,6,6,8,8-hexachlorocyclotetraphosphazatetraene (**6**) and 2,6-mono-ansa-(1′,5′-pentanedioxy)-2,4,6,6,8,8-hexachlorocyclotetraphosphazatetraene (**7**); one 2,2,6,6-dispiro-(1′,5′-pentanedioxy)-4,4,8,8-tetrachlorocyclotetraphosphazatetraene, $N_4P_4Cl_4[O(CH_2)_5O]_2$ (**8**); two isomeric 2,4,6,8-bisansa-(1′,5′-pentanedioxy)-2,4,6,8-tetrachlorocyclotetraphosphazatetraene (**9**) and 2,6,4,8-bisansa-(1′,5′-pentanedioxy)-2,4,6,8-tetrachlorocyclotetraphosphazatetraene (**10**); one 4,4,8,8-dispiro-2,6-ansa- (1′,5′-pentanedioxy)-2,6-dichlorocyclotetraphosphazatetraene, $N_4P_4Cl_2[O(CH_2)_5O]_3$ (**11**), one 2,2,4,4,6,6-trispiro-(1′,5′-pentanedioxy)-8,8-dichlorocyclotetraphosphazatetraene, $N_4P_4Cl_2[O(CH_2)_5O]_3$ (**12**); and a 2,2,4,4,6,6,8,8-tetraspiro-(1′,5′-pentanedioxy)-cyclotetraphosphazatetraene derivative, $N_4P_4[O(CH_2)_5O]_4$, (**13**). The respective structures were deduced by means of elemental analysis, mass spectrum, and ^{31}P, ^{1}H, and ^{13}C *nuclear magnetic resonance* spectroscopic investigations.

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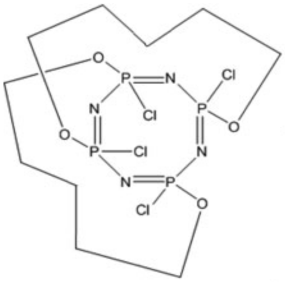
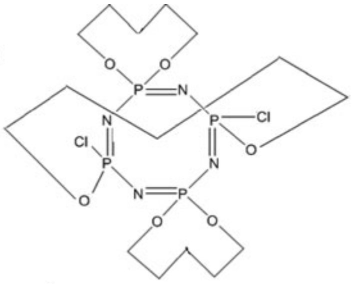
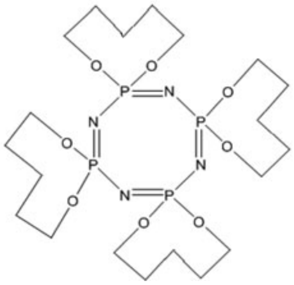
GRAPHICAL ABSTRACT







Introduction

The reactions of six- and eight-membered cyclophosphozene ring systems, $N_3P_3Cl_6$ (**2**) and $N_4P_4Cl_8$ (**1**), with difunctional reagents have been of significant interest, particularly from the perspective of observing regioisomerism in nucleophilic substitution reactions as well as the formation of spiro, ansa, and bridged derivatives and their mixtures.[1–3,5–8,18,39,49]

The octachlorocyclophosphazene (**1**) is more reactive than hexachlorocyclophosphazene (**2**); the former can also, in principle, give rise to a much larger number of products, and hence structure determination is more difficult.[1–54] In contrast to the reactions of cyclophosphazenes $(NPX_2)_3$ ($X = Cl$ or F) with monofunctional reagents, reactions with difunctional reagents generally proceed pairwise and can lead to “spiro,”

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"ansa," or "intermolecular" condensation products in which the phosphazene ring is retained.[1a–c,18b,44,46b,g] Since the relatively larger ring flexibility coupled with the larger number of replaceable chlorines makes the reaction of octachlorocyclotetraphosphazene, $N_4P_4Cl_8$ (**1**), more complex than that of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ (**2**), the treatment of the former with difunctional reagents can lead to a more diverse range of products.[19,44,46c,53,54] For example, the reactions of *tert*-butylamine with (**2**) actually gives geminal 2,2-N_3P_3(NH-*t*-Bu)$_2Cl_4$ at the bis stage of substitution,[51] while the analogous reaction with (**1**) gives the non-geminal 2,4- and 2,6-N_4P_4(NH-*t*-Bu)$_2Cl_6$,[4b,15] and hence it may be expected that the formation of an "ansa" product would be more favored in the reactions of difunctional reagents with (**1**) than with (**2**). Due to the reactivity of octachloride (**1**), it can also be nodded that different type of spiro-ansa, cross-linked products (1,5-ansa, cis-, and *trans*-bis-ansa) and tetrakis-ansa derivatives are also possible at this stage of substitution.[15,40,52,54]

The reactions of octachlorocyclotetraphosphazene (**1**) with 1,3-propane- and 1,4-butane-diols[2] gave only spiro derivatives (mono, bis, tris, and tetrakis).[2] The reactions of octafluorocyclotetraphosphazenes, $N_4P_4F_8$ with the silyl derivative of 2,2,3,3 tetrafluorobutane-1,4-diol gave both mono-spiro and singly bridged products.[49]

However, reactions of octafluorocylotetraphosphazene ($N_4P_4F_8$) with tetrafluorobutane-1,4-,[41] with octafluorohexane-1,6-diols,[40] and with the present studies in different molar ratios gave mixtures of regioisomers comprising compounds with spiro and/or ansa moieties, viz. mono-spiro, mono-ansa, bis-spiro, bis-ansa, tris- and tetrakis-spiro, dispiro-mono-ansa, and mono-spiro-bis-ansa derivatives.

In this paper, the synthesis and structural characterization of 10 new ansa- and spiro-cyclic cyclotetraphosphazene derivatives **4-13** are reported (Figure 1). A detailed comparative analysis of the ^{31}P, ^{1}H, and ^{13}C nuclear magnetic resonance (NMR) spectra is also discussed.

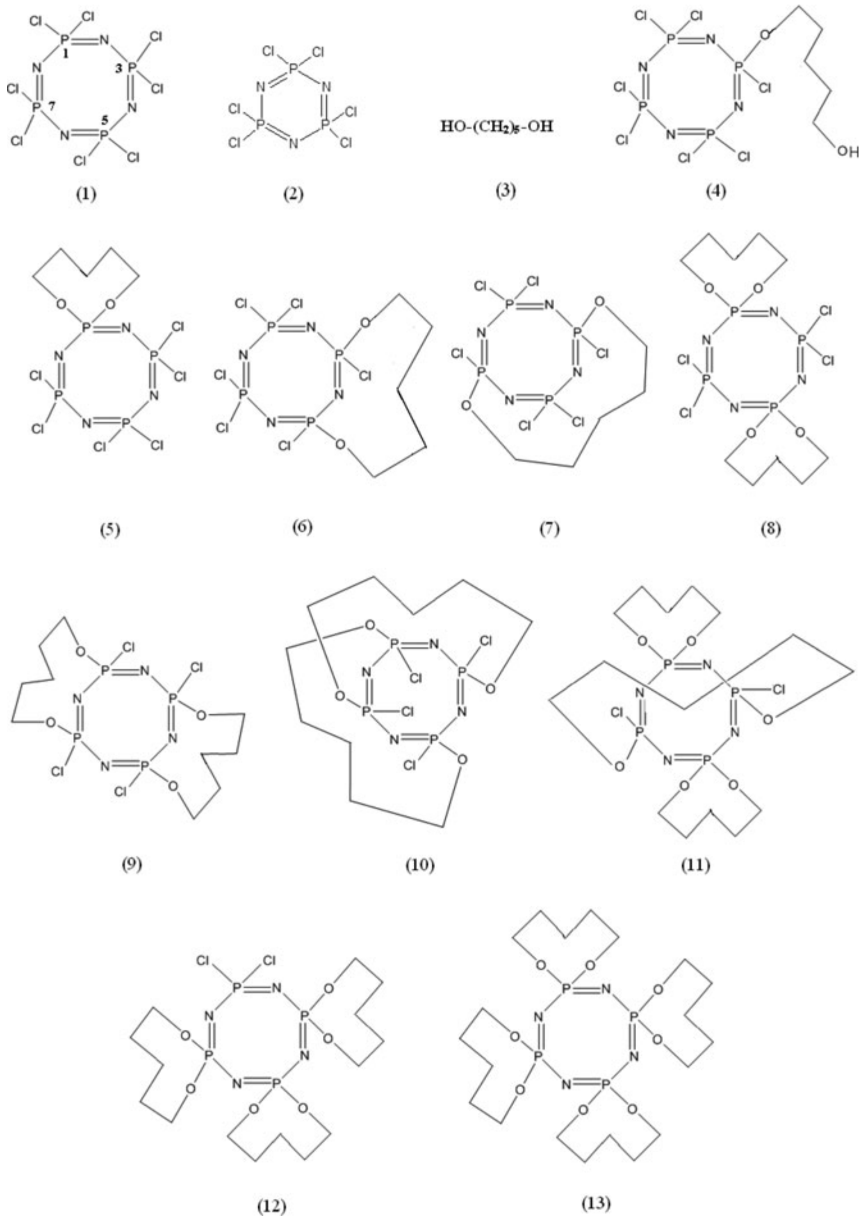

Figure 1. Structures of compounds.

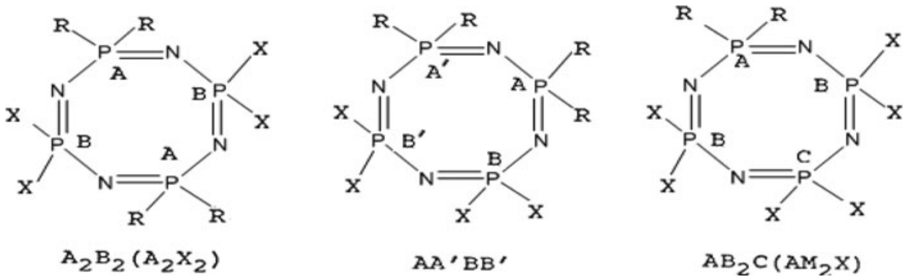

Figure 2. Replacement patterns of octachlorotetraphosphazene (**1**).

Results and discussion

From the reactions of $N_4P_4Cl_8$ (**1**) with pentane-1,5-diol, four types of products are formed: one 2-openchain-(1′-oxy-5′-hidroxy-pentane)-2,4,4,6,6,8,8-heptachlorocylotetraphosphazatetraene, $N_4P_4Cl_7[O(CH_2)_5OH]$, (**4**, 0.23 g, 7.2%); three isomeric $N_4P_4Cl_6[(O(CH_2)_5O]$; 2,2-mono-spiro-(1′,5′-pentanedioxy)-4,4,6,6,8,8-hexachlorocyclotetraphosphazatetraene, (**5**, 0.79 g, 23.2%), 2,4-mono-ansa-((1′,5′-pentanedioxy)-2,4,6,6,8,8-hexachlorocyclotetraphosphazatetraene, (**6**, 0.60 g, 18.3%) and 2,6-mono-ansa-(1′,5′-pentanedioxy)-2,4,6,6,8,8-hexachlorocyclotetraphosphazatetraene, (**7**, 0.61 g, 19.7%); three isomeric, $N_4P_4Cl_4[(OCH_2)_5O]_2$, 2,2,6,6-dispiro-(1′,5′-pentanedioxy)-4,4,8,8-tetrachlorocyclotetraphosphazatetraene, (**8**, 0.92 g, 26.9%), 2,4,6,8-bisansa-(1′,5′-pentanedioxy)-2,4,6,8-tetrachlorocyclotetraphosphazatetraene, (**9**, 1.2 g, 35.2%) and 2,6,4,8-bisansa-(1′,5′-pentanedioxy)-2,4,6,8-tetrachlorocyclotetraphosphazatetraene, (**10**, 0.81 g, 23.3%); two isomeric, $N_4P_4Cl_2[(OCH_2)_5O]_3$, 4,4,8,8-dispiro-2,6-ansa-(1′,5′-pentanedioxy)-2,6-dichlorocyclotetraphosphazatetraene, (**11**, 0.73 g, 33.7%) and 2,2,4,4,6,6-trispiro-(1′,5′-pentanedioxy)-8,8-dichlorocyclotetraphosphazatetraene, (**12**, 0.35 g, 16.2%); a 2,2,4,4,6,6,8,8-tetraspiro-(1′,5′-pentanedioxy)-cyclotetraphosphazatetraene derivative, $N_4P_4[(OCH_2)_5O]_4$, (**13**, 0.26 g, 12.3%). In general, during the purification and separation of the products, the proportional quantity of the open chain, mono-ansa, and tris-spiro derivatives decreased. This is attributed to the structural flexibility of $N_4P_4Cl_8$ (**1**) and the reactivity of P-Cl bonds (after substitution of one of the chlorine atoms, the remaining P-Cl bonds become very reactive and give multiple substituted products).[44,45,52] The percentage yields of **4-13** in 1:1, 1:2, and 1:3 mole ratios are presented in Table 5.

^{31}P NMR studies

^{31}P NMR spectra of tetramer derivatives (2) with four spins are obviously more complicated than those of the trimer (1) with only three spins. There is also a possibility that in addition to two-bond $^2J(\underline{PP})$, four-bond coupling $^4J(PP)$ might further complicate the spectra.[19,51] We did not observe any of the latter in our analysis; examples of this are, however, known.[54,28–29a,b] From the above group of compounds, A_2MX (A_2BX), AA'XX' (AA'BB'), $A_2\times_2$ (A_2B_2), and A_4 types of spectra were observed. Replacement patterns of octachloride (2) are presented in Figure 2. Selected ^{31}P NMR data for compounds 4–13 may be found in Table 1.

The proton-decoupled ^{31}P NMR spectra of compounds **4**, **5**, and **12** show an A_2BX (A_2MX)-type spin system. In these derivatives, two phosphorus nuclei would be magnetically equivalent (≡PCl_2 groups in the mono-spiro and open chain and ≡Pspiro in the tris-derivatives), while the other two phosphorus nuclei are different, and different groups of triplets were observed in the proton-decoupled ^{31}P NMR spectrum of compound **4**. The proton-coupled spectrum showed that only part of signals at low frequency collapsed as a triplet structure associated with the ≡P(OR)Cl group, whereas all other signals associated with the ≡PCl_2 groups remained unchanged. The proton-decoupled ^{31}P NMR spectrum of this compound showed that the two equivalent ≡PCl_2 groups were situated relatively at high frequency, and the two overlapping ^{31}P NMR signals at low frequency related to the remaining ≡PCl_2 group. The

Table 1. Selected ^{31}P NMR parameters of compounds **4-13**^{a}.

Compound	δ Cl_2^{a}	δ $P(OR)_2$^{a}	δ P(OR)Cl^a	$^2J(P(OR)_2\text{-}PCl_2)$^{b}	$^2J(PX_2\text{-}PX_2)$^{b}
(**1**)	−6.5				
(**4**)	−5.2 (2)^c −7.7 (1)^c		−7.9		57.2 (X_2 = Cl_2-(OR)Cl
(**5**)	−4.9 (2)^c −2.4 (1)^c		−6.0	58.4	28.7 (X_2 = Cl_2)
(**6**) 1,3-ansa	−0.9		−6.4		39.6 (X_2 = Cl_2-(OR)Cl
(**7**) 1,5-ansa	−7.3		−2.4		54.1 (X_2 = Cl_2-(OR)Cl
(**8**)	−1.8		−7.5	60.2	
(**9**)			−0.9		
(**10**)			−0.71		
(**11**)	5.1		−3.5		81.4 (X_2 = spiro-(OR)Cl
(**12**)	−0.5	5.9 (1)^c 2.6 (2)^c		55.2	90.8 (X_2 = spiro)
(**13**)		7.8			

[a] In $CDCl_3$ (referenced to external 85% H_3PO_4) at 161.83 MHz (room temperature), in ppm.
[b] In Hz.
[c] Relative number of nuclei are in parentheses.

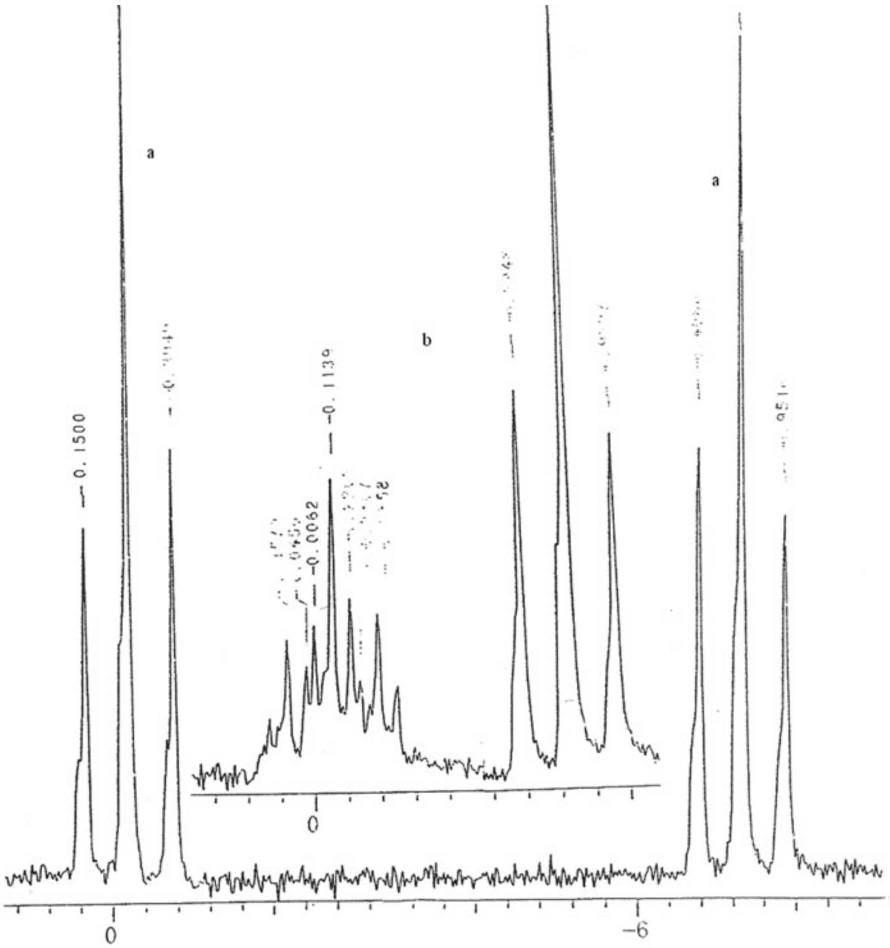

Figure 3. ^{31}P NMR spectra of compound **7**: (a) ^{31}P-^{1}H spectrum, (b) $^{31}P\{^{1}H\}$ spectrum, in $CDCl_3$ at 161.83 MHz (room temperature), referenced to external 85% H_3PO_4.

phosphorus-proton-coupled spectra help to identify the ≡Pspiro, ≡PCl2, and ≡P(OR)Cl groups by leaving ≡PCl2 groups unchanged, while ≡Pspiro and = P(OR)Cl groups exhibited further splitting.

The proton-coupled ^{31}P NMR spectrum of compounds **5** and **12** allow unambiguous assignments to ≡Pspiro and ≡PCl_2 moieties, indicating three different phosphorus environments in compound **5**, one of which corresponds to a substituted P atom (1P, at −6.0 ppm); according to the proton coupled ^{31}P NMR spectrum, the other two signals at −4.94 ppm (2P) and −2.4 ppm (1P) remained unchanged. In compound **12**, two of them correspond to two different ≡Pspiro groups (2P at 2.6 ppm and 1P at 5.9 ppm), and the other unchanged signal at −05 associated with the ≡PCl_2 group.

The proton-decoupled ^{31}P NMR spectra of compounds **7**, **8**, and **11** exhibit $A_2 \times_2$ type. The spin–spin coupling constant is readily obtained from the difference between the outer and middle transitions, and is equal in both multiplets for compound **11**. The ^{31}P NMR spectra of $A_2 \times_2$ type, viz. that of compounds **7** and **11** are presented in Figures 3 and 4. The ^{31}P NMR spectra of compound **6** exhibiting the AA'XX' (AA'BB') spin system comprises two basic multiplets, which are identical in appearance and display mirror image symmetry with respect to their frequency canters V_A and V_X and as a result of spin–spin interaction among neighboring ≡P(OR)Cl and ≡PCl_2 nuclei, which is the solid confirmation of the structure. The proton-coupled ^{31}P NMR spectrum showed 10 lined signals for each basic multiplet. The ≡PCl_2 groups were associated with the (AA') part of spectrum and resonate at −0.95 ppm, while the (XX') part collapsed with further splitting at −6.41 ppm.

The A_4-type spin systems are very simple, which give rise to a single line transition. An A_4 spin system arises when the four phosphorus nuclei of the tetramer have identical or very similar environments. Isomeric bis-ansa structures **9** and **10**, where the identical = P(OR)Cl nuclei resonate at −0.71 and −0.98 ppm, giving rise to single line transitions. The tetrakis-spiro compound **13** displays an A_4 spin system as well, resonating at 7.8 ppm. Comparison of selected ^{31}P NMR parameters of spiro and ansa derivatives of octachlorocyclotetraphosphazene (**1**) with relative diols are presented in Tables 1 and 2.

^{1}H NMR studies

The spiro (**5**) and ansa (**6**) derivatives basically would be expected to have similar ^{1}H NMR multiplets to the analogue spiro or ansa derivatives of trimer (**2**).[2,41–43] The extra phosphorus nucleus would provide a chance for more isomers to be formed at the stage of bis-spiro and ansa derivatives, which may have different ^{1}H NMR spectra depending on the position of the second spiro group. In this system, the methylene protons occur in three different chemical environments depending on where they are situated: α-, β-, or γ-.

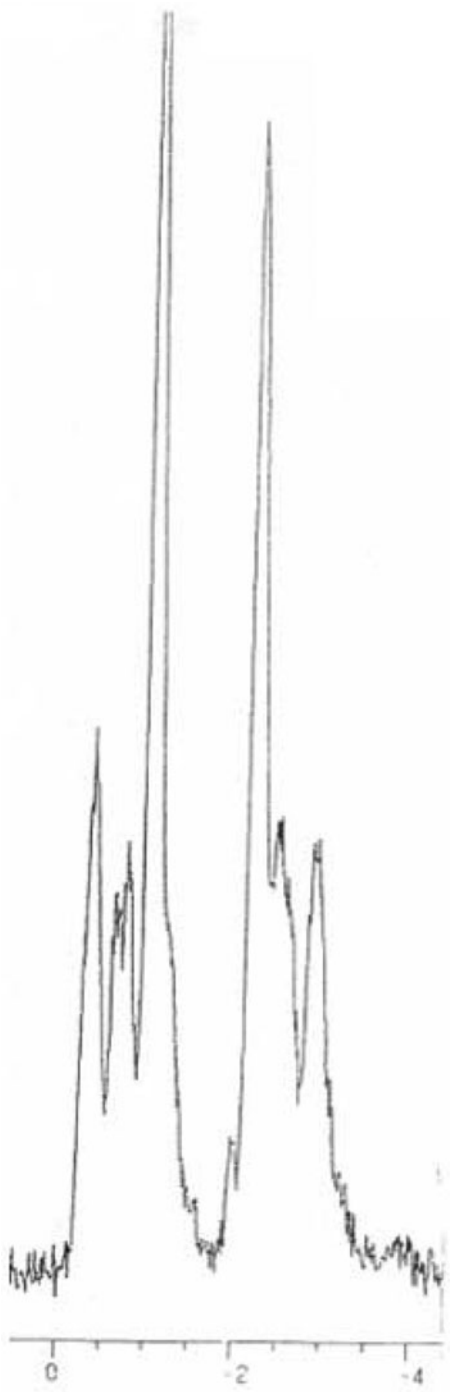

Figure 4. $^{31}P\{^1H\}$ NMR spectrum of compound **11** in $CDCl_3$ at 161.83 MHz, (room temperature), referenced to external 85% H_3PO_4.

When comparing with derivatives of lower homologue, $N_3P_3Cl_6$ (**2**) with pentane-1,5-diol,[43] we did not observe much change in the present series of compounds for the chemical shifts of α-, β-, or γ-methylene protons. As in the case of the homologue $N_4P_4Cl_8$ (1) with the bis(2-hydroxyethyl) ether, the present series shows that the $^3J(\underline{P}OC\underline{H}_2)$ values are higher for the mono-spiro **5** (17.1 Hz) and mono-ansa **6** (15.4) derivatives. The mono-spiro (**5**) and tetrakis-spiro (**13**) derivatives give rise to a simple proton NMR spectra, similar in appearance to those described for the analogue trimer (**2**) derivatives.[41–43] In the bis-spiro derivative **7**, the degree of complexity depends on the second spiro group. If the second spiro group is remote from the first spiro ring, then the spectrum is relatively simple, and therefore in compound **7**, the α-methylene protons are magnetically equivalent. They would see chlorine atoms on both sides, and give rise to a six-line multiplet from coupling with the phosphorus nucleus and adjacent $POCC\underline{H}_2$ protons. On the other hand, the β-methylene protons ($POCH_2$-CH_2-CH_2) are also magnetically identical and give two quintet spectra at 1.61 ppm due to coupling with two α-protons, two γ-protons, and with the phosphorus nucleus. In the case of the γ-methylene protons, a quintet structure is observed at 1.31 ppm. This signal does not exhibit any kind of coupling with the phosphorus nucleus, since the protons are too far away from the phosphorus nucleus, and therefore no further splitting is expected.

As for derivatives of $N_4P_4Cl_8$, (**1**) with the bis(2-hydroxyethyl) ether, the ^1H NMR spectra of the mono-ansa **6**, cis-1,3;5,7-ansa **9,** and cis-1,5;3,7-ansa **10** compounds show complex and unresolved spectra due to the non-equivalence of α- and β-methylene protons. Discussions are as those of the ansa derivatives of trimer (**1**).[41–43] The bis-ansa derivatives show somewhat more complicated ^1H NMR spectrum than mono-ansa derivatives. This is probably due to the virtual coupling effects; the chemical shift between the non-equivalent methylene groups of ansa rings is increased by replacing two chlorine atoms by a second ansa ring. Chemical shift differences and coupling constants are presented in Table 3.

^{13}C NMR studies

The ^{13}C NMR spectra are similar to those in our earlier investigations. With the help of these earlier investigations,[43] the interpretation of the present derivatives has been made easier. In general, for all pentane-1,5-diol derivatives, three carbon environments were observed at 50.27 and 100.53 MHz, except for the open chain **4** (where five different carbon environments were observed), tris-piro **12**, and the spiro-ansa **11** derivatives depending on whether they are α-, β-, or γ- relative to oxygen atoms. ^{13}C NMR spectra of open chain **4** and 1,3-mono-ansa **6** derivatives are presented in Figures 5 and 6.

As in the case of the proton NMR spectrum of spiro-ansa derivative **11**, the α- and β-carbon nuclei of the spiro ring may show nonequivalence due to different chemical environments (ansa moiety and chlorine atoms respectively) above and below the plane of the ring. Thus, if sufficiently resolved, the spiro-ansa compounds may show eight carbon environments; three from the ansa group (α-, β-, and γ-carbons) and five from spiro moiety (two α-, two β-, and one for γ-nuclei).

We observed in our earlier studies, on the bis(2-hydroxyethyl) ether with octochloride (**1**), that the chemical shifts of α- and β-carbon nuclei were close together, as both are adjacent to oxygen atoms. By contrast, for the pentane-1,5-diol system, different chemical environments are well separated.

The investigations of chemical shifts δ POC and POCC in the tris-spiro derivative **12** are noteworthy as more deshielded POC signals arise from the two spiro groups, which are flanked on

Table 2. Comparison of selected ^{31}P NMR parameters of spiro and ansa derivatives of octachlorocyclotetraphosphazene (**1**) with relative diols.

		^{31}P Chemical shift (ppm)			$^2J_{PNP}$ (Hz)		
Compound		2 × PCl_2 (1)	1 × PCl_2 (2)	$P(OR)_2$ (3)	1,2	1,3	
		Mono-spiro (A_2BC spin system)					
$N_4P_4Cl_6[O(CH_2)_3O]$[a]		−4.3	−5.5	−10.5	29.9	59.0	
$N_4P_4Cl_6[O(CH_2)_4O]$[a]		−4.1	−5.7	−2.05	29.3	62.5	
$N_4P_4Cl_6[O(CH_2)_5O]$[b]		−4.9	−6.0		28.7	58.4	
		−2.4					
$N_4P_4Cl_6[O(CH_2)_2O(CH_2)_2O]$[b]		−5.1	−6.6	−11.2	25.7	54.9	
$N_4P_4Cl_6(OCH_2CF_2CF_2CH_2O)$[c]		−1.9	−5.2	−6.1	30.5	63.5	
$N_4P_4Cl_6[OCH_2(CF_2)_4CH_2O]$[d]		−4.60	−6.29	−2.80	28.6	58.3	
Cis-dispiro **(**AA′BB′ spin system)		PCl_2 (1)	$P(OR)_2$ (2)		1,2	2,2	1,1
$N_4P_4Cl_4[O(CH_2)_3O]_2$[a]		−4.7	−6.6		58.2	82.85	
$N_4P_4Cl_4[O(CH_2)_4O]_2$[a]		−2.6	1.4		60.7	89.20	
$N_4P_4Cl_4[O(CH_2)_2O(CH_2)_2O]_2$[b]		−5.1	−7.4		56.37	70.44	
$N_4P_4Cl_6(OCH_2CF_2CF_2CH_2O)$[c]		−1.6/−1.6	−2.0/−2.0		70.2	93.4	35.2
Trans-dispiro **(**A_2B_2 spin system)		PCl_2 (1)		$P(OR)_2$ (2)	1,2	1,1	
$N_4P_4Cl_4[O(CH_2)_3O]_2$[a]		−2.3		−9.6	57.9	36.5	
$N_4P_4Cl_4[O(CH_2)_4O]_2$[a]		−1.0	Accidental isochrony	−1.0			
$N_4P_4Cl_4[O(CH_2)_5O]_2$[a]		−1.8		−7.5			60.25
$N_4P_4Cl_4[O(CH_2)_2O(CH_2)_2O]_2$[b]		−4.4		−9.4	49.1	34.6	
$N_4P_4Cl_6(OCH_2CF_2CF_2CH_2O)_2$[c]		1.5		−5.6	63.3		
Tris-spiro **(**A_2BX spin system)		PCl_2 (1)	1 × $P(OR)_2$ (2)	2x$P(OR)_2$ (3)	1,2	2,3	1,3
$N_4P_4Cl_2[O(CH_2)_3O]_3$[a]		−2.6	−2.1	−5.7	53.7	79.4	
$N_4P_4Cl_2[O(CH_2)_4O]_3$[a]		−0.2	5.5	2.2	54.2	86.1	
$N_4P_4Cl_2[O(CH_2)_5O]_3$[a]		−0.5	5.9	2.6	55.2	90.8	
$N_4P_4Cl_2(OCH_2CF_2CF_2CH_2O)_3$[c]		2.1	1.9	−1.4		85.2	62.6
Tetrakis-spiro (A_4 spin system)				$P(OR)_2$			
$N_4P_4[O(CH_2)_4O]_4$[a]				7.1			
$N_4P_4Cl_6[O(CH_2)_5O]_4$[b]				7.8			
$N_4P_4[O(CH_2)_2O(CH_2)_2O]_4$[b]				2.9			
$N_4P_4(OCH_2CF_2CF_2CH_2O)_4$[e]				3.5			
Mono-ansa **(**AA′BB′ spin system)	PCl_2 (1)		P(OR)Cl (2)		1,2	2,2	1,1
$N_4P_4Cl_6[O(CH_2)_5O]$[b]	1,3-ansa	−0.9	−6.4		39.6		
$N_4P_4Cl_6[O(CH_2)_5O]$[b]	1,5-ansa	−7.3	−2.4		54.1		
$N_4P_4Cl_6[O(CH_2)_2O(CH_2)_2O]$[b]	1,3-ansa	4.60	−7.6		57.6		
$N_4P_4Cl_6[O(CH_2)_2O(CH_2)_2O]$[b]	1,5-ansa	−2.77	−9.3		48.9		
$N_4P_4Cl_6(OCH_2CF_2CF_2CH_2O)$[c]	1,3-ansa	−3.9	0.11		30.9	15.5	15.5
$N_4P_4Cl_6[OCH_2(CF_2)_4CH_2O]$[d]	1,5-ansa	0.39	−0.9		36.8		
Bis-ansa (A_4 spin system)			P(OR)Cl				
$N_4P_4Cl_6[O(CH_2)_5O]_2$ [b]	cis-1,3-5,7-bis ansa		−0.9				
$N_4P_4Cl_4[O(CH_2)_2O(CH_2)_2O]_2$[b]	cis-1,3-5,7-bis ansa		−1.5				
$N_4P_4Cl_4[O(CH_2)_2O(CH_2)_2O]_2$[b]	cis-1,5-3,7 bis ansa		−1.1				
$N_4P_4Cl_4[OCH_2(CF_2)_4CH_2O]_2$[d]	cis-1,3-5,7-bis ansa		−2.2				
Tetrakis-ansa (A_4 spin system)			$P(OR)_2$				
$N_4P_4[OCH_2(CF_2)_4CH_2O]_4$[d]			−1.2				

(**1**) with relative diols[39,40,54], and the present work

[a] At 80.98 and 161.83 MHz, ^{31}P NMR chemical shifts (ppm) in $CDCl_3$ with respect to external 85% H_3PO_4.

[b] At 161.83 MHz (room temperature), ^{31}P NMR chemical shifts (ppm) in $CDCl_3$ with respect to external 85% H_3PO_4.

[c] At 202.38 MHz, ^{31}P NMR chemical shifts (ppm) in $CDCl_3$ with respect to external 85% H_3PO_4.

[d] At 202.38 MHz, ^{31}P NMR chemical shifts (ppm) in $CDCl_3$ with respect to external 85% H_3PO_4; $^2J_{PNP}$ values are checked by spin simulation.

[e] At 202.38 MHz, ^{31}P NMR chemical shifts (ppm) in THF-d_8.

one side by $\equiv PCl_2$ moiety. Those of the same groups have more shielded $POC\underline{C}$ nuclei as well.[28b] The tetrakis derivative exhibits a quintet signal for $PO\underline{C}$ nuclei due to virtual coupling with four ^{31}P nuclei.

The three-bond coupling constants $^3J(PCC)$ are very much larger than the two-bond couplings $^2J(PC)$, and hence the expected multiplicities can be readily seen in the former, but only rarely in the latter. Most pronounced are the differences in two- and three-bond coupling constants in compound **4**, which is significantly larger than in spiro and ansa compounds.

When comparing the results of the present study with earlier one on lower homologue trimer (**2**) derivatives with pentane-1,5-diol system,[43] coupling constants show much larger differences than chemical shifts. Two bond couplings $^2J(POC)$ are marginally lower in tetramer derivatives. The eight-membered spiro and ansa rings are stable in each of the octachloride (**1**) and hexachloride (**1**) but rather more stable in the lower homologue trimer (**2**) toward the diols investigated. The ^{13}C NMR chemical shifts and their coupling constants are presented in Table 4.

Table 3. Selected ^{1}H NMR parameters of compounds **4-13**^{a}.

Compound	δ POC$\underline{\mathrm{H}}_2$^{b}	δ POCC$\underline{\mathrm{H}}_2$^{b}	δ POCCC$\underline{\mathrm{H}}_2$^{b}	^3J(POC$\underline{\mathrm{H}}_2$)^c
(**4**)	4.3	1.8	1.5 4.5 (-O$\underline{\mathrm{H}}$)	13.9
(**5**)	4.4	1.6	1.5	17.1
(**6**)	4.2	1.6	1.3	15.4
(**7**)	4.2	1.6	1.3	13.0
(**8**)	4.3	1.6	1.5	13.5
(**9**)	4.2	1.6	1.3	16.5
(**10**)	4.2	1.6	1.30	16.3
(**11**) spiro-part	4.3	1.6	1.4	15.1
ansa-part	4.2	1.6	1.3	13.6
(**12**)	4.3	1.6	1.5	Complex multiplets
(**13**)	4.4	1.7	1.5	Complex multiplets

[a] In $CDCl_3$ (referenced to internal TMS), at 199.5 and 399.95 MHz (room temperature).
[b] In ppm.
[c] In Hz.

Experimental

Materials

Chemicals were obtained as follows: Reagent-grade solvents were used throughout the work, THF, benzene, light petroleum (b.p. 40–60°C), anhydrous diethyl ether and chloroform (May and Baker Ltd., London), 1,4-dioxane (Fisons Scientific Apparatus), deuteriated solvents for NMR spectroscopy, pentane-1, 5-diol (Aldrich Chem. Co. Ltd., Gillingham, England), pyridine, dichloromethane (B.D.H. Chemical Co. Ltd. East Yorkshire, England), octachlorocyclotetraphosphazatetraene (Shin Nisso Kako Co. Ltd., Tokyo). Solvents were dried by conventional methods.

Methods

All reactions were monitored by using Kieselgel 60° 254 (silica gel) pre-coated TLC plates and sprayed with Ninhydridine (0.5% w/v) in butanol solution, and developed at approximately 130°C. Separation of products was carried out by column chromatography using Kieselgel 60. Melting points were determined with a Reichart–Kofler micro heating stage and a Mettler FB 82 hot stage connected to an FP 800 central processor, both fitted using a polarizing microscope. ^{1}H NMR spectra were recorded using a JEOL FX-200 spectrometer operating at 199.5 MHz, a Bruker WH 250 spectrometer operating at 250.48 MHz (King's College, London), and a Varian XL-400 spectrometer operating at 399.5 MHz (King's College, London). Samples were dissolved in $CDCl_3$ and placed in 5-mm NMR tubes. Measurements were carried out using $CDCl_3$ lock, TMS as internal reference, and sample concentrations of 15–20 mg cm^3. ^{31}P NMR spectra were recorded using a Varian XL-200 spectrometer operating at 80.96 MHz (King's College, London) and a Varian 400 spectrometer operating at 162.0 MHz (King's College, London); 85% H_3PO_4 was used as external reference. ^{13}C NMR spectra were recorded using a JEOL FX-200 spectrometer operating at 50.10 MHz and a Varian VXR 400 spectrometer operating at 100.577 MHz (King's College, London). TMS was used as internal reference. The mass spectra were recorded using a VG 7070H mass spectrometer with Finingan INCOS Data System at King's College, London, and a VG 2AB IF mass spectrometer at the School of Pharmacy. Microanalyses were carried out by King's College, London micro analytic service.

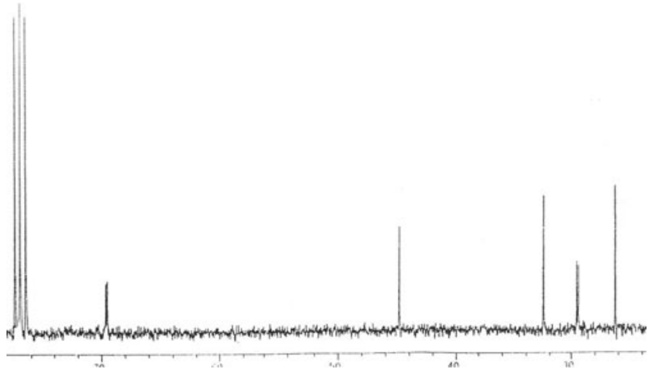

Figure 5. ^{13}C NMR spectrum of the open chain derivative **4** in $CDCl_3$ at room temperature at 100.13 MHz.

Reactions of octachlorocyclotetraphosphazatetraene with pentane-1,5-diol

One equivalent of compound 2

Tetramer (2), (4 g, 8.7 mmol) and pentane-1,5-diol, (3), (0.90 g, 8.7 mmol) were placed in dichloromethane (150 mL) in a 300-mL three-necked round-bottom flask and the solution was stirred at room temperature for approximately 1 h. The reaction mixture was cooled in an ice-bath, and anhydrous pyridine (1.39 g, 17.5 mmol) in dichloromethane (40 mL) was added dropwise as a hydrogen chloride acceptor. The reaction mixture was allowed to warm to room temperature and left for a further 15-h stirring. The reaction resulted in the formation of a precipitate. After 15 h, TLC showed the completion of the reaction. On attaining room temperature, the pyridine hydrochloride was removed by filtration and the filtrate was concentrated to 15 cm^3. Examination of the reaction mixture showed essentially the formation of three major and one minor products. The filtrate was concentrated to 8 mL and applied to a column packed with silica gel (60 g) and eluted with dichloromethane/benzene (3:1). Four products were separated and recrystallized from benzene/diethylether (2:1) in the following order: (i) 2,6-mono-ansa-(1′,5′-pentanedioxy)-2,4,6,6,8,8-hexachlorocyclotetraphosphazatetraene, $N_4P_4Cl_6[O(CH_2)_5O]$ (7), m.p. 168–171°C; yield, 0.61 g, (19.7%); Found C, 12.15; H, 1.98; N, 11.36%; M+, 492; $C_5H_{10}O_2N_4P_4Cl_6$ requires;

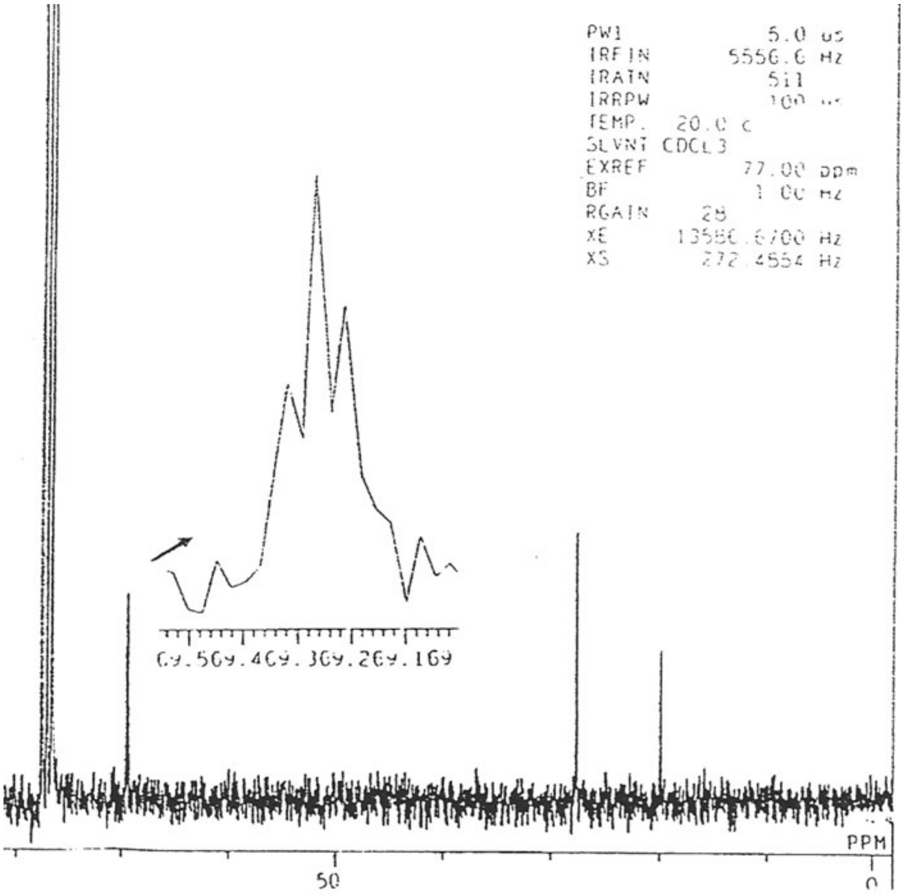

Figure 6. ^{13}C NMR spectrum of mono-1,3-ansa derivative **4** in CDCl$_3$ at room temperature at 100.13 MHz.

C, 12.19; H, 2.03; N, 11.38%; M, 492. ^{1}H NMR (CDCl$_3$), δ POC$\underline{H}_2$: 4.2, δ POCC$\underline{H}_2$: 1.6, δ POCCC$\underline{H}_2$: 1.3, ^3J(PH): 13.0 Hz. ^{31}P NMR, (CDCl$_3$), δ PCl$_2$: −7.3, δ P(OR)Cl: −2.4, ^2J[PCl$_2$–P(OR)Cl]: 54.1 Hz. ^{13}C NMR (CDCl$_3$), δ PO$\underline{C}$: 67.9, δ POC$\underline{C}$: 27.3, δ POCC$\underline{C}$: 17.6, ^2J(PC): 3.7 Hz, ^3J(PC): 7.5 Hz. (ii) 2-mono-spiro-(1′,5′-pentanedioxy)-4,4,6,6,8,8-hexachlorocyclotetraphosphazatetraene, N$_4$P$_4$Cl$_6$[O(CH$_2$)$_5$O] (**5**), m.p. 190–191 °C; yield, 0.79 g (23.2%); Found C, 12.07; H, 2.01; N, 11.36%; M+, 492; C$_5$H$_{10}$O$_2$N$_4$P$_4$Cl$_6$ requires; C, 12.19; H, 2.03; N, 11.38%; M, 492. ^{1}H NMR (CDCl$_3$), δ POC$\underline{H}_2$: 4.4, δ POCC$\underline{H}_2$: 1.6, δ POCCC$\underline{H}_2$: 1.5, ^3J(PH): 17.1 Hz. ^{31}P NMR, (CDCl$_3$), δ 2 × PCl$_2$: −4.9, δ 1×PCl$_2$: −2.4, δ P(OR)$_2$: −6.0, ^2J[PCl$_2$-P(OR)$_2$]: 58.4 Hz, ^2J[PCl$_2$-PCl$_2$]: 28.7 Hz. ^{13}C NMR (CDCl$_3$), δ PO$\underline{C}$: 67.6, δ POC$\underline{C}$: 29.1, δ POC$\underline{C}$: 18.1, ^2J(PC): 4.1 Hz, ^3J(PC): 7.9 Hz. δ POCC: 29.1, δ POCC: 18.1, ^2J(PC): 4.1 Hz, ^{3}J(PC): 7.9 Hz. (iii) 2-openchain-(1′-oxy-5′-hidroxy-pentane)-2,4,4,6,6,8,8-heptachlorocylotetraphosphazatetraene, N$_4$P$_4$Cl$_7$[O(CH$_2$)$_5$OH] (**4**), m.p. 236–239°C; yield, 0.23 g (7.2%); Found: C, 11.31; H, 2.1; N, 10.61%; M$^+$ 528; C$_5$H$_{11}$O$_2$N$_4$P$_4$Cl$_2$ requires, C, 11.36; H, 2.08; N, 10.60%; M, 528. ^{1}H NMR (CDCl$_3$), δ POC$\underline{H}_2$: 4.3, δ POCC$\underline{H}_2$: 1.8, δ POCCC$\underline{H}_2$: 1.46, (-O$\underline{H}$): 4.5, ^3J(PH): 13.9 Hz, C$_4$ = 24.6, C$_5$ = 32.4, C$_6$ = 44.9. ^{31}P NMR (CDCl$_3$), δ PCl$_2$: −5.2, δ P(OR)Cl: −7.9, ^2J[PCl$_2$–P(OR)Cl]: 57.2 Hz. ^{13}C NMR (CDCl$_3$), δ PO$\underline{C}$: 69.6, δ POC$\underline{C}$: 29.9, δ POCC$\underline{C}$: 26.3, C$_4$: 24.4, C$_5$: 32.4, C$_6$: 44.9 ^2J(PC): 6.8 Hz, ^3J(PC): 9.1 Hz. (iv) 2,2,6,6-di-spiro-(1′,5′-pentanedioxy)-4,4,8,8-tetrachlorocyclotetraphosphazatetraene, N$_4$P$_4$Cl$_4$[O(CH2)$_5$O]$_2$ (**8**), m.p. 210–211°C; yield, 0.92 g, (26.9%); Found C, 23.01; H, 3.87; N, 10.68%; M$^+$, 524; C$_{10}$H$_{20}$O$_4$N$_4$P$_4$Cl$_6$ requires C, 22.9; H, 3.82; N, 10%; M, 492. ^{1}H NMR (CDCl$_3$), δ POC$\underline{H}_2$: 4.31, δ POCC$\underline{H}_2$: 1.61, δ POCCC$\underline{H}_2$: 1.53 ^3J(PH): 13.5 Hz. ^{31}P NMR (CDCl$_3$), δ PCl$_2$: −1.8, δ P(OR)$_2$: −7.5, ^2J[P(OR)$_2$–PCl$_2$]: 60.25 Hz. ^{13}C NMR (CDCl$_3$), δ PO$\underline{C}$: 68.3, δ POC$\underline{C}$: 29.2, δ POCC$\underline{C}$: 18.2, ^2J(PC): 4.9 Hz, ^3J(PC): 7.1 Hz.

Two equivalents of compound 2

Following the same procedure as illustrated in reaction (a), tetramer (2) (4 g, 8.7 mmol), pentane-1,5-diol (3), (1.80 g, 17.4 mmol), pyridine (2.74 g, 34.60 mmol), stirring time was 24 h. In addition to compound (5), three new products were observed by TLC. The solvent was removed under reduced pressure and the resulting white solid material was subjected to column chromatography, using a mixture of dichloromethane/benzene (4:1) as an eluent. Products were recrystallized from benzene containing a few drops of light petroleum (b.p. 40–60°C). Four main phosphazene fractions were obtained: (i) 2,2-mono-spiro-(1′,5′-pentanedioxy)-4,4,6,6,8,8-hexachlorocyclotetraphosphazatetraene, (**5**, 11.2%). (ii) 2,4-mono-ansa-((1′,5′-pentanedioxy)-2,4,6,6,8,8-hexachlorocyclotetraphosphazatetraene, N$_4$P$_4$Cl$_6$[O(CH$_2$)$_5$O] (**6**), m.p. 159–161 °C, yield, 0.60 g (18.3%); Found: C, 12.21; H, 2.05; N, 11.36%; M$^+$ 459; C$_5$H$_{10}$O$_2$N$_4$P$_4$Cl$_6$ requires, C,

Table 4. Selected ^{13}C NMR parameters of compounds **4-13**^{a}.

Compound	δ PO$\underline{\text{C}}^{b}$	δ POC$\underline{\text{C}}^{b}$	δ POCC$\underline{\text{C}}^{b}$	^{2}J(PO$\underline{\text{C}}$)^{c}	^{3}J(POC$\underline{\text{H}}_2$)^{c}
(**4**)	69.6 $C_4 = 24.6$, $C_5 = 32.4$, $C_6 = 44.9$	29.9	26.3	6.8	9.1
(**5**)	67.6	29.1	18.1	4.1	7.9
(**6**)	68.1	27.1	18.2	3.4	7.7
(**7**)	67.9	27.3	17.6	3.7	7.5
(**8**)	68.3	29.2	18.2	4.9	7.1
(9)	67.0	27.6	17.7	3.4	00
(**10**)	67.2	27.4	17.1	3.7	00
(**11**) spiro part	67.8	29.3	17.8	4.2	7.0
ansa part	67.2	27.6	17.3	3.6	00
(**12**)	67.1	29.3		4.6	00
	66.8	29.0		4.8	00
(**13**)	66.2 (qui)	28.8	17.5	4.7	00

[a] In $CDCl_3$ (room temperature) at 50.1 and 100.577 MHz.
[b] in ppm.
[c] In Hz.

12.19; H, 2.03; N, 11.38%; M, 4.92. ^{1}H NMR ($CDCl_3$), δ POC$\underline{\text{H}}_2$: 4.23, δ POCC$\underline{\text{H}}_2$: 1.62, δ POCCC$\underline{\text{H}}_2$: 1.27, ^{3}J(PH): 15.4 Hz. ^{31}P NMR ($CDCl_3$), δ PCl_2: −0.95, δ P(OR)Cl: −6.41, ^{2}J[PCl_2–P(OR)Cl]: 39.6 Hz. ^{13}C NMR ($CDCl_3$), δ PO$\underline{\text{C}}$: 68.1, δ POC$\underline{\text{C}}$: 27.1, δ POCC$\underline{\text{C}}$: 18.2, ^{2}J(PC): 3.4, ^{3}J(PC): 7.7 Hz. (iii) 2,4,6,8-bisansa-(1′,5′-pentanedioxy)-2,4,6,8-tetrachlorocyclotetraphosphazatetraene, $N_4P_4Cl_4[O(CH_2)_5O]_2$ (**9**), m.p. 226 °C, yield 1.2 g (35.2%,); Found: C, 22.96; H, 3.87; N, 10.68%; M+ 528; $C_{10}H_{20}O_4N_4P_4Cl_4$ requires C, 22.9; H, 3.82; N, 10.68%; M, 528. ^{1}H NMR ($CDCl_3$), δ POC$\underline{\text{H}}_2$: 4.2, δ POCC$\underline{\text{H}}_2$: 1.6, δ POCCC$\underline{\text{H}}_2$: 1.3 ^{3}J(PH): 16.5 Hz. ^{31}P NMR, ($CDCl_3$), δ $P(OR)_2$: −0.98. ^{13}C NMR ($CDCl_3$), δ PO$\underline{\text{C}}$: 67.0, δ POC$\underline{\text{C}}$: 27.6, δ POCC$\underline{\text{C}}$: 17.7, ^{2}J(PC): 3.4, ^{3}J(PC): 00 Hz. (iv) 2,6,4,8-bisansa-(1′,5′-pentanedioxy)-2,4,6,8-tetrachlorocyclotetraphosphazatetraene, $N_4P_4Cl_4[O(CH_2)_2O(CH_2)_2O]_2$ (**10**), m.p. 238–239°C, yield 0.81 g (23.3%); Found: C, 22.93; H, 3.81; N, 10.68%; M^{+} 528; $C_{10}H_{20}O_4N_4P_4Cl_4$ requires C, 22.9; H, 3.82; N, 10.68%; M, 528. ^{1}H NMR ($CDCl_3$), δ POC$\underline{\text{H}}_2$: 4.2, δ POCC$\underline{\text{H}}_2$: 1.6, δ POCCC$\underline{\text{H}}_2$: 1.3 ^{3}J(PH): 16.3 Hz. ^{31}P NMR, ($CDCl_3$), δ $P(OR)_2$: −0.7. ^{13}C NMR ($CDCl_3$), δ PO$\underline{\text{C}}$: 67.2, δ POC$\underline{\text{C}}$: 27.6, δ POCC$\underline{\text{C}}$: ^{2}J(PC): 3.7, ^{3}J(PC): 00 Hz.

Three equivalents of compound 2

The apparatus for this preparation comprises a 500-mL three-necked round-bottom flask provided with an efficient stirrer and a water condenser fitted with a calcium chloride tube.

Table 5. Percentage yields of **4-13** in 1:1, 1:2, and 1:3 mole ratios.

Compound (%)	1:1	1:2	1:3
4	7.2		
5	23.2	11.2	
6		18.3	
7	19.7		12
8	26.9		19
9		35.2	
10		23.3	
11			33.7
12			16.2
13			12.3

$N_4P_4Cl_8$ (1) (4 g, 8.7 mmol) and pentane-1,5-diol, (3) (2.70 g. 26.1 mmol) were dissolved in dichloromethane (150 mL) and placed into 500-mL three-necked round-bottom flask and the solution was stirred at room temperature for approximately 1 h. To the remaining suspension, six equivalents of pyridine (4.12 g. 52.2 mmol) in dichloromethane were added dropwise with stirring. The mixture was then allowed to reflux at 60°C for approximately 20 h, until the reaction was completed. TLC revealed essentially the formation of four major and one minor products, which could be isolated. The solid material was extracted with a further quantity of dichloromethane, the dichloromethane solutions were combined and the insoluble material was filtered off and the solvent removed from the filtrate. Individual phosphazene derivatives were separated by column chromatography using a mixture of benzene/dichloromethane 5:2 as a mobile phase. Two known and three new products were obtained and recrystallized from benzene containing a few drops of light petroleum (b.p. 40–60°C): (i) 2,6-mono-ansa-(1′,5′-pentanedioxy)-2,4,6,6,8,8-hexachlorocyclotetraphosphazatetraene (**7**, 12%). (ii) 2,2,6,6-di-spiro-(1′,5′-pentanedioxy)-4,4,8,8-tetrachlorocyclotetraphosphazatetraene, (iii) 4,4,8,8-di-spiro-2,6-ansa-(1′,5′-pentanedioxy)-2,6-dichlorocyclotetraphosphazatetraene, $N_4P_4Cl_2[O(CH2)_5O]_3$ (**11**), m.p. 274–275°C, yield 0.73 g (33.7%); Found: C, 32.4; H, 5.41; N, 10.07%; M^{+} 556; $C_{15}H_{30}O_6N_4P_4Cl_4$ requires, C, 32.37; H, 5.39; N, 10.07%; M, 556. ^{1}H NMR ($CDCl_3$), (spiro part) δ POC$\underline{\text{H}}_2$: 4.3, δ POCC$\underline{\text{H}}_2$: 1.6, δ POCCC$\underline{\text{H}}_2$: 1.4, ^{3}J(PH): 15.1 Hz, (ansa part) δ POC$\underline{\text{H}}_2$: 4.2, δ POCC$\underline{\text{H}}_2$: 1.6, δ POCCC$\underline{\text{H}}_2$: 1.3, ^{3}J(PH): 13.6 Hz. ^{31}P NMR, ($CDCl_3$), δ $P(OR)_2$: 5.1, δ P(OR)Cl: −3.5, ^{2}J[$P(OR)_2$ P(OR)Cl]: 81.4 Hz. ^{13}C NMR ($CDCl_3$), spiro-part, δ PO$\underline{\text{C}}$: 67.8, δ POC$\underline{\text{C}}$: 29.3, δ POCC$\underline{\text{C}}$: 17.8, ^{2}J(PC): 4.2, ^{3}J(PC): 7.0 Hz, ansa-part, δ PO$\underline{\text{C}}$: 67.2, δ POC$\underline{\text{C}}$: 27.6, δ POCC$\underline{\text{C}}$: 17.3, ^{2}J(PC): 3.6, ^{3}J(PC): 00 Hz. (iv) 2,2,4,4,6,6-tri-spiro-(1′,5′-pentanedioxy)-8,8-dichlorocyclotetraphosphazatetraene, $N_4P_4Cl_2[O(CH2)_5O]_3$ (**12**), m.p. 256°C, yield 0.35 g (16.2%); Found: C, 32.36; H, 5.43; N, 10.07%; M^{+} 556; $C_{15}H_{30}O_6N_4P_4Cl_4$ requires, C, 32.37; H, 5.39; N, 10.07%; M, 556. ^{1}H NMR ($CDCl_3$), δ POC$\underline{\text{H}}_2$: 4.3, δ POCC$\underline{\text{H}}_2$: 1.6, δ POCCC$\underline{\text{H}}_2$: 1.5, ^{3}J(PH): complex multiplets. ^{31}P NMR, ($CDCl_3$), δ PCl_2: −0.5, δ $P(OR)_2$

(1): 5.9, δ P(OR)$_2$ (2): 2.6, ^2J(P(OR)$_2$-PCl$_2$): 55.2, ^2J(P(OR)$_2$-P(OR)$_2$): 90.8 Hz. ^{13}C NMR (CDCl$_3$), δ PO$\underline{C}$: 67.1/66.8, δ POC$\underline{C}$: 29.3/29.0, ^2J(PC): 4.6, ^3J(PC): 00 Hz. (v) 2,2,4,4,6,6,88-tetra-spiro-(1,5-pentanedioxy)-cyclotetraphosphazatetraene derivative, $N_4P_4Cl_6[O(CH2)_5O]_4$ (**13**), m.p. 291–292°C, yield 0.26 g (12.3%); Found: C, 40.79; H, 6.81; N, 9.52%; M$^+$ 588; $C_{20}H_{40}O_8N_4P_4Cl_4$ requires, C, 40.81; H, 6.8; N, 9.52%; M, 588. ^{1}H NMR (CDCl$_3$), δ POC$\underline{H}_2$: 4.4, δ POCC$\underline{H}_2$: 1.7, δ POCCC$\underline{H}_2$: 1.5 ^3J(PH): complex multiplets. ^{31}P NMR, (CDCl$_3$), δ P(OR)$_2$: 7.8. ^{13}C NMR (CDCl$_3$), δ PO$\underline{C}$: 66.2 (qui), δ POC$\underline{C}$: 28.8, δ POCC$\underline{C}$: 17.5, ^2J(PC): 4.7, ^3J(PC): 00 Hz.

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