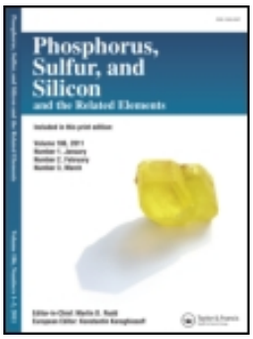

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THE REACTIONS OF OCTACHLOROCYCLOTETRAPHOSPHAZENE WITH DIFUNCTIONAL BIS(2-HYDROXYETHYL) ETHER. NUCLEAR MAGNETIC STUDIES OF THE PRODUCTS

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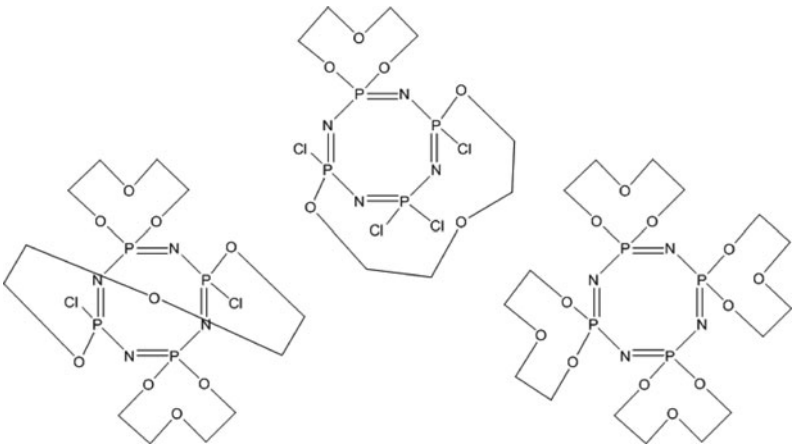
GRAPHICAL ABSTRACT



Abstract *The reactions of octochlorocyclotetraphosphazatetraene, $N_4P_4Cl_4$ (**1**) with difunctional bis(2-hydroxyethyl) ether gave the following isolated and characterized products: one mono-spiro, $N_4P_4Cl_6[(OCH_2)_2\text{-}(CH_2)_2O]$ (**4**); its isomers 1,3- (**5**) and 1,5-ansa (**6**); two isomeric cis-bis- and trans-bis-spiro, $N_4P_4Cl_4[(OCH_2)_2\text{-}(CH_2)_2O]_2$ (**7** and **8**); their isomers cis-1,3;5,7-ansa (**9**), cis-1,5;5,7-ansa (**10**), and spiro-ansa (**11**); as well as one bis-spiro mono-ansa, $N_4P_4Cl_2[(OCH_2)_2\text{-}(CH_2)_2O]_3$ (**12**), and a tetrakis, $N_4P_4[O(CH_2)_2O(CH_2)_2O]_4$ (**13**) derivatives. ^{31}P, ^{1}H, and ^{13}C NMR spectroscopic investigations indicated all bis(2-hydroxyethyl) ether substituted cyclochlorophosphazene derivatives to have four types of spectra: A_2MX (A_2BX), AA'XX' (AA'BB'), $A_2\times_2$ (A_2B_2), and A_4.*

Keywords Octachlorocyclotetraphosphazatetraene; bis(2-hydroxethyl) ether; spiro compounds; ansa compounds; spiro-ansa compounds; NMR studies

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INTRODUCTION

The nucleophilic substitution reactions of the eight-membered ring system, $N_4P_4Cl_8$ (**1**) with monofunctional[18] and difunctional[1a,1c,2,49] reagents have received much less attention than those of its lower homologue, $N_3P_3Cl_6$ (**2**). The reactions of difunctional reagents with both of the cyclophosphazenes (**1** and **2**) have been of significant interest because they lead to the formation of regioisomers in substitution reactions: spiro-, ansa-, bridged-derivatives and their mixtures.[1–35,39–54] The octachlorocyclophosphazene (**1**), is more reactive than the hexachlorocyclophosphazene (**2**); the former can also, in principle, give rise to a much larger number of products, and hence structure determination is more difficult.[2,19,51]

The reactions of secondary amines, NHR_2, gave mainly nongeminal products, although stoichiometry, reaction temperature, and solvent influence the nature of the products and their relative proportions.[3,4,19,51]

From the reactions of primary amines, NH_2R, quite a lot of resinous materials were observed, probably polymeric in nature, due to cross-linking reactions, which in essence, make the primary amines difunctional. An excellent example of difunctionality are the bicylic cyclotetraphosphazatetraenes obtained in the exhaustive aminolysis of the octachlorocyclophosphazene (**1**).[5,16]

It has been already mentioned that octachlorocyclotetraphosphazatetraene, $N_4P_4Cl_8$ (**1**), is more reactive than its lower homologue, $N_3P_3Cl_6$ trimer (**2**). The same pertains, with even greater force to the less investigated difunctional reagents and hitherto little was known in the literature.[2,45,48,49,52,53] Only two derivatives of (**1**), $N_4P_4Cl_6[NMe(CH_2)_2NMe]$,[1a-c] and $N_4P_4Cl_6[NH(CH_2)_3NH]$,[1] had been isolated as such, two further ones, $N_4P_4Cl_6[NH(CH_2)_2NH]$,[1] and $N_4P_4Cl_6[NH(CH_2)_2NH]$,[1] merely on derivatization. Only resinous material was obtained from the reactions with ethylene glycol and diaminoethane.[1]

As in the case of the former reports,[1a-c] the reaction products of the octachloride, (**1**), with ethylene glycol too unstable to be isolated. This instability was also noticed, although to a lesser extent, with 1,3-propane-diol.[2] But, reactions with 1,4-butanediol gave stable derivatives. From the reactions of 1,3-propane-diol, one mono-, $N_4P_4Cl_6[O(CH_2)_3O]$, two isomeric bis- $N_4P_4Cl_4[O(CH2)_3O]_2$, and one tris derivative, $N_4P_4Cl_2[O(CH_2)_3O]_3$ were isolated.[2] The homologue 1,4-butanediol,[2] yielded one mono-, $N_4P_4Cl_6[O(CH_2)_4O]$, two isomeric bis-, $N_4P_4Cl_4[O(CH_2)_4O]_2$, one tris-, $N_4P_4Cl_2[O(CH_2)_4O]_3$, and a tetrakis derivative, $N_4P_4[O(CH_2)_4O]_4$.

In general, the reactions of **1** with difunctional reagents (diols, amino-alcohols, and di-amines) showed a preference for the formation of spiro derivatives.[2,39,40,44,45] On the other hand, the reactions of **1** with 1,1′-ferrocendiol lead to the formation of the mono-ansa product, 1,3-$N_4P_4Cl_6(FcO_2)$,[46] whereas reactions with the corresponding dithia or diselena derivatives gave mono-spiro derivatives.[47,48] The reactions of octafluorocyclotetraphosphazenes, $N_4P_4F_8$ with the silyl derivative of 2,2,3,3-tetrafluorobutane-1,4-diol gave only monospiro and singly-bridged products.[49]

However, reactions of octachlorocyclotetraphosphazenes, $N_4P_4Cl_8$ (**1**) with 2,2,3,3-tetrafluorobutane-1,4-diol,[49] octafluorocylotetraphosphazene ($N_4P_4F_8$) with tetrafluorobutane-1,4-,[39] and octafluorohexane-1,6-diols,[40] and reactions of **1** in the present study in different molar ratios gave mixtures of regio-isomers consisting of compounds with spiro and/or ansa moieties, viz. mono-, bis-, tris-, and tetrakis-spiro, mono-, and bis-ansa and spiro-ansa derivatives.

The five-membered spiro rings are somewhat unstable in the $N_3P_3Cl_6$ system, and were too unstable to be isolated for $N_4P_4Cl_8$ rings. The six-membered spiro rings are stable with the lower homologue, $N_3P_3Cl_6$ (**2**) but rather unstable (when P-Cl bonds are present) in the higher homologue, $N_4P_4Cl_8$ (**1**). The seven- and eight-membered spiro derivatives appear to be stable in both systems. A detailed comparative analysis of the ^{31}P, ^{1}H, and ^{13}C NMR data are reported here.

RESULTS AND DISCUSSION

From the reactions of $N_4P_4Cl_8$ (**1**) with bis(2-hydroxyethyl) ether (**3**), we isolated a total of 10 compounds: one mono-spiro, $N_4P_4Cl_6[(OCH_2)_2O(CH_2)_2O]$, (**4**, 0.65 g, 24.25%); its isomers 1,3-ansa (**5**, 0.60 g, 15.3%), and 1,5-ansa (**6**, 1.10 g, 48.5%); two isomeric, $N_4P_4Cl_4[(OCH_2)_2O(CH_2)_2O]_2$, *cis*-bis-spiro (**8**, 0.87 g, 22.2%), and *trans*-bis-spiro (**7**, 1.6 g, 43.1%); their isomeric *cis*-1,3;5,7-bis-ana (**9**, 0.35 g, 17.1%), *cis*-1,5;3,7-bis-ansa (**10**, 0.30 g, 16.2%), and spiro-ansa (**11**, 0.43 g, 21.75%); one bis-spiro mono-ansa, $N_4P_4Cl_2[(OCH_2)_2O(CH_2)_2O]_3$, (**12**, 0.69 g, 24.6%), and a tetrakis-derivative, $N_4P_4[O(CH_2)_2O(CH_2)_2O]_4$, (**13**, 0.22 g, 10.3%).

In spite of repeated attempts, we failed to obtain any singly- or doubly-bridged derivatives from this system.

^{31}P NMR Studies

^{31}P NMR spectroscopy is a very powerful tool to characterize the structures of the cyclophosphazene derivatives. ^{31}P NMR spectra of tetramer derivatives (**1**) with four spins are obviously more complicated than those of the trimer (**2**) with only three spins. There is also the possibility that, in addition to two-bond ^{2}J(PP), four-bond coupling ^{4}J(PP) might further complicate the spectra.[19,51] We did not observe any of the latter in our analysis; examples of it are, however, known.[28,29a,b] From the above group of compounds, we observed spectra of four types: A_2MX (A_2BX), AA'XX' (AA'BB'), $A_2\times_2$ (A_2B_2), and A_4. Replacement patterns of the octochloride (**1**) are presented in Figure 2.

There is usually no difficulty in recognizing AA'BB' and A_2B_2 spectra. Although the latter may not always be fully resolved if A and B chemical shifts are close, examples are common, as 2,6-substitution is encountered in all reactions of **1** with primary or secondary amines.[3,4] In contrast, surprisingly few examples are known elsewhere in which true magnetic equivalence of A and B nuclei is found. Geometrical isomers can be differentiated in this way, since the spin system would remain the same, and possible differences in ring conformation is that conformational changes are very rapid on the NMR time scale to affect the ^{31}P spectra significantly.

In general, most of the two bond couplings ^{2}J(PP), are less positive than those of the analogue trimer (**2**) derivatives, an observation that is unexpected considering the larger bond angle at endocylic phosphorus.

Fortunately, in these compounds, the spin coupling between remote phosphorous nuclei ^{4}J(PP) were negligible compared to the chemical shift differences $\delta_A - \delta_C$, and $\delta_B - \delta_D$ and hence, assignments of chemical shift values and coupling constants were relatively simpler than those for the four-spin systems, where ^{4}J(PP) has to be taken into consideration.[25]

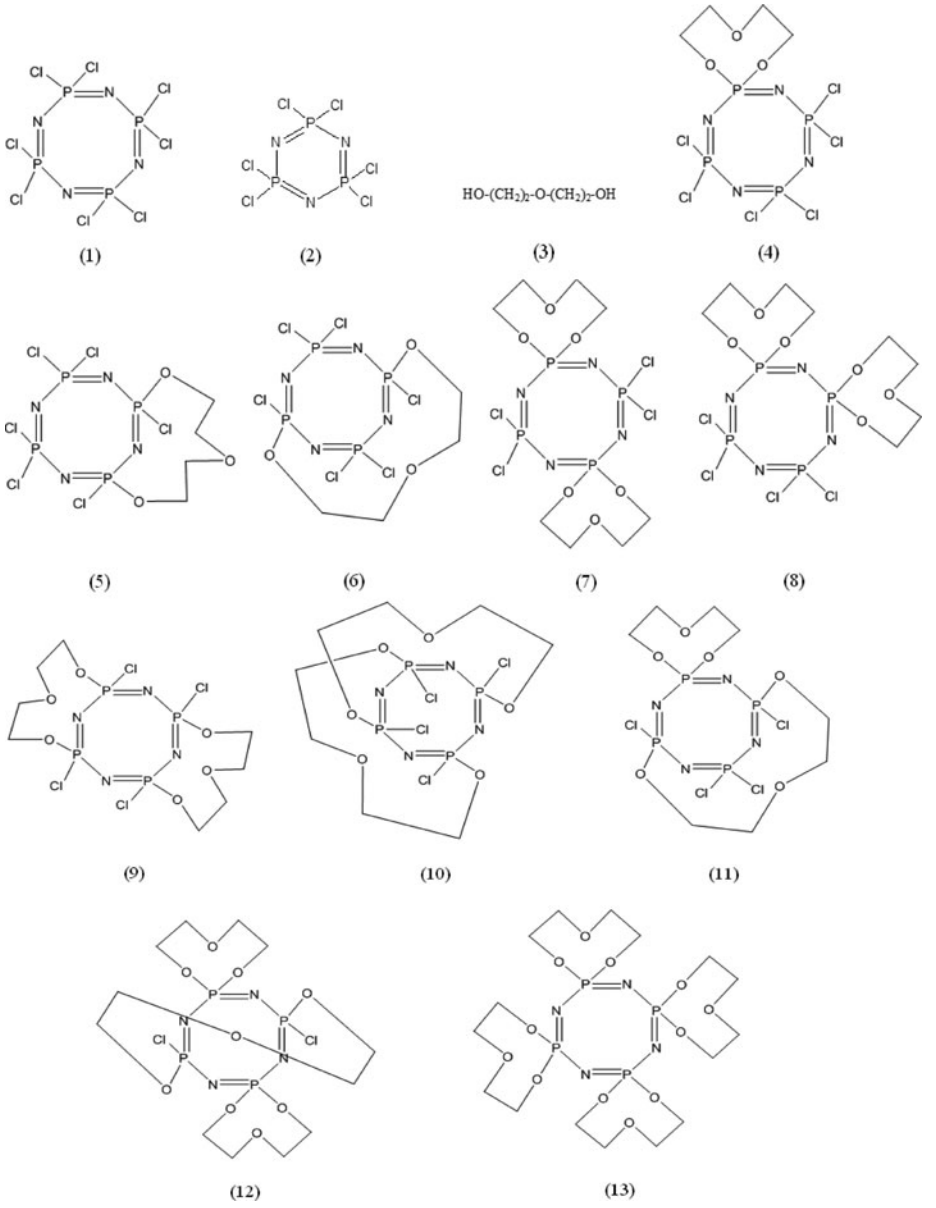

Figure 1 Structures of compounds.

Proton coupled spectra allow in this case, as in all the others, unambiguous assignments, which phosphorus nuclei do or do not have substituent attached as ≡Pspiro, ≡P(OR)Cl, and ≡PCl_2 moieties (see Fig. 1). Previous work on propane-1,3- and butane-1,4-diols[2] revealed that a graphical representation of all the 31P NMR shifts of the compounds showed that replacement of a spiro propanedioxy by a spiro butanedioxy group causes a deshielding of the ≡Pspiro nucleus, which brings it into region of absorption for the ≡PCl_2 nuclei and thus gives rise to an accidental isochrony. Such close chemical shifts

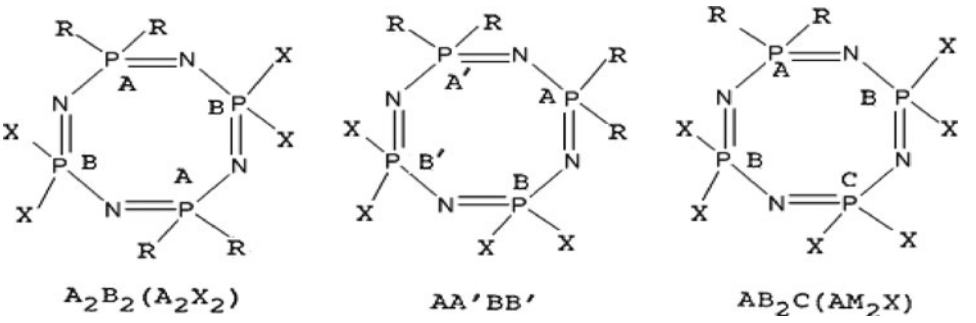

Figure 2 Replacement patterns of octochlorotetraphosphazene (**1**).

may cause originally to assign on spectroscopic grounds an erroneous structure to derived compounds.[2,54]

A detailed comparison of the spectrum, suggests that a 2,2,6,6-bis spiro butanedioxy derivative should have ^{31}P NMR absorptions for both the ≡PCl_2 and ≡Pspiro nuclei around –1 ppm, and these might well be isochronous. Further, this graph allows a prediction of chemical shift of also approximately-1 ppm for the, so unknown tetrakis-spiro propanedioxy derivative, $N_4P_4[O(CH_2)_3O]_4$.[2]

The phosphorus ^{31}NMR measurements made in this study were obtained at 80.95 and 162.0 MHz. ^{31}NMR chemical shifts and coupling constants values obtained in this series are presented in Table 1.

(a) A_2BX (A_2MX) type spin system

An A_2BX (A_2MX) type spin system would be anticipated in particular for the mono-, and tris-spiro derivatives. Hence, in these derivatives, two phosphorus nuclei would be magnetically equivalent (≡PCl2 in the mono-, and ≡Pspiro in the tris-derivatives), while the other two phosphorus nuclei would be different.

Compounds, N4P4CI6[O(CH2)2(CH2)2O] (**4**) and N4P4Cl4[O(CH2)2(CH2)2O]$_2$ (**11**), display spectra of A_2BX (A_2MX) type, establishing that compound **4** is the mono-spiro and compound **11** is the spiro-1,5-ansa derivative (we expect to observe an ABCX type spectrum for the spiro-1,3 isomer).

Proton coupled spectra allow unambiguous assignments to ≡Pspiro and ≡PCl_2 moieties. For mono-spiro compound **4**, the A_2 part is associated with the two ≡PCl_2 groups and gives rise to a relatively downfield four lines band arising from coupling with the ≡Pspiro and unique ≡PCl_2 group. The B part, the unique ≡PCl_2 group is slightly shifted upfield, shoving a three line multiplet arising from coupling with the remaining two equivalent ≡PCl_2 nuclei. The spiro groups (≡Pspiro), which totally collapsed, when the P-H technique was applied to the spectrum, displayed a clear triplet, arising from coupling with the near two ≡PCl_2 nuclei. Phosphorus–phosphorus four bond coupling to the ≡PCl_2 and ≡Pspiro nuclei is not detected.

The spiro-1,5-ansa derivative **11**, showed second order ABX_2 (A_2BX) type spectra. Four transitions are observed in the A part of the spectra for ≡Pspiro nuclei, which totally collapse when the phosphorus-proton coupling techniques were applied. The chemical shift of the spiro group of this compound **11**, dramatically moved downfield relative to that of the spiro group in compounds **4**.

Table 1 Selected ^{31}P NMR parameters of compounds **4–13**[a]

	^{31}P Chemical shift (ppm)				$^{2}J_{PNP}$ (Hz)[c]				
Compound	2×PCl_2 (1)[b]	1×PCl_2 (2)[b]	P(OR)Cl (3)[b]	$P(OR)_2$ (4)[b]	1,2	1,3	1,4	3,4	4,4
(1)		−6.50							
(4)	−5.11	−6.62		−11.17	25.70		54.90		
(5)	−4.60		−7.65			57.60			
(6)	−9.30		−2.77			48.90			
(7)	−4.36		−9.41		34.60		49.14		
(8)	−5.11		−7.40				56.37		70.44
(9)			−1.48						
(10)			−1.07						
(11)	−8.94		−2.19	3.03		63.50	55.90		
(12)			−4.12	6.70			69.50		
(13)	2.87								

[a]In $CDCl_3$ (referenced to external 85% H_3PO_4) at 161.83 MHz (room temperature).
[b]In ppm.
[c]In Hz.

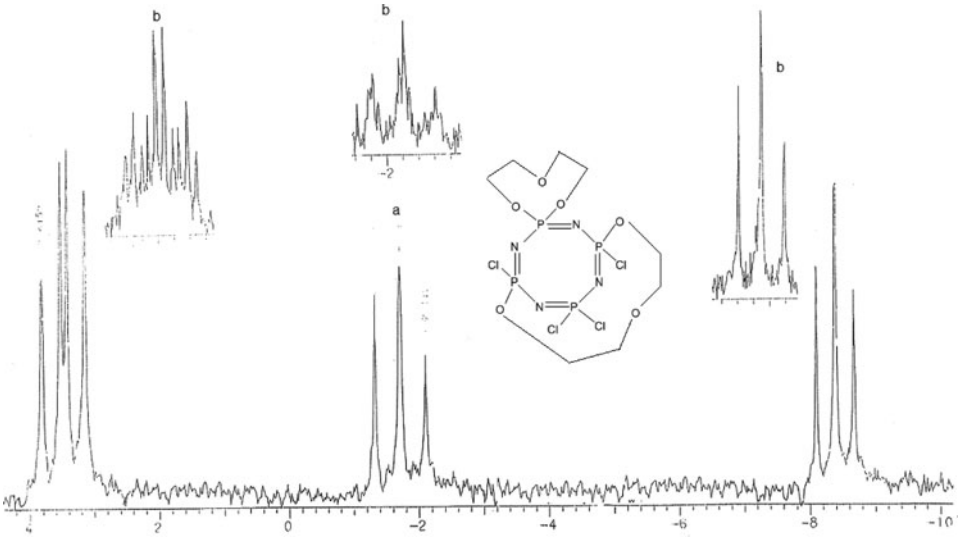

Figure 3 ^{31}P NMR spectra of compound **11**: (a) proton decoupled spectrum, (b) proton coupled spectrum, in $CDCl_3$ at 161.83 MHz, (room temperature), referenced to external 85% H_3PO_4.

The X_2 part [≡P(OR)Cl] displays a three line spectrum, arising from coupling with ≡Pspiro and ≡PCl_2 nuclei. Phosphorus coupled spectrum shows additional splitting patterns in this region as well. The B part of the compound indicates the ≡PCl_2 group, showing three symmetrical transitions arising from coupling with two ≡P(OR)Cl nuclei. The ^{31}P NMR spectrum of the A_2MX type, viz. that of compound **11** is shown in Figure 3.

(b) The $A_2\times_2$ (A_2B_2) spin system

$A_2\times_2$ type spectra were observed for compounds, $N_4P_4Cl_6[O(CH_2)_2(CH_2)_2O]$ (**6**), $N4P_4Cl_4[O(CH_2)_2(CH_2)_2O]_2$ (**7**), and $N_4P_4Cl_2[O(CH_2)_2(CH_2)_2O]_3$ (**12**). The phosphorus-proton coupled spectra help to identify the ≡Pspiro, ≡PCl_2, and the ≡P(OR)Cl groups by leaving ≡PCl_2 groups unchanged while ≡Pspiro and the = P(OR)Cl groups collapsed with further splitting. 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 **12**.

^{31}P NMR spectra of compounds **6** and **12** are represented in figure 4 and 5.

The AA'XX' spin system

The AA'XX' (AA'BB') spin system consists of two basic multiplets, which are identical in appearance and display mirror image symmetry with respect to their frequency centers V_A and V_X. In our compounds, this type of spin system was exemplified in the mono-ansa **5** and 2,2,4,4-bis-spiro **8** derivatives, as a result of the spin–spin interaction amongst the neighboring ≡P(OR)Cl and ≡Pspiro groups and the two chlorine carrying phosphorus nuclei which establish the structures. The spin–spin coupling between the phosphorus nuclei are illustrated below in Figure 6.

Theoretically, each basic multiplet should give rise to 10 transitions which consists of two basic *ab* subspectra and two strong N-lines. The two outermost and two innermost lines together constitute an *ab* type subspectrum.

The apparent chemical shifts and spin–spin coupling constants of the two *ab* subspectra are evaluated by the standard procedure of analyzing an *ab* system.[1b,2,19,39,40,51]

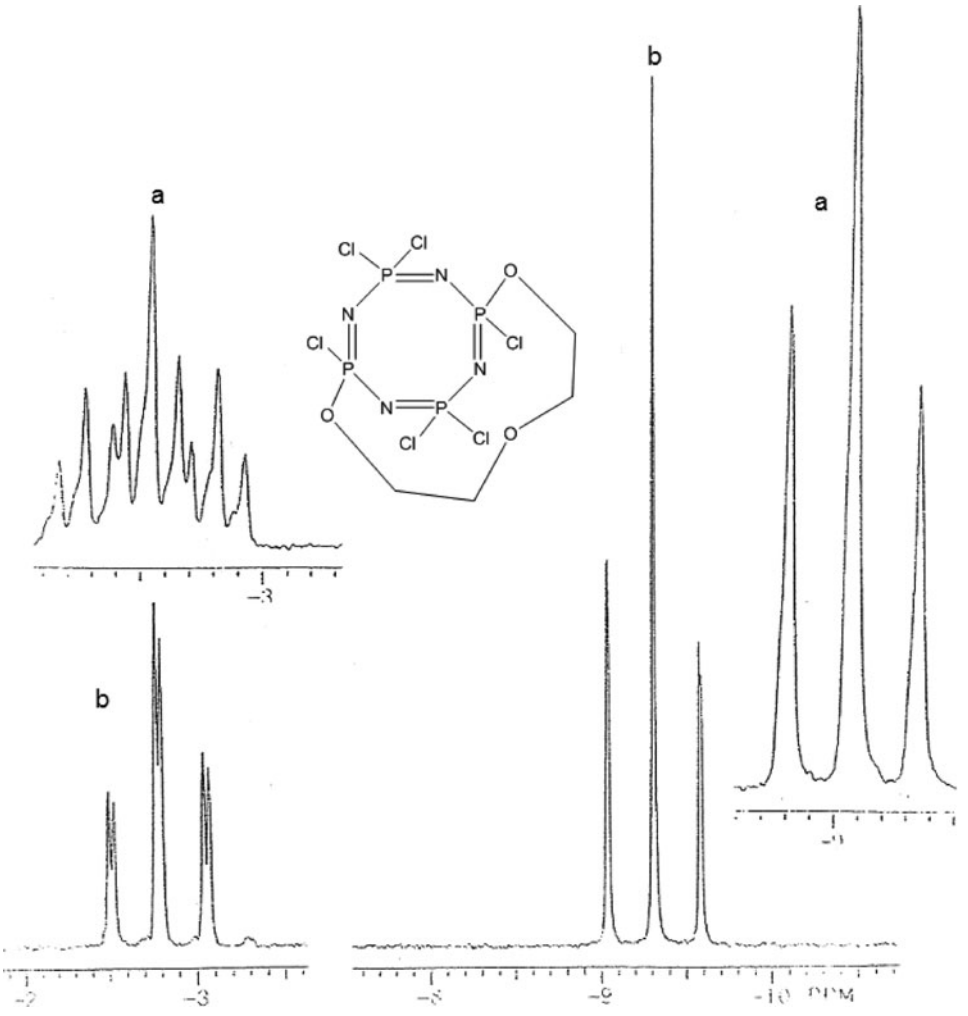

Figure 4 ^{31}P NMR spectra of compound **6**: (a) ^{31}P-^{1}H spectrum, (b) ^{31}P{^{1}H} spectrum, in $CDCl_3$ at 161.83 MHz, (room temperature), referenced to external 85% H_3PO_4.

In compound **5**, 10 lines were observed for each basic multiplet. The $\equiv PCl_2$ groups were associated with the AA' part of the spectrum, and resonate at –7.65 ppm; this was confirmed by using phosphorus–phosphorus coupling techniques. The XX' part collapsed with further splitting. ^{31}P NMR spectra of compound **5** are shown in Figure 7.

(c) The A_4 spin system

The A_4 type spin systems are very simple, which gives 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, $N_4P_4Cl_4[O(CH_2)_2O(CH_2)_2O]_2$ (**9** and **10**), where the identical $=P(OR)Cl$ nuclei resonate at –1.45 and –1.07 ppm giving rise to single line transitions. The tetrakis-spiro compound, $N_4P_4[O(CH_2)_2O(CH_2)_2O]_4$ (**13**), displays an A_4 spin system as well resonating at 2.87 ppm.

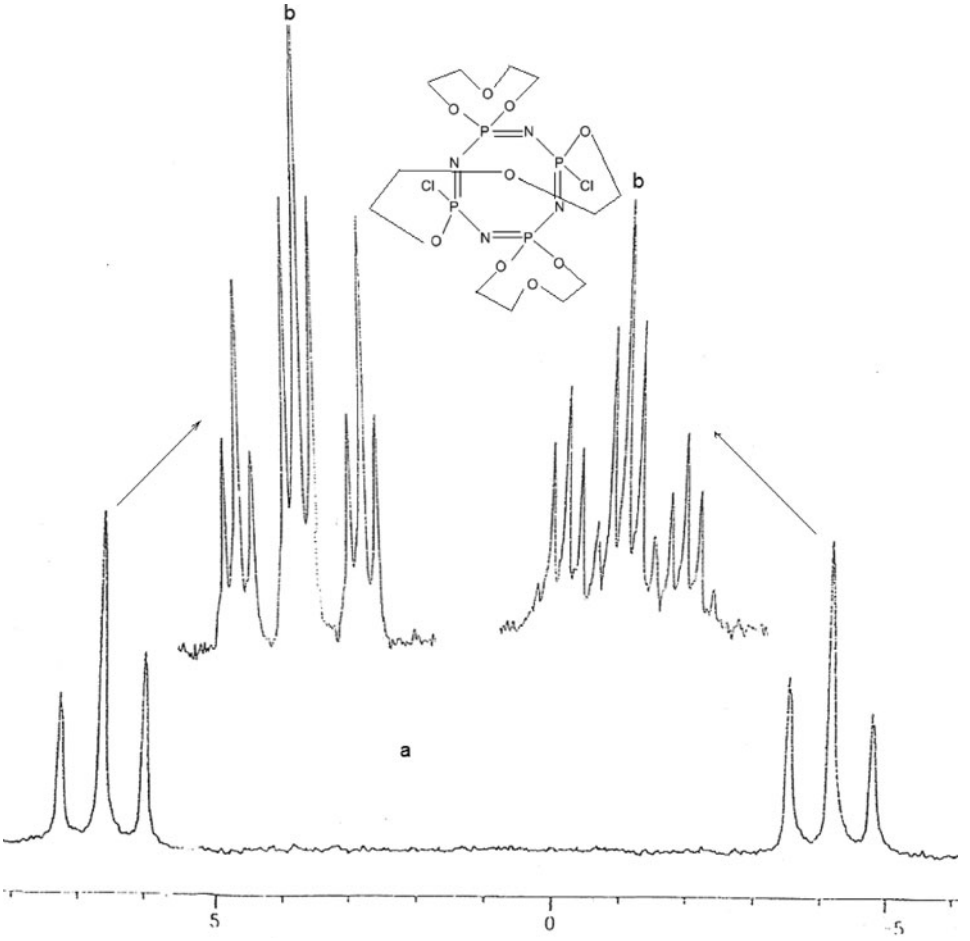

Figure 5 ^{31}P NMR spectra of compound 12: (a) ^{31}P{^{1}H}spectrum, (b) ^{31}P-^{1}H spectrum, in $CDCl_3$ at 161.83 MHz, (room temperature), referenced to external 85% H_3PO_4.

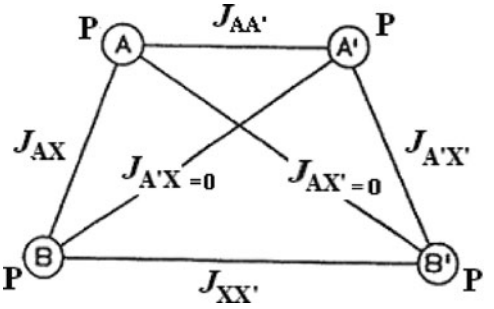

Figure 6 AA'XX' spin–spin coupling between phosphorus nuclei.

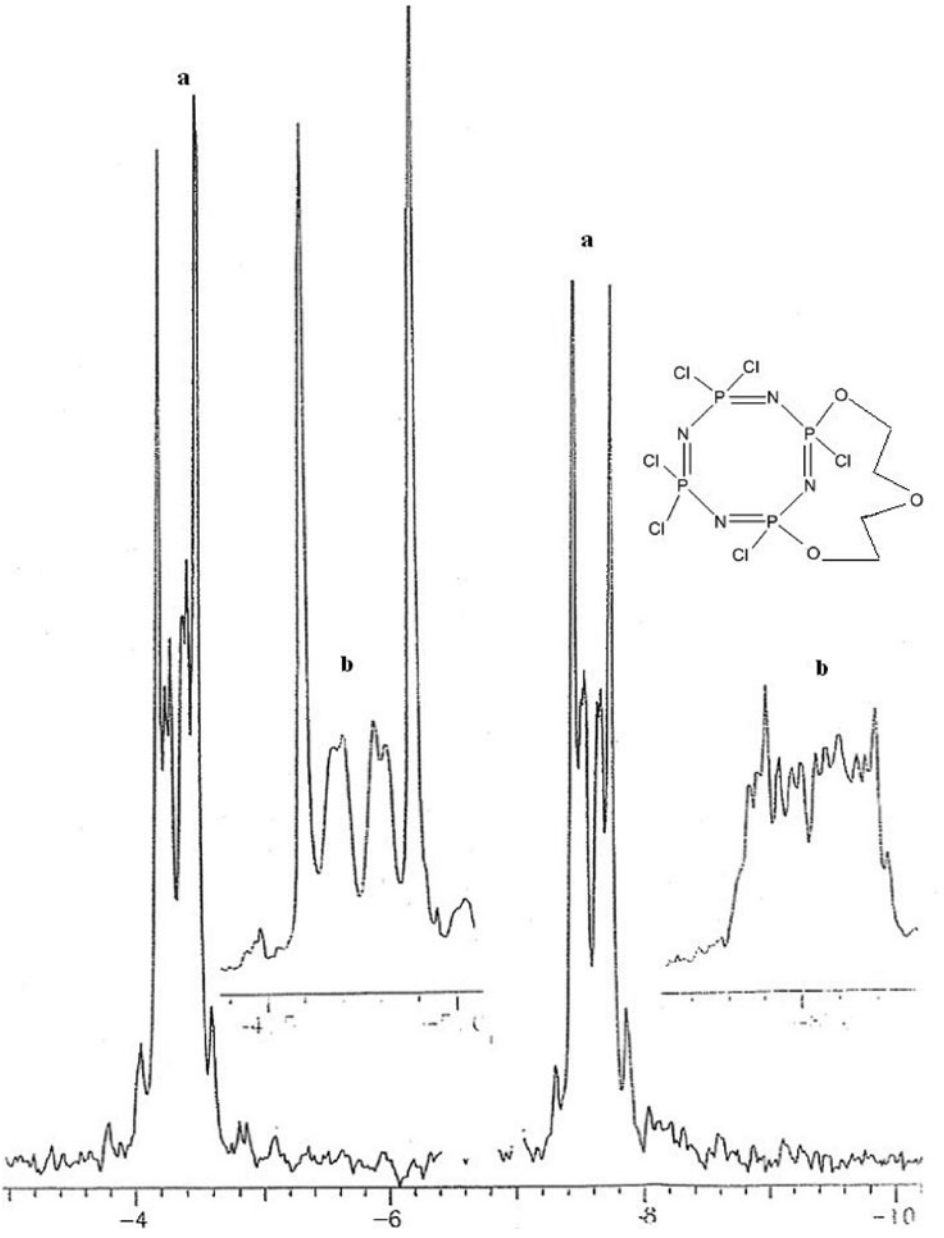

Figure 7 ^{31}P NMR spectra of compound **5**: (a) ^{31}P-^{1}H spectrum, (b) ^{31}P{^{1}H} spectrum, in $CDCl_3$ at 161.83 MHz, (room temperature), referenced to external 85% H_3PO_4.

In the foregoing spin system, second order effects are pronounced, especially in the ethoxy derivatives [40c]. Deviation from first order behavior is most conspicuous in the intensity distribution of the multiplet lines.[55–58] Thus, in the first order spectra the multiplet patterns display mirror–image symmetry with respect to their center frequency; in some compounds this mirror–image symmetry is lost in a manner which increase the

intensities of the bands, which are nearest to each other at the expense of the intensities of the outer parts of the multiplets. This roofing effect is discernible in compound **4**. In compounds where the second order effect is dominating, the second order effect will results in further lines splitting and the spacing of each multiplet will be increased and will then no longer depend on the spin coupling. It is found that the second order effect exists only if the perturbation parameter (λ) value is too large.[1b]

$$^{\lambda}AB = \frac{J_{AB}}{(v_A - v_B)}$$

In both tetramer (**1**) and trimer (**2**) derivatives, the chemical shift value of the =Pspiro and $=PCl_2$ nuclei are further moved downfield upon further replacement of chlorine atoms by another spiro group. When we consider the values of the coupling constants, we will confine ourselves to ^2J(Pspiro-PCl_2) values. Those of the trimer (**2**) derivatives are greater than the corresponding values for the tetramer (**1**) by ~16 Hz. The ^2J[Pspiro-PCl_2] values of the trimer derivatives increased by progressive substitution of the spiro groups. The same pertains also in the tetramer system. Comparison of ^{31}P NMR data for selected spiro and ansa derivatives of cyclotetraphosphazene (**1**) with relative diols are shown in Table 2.

^{1}H NMR Studies

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 two different chemical environments depending on whether they are situated, α- or β- with respect to the oxygen atoms.

The mono spiro **4**, 1,5-mono-ansa **6** 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] The methylene protons in each of these two compounds are equivalent, and are split by coupling with the adjacent methylene protons and with the phosphorus nucleus. The six lines of the $POCH_2$ protons are well resolved in both of the compounds **4** and **6**. The $POCCH_2$ protons appeared as a triplet for compound **4** and further splitting by the phosphorus nucleus is observed as well, giving a total of 6 lines.

In the bis spiro derivatives, $N_4P_4Cl_4[O(CH_2)_2(CH_2)_2O]_2$, (**7** and **8**) 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 alpha-methylene protons are magnetically equivalent. They would see chlorine atoms in both sides, and give rise to a six line multiplet, from coupling with the phosphorus nucleus and adjacent $POCH_2$ protons (centered at 4.36 ppm). The $POCCH_2$ protons are also magnetically identical; a triplet structure is shown coupling with the $POCH_2$ protons, with further splitting from the phosphorous nucleus, six lines are observed, centered at 3.72 ppm. However, a very complex spectrum is observed for the isomeric bis-spiro derivative **8**. The two spiro rings are equivalent as are the α- and the β-methylene groups above and below the rings. Since the each spiro group is flanked on one side by two chlorine atoms and on the other side by another spiro group, the two protons within each methylene group are nonequivalent. Whether this is observed will depend on the conformation of the spiro ring and how pronounced this nonequivalence is. If such a nonequivalence is observed all the methylene groups could in principle give rise to AB quartets with further coupling

Table 2 Comparison of selected ^{31}P NMR parameters of spiro and ansa derivatives of octachlorocyclotetraphosphazene (**1**) with relative diols [39,40 and the present work]

	^{31}P Chemical shift (ppm)			$^{2}J_{PNP}$ (Hz)		
Compound	$2\times PCl_2$ (1)	$1\times PCl_2$ (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	
$N_4P_4Cl_6[O(CH_2)_2O(CH_2)_2O]$[b]	−5.11	−6.62	−11.17	25.7	54.9	
$N_4P_4Cl_6(OCH_2CF_2CF_2CH_2O)$[c]	−1.89	−5.22	−6.10	30.5	63.46	
$N_4P_4Cl_6[OCH_2(CF_2)_4CH_2O]$[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]	−5.11	−7.4	56.37	70.44		
$N_4P_4Cl_6(OCH_2CF_2CF_2CH_2O)$[c]	−1.58/ − 1.58	−2.00/ − 2.00		70.23	93.44	35.25
Trans-dispiro (A_2B_2spin 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		
$N_4P_4Cl_4[O(CH_2)_2O(CH_2)_2O]_2$[b]	−4.36			−9.41	49.14	34.6
$N_4P_4Cl_6(OCH_2CF_2CF_2CH_2O)_2$[c]	1.54			−5.58	63.30	
Tris-spiro (A_2BX spin system)	PCl_2 (1)	$1\times P(OR)_2$ (2)	$2\times P(OR)_2$ (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	
$N_4P_4Cl_2(OCH_2CF_2CF_2CH_2O)_3$[c]	2.13	1.91	−1.39		85.22	62.60
Tetrakis-spiro (A_4 spin system)	$P(OR)_2$					
$N_4P_4[O(CH_2)_4O]_4$[a]		7.1				
$N_4P_4[O(CH_2)_2O(CH_2)_2O]_4$[b]	2.87					
$N_4P_4(OCH_2CF_2CF_2CH_2O)_4$[e]	3.52					
Mono-ansa (AA'BB' spin system)	PCl_2 (1)	P(OR)Cl (2)		1,2	2,2	1,1
$N_4P_4Cl_6[O(CH_2)_2O(CH_2)_2O]$[b]	1,3-ansa	4.60	−7.65	57.60		
$N_4P_4Cl_6[O(CH_2)_2O(CH_2)_2O]$[b]	1,5-ansa	−2.77	−9.30	48.9		

(Continued on next page)

Table 2 Comparison of selected ^{31}P NMR parameters of spiro and ansa derivatives of octachlorocyclotetraphosphazene (**1**) with relative diols [39,40 and the present work] *(Continued)*

	^{31}P Chemical shift (ppm)			$^{2}J_{PNP}$ (Hz)		
Compound	$2\times PCl_2$ (1)	$1\times PCl_2$ (2)	$P(OR)_2$ (3)	1,2	1,3	
Mono-spiro (A_2BC spin system)						
$N_4P_4Cl_6(OCH_2CF_2CF_2CH_2O)$[c]	1,3-ansa	−3.96	0.11	30.88	15.47	15.50
$N_4P_4Cl_6[OCH_2(CF_2)_4CH_2O]$[d]	1,5-ansa	0.39	−0.95	36.8		
Bis-ansa (A_4 spin system)		P(OR)Cl				
$N_4P_4Cl_4[O(CH_2)_2O(CH_2)_2O]_2$[b]	cis-1,3-5,7-bis ansa	−1.48				
$N_4P_4Cl_4[O(CH_2)_2O(CH_2)_2O]_2$[b]	cis-1,5-3,7 bis ansa	−1.07				
$N_4P_4Cl_4[OCH_2(CF_2)_4CH_2O]_2$[d]	cis-1,3-5,7-bis ansa	−2.21				
Tetrakis-ansa (A_4 spin system)	$P(OR)_2$					
$N_4P_4[OCH_2(CF_2)_4CH_2O]_4$[d]	−1.23					

[a]At 80.98 MHz 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, $^{2}J_{PNP}$ values checked by spin simulation.
[e]At 202.38 MHz ^{31}P NMR chemical shifts (ppm) in THF-d_8.

Table 3 Selected ^{1}H NMR data for compounds **4–13**[a]

Compound	δ $POCH_2$[b]	δ $POCCH_2$[b]	$^3J(POCH_2)$[c]
(4)	4.43	3.70	16.79
(5)	4.27	3.75	18.00
(6)	4.34	3.63	16.72
(7)	4.36	3.72	17.10
(8)	4.39	3.66	18.10
(9)	4.31	3.71	17.45
(10)	4.30	3.69	17.80
(11) spiro part	4.32	3.72	17.10
ansa part	4.32	3.70	18.53
(12) spiro part	4.30	3.87	17.60
ansa part	4.26	3.70	18.50
(13)	4.36	3.66	17.10

[a]In CDCl3 (referenced to internal TMS), at 199.5 MHz and 399.95 MHz (room temperature).
[b]In ppm.
[c]In Hz.

to neighboring nuclei. Long-range virtual coupling with the two equivalent phosphorus nuclei will make a triplet of quartets for the α-methylene protons and coupling with the β-methylene protons might, depending on Karplus relationship,[38-40] give rise to 36 or 48 lines. We observed a very complex and unresolved absorptions from the α- and β-methylene protons. The complexity arises, as described above, from the nonequivalence of the $POCH_2$ and POC-CH_2 protons respectively.

The ^{1}H NMR spectra of mono-ansa, $N_4P_4Cl_6[O(CH_2)_2O(CH_2)_2O]$ (**5**) and bis-ansa, $N_4P_4Cl_4[O(CH_2)_2O(CH_2)_2O]_2$ (**9**) derivatives also show complex and unresolved spectra due to the nonequivalence of the methylene protons. Arguments are similar to those of the ansa derivatives of the trimer (**2**).[41–43] Nonequivalence would allow the protons of each group to interact giving rise to an AB quartet, which will be further split by the neighboring protons and phosphorus nuclei leading to complex spectra. Therefore, various multiplets may be anticipated for the $POCH_2$ and the $POCCH_2$ protons. The α-methylene protons would be expected to split into a triplet of quartets by coupling with the β-methylene protons which should be split by virtual coupling with the two equivalence ansa carrying P nuclei into triplet of triplets of quartets. By similar arguments, the β-methylene protons should give as in the case of the α-group, a 36 line spectrum with virtual coupling 48 lines would be observed. The bis-ansa derivative shows a somewhat more complicated ^{1}H NMR spectrum than the mono-ansa compound. This is probably due to the virtual coupling effects. The chemical shift between the nonequivalent methylene groups of the ansa rings are increased by replacing two chlorine atoms by a second ansa ring. The $POCH_2$ and $POCCH_2$ methylene protons are located, as in the case of mono-ansa compound (**5**), as two broad bands with central humps at 4.31 and 3.79 ppm. ^{1}H NMR spectra of compound **6** are shown in figure 8.

Due to the similarity of the proton environments, the chemical shift differences ($POCH_2$ and $POCCH_2$) are very small in each group. Therefore, distinctive signals for each group would be less likely to be detected; instead, overlapping signals are observed. It is also observed that chemical shifts of these derivatives are little affected by the progressive replacement of the chlorine atoms by spiro or ansa groups. Chemical shift differences and coupling constants are presented in the Table 3

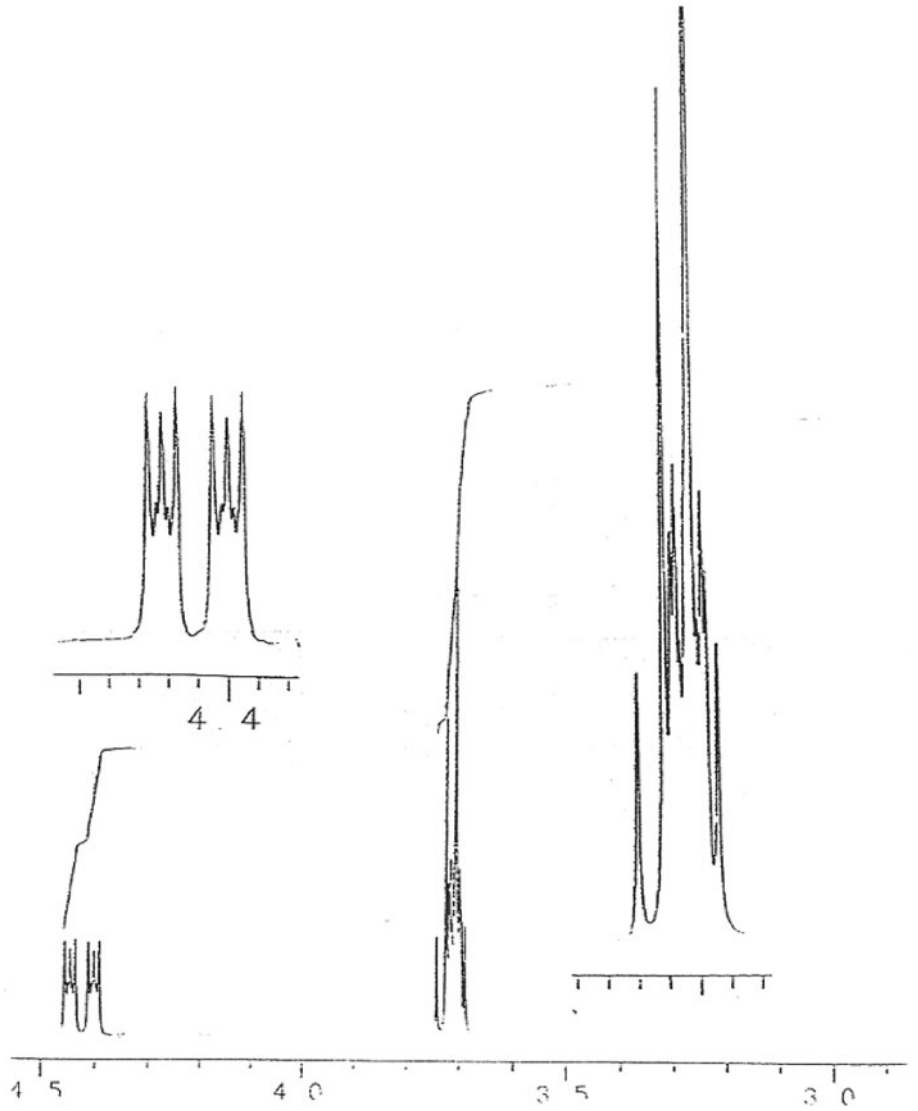

Figure 8 ^{1}H NMR spectrum of compound **6** in $CDCl_3$ at 399.95 MHz and at room temperature, referenced to internal TMS.

^{13}C NMR Studies

The splitting pattern provides more information about the number of the carbon environments. Information was obtained from chemical shifts as well as from coupling constants.

In general, two carbon environments were observed at 50.27 and 100.53 MHz, depending on whether they are alpha-, or beta-carbons relative to the oxygen atoms.

Coupling over two bonds to the phosphorus nuclei is likely, though over three bonds the Karplus[36–38] relationships might reduce the couplings so to be nonobservable. Similar to

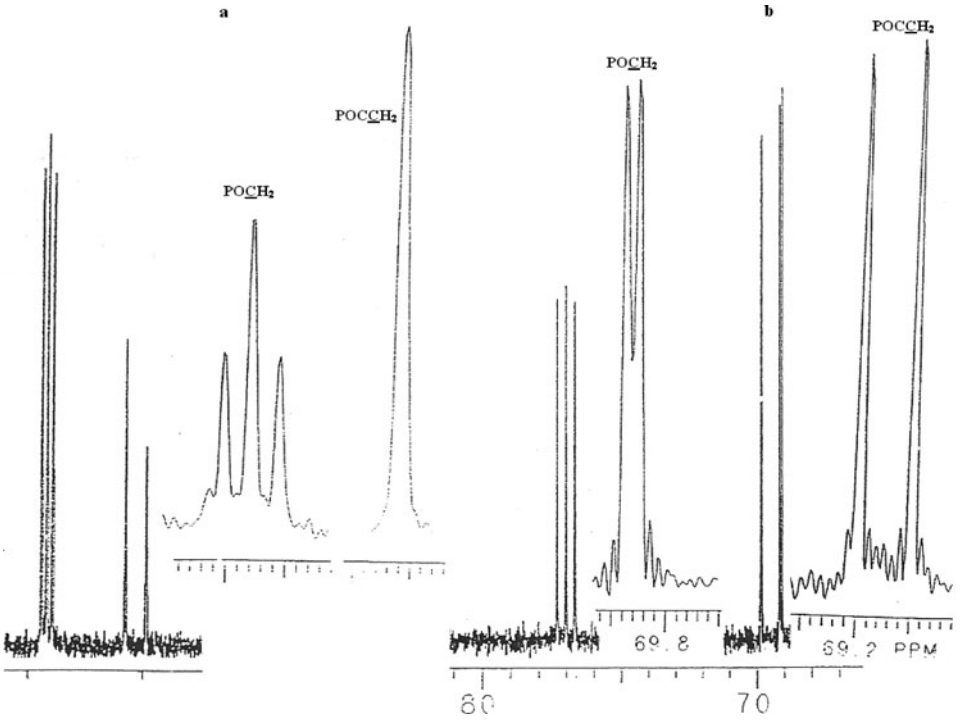

Figure 9 ^{13}C NMR spectra of isomeric ansa derivatives: (a) compound **5**, (b) compound **6**, in $CDCl_3$, at room temperature, at 100.58 MHz.

the homologue trimer (**2**) derivatives, doublets were observed for the $POCH_2$, and $POCCH_2$ carbon nuclei. Upon progressive substitutions of the Chlorine atoms by spiro groups, the doublet structures become subject to further splitting. Those additional lines of the ^{13}C resonances may be attributed to long range virtual coupling effects through interaction of carbon nucleus with a remote phosphorus nucleus. In the series of the compounds, the ^{31}P chemical shift differences between the phosphorus nuclei carrying the spiro group are zero or very small due to the equivalency of the spiro nuclei, which provide the basic condition for virtual coupling to operate.

From the 1,5-mono-ansa **5** and 1,5;3,7-bisansa **11** derivatives, the $POCH_2$ and $POCCH_2$ carbons in the P(OR)Cl linkage are equivalent, hence doublets are observed for the alpha- and the beta-carbons. A three line spectrum is observed for the α-carbons of the bis-spiro derivative **7**, resulting from coupling between the two magnetically and chemically equivalent phosphorus and carbon nuclei (POC). The $POCCH_2$ carbons surprisingly, display a triplet at 68.30 ppm. At higher field (100.53 MHz), no splitting is observed for this region.

The cis-1,3;5,7-bis ansa derivative **9**, gives a triple-lined spectrum for the α-carbon nuclei at 70.06 ppm. Theoretically, it would show a quintet structure, since four phosphorus nuclei are in identical chemical environments and linked to similar groups. Nevertheless, more resolution enhancement of the $POCH_2$ carbon signals did not reveal any alteration. On the other hand, the beta-methylene carbons give rise to a quintet structure at 68.26 ppm

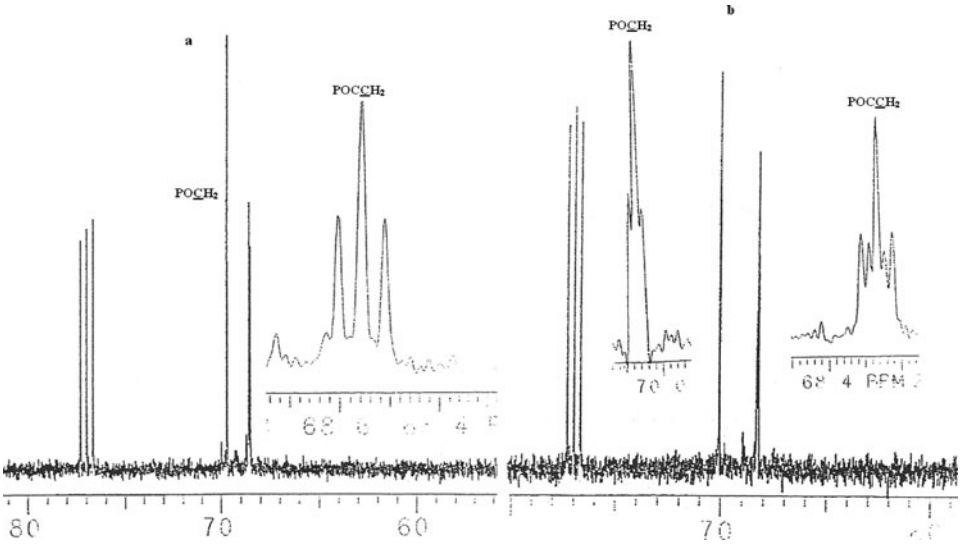

Figure 10 ^{13}C NMR spectra of isomeric bis-spiro and bis-ansa derivatives: (a) compound **7**, (b) compound **9**, in $CDCl_3$, at room temperature, at 100.58 MHz.

as expected. ^{13}C NMR spectra of compounds **5**, **6**, **7**, and **9** are presented in Figures 9 and 10.

When comparing the results of the present study with earlier one on the lower homologue trimer (**2**) derivatives, with bis(2-hydroxyethyl) ether system,[42] coupling constants show much larger differences than chemical shifts. Two bond couplings ^2J(POC) are marginally lower in the tetramer derivatives. The alteration in the three bond coupling is more dramatic and ^3J(POC) values are considerably higher in the tetramer derivatives. ^{13}C NMR NMR data are given in Table 4.

Table 4 Selected ^{13}C NMR data for compounds **4–13**[a]

Compound	δ ($POCH_2$)[b]	δ ($POCCH_2$)[b]	^2J(POC)[c]	^3J(POCC)[c]
(4)	69.93	69.17		9.77
(5)	69.17	68.55		9.40
(6)	69.86	69.14	2.40	9.90
(7)	70.11	68.30		9.20
(8)	70.47	67.91	3.11	9.77
(9)	70.10	68.26	3.50	8.60
(10)	70.94	67.81		9.10
(11)	71.01	68.67		9.20
	69.70	66.80		8.70
(12)	71.81	68.37		9.11
	69.70	68.10		8.71
(13)	68.63	66.51		8.72

[a]In $CDCl_3$ (room temperature) at 50.1 MHz and 100.58 MHz.
[b]In ppm.
[c]In Hz.

EXPERIMENTAL

Materials

Reagent grade solvents were used through the work, THF, benzene, light petroleum (b.p. 40–60°C), anhydrous diethyl ether and chloroform (May and Baker Ltd., London, England), 1,4-dioxane (Fisons Scientific Apparatus, London, England), deuteriated solvents for NMR spectroscopy, bis(2-hydroxyethyl)ether (Aldrich Chem. Co. Ltd., Gillingham, England), pyridine, dichloromethane (B.D.H. Chemical Co. Ltd., East Yorkshire, England), octachlorocyclotetraphosphazatetraene (**1**) (Shin Nisso Kako Co. Ltd., Tokyo, Japan). Solvents were dried by conventional methods.

Methods

All reactions were monitored by using Kieselgel 60° 254 (silica gel) precoated TLC plates and sprayed with Ninhydridine (0.5% w/v) in butanol solution, and developed at approximately 130°C. Separations of products were 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 a 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.

Reactions of Octachlorocyclotetraphosphazatetraene With Bis(2-Hydroxyethyl) Ether

One Equivalent of Compound 2. Tetramer (**1**), (4 g, 8.7 mmol) and bis(2-hydroxethyl) ether (0.91 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 2 h. The reaction mixture was cooled in an ice-bath and anhydrous pyridine (1.37 g, 17.3 mmol) in dichloromethane (30 mL) was added dropwise as a hydrogen chloride acceptor. The reaction mixture was allowed to warm to room temperature and left for a further 16 h stirring. The reaction resulted in the formation of a precipitate. The course of the reaction was followed by TLC with silica gel plates using benzene/dichloromethane (1:6). Stirring was stopped and the apparatus was cooled to room temperature.

Then, the bulk of the pyridine hydrochloride was filtered off and the remaining was removed by column chromatography using a mixture of dichloromethane/benzene (6:1).

Examination of the reaction mixture showed essentially the formation of two major and one minor products. The filtrate was concentrate to 10 mL and about half of the filtrate was applied to a column packed with silica gel (70 g) using dichloromethane/benzene mixture (6:1) as an eluent. (i) The first compound was identified as 1,5-mono-ansa $N_4P_4Cl_6[O(CH_2)_2O(CH_2)_2O]$ (**6**), which was recrystallized from benzene/diethylether (2 : 1), m.p. 187–189°C, yield, 1.10 g (48.5%). Found: C, 9.74; H, 1.65; N, 11.30%; M^+ 494; $C_4H_8O_3N_4P_4Cl_6$ requires, C, 9.71; H, 1.61; N, 11.33%; M, 494. ^{1}H NMR ($CDCl_3$), δPOCH$_2$: 4.34, δPOCCH$_2$: 3.63, ^3J(PH): 16.72 Hz. ^{31}P NMR, ($CDCl_3$), δPCl_2: –9.30, δP(OR)Cl: –2.77, ^2J[PCl$_2$–P(OR)Cl]: 48.9 Hz. ^{13}C NMR ($CDCl_3$), δPOC: 69.86, δPOCC: 69.14, ^2J(PC): 2.40 Hz, ^3J(PC): 9.90 Hz.

(ii) The second compound was identified as mono-spiro, $N_4P_4Cl_6[O(CH_2)_2O(CH_2)_2O]$ (**4**), m.p. 194–197°C, yield, 0.65 g (24.25%). Found: C, 9.75; H, 1.66; N, 11.31%; M^+ 494; $C_4H_8O_3N_4P_4Cl_6$ requires, C, 9.71; H, 1.61; N, 11.33%; M, 494. ^{1}H NMR ($CDCl_3$), δPOCH$_2$: 4.43, δPOCCH$_2$: 3.70, ^3J(PH): 16.79 Hz. ^{31}P NMR, ($CDCl_3$), $\delta 2\times PCl_2$: –5.11, $\delta 1\times PCl_2$: –6.62, δP(OR)$_2$: –11.17, ^2J[PCl$_2$-P(OR)$_2$]: 54.90 Hz, ^2J[PCl$_2$-PCl$_2$]: 25.7 Hz. ^{13}C NMR ($CDCl_3$), δPOC: 69.93, δPOCC: 69.17, ^3J(PC): 9.77 Hz.

(iii) The last compound was identified as bis-spiro mono ansa, $N_4P_4Cl_2[O(CH_2)_2(CH_2)_2O]_3$ (**12**), recrystallized from benzene:diethylether (2:1), m.p. 238–241°C; yield, 0.69 g (24.6%). Found: C, 25.58; H, 3.96; N, 9.99%; M^+ 562; $C_{12}H_{24}O_9N_4P_4Cl_2$ requires, C, 25.61; H, 4.27; N, 9.96%; M, 562. ^{1}H NMR ($CDCl_3$), (spiro part) δPOCH$_2$: 4.30, δPOCCH$_2$: 3.87, ^3J(PH): 17.60 Hz, (ansa part) δPOCH$_2$: 4.26, δPOCCH$_2$: 3.70, ^3J(PH): 18.50 Hz. ^{31}P NMR ($CDCl_3$), δP(OR)Cl: –4.12, δP(OR)$_2$: 6.70, ^2J[P(OR)$_2$–P(OR)Cl]: 69.50 Hz. ^{13}C NMR ($CDCl_3$), δPOC: 71.81/69.70, δPOCC: 68.37/68.10, ^3J(PC): 9.11/8.71 Hz.

Two Equivalents of Compound 2. The same procedure as described above was applied; tetramer (**1**) (4 g, 8.7 mmol), bis(2-hydroxyethy) ether (**3**), (1.82 g, 17.5 mmol), pyridine (2.74 g, 34.60 mmol), stirring time was 24 h. In addition to compound **6**, 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/diethyl ether (4:1) as 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) 1,5-mono-ansa derivative (**6**, 0.67 g, 17.1%), (ii) 1,3-mono-ansa, $N_4P_4Cl_6[O(CH_2)_2(CH_2)_2O]$ (**5**), m.p. 135–138°C, yield, 0.60 g (15.3%). Found: C, 9.73; H, 1.63; N, 11.36%; M^+ 494; $C_4H_8O_3N_4P_4Cl_6$ requires, C, 9.71; H, 1.61; N, 11.33%; M, 4.94. ^{1}H NMR ($CDCl_3$), δPOCH$_2$: 4.27, δPOCCH$_2$: 3.75, ^3J(PH): 18.00 Hz. ^{31}P NMR, ($CDCl_3$), δPCl_2: –4.60, δP(OR)Cl: –7.65, ^2J[PCl$_2$–P(OR)Cl]: 57.60 Hz. ^{13}C NMR ($CDCl_3$), δPOC: 69.17, δPOCC: 68.55, ^3J(PC): 9.40 Hz.

(iii) *trans*-bis-spiro, $N_4P_4Cl_4[O(CH_2)_2O(CH_2)_2O]_2$ (**7**), m.p. 259–261°C, yield 1.6 g (40.8%,). Found: C, 18.1; H, 3.02; N, 10.68%; M+ 528; $C_8H_{16}O_6N_4P_4Cl_4$ requires, C, 18.2; H, 3.03 N, 10.60%; M, 528. ^{1}H NMR ($CDCl_3$), δPOCH$_2$: 4.36, δPOCCH$_2$: 3.72, ^3J(PH): 17.10 Hz. ^{31}P NMR, ($CDCl_3$), δPCl_2: –4.36, δP(OR)$_2$: –9.41, ^2J[P(OR)$_2$–PCl$_2$]: 49.14 Hz, ^2J[PCl$_2$–PCl$_2$]: 34.6. ^{13}C NMR ($CDCl_3$), δPOC: 70.11, δPOCC: 68.30, ^3J(PC): 9.20 Hz.

(iV) *cis*-bis-spiro, $N_4P_4Cl_4[O(CH_2)_2O(CH_2)_2O]_2$ (**8**), m.p. 230–231°C, yield 0.87 g (22.2%). Found: C, 18.24; H, 3.02; N, 10.63%; M^+ 528; $C_8H_{16}O_6N_4P_4Cl_4$ requires, C, 18.2; H, 3.03 N, 10.60%; M, 528. ^{1}H NMR ($CDCl_3$), δPOCH$_2$: 4.39, δPOCCH$_2$: 3.66, ^3J(PH): 18.10 Hz. ^{31}P NMR, ($CDCl_3$), δPCl_2: -5.11, δP(OR)$_2$: –7.4, ^2J[P(OR)$_2$–PCl$_2$]: 56.37 Hz, ^2J[P(OR)$_2$–P(OR)$_2$]: 70.44 Hz. ^{13}C NMR ($CDCl_3$), δPOC: 70.47, δPOCC: 67.91, ^2J(PC): 3.11, ^3J(PC): 9.77Hz.

Three Equivalents of Compound 2. The apparatus for this preparation consists of a 500 mL three-necked round-bottom flask provided with an efficient stirrer and a water condenser fitted with a calcium chloride tube.

$N_4P_4Cl_8$ (**1**) 4 g (8.7 mmol) and bis(2-hydroxethyl) ether (2.73 g. 26.1 mmol) were placed in dichloromethane (150 mL) into the reaction flask and the solution was stirred at room temperature for approximately 2 h. Then, the contents of the flask were stirred and boiled under reflux on a hot place for 20 min. The reaction flask was then cooled to room temperature and to this solution 6 equivalents of pyridine (4.12 g. 52.2 mmol) was added dropwise while stirring. The suspended material was allowed to settle. The mixture was then allowed to reflux at 45–50°C, for approximately 13 h, after which time the reaction was complete. Pyridine hydrochloride precipitated as long thin needle crystals. TLC revealed essentially the formation of four major and one minor product. The solid material was extracted with a further quantity of dichloromethane add the dichloromethane solutions were combined and filtered. The residue was purified by vacuum distillation. An intense spot was observed on the base line of the TLC plate due to pyridine hydrochloride and polymeric materials. The individual phosphazene derivatives were separated by column chromatography using a mixture of benzene and dichloromethane (2:5) as the mobile phase. The products were recrystallized from benzene containing a few drops of light petroleum (b.p. 40–60 °C). (i) The first derivative was identified as 1,5-mono-ansa (**6**, 11.1%).

(ii) *cis*-1,3;5,7-bis-ansa, $N_4P_4Cl_4[O(CH_2)_2O(CH_2)_2O]_2$ (**9**), m.p. 251–252°C, yield 0.35 g (17.1%). Found: C, 18.22; H, 3.07; N, 10.58%; M^+ 528; $C_8H_{16}O_6N_4P_4Cl_4$ requires, C, 18.2; H, 3.03; N, 10.60%; M, 528. ^{1}H NMR ($CDCl_3$), $\delta POCH_2$: 4.31, $\delta POCCH_2$: 3.71, ^3J(PH): 17.45 Hz. ^{31}P NMR, ($CDCl_3$), δP(OR)Cl: –1.48. ^{13}C NMR ($CDCl_3$), δPOC: 70.10, δPOCC: 68.26, ^2J(PC): 3.50 Hz, ^3J(PC): 8.60 Hz.

(iii) monospiro-ansa derivative, $N_4P_4Cl_4[O(CH_2)_2(CH_2)_2O]_2$ (**11**), m.p. 254–256°C, yield 0.43g (21.75%). Found: C, 18.16; H, 3.06; N, 10.61%; M+ 528; $C_8H_{16}O_6N_4P_4Cl_4$ requires, C, 18.2; H, 3.03; N, 10.60%; M, 528. ^{1}H NMR ($CDCl_3$), (spiro part) $\delta POCH_2$: 4.32, $\delta POCCH_2$: 3.72, ^3J(PH): 17.10 Hz, (ansa part) $\delta POCH_2$: 4.32, $\delta POCCH_2$: 3.70, ^3J(PH): 18.53 Hz. ^{31}P NMR, ($CDCl_3$), δPCl_2: -8.94, $\delta P(OR)_2$: 3.03, δP(OR)Cl: –2.19, $^2J[PCl_2–P(OR)_2]$: 63.50 Hz, ^2J[P(OR)Cl–P(OR)$_2$]: 55.90 Hz.^{13}C N.M.R ($CDCl_3$), δPOC: 71.01/69.70, δPOCC: 68.67/66.80, ^3J(PC): 9.20/8.70 Hz.

(iv) *cis*-1,5;3,7-bis ansa, $N_4P_4Cl_4[O(CH_2)_2O(CH_2)_2O]_2$ (**10**), m.p. 225–226°C, yield 0.30 g (16.2%). Found: C, 18.11; H, 3.09; N, 10.56%; M^+ 528; $C_8H_{16}O_6N_4P_4Cl_4$ requires, C, 18.2; H, 3.03; N, 10.6%; M, 528. ^{1}H NMR ($CDCl_3$), $\delta POCH_2$: 4.30, $\delta POCCH_2$: 3.69, ^3J(PH): 17.80 Hz. ^{31}P NMR, ($CDCl_3$), δP(OR)Cl: –1.07. ^{13}C NMR ($CDCl_3$), δPOC: 70.94, δPOCC: 67.81, ^3J(PC): 9.1Hz.

(v) The last fraction was assigned as a tetrakis-spiro derivative, $N_4P_4[O(CH_2)_2O(CH_2)_2O]_4$ (**13**), m.p. 264–267°C, yield 0.22 g (10.3%). Found: C, 32.33; H, 5.41; N, 9.38%; M^+ 596; $C_8H_{16}O_6N_4P_4Cl_4$ requires, C, 32.21; H, 5.36; N, 9.4%; M, 596. ^{1}H NMR ($CDCl_3$), $\delta POCH_2$: 4.36, $\delta POCCH_2$: 3.66, ^3J(PH): 17.10. ^{31}P NMR, ($CDCl_3$), $\delta P(OR)_2$: 2.87. ^{13}C NMR ($CDCl_3$), δPOC: 68.63, δPOCC: 66.51, ^3J(PC): 8.72 Hz.

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