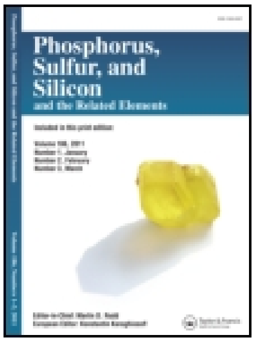

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Phosphorus-Nitrogen Compounds: The Reactions of Hexachlorocyclotriphosphazatriene with Pentane-1,5-Diol. Nuclear Magnetic Resonance Studies of The Products

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PHOSPHORUS-NITROGEN COMPOUNDS: THE REACTIONS OF HEXACHLOROCYCLOTRIPHOSPHAZATRIENE WITH PENTANE-1,5-DIOL. NUCLEAR MAGNETIC RESONANCE STUDIES OF THE PRODUCTS

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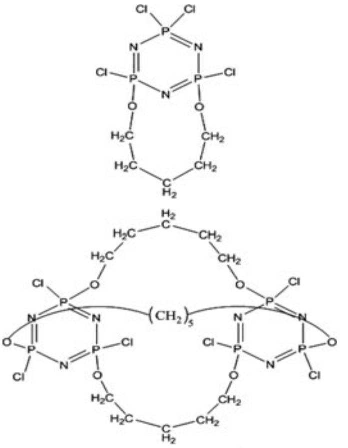
GRAPHICAL ABSTRACT



Abstract *From the reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$ (1) with pentane-1,5-diol (2) in dichloromethane solution, the following derivatives have been isolated: 2,2-spiro(1′,5′-pentanedioxy)-4,4,6,6-tetrachlorocyclotriphosphazatriene, $N_3P_3Cl_4[O(CH_2)_5O]$ (3); its ansa isomer, 1,3-ansa(1′,5′-pentanedioxy)-1,3,5,5-tetrachlorocyclotriphosphazatriene, (4); bis spiro(1′,5′-pentanedioxy)-6,6-dichlorocyclotriphosphazatriene, $N_3P_3Cl_2[O(CH_2)_5O]_2$ (5); its spiro-ansa isomer, (1′,5′-pentanedioxy)-1,3-dichlorocyclotriphosphazatriene (6); as well as the bino(1,5-pentanedioxy)-di-(pentachlorocyclotriphosphazatriene), $N_3P_3Cl_5[O(CH_2)_5O]N_3P_3Cl_5$ (7), and tri-bino(1,5-pentanedioxy)-di (trichlorocyclotriphosphazatriene), $N_3P_3Cl_3[O(CH_2)_5O]_3N_3P_3Cl_3$, (8) derivatives. Their structures were established by*

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MS and NMR with the use of ^{1}H, ^{13}C, and ^{31}P spectroscopy. Product types and relative yields are compared with those of the previously investigated diol derivatives. The yield of the mono-ansa product (25%) obtained in this system was considerably increased relative to those of the propane-1,3-diol derivative (11.2%) and decreased relative to the 2,2-dimethyl-propane-1,3-diol (36.2%), and bis(2-hydroxyethyl) ether (34.5%) derivatives.

[Supplementary materials are available for this article. Go to the publisher's online edition of Phosphorus, Sulfer, and Silicon and the Related Elements *for the following free supplemental files:* Additional tables and figures.*]*

Keywords Hexachlorocyclotriphosphazatriene; pentane-1,5-diol; ansa structure; spiro compounds; bridged structures; NMR studies

INTRODUCTION

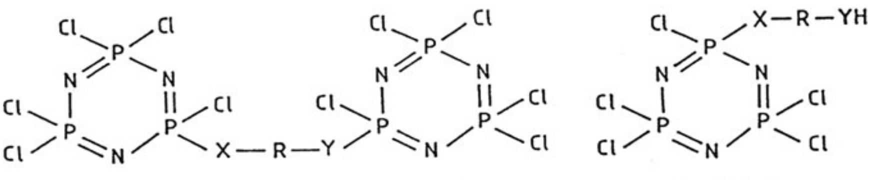
The reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$ (1), and octachlorocyclotetraphosphazatetraene $N_4P_4Cl_8$ (2), with various diols have been previously reported.[1–24] The reactions of the hexachloride, (1) with ethane-1,2-, propane-1,3-, and butane-1,4-diols have been the subject of systematic investigations[3,5] which gave examples of all four structural types: spiro, $N_3P_3[O(CH_2)_nO]_xCl_{6\text{-}y}$ ($n = 2, 3, 4, x = 1, 2, 3; y = 4, 2, 0$), and ansa, $N_3P_3[O(CH_2)_nO]Cl_4$ ($n = 3, 4$); spiro-ansa, $N_3P_3[O(CH_2)_nO]_2Cl_2$ ($n = 3, 4$); bridging, $N_3P_3Cl_{6\text{-}x}[O(CH_2)_nO]N_3P_3Cl_{6\text{-}x}$ ($n = 3, 4; x = 1, 2, 3$), and dangling, $N_3P_3[O(CH_2)_nOH]_xCl_5$ ($n = 3, 4$), with the first predominating.[3] General examples of the structural types are presented in Figure 1.

When the central CH_2 group in propane-1,3-diol was exchanged for an electron-donating CMe_2 group in 2,2-dimethylpropane-1,3-diol,[4] ansa moieties were increased relative to spiro units when compared to propane-1,3-diol.[3] By contrast, replacement of the CH_2 grouping by an electron-withdrawing $C(CO_2Et)_2$ moiety gave exclusively spiro products.[5,19]

Crystal structures of some of these have been reported (spiro, ansa, and bridged derivatives)[9–11,16–23] as well as the ^{35}Cl n.q.r. spectra of three of the mono-spiro derivatives $N_3P_3[O(CH_2)_nO]_xCl_{6\text{-}y}$ ($n = 2, 3, 4, x = 1; y = 2$).[12]

Spiro (1)

Ansa (2)



Bridging (3)

Open Chain (4)
(Dangling)

Figure 1 General examples of the structural types.

We now report our findings for pentane-1,5-diol. The spiro derivatives were by far the major products, especially for the ethane- and propane-diols.[3,5] Bridged derivatives assumed significant importance with butane-diol.[3] The spiro-ansa compounds were in considerably smaller amounts than their dispiro isomers in the pentane-1,5-diol system. The ansa derivatives were isolated in only trace amounts in the propane-1,3- and butane-1,4-diols,[3,5] but in considerably higher amounts in 2,2-dimethyl-propane-1,3–[4] and pentane-1,5-diols and in bis(2-hydroxyethyl) ether.[1] Bridged compounds were obtained in better yields than danglers.[2,3,8]

In the reactions of pentane-1,5-diol, in the presence of pyridine, as an HCl scavenger and using dichloromethane as a solvent, mono-ansa (25%) and spiro-ansa (21%) formations slightly predominate over their mono-spiro (22.9%) and dispiro (20.7%) isomers. The mono-ansa compound was also isolated as the major product in this system. However, in the reactions, using dioxane as a solvent and pyridine as tertiary base, mono-spiro (31.5%) and dispiro (24.6%) formations predominate over their isomeric mono-ansa (23.1%) and spiro-ansa (17.5%) structures. The same observations also pertain to the reactions of 2,2-dimethyl-propane-1,3-diol,[1] when dichloromethane was used as a solvent, mono-ansa (36.2%) and spiro-ansa (17.1%) derivatives predominated over their mono-spiro (24%) and dispiro (14.1%) isomers. As in the earlier investigations, the solvent systems have a great influence over product types and relative yields of cyclophosphazenes. The structures of compounds from pentane-1,5-diol (1–8) are presented in Figure 2.

RESULTS AND DISCUSSION

Structural characterization for the compounds reported were based at first on the ^{31}P proton-coupled ^{31}P [+{^{1}H}] and decoupled ^{31}P{-^{1}H-} spectra. ^{1}H and ^{13}C NMR and elemental analysis were applied for auxiliary support.

The existence of all isomeric forms was confirmed further by the fact that the observed fine splitting by proton coupled spectroscopic experiments gave unambiguous structural assignments.

Isomeric compounds were distinguished by recording proton-coupled ^{31}P NMR spectra, when fine structure was observed for the ≡Pspiro and ≡P(OR) parts of the compounds. These experiments left the ^{31}P NMR spectra of the ≡PCl_2 moiety unaltered. This indicates that the splitting are due to phosphorus-proton couplings for P nuclei, which carry spiro, ansa, bridging or dangling moieties within the -P-N-P- subunits. We now discuss their structure based on NMR spectroscopic studies.

^{31}P NMR Studies

Compounds (3) and (4), whose analysis and mass spectra showed these to be isomers of $N_3P_3Cl_4[O(CH_2)_5O]$, could have in principle two structures: Spiro (3) or ansa (4). Both types are known from propane-1,3-, 2,2-dimethyl-propane-1,3-diols, and bis(2-hydroxyethyl) ether. Experience with these two isomers shows that the ansa compound has an AB_2 spectrum, while that of the spiro isomer is of the A_2X type. Proton coupling affects the B_2 part of the former and X part of the latter. The spectrum of compound (3) is of the A_2X type, with the X part showing further splitting on proton coupling. Thus, this compound can be assigned with confidence the spiro structure (3). Its isomer has an AB_2 spectrum and its B_2 part is affected by proton coupling. It is thus assigned the ansa structure

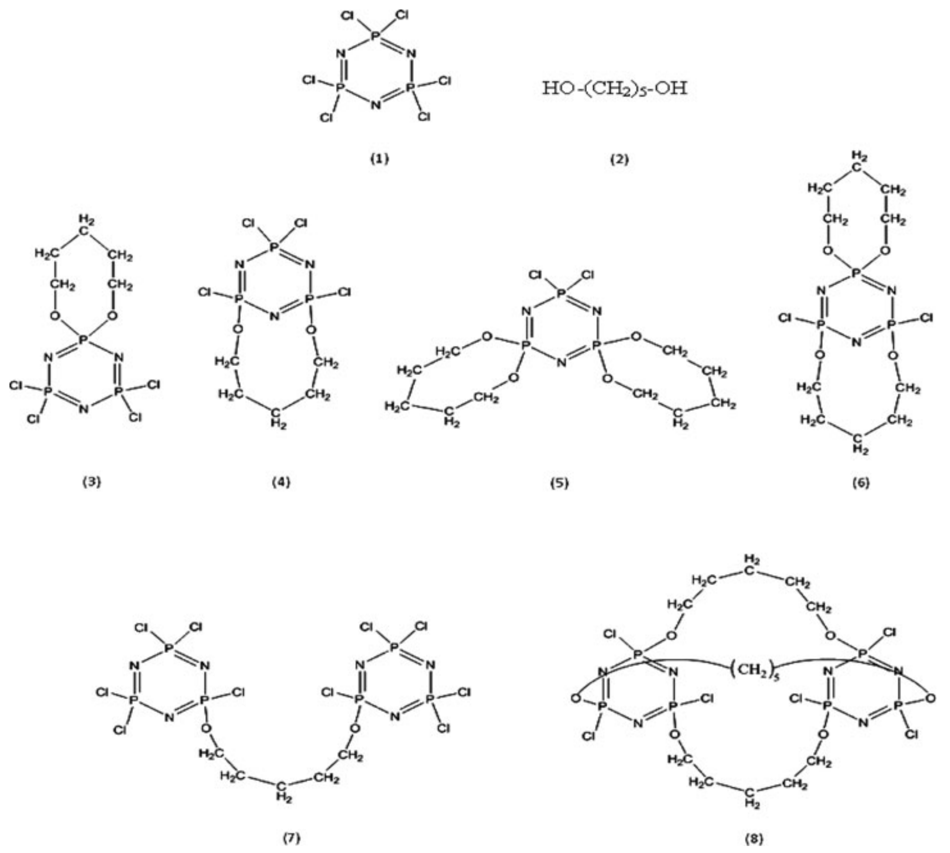


Figure 2 Structures of compounds.

(4). The ^{31}P NMR spectra at 24.15 MHz and 162.0 MHz of the four mono-spirodioxy derivatives, $N_3P_3[O(CH_2)_nO]Cl_4$ ($n = 2$, 3, 4, and 5), are given in Figure 3.

The isomeric compounds (5) and (6) exhibit A_2X and AB_2 type spectra, respectively. ^{31}P NMR proton-coupled spectrum of the spiro-ansa structure allows identification of the lines due to the ≡Pspiro and ≡P(OR)Cl groups, where each group split into further lines. Proton coupling experiments as well as comparison with the analogues propane-1,3-diol, bis(2-hydroxyethyl) ether and 2,2-dimethylpropane-1,3-diol derivatives allow unambiguous assignments of structures. Compound (5) is the dispiro and its isomer is the spiro-ansa (6). The ^{31}P NMR proton-coupled and decoupled spectra of compound (6) are exhibited in Figure 4.

Compound (7) has an A_2B type spectrum, consisting of two distinct groups of signals representing the ≡P(OR)Cl and the $\equiv PCl_2$ groups, respectively, and shows that the two phosphazene rings are chemically equivalent. The phosphorus proton-coupled spectrum suggests that the A_2 part of the spectrum arises from $\equiv PCl_2$ groups, since it remains unaffected, whereas the B part, which splits into further lines, is assigned to the ≡P(OR)Cl groups. We, therefore, assign a single-bridged structure (7) to this. In contrast to the butane-1,4-diol[3] and the bis(2-hydroxethyl) ether[1] systems, here compound (7) is in lower yield. In the case of compound (8), which was purified with great difficulties, where the ^{31}P NMR

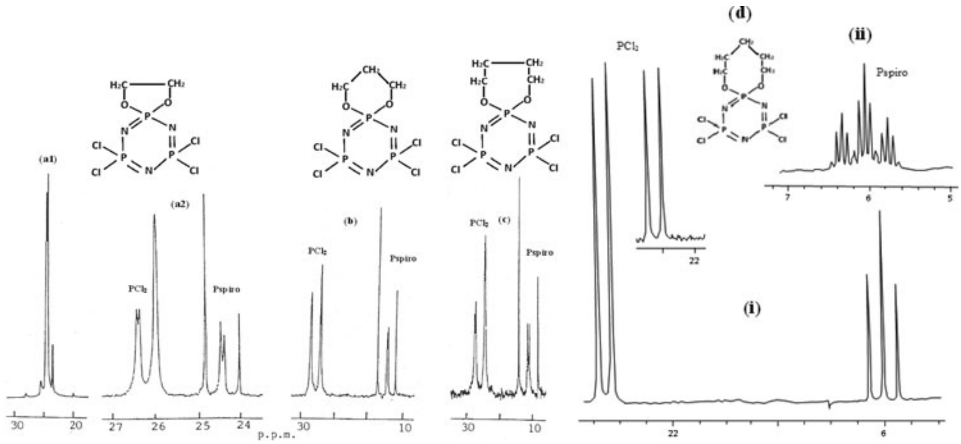


Figure 3 ^{31}P NMR spectra of mono-spiro derivatives, $N_3P_3Cl_4[O(CH_2)_2O]$ (a1, a2); $N_3P_3Cl_4[O(CH_2)_3O]$ (b); $N_3P_3Cl_4[O(CH_2)_4O]$ (c); $N_3P_3Cl_4[O(CH_2)_5O]$ (d), (i) proton decoupled, (ii) proton-coupled spectra, at room temperature, in $CDCl_3$, (a1, b, and c) at 24.15 MHz, (a2 and d) at 162.00 MHz, referenced to external 85% H_3PO_4.

spectrum is of the A_3 spin type. An A_3 spin system arises, when the phosphorus nuclei in the two bridgeheads have identical or very similar environments. The ≡P(OR)Cl groups are in identical environments and linked to similar groups; therefore, one single line is observed for this compound. The ^{31}P NMR proton-coupled spectra of compounds (4) and (5) are presented in Figure 5.

The following points are noteworthy: (a) the ≡Pspiro nuclei are deshielded in the order -6-membered > 7-membered > 5-membered spiro rings. (b) The effect of the spiro substituent on the ≡PCl_2 nuclei shows the same order, giving rise to some of the most

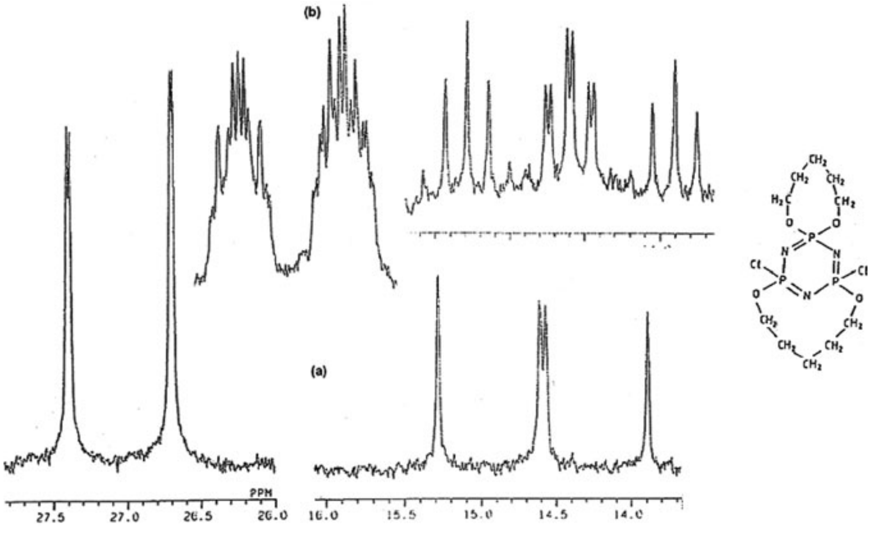


Figure 4 ^{31}P NMR spectra of spiro-ansa compound, $N_3P_3Cl_2[O(CH_2)_5O]_2$, (a) proton-decoupled spectrum, (b) proton-coupled spectrum, at room temperature, in $CDCl_3$, at 162.00 MHz, referenced to external 85% H_3PO_4.

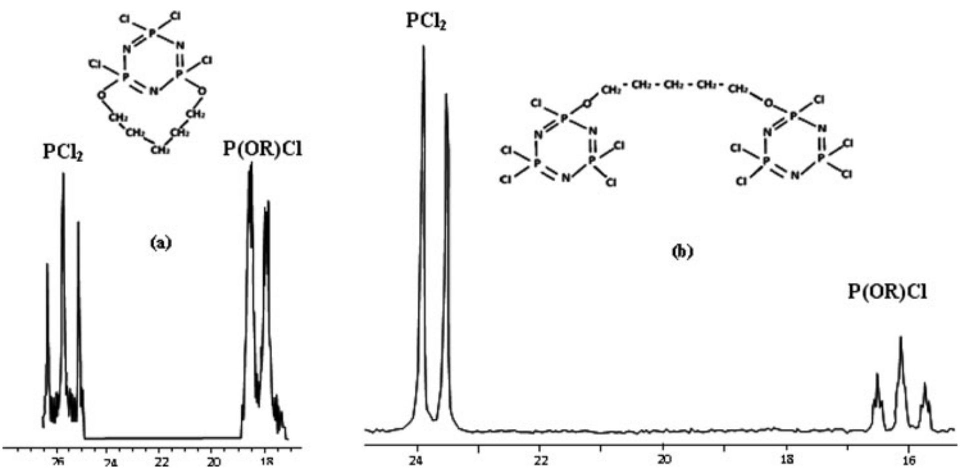


Figure 5 ^{31}P NMR proton-coupled spectra of mono-ansa compound, $N_3P_3Cl_4[O(CH_2)_5O]$ (a), (4) and bino cyclophosphazene derivative, $N_3P_3Cl_5[O(CH_2)_5O]N_3P_3Cl_5$ (b), (7), at room temperature, in $CDCl_3$, at 162.00 MHz, referenced to external 85% H_3PO_4.

deshielded $\equiv PCl_2$ nuclei recorded. (c) While the chemical shifts of the $\equiv$Pspiro nuclei cover a large range (27–34 ppm), the shifts of the $\equiv$P(OR)Cl nuclei vary little from $\delta = 16$, if the OR group is acyclic, but changes drastically for the ansa compounds to δ 30–31. This may be related to the ring compression, which has been observed, and is due to a reduced *trans-annular* distance.[11] (d) All two bond coupling constants, ^2J (PP), are large and in the range of 57–77 Hz.

The chemical shift values with the phosphorus–phosphorus spin–spin coupling constant values are given in Table 1 and comparative, related diol derivatives are presented in Table 2.

Table 1 ^{31}P NMR data of derivatives (1), (3–8)[a]

Compound	δPCl$_2$[b]	δPspiro[b]	δP(OR)Cl[b]
1.	19.9		
3.[c]	23.1	5.3	
4.[d]	26.8		18.7
5.[e]	25.4	10.3	
6.[f]		14.6	27.0
7.[g]	23.8		16.1
8.			21.7

[a] In $CDCl_3$, referenced to external 85% phosphoric acid (H_3PO_4), at room temperature, at 162.0 MHz.

[b] In ppm.

[c] ^{2}J(Pspiro-PCl$_2$:71.4 Hz.

[d] ^{2}J[P(OR)Cl-PCl$_2$]: 67.4 Hz.

[e] ^{2}J(Pspiro-PCl$_2$): 74.3Hz.

[f] ^{2}J[Pspiro-P(OR)Cl]: 80.6 Hz.

[g] ^{2}J[P(OR)Cl-PCl$_2$]: 62.3 Hz.

Table 2 ^{31}P NMR data for the diol derivatives of $N_3P_3Cl_6$ (1)

Compound Mono-spiro	$\delta\underline{P}Cl_2$	$\delta\underline{P}(OR)_2$	$^2J_{PNP}$ (Hz)
Gem-$N_3P_3Cl_4(OMe)_2$[25]	25.1	9.2	65.0
$N_3P_3Cl_4[NH(CH_2)_2NH]$[3]	24.9	24.4	56.2
$N_3P_3Cl_4[O(CH_2)_2NH]$[3]	23.5	22.9	47.1
$N_3P_3Cl_4[O(CH_2)_2O]$[3,25]	26.5	24.4	68.0
$N_3P_3Cl_4[O(CH_2)_3O]$[3,25]	24.1	3.4	69.2
$N_3P_3Cl_4[O(CH_2)_4O]$[3]	24.1	10.3	70.5
$N_3P_3Cl_4[O(CH_2)_5O]$ (3)	23.1	5.3	71.4
$N_3P_3Cl_4[O(CH_2)_6O]$[23]	23.2	4.8	64.9
$N_3P_3Cl_4[(OCH_2CH_2)_2O]$[1]	23.2	4.9	70.8
$N_3P_3Cl_4[OCH_2C(Me)_2CH_2O]$[4]	23.3	2.2	69.3
$N_3P_3Cl_4[OCH_2(CF_2)_2CH_2O]$[16]	25.2	8.6	75.0
$N_3P_3Cl_4[OCH_2(CF_2)_3CH_2O]$[16]	24.8	7.5	74.6
$N_3P_3Cl_4[OCH_2CH(OC(O) = CH_2)O]$[25]	26.1	24.0	68.5
$N_3P_3Cl_4[OCH_2CMe(CH_2OC(O) = CH_2)$ $CH_2O]$[a][25]	25.2, 23.3	3.5	76.1[b], 61.8[b], 60.6[c]
Bis-spiro	$\delta\underline{P}Cl_2$	$\delta\underline{P}(OR)_2$	$^2J_{PNP}$ (Hz)
$N_3P_3Cl_2[O(CH_2)_2O]_2$[3]	31.3	30.9	76.8
$N_3P_3Cl_2[O(CH_2)_3O]_2$[3]	26.5	9.1	70.8
$N_3P_3Cl_2[O(CH_2)_4O]_2$[3]	27.8	16.0	76.9
$N_3P_3Cl_2[O(CH_2)_5O]_2$ (5)	25.4	10.3	74.3
$N_3P_3Cl_2[(OCH_2CH_2)_2O]_2$[1]	25.9	10.2	59.3
$N_3P_3Cl_2[OCH_2C(Me)_2CH_2O]_2$[4]	26.1	8.7	70.4
$N_3P_3Cl_2[OCH_2(CF_2)_2CH_2O]_2$[16]	29.5	14.4	81.5
$N_3P_3Cl_2[OCH_2(CF_2)_3CH_2O]_2$[16]	28.6	12.9	79.6
Tris-spiro		$\delta\underline{P}(OR)_2$	
$N_3P_3[O(CH_2)_2O]_3$[3]		37.4	
$N_3P_3[O(CH_2)_3O]_3$[3]		14.1	
$N_3P_3[O(CH_2)_4O]_3$[3]		21.7	
$N_3P_3[(OCH_2CH_2)_2O]_3$[1]		15.3	
$N_3P_3[OCH_2C(Me)_2CH_2O]_3$[4]		13.9	
$N_3P_3[OCH_2(CF_2)_2CH_2O]_3$[16]		19.9	
$N_3P_3[OCH_2(CF_2)_3CH_2O]_3$[16]		17.8	
Mono-ansa	$\delta\underline{P}Cl_2$	$\delta\underline{P}(OR)Cl$	$^2J_{PNP}$ (Hz)
$N_3P_3Cl_4[O(CH_2)_3O]$[3]	29.5	30.5	56.9
$N_3P_3Cl_4[O(CH_2)_5O]$ (4)	26.8	18.7	67.4
$N_3P_3Cl_4[O(CH_2)_6O]$[23]	26.9	19.9	67.3
$N_3P_3Cl_4[(OCH_2CH_2)_2O]$[4]	27.6	22.3	75.3
$N_3P_3Cl_4[OCH_2C(Me)_2CH_2O]$[4]	23.5	25.0	64.2
$N_3P_3Cl_4[OCH_2(CF_2)_2CH_2O]$[16]	25.2	23.6	65.0
$N_3P_3Cl_4[OCH_2(CF_2)_3CH_2O]$[16]	25.3	20.1	67.9
$N_3P_3Cl_4[OCH_2(CF_2)_4CH_2O]$[17]	26.7	19.6	69.2
Spiro-ansa	$\delta\underline{P}(OR)_2$	$\delta\underline{P}(OR)Cl$	$^2J_{PNP}$ (Hz)
$N_3P_3Cl_2[O(CH_2)_3O]_2$[3]	10.1	31.2	73.0
$N_3P_3Cl_2[O(CH_2)_4O]_2$[3]	17.2	28.2	79.3
$N_3P_3Cl_2[O(CH_2)_5O]_2$ (6)	14.6	27.0	80.6
$N_3P_3Cl_2[O(CH_2)_6O]_2$[3]	13.7	26.5	72.0
$N_3P_3Cl_2[(OCH_2CH_2)_2O]_2$[1]	14..4	27.1	75.3
$N_3P_3Cl_2[OCH_2C(Me)_2CH_2O]_2$[4]	9.8	31.8	70.9
$N_3P_3Cl_2[OCH_2(CF_2)_3CH_2O]_2$[16]	12.6	24.8	86.8
$N_3P_3Cl_2[OCH_2(CF_2)_2CH_2O]_2$[16]	2.9	28.5	86.5
Bino	$\delta PCl2$	$\delta\underline{P}(OR)Cl$	$^2J_{PNP}$ (Hz)

Table 2 ^{31}P NMR data for the diol derivatives of $N_3P_3Cl_6$ (1) *(Continued)*

Compound Mono-spiro	$\delta\underline{P}Cl_2$	$\delta\underline{P}(OR)_2$	$^{2}J_{PNP}$ *(Hz)*
$N_3P_3Cl_5[O(CH_2)_3O]N_3P_3Cl_5$[3]	23.4	16.0	63.0
$N_3P_3Cl_5[O(CH_2)_4O]N_3P_3Cl_5$[3]	23.5	15.9	61.9
$N_3P_3Cl_5[O(CH_2)_5O]N_3P_3Cl_5$ (7)	23.8	16.1	62.3
$N_3P_3Cl_5[O(CH_2)_6O]N_3P_3Cl_5$[23]	23.7	16.1	62.1
$N_3P_3Cl_5[O(CH_2)_8O]N_3P_3Cl_5$[23]	23.6	16.1	62.1
$N_3P_3Cl_5[(OCH_2CH_2)_2O]N_3P_3Cl_5$[1]	23.5	25.8	49.3
$N_3P_3Cl_5[OCH_2C(Me)_2CH_2O]N_3P_3Cl_5$[4]	24.6	8.1	63.5
$N_3P_3Cl_5[OCH_2(CF_2)_4CH_2O]N_3P_3Cl_5$[17]	23.8	17.6	65.2
Bis-bino	δPCl2	$\delta\underline{P}(OR)Cl$	$^{2}J_{PNP}$ *(Hz)*
$N_3P_3Cl_4[O(CH_2)_6O]_2N_3P_3Cl_4$[23]	26.5	27.7	63.4
$N_3P_3Cl_4[O(CH_2)_8O]_2N_3P_3Cl_4$[23]	23.6	16.2	62.1
$N_3P_3Cl_4[(OCH_2CH_2)_2O]_2N_3P_3Cl_4$[1]	25.8	26.1	61.8
$N_3P_3Cl_4[OCH_2C(Me)_2CH_2O]_2N_3P_3Cl_4$[4]	26.4	27.5	57.6
$N_3P_3Cl_4[OCH_2(CF_2)_4CH_2O]_2N_3P_3Cl_4$-anti[17]	26.0	20.4	67.3
$N_3P_3Cl_4[OCH_2(CF_2)_4CH_2O]_2N_3P_3Cl_4$-syn[17]	26.1	20.4	67.7
Tri-bino		$\delta\underline{P}(OR)Cl$	
$N_3P_3Cl_3[O(CH_2)_5O]_3N_3P_3Cl_3$ (8)		22.7	
$N_3P_3Cl_3[O(CH_2)_6O]_3N_3P_3Cl_3$[23]		22.1	
$N_3P_3Cl_3[O(CH_2)_8O]_3N_3P_3Cl_3$[23]		22.3	
$N_3P_3Cl_3[(OCH_2CH_2)_2O]_3N_3P_3Cl_3$[1]		24.6	
$N_3P_3Cl_3[OCH_2C(Me)_2CH_2O]_3N_3P_3Cl_3$[4]		25.2	
$N_3P_3Cl_3[OCH_2(CF_2)_4CH_2O]_3N_3P_3Cl_3$[17]		23.1	

[a]Exhibits an ABX spin system, [b]PCl_2-P(spiro) coupling [c]PCl_2- Cl_2 coupling.

^{1}H NMR Studies

The ^{1}H NMR spectra are similar to those in our earlier investigations. With the help of these earlier investigations[1–24] the interpretation of the present derivatives has been made easier. The $OC\underline{H}_2$ protons are about 0.45 ppm more shielded than those of the corresponding 1,3-propane-diol derivatives. The ansa (4), the dispiro (5), the ansa portion of the spiro-ansa (6), and compound (8) show remarkable similarity in $OC\underline{H}_2$ chemical shifts. $^{3}\underline{J}(\underline{PH})$ values fall into three distinct groups; (i) mono spiro (3), and the spiro section of the spiro-ansa derivative (6); (ii) ansa (4), ansa section of compound (6), compounds (7) and (8); (iii) dispiro compound (5).

In this system, methylene protons occur in three different chemical environments depending on whether they are situated, α-, β- or γ- with respect to the oxygen atoms. When pentane-1,5-diol forms part of a ring, further nonequivalence may occur. Thus, for example, in the spiro part of the spiro-ansa compound the α-methylene protons as well in the β-methylene protons are nonequivalent as the group above and below the phosphazene ring are in different chemical environments, those above the ring seeing the ansa group, those below the chlorine atoms. However, within each methylene group the two protons are equivalent. By contrast, in the ansa moiety the two α-methylene groups are equivalent. The same applies to the β-methylene groups, but all the methylene groups α-, β- and γ-methylene protons have nonequivalent protons.

The α-, β-methylene protons of the mono-spiro compound within each methylene group are equivalent. In the ansa moiety the two α- and the two β-methylene groups are equivalent, but the two methylene protons within each methylene group are nonequivalent as one faces toward the other away from the N_3P_3 ring and its spiro group. The integrated signals from the α-, β- and γ-methylene protons are as expected in the ratio of 4:4:2. In formally saturated systems one may expect coupling over two and three bonds, though in the latter case this will depend on the Karplus relationship.[6,7] More rarely one can observe small four-bond coupling. The α-methylene protons, which, subject to the Karplus relationship, will give rise to two triplets by coupling with the adjacent phosphorus nucleus and the β-methylene protons. The β-methylene protons might be expected to couple with two α- and two γ-methylene protons and, subject to the Karplus relationship, may give rise either to quintet or two triplets. The gamma methylene protons would show up to five lines.

The mono-spiro derivative has a relatively simple proton spectrum, giving a six-line spectrum for the methylene protons ($POC\underline{H}_2$) at 4.22 ppm, from coupling with the neighboring β-methylene protons and the phosphorus nucleus. On the other hand, the β-methylene protons ($POCH_2$-$C\underline{H}_2$-CH_2) give two quintets spectra at 1.80 ppm due to coupling with the two α-, two γ-protons, and with the phosphorus nucleus.

In the case of the γ-methylene protons, a quintet structure is observed at 1.57 ppm. This signal does not manifest any kind of coupling with the phosphorus nucleus, since the protons are too far away from the phosphorus nucleus and, therefore, no further splitting would be expected.

The mono-ansa (4) and spiro-ansa (6) compounds give rise to very complex ^1H spectra. For reasons, which have been enumerated above.

At 200 and 400 MHz, very complex spectra were observed suggesting that the α-methylene protons are not sufficiently resolved. Accidental coincidence leads to fewer lines than expected. Detailed consideration of the ^1H NMR spectrum of the spiro-ansa (6) derivative was not possible due to the complexity of the $POC\underline{H_2}$ and $POCC\underline{H}_2$ protons of the spiro and the ansa groups. That may be attributed to the coalescence of large number of lines and because of the closeness of the chemical shifts. Therefore, it is difficult to make an assignment between the signals of the specific protons in the spiro and ansa rings. The $^3J(\underline{PH})$ values of the ansa portion of the spiro-ansa compound (6) are noticeably smaller than those of the others.

The ^1H NMR spectra of the bis-spiro derivatives are by far the most complex and also the most interesting. The protons of the two $OC\underline{H}_2$ and the two $CC\underline{H}_2$ methylene groups are equivalent, but within each methylene group the two protons are nonequivalent due to their being part of a cyclic moiety and, therefore, the two protons of each methylene group see a different environment. This is most pronounced for the 6-membered and least for the 8- and 10-membered rings.

In dispiro structures, the two spiro rings are equivalent as are the α- and the β-methylene groups above and below the rings. However, because 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. In the propane-1,3-diol system,[3] this nonequivalence was quite noticeable for the α-methylene protons and even more pronounced for the β-methylene protons. With the pentane dioxy system, nonequivalence might be observed at any one or all of the α-, β- and γ-methylene protons. If such a nonequivalence is observed, all the methylene groups could in principle give rise to AB quartets with further coupling 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,[6,7] give rise to 36 or 48 lines. However, 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 $POC\underline{H}_2$ and POC-$C\underline{H}_2$, protons, respectively. For the α-methylene protons, a complex overlap of signals, occurred at 4.17 ppm, predicted about 34 lines. Very complex overlap signals for the POC-$C\underline{H}_2$, protons are also observed centered at 1.78 ppm. The γ-methylene (POC-C-$C\underline{H}_2$) protons displayed a symetrical five-line spectrum, centered at 1.41 ppm, arising from coupling with the four nonequivalent adjacent methylene protons; no further coupling with the phosphorus nucleus was observed.

The NMR spectrum of the dispiro derivative[3] $N_3P_3Cl_2[O(CH_2)_2O]_2$ displays a better fine structure than that of the dispiro compound $N_3P_3Cl_2[O(CH_2)_5O]_2$ (5). In the former, the nonequivalence of the methylene protons is considerably more pronounced.

Compound (7) shows three different environments as expected for the α-, β- and γ-methylene protons. The α-methylene protons are equivalent and give rise to a six-line band, located about at 4.18 ppm, three lines from coupling with the adjacent β-methylene protons, which are further split into six lines from coupling with the phosphorus nucleus. The β-methylene protons show a five-line multiplet centered at 1.83 ppm, arising from coupling with the four neighboring α- and γ-methylene protons. Even when the resolution of the spectrum is enhanced, no coupling with the phosphorus nucleus is observed. The γ-methylene ($POCH_2$-CH_2-$C\underline{H}_2$) protons give rise to a five-line multiplet at 1.53 ppm, arising from coupling with adjacent $POCC\underline{H}_2$ protons.

We have noted above that in the reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, (1) with ethane-, propane-1,3-, and butane-1,4-diols the[2–4] spiro derivatives were the most prevalent products. These contained, with the above reagents, 5-, 6-, and 7-membered phosphate rings. By contrast, the ansa derivatives predominated within 2,2-dimethylpropane-1,3-diol, bis(hydroxethyl) ether and pentane-1,5-diol, which contained respectively 8-, 8-, and 10-membered phosphate rings. In a number of these, the $OC\underline{H}_2$ protons, and, where appropriate, the $CC\underline{H}_2$ protons were in different chemical environments. Differences in chemical shifts of these methylene protons were the most pronounced in the 6-membered phosphate rings, and these proved most useful for structural assignments. The ^1H data are presented in Table 3.

Table 3 ^1H NMR data of derivatives (1), (3–8)[a]

Compound	$\delta POC\underline{H}_2$[b]	$\delta POCH_2C\underline{H}_2$[b]	$\delta POCH_2CH_2C\underline{H}_2$[b]	$^3J(\underline{PH})$[c]
3	4.24	1.80	1.28	11.63
4	4.17	1.78	1.25	12.02
	4.13	1.71		
5	4.28	1.74	1.30	13.04
6 Spiro	4.35	1.75	1.27	12.11
	4.29	1.70		12.11
Ansa	4.23	1.66	1.23	8.25
	4.16	1.61		8.21
7	4.22	1.65		13.08
8	4.14	1.62		12.94

[a] In $CDCl_3$ (TMS internal reference) at 199.5 and 399.95 MHz (room temperature).

[b] In ppm.

[c] In Hz.

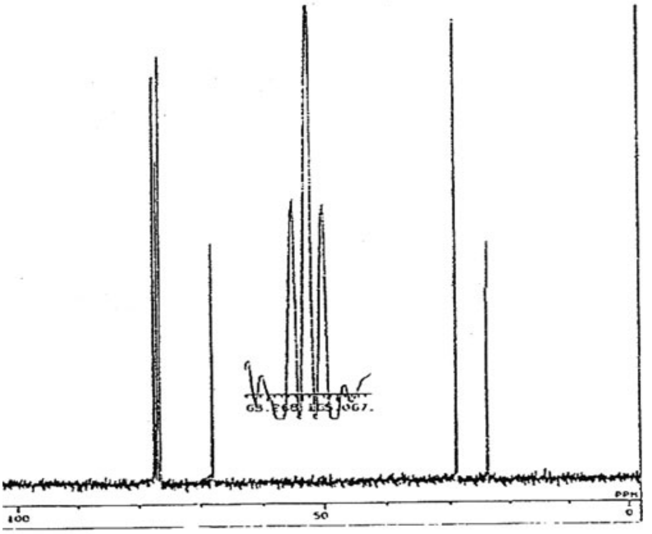


Figure 6 ^{13}C NMR spectrum of bis-spiro derivative, $N_3P_3Cl_2[O(CH_2)_5O]_2$ (5), in $CDCl_3$, at room temperature, at 100.13 MHz.

^{13}C NMR Studies

In general, for all pentane-1,5-diol derivatives, three carbon environments were observed at 50.27 MHz and 100.53 MHz, except for the spiro-ansa derivative (where eight different carbon environments were observed), depending on whether they are α-, β-, or γ-relative to the oxygen atoms. Coupling over two bonds to the phosphorus nuclei is likely, though over three bonds the Karplus[6,7] relationships might reduce the couplings so to be nonobservable. Unlike the proton NMR spectra, the bis-spiro derivatives will not exhibit any nonequivalence due to different methylene carbon environments, but like the proton

Table 4 ^{13}C N.M.R. data of derivatives (3–8)[a]

Compound	δPO$\underline{C}$[b]	δPOC$\underline{C}$[b]	δPOCC$\underline{C}$[b]	$\underline{^2}J(\underline{P\text{-}C})$[c]	$\underline{^3}J(\underline{P\text{-}C})$[c]
3	69.1	28.7	23.6	8.60	8.34
4	68.5	27.5	19.8	8.20	—
5	68.1	28.8	23.6	5.96	—
6 Spiro	69.2[d]	29.4[d]	21.2[d]	5.90	8.52
	69.5[d]	27.1[d]		5.87	8.09
Ansa	68.0[e]	28.4[e]	20.0[e]	7.59	—
7	69.3	29.0	21.5	7.53	8.59
8	68.1	28.9	22.5	7.73	10.22

[a] In $CDCl_3$ (TMS internal reference) at 100.3 MHz.

[b] In ppm.

[c] In Hz.

[d] spiro part.

[e] ansa part of the spiro-ansa compound.

Footnote: For compound 4 and ansa part of the spiro-ansa compound (5), $\underline{^3}J(\underline{P\text{-}C})$ values are not observable, the resolution was not good enough.

NMR spectrum, in the spiro-ansa derivative, the α- and the β-carbon nuclei of the spiro ring may show nonequivalence due to the different 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 the γ-carbons) and 5 from the spiro moiety (two α-, two β-, and one for the γ-nuclei).^{13}C NMR spectrum of compound (5) is presented in Figure 6.

We observed in our earlier studies, on the bis(2-hydroxyethyl) ether,[1] that the chemical shifts of the α- and the β- carbon nuclei were close together, as both are adjacent to oxygen atoms. By contrast for the pentane-1,5-diol system the different chemical environments are well separated. The three bond coupling constants $^3\underline{J}(\mathrm{PC\underline{C}})$ are very much larger than the two bonds coupling $^2\underline{J}(\mathrm{PC})$, and hence the expected multiplicities can be readily seen in the former, but only rarely in the latter. The three-bond coupling constant in compound 8 is significantly larger than in the spiro, ansa or singly-bridged groups. The ^{13}C NMR chemical shifts and their coupling constants are presented in Table 4.

CONCLUSIONS

All spiro, ansa, and bridged derivatives based on the above reaction system were synthesized, separated by column chromatography and characterized by elemental analyses, MS, and ^{31}P NMR spectroscopy with auxiliary use of $^{\mathbf{1}}$H and $^{\mathbf{13}}$C NMR spectra.

If we consider the present findings pertaining to the reactions of pentane-1,5-diol with the hexachlorocyclotriphosphazatriene (1), and compare these with our earlier observations, based on the lower analogue diols, we note resemblances as well as contrasts. While the reactions of ethane-1,2-diol, propane-1,3-diol and butane-1,4-diol gave predominantly spiro derivatives, the present study with pentane-1,5-diol gave predominantly ansa and bridged derivatives.

On the other hand, as in the 2,2-dimethylpropane-1,3-diol [4] and bis(2-hydroxyethyl) ether [1], we could not isolate any dangler formation from pentane-1,5-diol, whereas butane-1,4-diol [5] gives dangling derivative more readily.

A brief comparison of our data on pentane-1,5-diol (A) with that of the recently published results of its hexafluoro-analog (B) may be appropriate.[16] The percentage of diol residues in spiro, ansa, and bridging positions are (A):(B) for spiro 52:53, ansa 26:47, and bridging 22:0. The yields of spiro moieties are virtually identical, while we observed fewer ansa groups. Our yield for bridging entities is relatively large, in sharp contrast to the complete absence reported for the fluorinated diol. We note that there are two further differences, apart from the replacement of 6 H atoms by 6 F atoms, between the two reaction systems here compared. We used the neutral diol with pyridine as the hydrogen chloride acceptor; the other study used an anionic reagent. In addition, we used as solvent dichloromethane, while theirs was THF. We have already commented above that solvents effects could be important. Thus the relative yields of spiro, ansa, and bridging moieties will need further studies to systematize.

EXPERIMENTAL

Materials

Chemicals were obtained as follows:

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

Methods

All reactions were monitored using Kieselgel 60^0 254 (silica gel) precoated t.l.c. 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 flash column chromatography using Kieselgel 60. Melting points were determined on a Reichart-Kofler micro heating stage and a Mettler FB 82 hot stage connected to a FP 800 central processor both fitted with a polarising 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., University College, London). Samples were dissolved in $CDCl_3$ and placed in 5 mm NMR tubes. Measurements were carried out using a $CDCl_3$ 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., University College, London), a Varian 400 spectrometer (operating at 162.0 MHz., University College, London); 85% H_3PO_4 was used as an 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., University College, London), TMS was used as an internal reference. The mass spectra were recorded using a VG 7070H Mass Spectrometer with Finingan INCOS Data System at University College, London, and a VG 2AB IF mass spectrometer at the School of Pharmacy. Microanalyses were carried out by University College, London microanalytic service.

Reactions of Hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$ (1) with Pentane-1,5-diol, $[HO(CH_2)_5OH)]$ (2)

(a) With one equivalent of pentane-1,5-diol.

Hexachlorocyclotriphosphazatriene (4 g, 11.49 mmol) in dichloromethane (100 mL) was placed in a 500 mL single-necked round bottom flask. Pyridine anhydrous (1.8 g, 22.99 mmol) was added dropwise to this trimer (1) solution. The reaction mixture was cooled. Then pentane-1,5-diol (1.21 g, 11.65 mmol) was dissolved in dichloromethane (50 mL) and placed in a 150 mL dropping funnel. This solution was allowed to run with stirring into trimer/pyridine solution. On completion of the addition, the reaction mixture was allowed to attain room temperature and then stirred for 20 h.

The reaction mixture was filtered and the filtrate was concentrated (15 mL). T.l.c. revealed the formation of the two major components, accompanied by unreacted starting materials. An intense spot was observed on the base line of the t.l.c. plate, presumably due to pyridine hydrochloride and polymeric products. Separation of these compounds was achieved by using column chromatography (150 g, silica gel, and a solvent system of dichloromethane: benzene (5:1) as an eluent. Fractions containing the major compounds were collected, taken to dryness, and then the residue recrystallized from light petroleum containing a few drops of benzene. The first compound was characterized as 2,2-spiro(1′,5′-pentanedioxy)-4,4,6,6-tetrachlorocyclotriphosphazatriene, $N_3P_3Cl_4[O(CH_2)_5O]$ (3), m.p. 164°C, and yield 1 g. (22.9%). [Found: C, 15.85; H, 2.57; N, 11.16%; $\underline{M}^+$, 377, $C_5H_{10}O_2N_3P_3Cl_4$ requires: C, 15.91; H, 2.65; N, 11.14%; $\underline{M}$, 377]. ^{1}H NMR, δPOC$\underline{H}_2$: 4.24, δPOCH$_2$C$\underline{H}_2$: 1.80, δPOCH$_2$CH$_2$C$\underline{H}_2$: 1.28, $^3J(\underline{PH})$: 11.63 Hz. ^{31}P NMR, $\delta\underline{P}$Cl$_2$: 23.1, $\delta\underline{P}$spiro: 5.3, $^2J(\underline{P}$spiro-$\underline{P}$Cl$_2)$: 71.40 Hz. ^{13}C N.M.R, δPO$\underline{C}$: 69.1, δPOC$\underline{C}$: 28.7, δPOCC$\underline{C}$: 23.6, $^2J(\underline{P}$-$\underline{C})$: 8.60 Hz, $^3J(\underline{P}$-$\underline{C})$: 8.34 Hz.

The second compound was identified as bis-spiro(1′,5′-pentanedioxy)-6,6-dichlorocyclotriphosphazatriene, $N_3P_3Cl_2[O(CH_2)_5O]_2$ (5), m.p. 109–110°C; yield, 0.83 g., (20.75%); [Found: C, 29.62; H, 4.42; N, 10.53%; $\underline{M}^+$, 409, $C_{10}H_{20}O_4N_3P_3Cl_2$ requires, C, 29.33; H, 4.88; N, 10.26%; $\underline{M}$, 409]. ^{1}H NMR, δPOC$\underline{H}_2$: 4.28, δPOCH$_2$C$\underline{H}_2$: 1.74, δPOCH$_2$CH$_2$C$\underline{H}_2$: 1.30, $^3J(\underline{PH})$: 13.04 Hz. ^{31}P NMR, $\delta\underline{P}$Cl$_2$: 25.4, $\delta\underline{P}$spiro: 10.3, $^2J(\underline{P}$spiro-$\underline{P}$Cl$_2)$: 74.30 Hz. ^{13}C N.M.R, δPO$\underline{C}$: 68.1, δPOC$\underline{C}$: 28.8, δPOCC$\underline{C}$: 23.6, $^2J(\underline{P}$-$\underline{C})$: 5.96 Hz.

(b) With two equivalents of pentane-1,5-diol.

Trimer (1) hexachlorocyclotriphosphazatriene (4 g, 11.49 mmol) was dissolved in dichloromethane (100 mL) and the mixture stirred at room temperature for 15 min. A solution of anhydrous pyridine (2.75 g, 34.76 mmol, three equivalents) in 10 mL of dichloromethane was added dropwise to the reaction mixture. After the reaction mixture was cooled, pentane-1,5-diol (2.42 g, 23.30 mmol) was dissolved in dichloromethane (50 mL) and added to trimer/pyridine solution. The reaction mixture was allowed to attain room temperature. The stirring was continued for a further 2 h, and then the mixture was boiled under reflux for further 5 h. The reaction mixture was allowed to attain room temperature. The light brownish mixture was filtered off and the filtrate was concentrated. T.L.C. showed the presence of five major compounds. Separation of these compounds was achieved by using column chromatography (50 g, silica gel, and a solvent system of light petroleum (b.p. 40–60°C): benzene (3.5:2) as an eluent. Fractions were combined and evaporated to dryness.

The first compound was characterized as mono-spiro (3), yield 0.83 g. (19%). Characterization details are above as in (a).

The second compound was identified as the tri-bino(1,5-pentanedioxy)-di-(trichlorocyclotriphosphazatriene), $N_3P_3Cl_3[O(CH_2)_5O]_3N_3P_3Cl_3$, (8), m.p. 141°C, yield 0.31 g. (7.75%). [Found: C, 22.71; H, 3.81; N, 10.53%; $\underline{M}^+$, 786; $C_{15}H_{30}O_6N_6P_6Cl_6$, requires, C, 22.80; H, 3.80; N, 10.60%; $\underline{M}$, 786].^{1}H NMR, δPOC$\underline{H}_2$: 4.14, δPOCH$_2$C$\underline{H}_2$: 1.62, $^3J(\underline{PH})$: 12.94 Hz. ^{31}P NMR, $\delta\underline{P}$(OR)Cl: 21.7, ^{13}C N.M.R, δPO$\underline{C}$: 68.1, δPOC$\underline{C}$: 28.9, δPOCC$\underline{C}$: 22.5, $^2J(\underline{P}$-$\underline{C})$: 7.73 Hz, $^3J(\underline{P}$-$\underline{C})$: 10.22 Hz.

(c) With three equivalents of pentane-1,5-diol.

The reaction was carried out as in (a), but the stirring time was 12 h. Four major products were separated by column chromatography using a mixture of dichloromethane: benzene, (7:2.5) as eluent.

The mono-ansa derivative, 1,3-ansa(1′,5′-pentanedioxy)-1,3,5,5-tetrachlorocyclotriphosphazatriene, $N_3P_3Cl_4[O(CH_2)_5O]$ (4); m.p. 66.5–67°C, yield, 1.2 g, (25%). [Found: C, 15.94; H, 2.61; N, 10.99%; $\underline{M}^+$, 377; $C_5H_{10}O_2N_3P_3Cl_4$, requires, C, 15.91; H, 2.65; N, 11.14%; $\underline{M}$, 377]. ^{1}H NMR, δPOC$\underline{H}_2$: 4.17, 4.13; δPOCH$_2$C$\underline{H}_2$: 1.78, 1.71; δPOCH$_2$CH$_2$C$\underline{H}_2$: 1.25, $^3J(\underline{PH})$: 12.02 Hz. ^{31}P NMR, $\delta\underline{P}$Cl$_2$: 26.8, $\delta\underline{P}$(OR)Cl: 18.7, $^2J[\underline{P}$(OR)Cl$\underline{P}$Cl$_2]$: 67.40 Hz. ^{13}C N.M.R, δPO$\underline{C}$: 68.5, δPOC$\underline{C}$: 27.5, δPOCC$\underline{C}$: 19.8, $^2J(\underline{P}$-$\underline{C})$: 8.24 Hz.

The spiro-ansa compound, spiro-ansa(1′,5′-pentanedioxy)-1,3-dichlorocyclotriphosphazatriene, $N_3P_3Cl_2[O(CH_2)_5O]_2$ (6); m.p. 91.5–92°C; yield, 0.84 g, (21.00%). [Found: C, 29.48; H, 4.84; N, 10.29%; $\underline{M}^+$ 409; $C_{10}H_{20}O_4N_3P_3Cl_2$ requires C, 29.33; H, 4.88; N, 10.26%; $\underline{M}$, 409]. ^{1}H NMR, Spiro part, $\delta \mathrm{POC\underline{H}_2}$: 4.35, 4.29; $\delta \mathrm{POCH_2C\underline{H}_2}$: 1.75, 1.70, $\delta \mathrm{POCH_2CH_2C\underline{H}_2}$: 1.27, $^3\mathrm{J\underline{(PH)}}$: 12.11 and 12.11 Hz; Ansa part, $\delta \mathrm{POC\underline{H}_2}$: 4.23, 4.16, $\delta \mathrm{POCH_2C\underline{H}_2}$: 1.66, 1.61, $\delta \mathrm{POCH_2CH_2C\underline{H}_2}$: 1.23, $^3\mathrm{J\underline{(PH)}}$: 8.25 and 8.21 Hz. ^{31}P NMR, $\delta \mathrm{\underline{P}spiro}$: 14.6, $\delta \mathrm{\underline{P}(OR)Cl}$: 27.0, $^2\mathrm{J[\underline{P}spiro\text{-}\underline{P}(OR)Cl]}$: 80.60 Hz. ^{13}C N.M.R, Spiro part, $\delta \mathrm{PO\underline{C}}$: 69.2, 69.5, $\delta \mathrm{POC\underline{C}}$: 29.4, 27.1, $\delta \mathrm{POCC\underline{C}}$: 21.2, $^2\mathrm{J(\underline{P}\text{-}\underline{C})}$: 5.90 and 5.87 Hz, $^3\mathrm{J(\underline{P}\text{-}\underline{C})}$: 8.52 and 8.09 Hz; Ansa part, $\delta \mathrm{PO\underline{C}}$: 68.0, $\delta \mathrm{POC\underline{C}}$: 28.4, $\delta \mathrm{POCC\underline{C}}$: 20.0, $^2\mathrm{J(\underline{P}\text{-}\underline{C})}$: 7.59 Hz.

The bino(1,5-pentanedioxy)-di-(pentachlorocyclotriphosphazatriene) derivative, $N_3P_3Cl_5[O(CH_2)_5O]N_3P_3Cl_5$ (7), an oily product, yield, 0.57 g, (14.25%); [Found: C, 8.14; H, 1.22; N, 11.76%; $\underline{M}^+$ 722, $C_5H_{10}O_2N_6P_6Cl_{10}$ requires, C, 8.31; H, 1.38; N, 11.63%; $\underline{M}$, 722].^{1}H NMR, $\delta \mathrm{POC\underline{H}_2}$: 4.22, $\delta \mathrm{POCH_2C\underline{H}_2}$: 1.65, $^3\mathrm{J\underline{(PH)}}$: 13.08 Hz. ^{31}P NMR, $\delta \mathrm{\underline{P}Cl_2}$: 23.8, $\delta \mathrm{\underline{P}(OR)Cl}$: 16.1, $^2\mathrm{J[\underline{P}(OR)Cl\text{-}\underline{P}Cl_2]}$: 62.30 Hz. ^{13}C N.M.R, $\delta \mathrm{PO\underline{C}}$: 69.3, $\delta \mathrm{POC\underline{C}}$: 29.0, $\delta \mathrm{POCC\underline{C}}$: 21.5, $^2\mathrm{J(\underline{P}\text{-}\underline{C})}$: 7.53 Hz, $^3\mathrm{J(\underline{P}\text{-}\underline{C})}$: 8.59 Hz.

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