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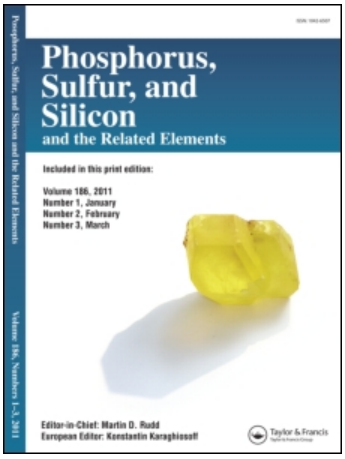

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PHOSPHORUS-NITROGEN COMPOUNDS. PART 68.[1] THE REACTIONS OF HEXACHLOROCYCLOTRIPHOSPHAZATRIENE ANDOCTACHLOROCYCLOTETRAPHOSPHAZATETRAENE WITH PENTAERYTHRITOL

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PHOSPHORUS-NITROGEN COMPOUNDS. PART 68.[1] THE REACTIONS OF HEXACHLOROCYCLOTRIPHOSPHAZATRIENE AND OCTACHLOROCYCLOTETRAPHOSPHAZATETRAENE WITH PENTAERYTHRITOL

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(Received May 2, 1990)

The reactions of hexachlorocyclotriphosphazatriene and octachlorocyclotetraphosphazatetraene with pentaerythritol give rise to spirane derivatives, $N_3P_3Cl_4[(OCH_2)_2C(CH_2O)_2]N_3P_3Cl_4$ and $N_4P_4Cl_6$-$[(OCH_2)_2C(CH_2O)_2]N_4P_4Cl_6$, as well as to a spiro/ansa, $N_3P_3Cl_4[(OCH_2)_2C(CH_2O)_2]N_3P_3Cl_4$ and a spiro-open-chain, $N_3P_3Cl_4[(OCH_2)_2C(CH_2OH)_2]$ derivative. N.m.r. investigations of these products are reported.

Key words: Hexachlorocyclotriphosphazatriene; octachlorocyclotetraphosphazatetraene, pentaerythritol; spirane derivative; spiro-ansa derivative; n.m.r. studies.

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INTRODUCTION

We have recently reported the reaction of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, (**1**), and of octachlorocyclotetraphosphazatetraene, $N_4P_4Cl_8$, (**2**) with difunctional and trifunctional aliphatic alcohols.[1–7] With the diols, we refer particularly to propane-1,3-diol, which with compound (**1**) gave rise mainly to spiro derivatives.[2] Additionally, however, ansa, open-chain and bridge derivatives were isolated and characterised. More recently we have investigated the reactions of compounds (**1**) and (**2**) with 2,2-dimethylpropane-1,3-diol.[3,6]

To our knowledge only one reaction of the six-membered ring phosphazene (**1**) with a tetrafunctional reagent has been reported[8] and none for the eight-membered ring analogue (**2**). The reaction of (**1**) with the tetrafunctional amine, spermine, gave the spiro-bridged structure (**3**).[8]

We now report the reactions of a tetrafunctional aliphatic hydroxy compound, pentaerythritol, (**4**), with the chlorophosphazenes (**1**) and (**2**). Our interest in this reagent arose (**a**) out of its tetrafunctionality and its potential as a model for phosphazene polymers and (**b**) as it could be regarded as a substituted propane-1,3-diol, $(HOCH_2)_2CR_2$, (**5**). We had earlier investigated the effect of varying the substituents (R = H[2], Me[3], CO_2Et[4]) on product type and relative yields. The C-methylated diol (**5**, R = Me) gave a rather higher ratio of ansa (**6**) to spiro isomer (**7**) than its parent diol (**5**, R = H). For our purposes it will be useful to compare

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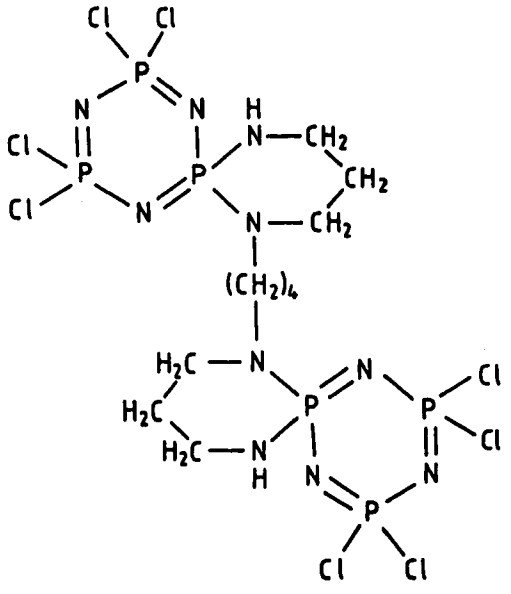

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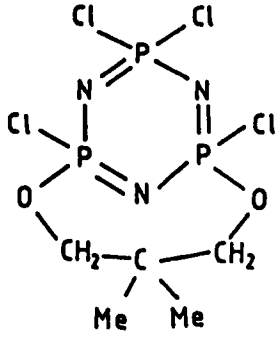

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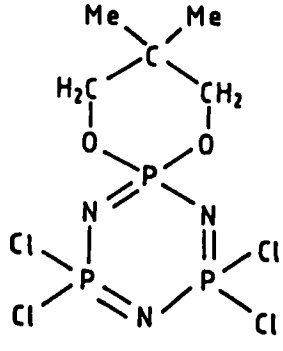

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the diols (**5**, R = Me) with pentaerythritol (**4**). We can regard the latter, (**4**), as a derivative of the former, by replacing in $(HOSH_2)_2C(CH_2R)_2$ R = OH by R = H.

RESULTS AND DISCUSSION

The reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, (**1**) and of its homologue, $N_4P_4Cl_8$, (**2**) with pentaerythritol $C(CH_2OH)_4$, (**4**) are very difficult, because of the sparing solubility of this tetra-ol in any kind of non-hydroxylic organic solvent. Hence yields of these derivatives are small.

The reactions of $N_3P_3Cl_6$ with 2,2-dimethylpropane-1,3 diol leads, in general, to the formation of spiro structures, although ansa structures, e.g. (**6**), have been isolated[3] in greater yields than in the unmethylated analogue.[2]

In the reaction of pentaerythritol with the hexachloride (**1**) a large number of

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possible products might theoretically be formed, since after the initial reaction with a single phosphazene ring to give a spiro or an ansa structure, two further functional groups remain free. These have the potential to react with a second phosphazene ring. In the reactions of compound (**1**) with pentaerythritol in the presence of pyridine using dichloromethane as a solvent, spiro formation predominates. The major compound isolated (**8**) contains two spiro units linking two phosphazene rings. This compound was also isolated as the major product (85% relative yield) in the reaction of pentaerythritol using acetonitrile as solvent and pyridine as tertiary base. However, in this case a second compound was isolated in low yield (15%). This compound again consists of two phosphazene rings linked through the pentaerythritol moiety, but in this case both ansa and spiro moieties are observed within the same molecular structure (**9**). When acetonitrile is used as solvent, but the tertiary base is changed to dimethylaminopyridine, $Me_2NC_5H_5N$, the major product is a mono spiro structure containing a single phosphazene unit in which only two ends of the tetrafunctional reagent have reacted leaving two free —OH groups (**10**). This can be described as a spiro-open-chain derivative.

The $^{31}P\{^1H\}$, ^{31}P-^1H, ^1H and ^{13}C n.m.r. spectra of the products are used to distinguish between these compounds.

In an extension of the studies of tetrafunctional reagents with compound (**1**) the reactions of its homologue, octachlorocyclotetraphosphazatetraene, $N_4P_4Cl_8$, (**2**) with pentaerythritol (**4**) have also been investigated. The reactions of pentaerythritol (**4**) with 2, 4, 6 or 8 equivalents of octachloride in acetonitrile gave only one derivative, $(N_4P_4Cl_6)_2[C(CH_2O)_4]$ (**11**), a dispiro structure. This was deduced by mass spectrometry and ^{31}P, ^{13}C and ^1H n.m.r. spectroscopy.

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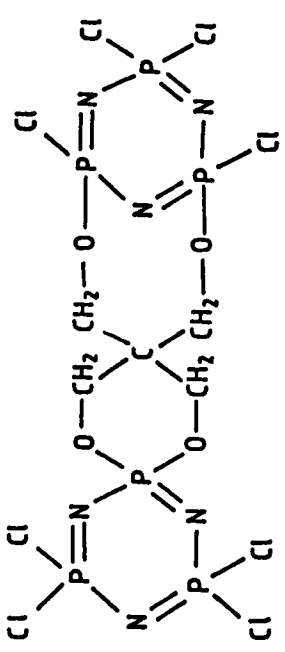
^{31}P N.m.r. Studies

The ^{31}P n.m.r. spectrum of compound (**8**) is of the A_2X type; it shows that the two phosphazene rings are chemically equivalent. The $\equiv PCl_2$ groups are magnetically equivalent in the two rings and so are the $\equiv$Pspiro groups. A similar ^{31}P n.m.r. absorption is observed for the spiro-open-chain derivative, (**10**). The phosphorus proton coupled spectra suggest that the A_2 part of the spectra of both compounds arises from the $\equiv PCl_2$ group, whereas the X part, which splits into further lines by proton coupling is associated with the $\equiv$Pspiro group.

The mass spectrum and elemental analysis of the third compound (**9**) is consistent with its being an isomer of (**8**). Phosphorus-31 n.m.r. spectroscopy was found very useful to characterise this particular compound. Two distinctly different types of systems are observed, an A_2X and an A_2B. The only explanation for this absorption is that the two phosphazene rings are substituted in a different manner. One ring is substituted by a spiro ring (the two functional groups attached to the same phosphorus atom), whilst the second ring is substituted by an ansa ring (two functional groups attached to two phosphorus nuclei in the same molecule), these two spectra would not be expected to interact.

^{31}P n.m.r. spectroscopy has been used[3] to distinguish between the mono-ansa (**6**) and mono-spiro structures (**7**). The spectrum of compound (**9**) is shown in Figure 1 and compared with the ^{31}P spectra of the two isomers (**6**) and (**7**) at the same field strength. It clearly supports the proposed spiro-ansa structure for the new product.



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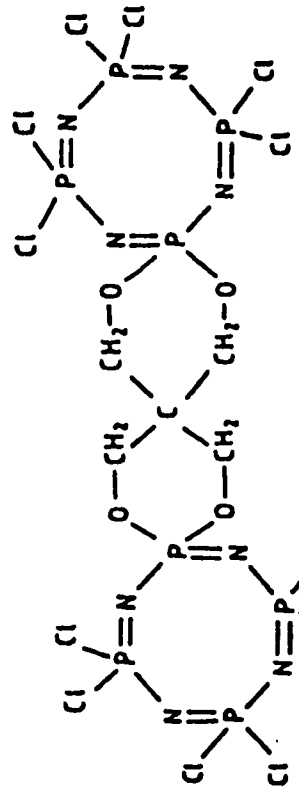

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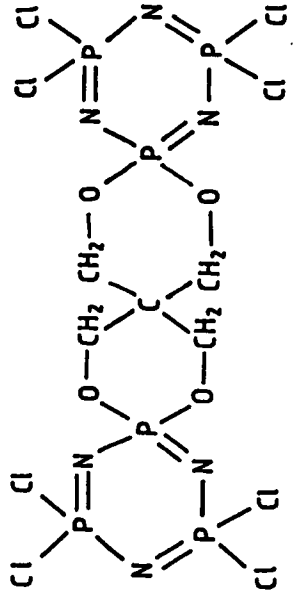

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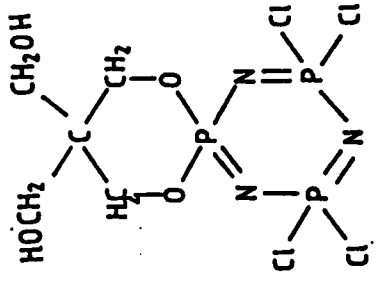

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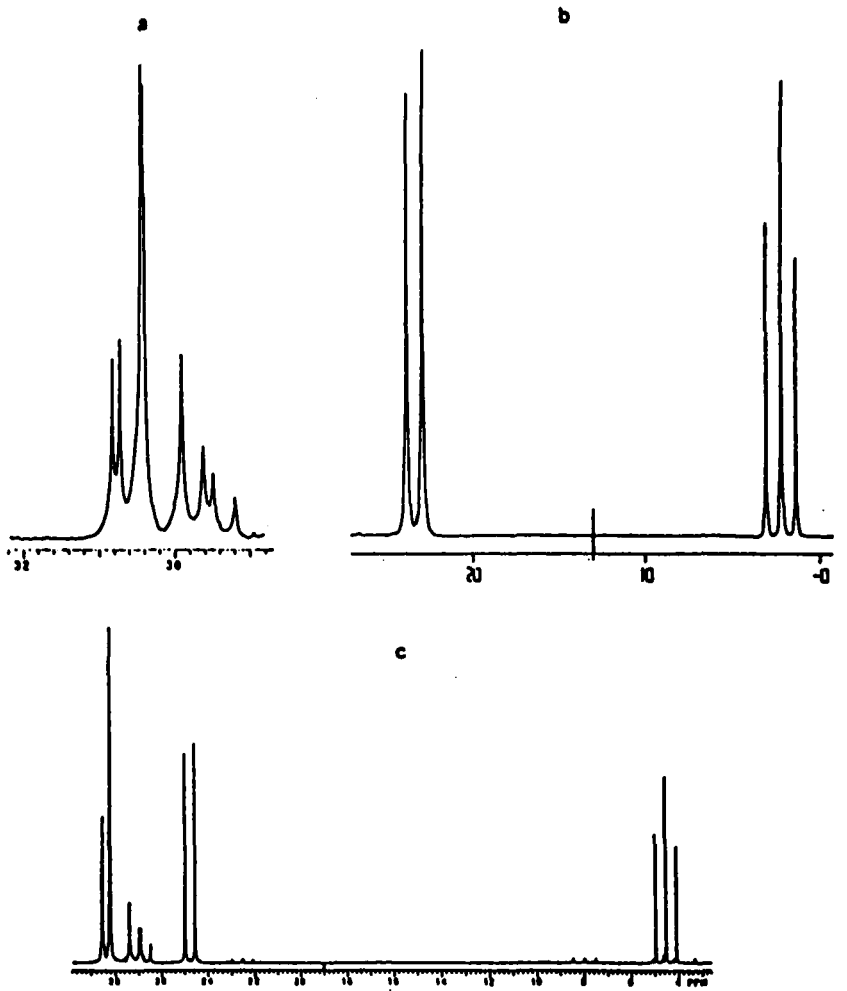

FIGURE 1 $^{31}P\{^1H\}$ nmr spectra at room temperature in $CDCl_3$ at 162.0 MHz (**a**) compound (**6**); (**b**) compounds (**7**) and (**8**); (**c**) compound (**9**).

The ^{31}P-^1H n.m.r. spectrum was used to help in the assignment of the lines arising from the $\equiv PCl_2$, and the $\equiv$Pspiro groups. The A_2 part of the spectrum, of the spiro phosphazene ring remains unsplit on proton coupling, suggesting that this is due to the $\equiv PCl_2$ groups. The X part of the spectrum, however, from the same phosphazene moiety gives rise to additional fine splitting on proton coupling, showing the presence of protons in this group. In the case of the ansa ring the A_2 part of the spectrum gives further splitting on proton coupling showing that, this part of the spectrum arises from the $\equiv P(OR)Cl$ group, whereas the B part remains unaffected and is associated with the $\equiv PCl_2$ unit.

The ^{31}P n.m.r. spectrum of the homologous compound, (**11**), is of an A_2BX type, indicating that the product is monospiro cyclic derivative linked to two equivalent phosphazene rings. It resembles that of the monospiro derivative, $N_4P_4Cl_6[(OCH_2)_2CMe_2]$, (**12**).

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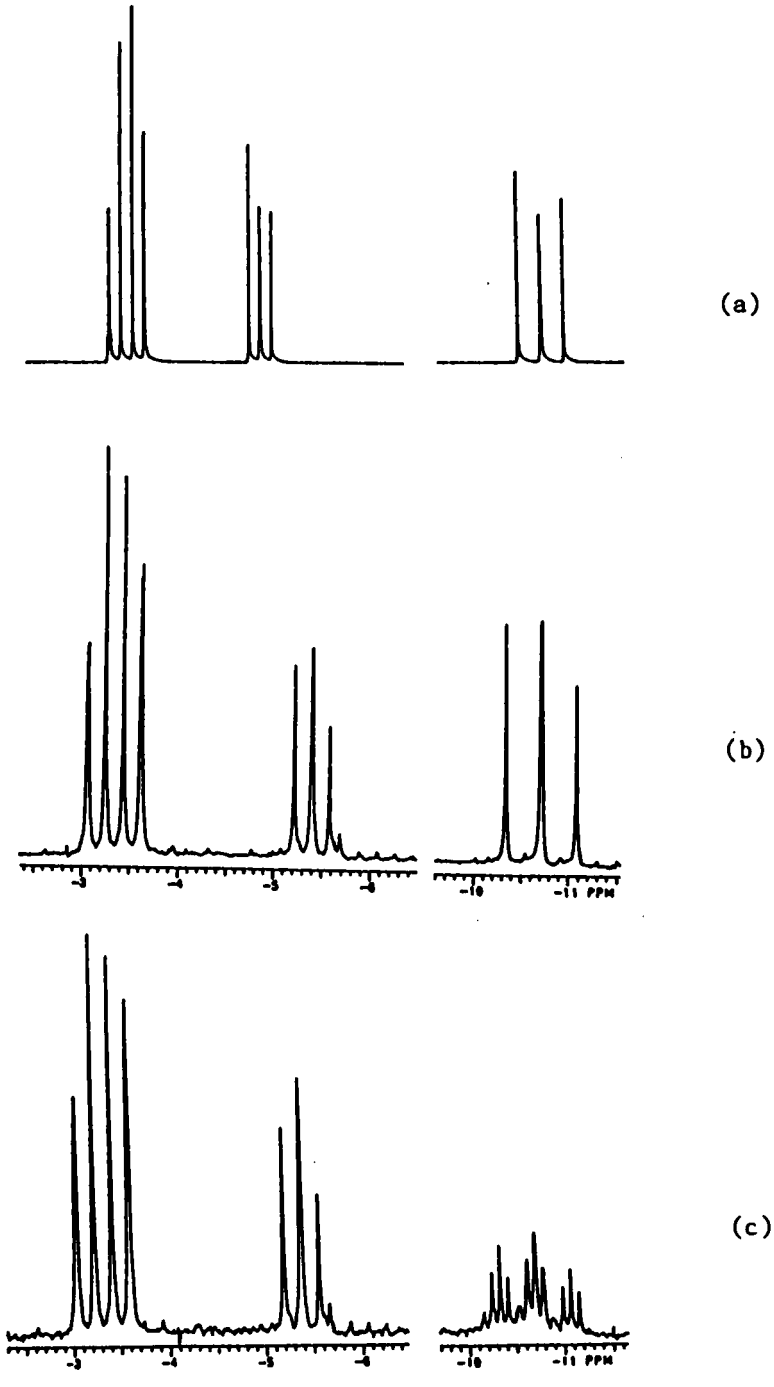

FIGURE 2 ^{31}P nmr spectrum of compound (**11**) in $CDCl_3$ at room temperature (**a**) simulation; (**b**) $^{31}P\{^1H\}$; (**c**) ^{31}P-^1H.

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The ^{31}P-^{1}H n.m.r. spectrum allows assignment of peaks due to the $\equiv$Pspiro and $\equiv PCl_2$ groups. The intensity of lines in the spectrum suggests that the two $\equiv PCl_2$ nuclei directly adjacent to the $\equiv$Pspiro group are found further upfield than the remote $\equiv PCl_2$ nucleus (Figure 2). The positions and relative intensities of the observed signals can be compared with those obtained by simulation. The ^{31}P data for the pentaerythritol derivatives together with those of some related structural types are given in Table I.

^{1}H N.m.r. Data

The proton n.m.r. data for the pentaerythritol derivatives are summarised in Table II together with that of related compounds. The spectra are similar to those of the 2,2-dimethylpropane-1,3-diol derivatives.[3] Thus the $OC\underline{H}_2$ methylene protons of the spiro ring for compounds (**8**) and (**10**) are observed as doublets, since these methylene groups are in identical environments and their protons are equivalent. The $C\underline{H}_2$—OH protons in the case of $N_3P_3Cl_4[(OCH_2)_2C(CH_2OH)_2]$, (**10**) give rise to a singlet. The absorption due to the O—$\underline{H}$ proton was observed as a sharp single line at 2.21 p.p.m., which disappeared on treatment of the sample with D_2O.

Two different methylene proton signals are observed in the spectrum for the spiro ansa pentaerythritol derivative (**9**). (**a**) The two methylene groups of the spiro ring observe two different environments. However, the methylene protons for each group are equivalent since they observe identical chemical environments. Thus, a fairly simple spectrum would be expected and two doublet structures were observed due to coupling of these protons with the spiro phosphorus nucleus. (**b**) The $OC\underline{H}_2$ ansa-methylene groups appear as two multiplets. The two methylene groups are in identical chemical environments, but their protons are non-equivalent, since they observe different environments towards and away from the phosphazene ring; hence an AB quartet structure would be expected. Coupling with the phosphorus nuclei will give rise to further splitting. Due to long range coupling a total of 12 lines might be observed. Because of the absorption between the peaks and the fact

TABLE I

^{31}P n.m.r. data

Compound	δ $\underline{P}Cl_2$[a]	δ $\underline{P}$spiro[a]	δ $\underline{P}$ansa[a]	$^{2}J(\underline{P}Cl_2\text{-}\underline{P}$spiro)[b]	$^{2}J(\underline{P}Cl_2\text{-}\underline{P}$ansa)[b]
(**1**)	19.9				
(**8**)	24.7	4.65		69.3	
(**10**)	24.6	4.4		68.7	
(**7**)[c]	23.3	2.2		69.3	
(**9**) spiro	24.6	4.5		70.3	
ansa	27.3		28.4		
(**6**)[c]	23.5		25.0	64.2	56.9
(**2**)	−6.5				
(**11**)[d]	−3.3(2)[e]	−10.7		60.1	
	−5.4(1)				
(**12**)[e,f,g]	−4.3(2)	−10.5		59.0	
	−5.5(1)				

[a] In p.p.m., [b] in Hz, [c] data from Reference 3, [d] $^{2}J(\underline{P}Cl_2\text{-}\underline{P}Cl_2)$ 29.8 Hz, [e] relative number of nuclei in brackets, [f] data from Reference 6, [g] $^{2}J(\underline{P}Cl_2\text{-}\underline{P}Cl_2)$ 29.9 Hz.

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TABLE II

^{1}H n.m.r. data

Compound		δ POCH$_2$[a]	^{3}J(P-H)[b]
(**8**)		4.48	13.6
(**10**)		4.38	13.6
(**7**)[c]		4.14	13.2
(**9**)	spiro	4.42, 4.30	13.85
	ansa	4.50, 4.28	12.5
(**6**)[c]		4.22, 3.86	7.9, 8.2
(**11**)		4.39	13.8
(**12**)[d]		4.48	13.5

[a] In p.p.m., [b] in Hz, [c] data from Reference 3, [d] data from Reference 6.

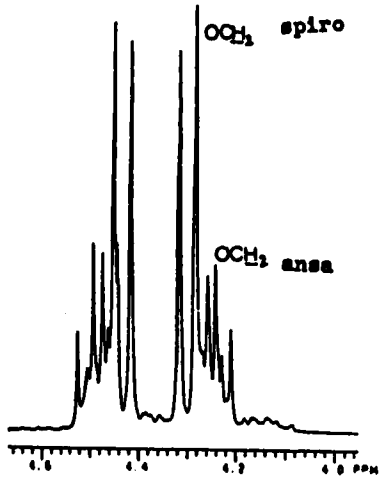

FIGURE 3 ^{1}H nmr spectrum of compound (**9**) in $CDCl_3$ at room temperature at 399.96 MHz.

that the doublets overlap, it is difficult to estimate reliably the relative number of the peaks in each environment (Figure 3).

^{13}C n.m.r. Data

Other evidence for the determination of the structures of the pentaerythritol derivatives is provided by their ^{13}C n.m.r. spectra. ^{13}C n.m.r. spectroscopy proved an extremely useful tool to determine the number of different chemical environments present and hence to deduce the structures of these compounds. We must take cognizance of the following facts: it has been shown by X-ray crystallography that the spirane structure postulated for compound (**8**) is correct.[10] The two halves of the spirane $N_3P_3Cl_4[(OCH_2)_2]C_{1/2}$ are therefore identical.

The ^{13}C n.m.r. spectrum of the spiro-open-chain compound, $N_3P_3Cl_4[(CH_2O)_2]$-$C(CH_2OH)_2]$ (**10**) exhibits two different signals for the O$\underline{C}$H$_2$ nuclei. The downfield doublet at 70.0 p.p.m. corresponds to the methylene carbons, which are attached to the phosphazene ring through the dioxy linkage, where coupling between the phosphorus nucleus and carbon nuclei is observed, whilst there is no phosphorus coupling with the second methylene carbon nuclei (—$\underline{C}$H$_2$OH). Hence the expected one line signal was observed.

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TABLE III

^{13}C n.m.r. data

Compound	δ POCH$_2$[a]	δ POCC[a]	^2J(PC)[b]	^3J(PC)[b]
(**8**)	68.7	36.4	6.6	4.8
(**10**)[c]	70.0	41.5	6.45	4.7
(**7**)	77.0	32.2	6.45	5.9
(**9**) spiro	68.3	41.2	6.45	4.6
ansa	67.2		2.8	
(**6**)	76.6	32.1	6.8	5.9
(**11**)	68.7	36.45	6.2	4.8
(**12**)[d]	77.1	32.6	5.9	5.7

[a] In p.p.m., [b] in Hz, [c] singlet at 62.4 p.p.m. refers to CCH$_2$OH, [d] data from Reference 6.

The ^{13}C spectrum permitted a distinction to be drawn between the spiro- and ansa-methylene carbon groups of compound (**9**). The ansa-carbon group was identified by its high field signal at δ 67.2 (a triplet structure due to the presence of virtual coupling), and the spiro-carbon group signal was identified by its lower field signal, δ 68.3. The downfield multiplet is associated with the carbons of the —OCH$_2$ groups of the spirodioxy ring. Since the two carbon nuclei are non-equivalent two doublet structures are observed due to the two-bond phosphorus coupling.

For compound (**8**) the carbon n.m.r. absorption of the β-carbon (nonprotonated centre carbon) is observed as a triplet structure, due to the direct coupling with one phosphorus nucleus from each phosphazene ring, whereas for the compound (**10**) the absorption for the same nucleus was observed as a doublet. In the case of the spiro-ansa compound (**9**) the situation is different. The central carbon nucleus is linked to two different phosphorus nuclei (spiro-phosphorus and ansa-phosphorus). Therefore two types of coupling would be expected. A doublet due to the coupling with the spiro phosphorus nucleus, and further splitting to a triplet from the coupling with the ansa-phosphorus nuclei would be expected. At 50.10 MHz the expected signals were observed. Because the data points at 99.95 MHz were fewer than those at 50.10 MHz only one doublet was observed. The ^{13}C data are given in Table III.

EXPERIMENTAL

Chemicals were obtained as follows: benzene, light petroleum (b.p. 40–60°C), anhydrous diethyl ether, dichloromethane (May and Baker Ltd.), tetrahydrofuran (Fluka-Garantie 99.5%), deuteriated solvents for n.m.r. spectroscopy, 4-dimethylaminopyridine (Aldrich Chem. Co. Ltd.), pentaerythritol (B.D.H. Chemical Ltd.), hexachlorocyclotriphosphazatriene and octachlorocyclotetraphosphazatetraene (Shin Nisso Kako Co. Ltd.). Solvents were dried by conventional methods.

All reactions were monitored by using Kieselgel 60 F 524 (Silica gel) precoated t.l.c. plates and sprayed with Ninhydrin (0.5 w/v%) in butanol solution, and developed at approximately 130°C. Separation of products were carried out by flash column chromatography[9] using Kieselgel 60. Melting points were determined on a Reichert-Kofler microheating stage and a Mettler FB 82 hot stage connected to a FP 800 Central Processor both fitted with a polarising microscope.

^1H n.m.r. spectra were recorded using a JEOL FX 200 spectrometer (operating at 199.5 MHz) and a Varian XL 400 spectrometer (operating at 399.95 MHz—University College, London). Samples were dissolved in $CDCl_3$ and placed in 5 mm n.m.r. 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 n.m.r. spectra were recorded using a JEOL JNM FX-60 spectrometer (operating at 24.15 MHz), a Varian XL-200 spectrometer (operating at 80.98 MHz—University College, London), and a Varian VXR 400 spectrometer

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(operating at 162.0 MHz—University College, London). 85% H_3PO_4 was used as an external reference. ^{13}C n.m.r. spectra were recorded using a JEOL-JNM FX200 spectrometer (operating at 50.10 MHz) and VARIAN XL-400 spectrometer (operating at 99.95 MHz—University College, London). Samples were dissolved in $CDCl_3$ and placed in 5 mm n.m.r. tubes. $CDCl_3$ was used as a "lock" solvent and chemical shifts were measured relative to TMS (0 p.p.m.).

The mass spectra were recorded using a VG 7070 H mass spectrometer with Finnigan INCOS Data System at University College, London. Measurements and calculations are based on mass of most abundant isotopes.

1) The hexachloride, $N_3P_3Cl_6$, (**1**), (6 g, 17.24 mmol) was dissolved in CH_2Cl_2 (200 cm^3). To this solution, pyridine (2.7 g, 34.18 mmol) was added dropwise. Solid pentaerythritol (1.2 g, 8.82 mmol) was then added to this mixture. The reaction was boiled under reflux for approximately 24 h. After cooling t.l.c. showed the formation of one compound. Column chromatography was used [dichloromethane/light petroleum (b.p. 40–60°C) (3:2) as eluent] to remove polymeric products and pyridine hydrochloride. The phosphazene derivative was identified as the spirane compound, (**8**), m.p. 239°C, yield 0.9 g (15%) [Found: C, 8.9; H, 1.2; N, 12.3%; $\underline{M}^+$, 682. $C_5H_8O_4N_6P_6Cl_8$ requires C, 8.8; H, 1.2; N,12.25%; $\underline{M}$, 682).

2) Pyridine (2.7 g, 34.18 mmol) was added dropwise to a solution of the hexachloride (**1**) (6 g, 17.24 mmol) in acetonitrile (200 cm^3). Pentaerythritol (1.2 g, 8.82 mmol) was added to the stirred solution. The reaction was then boiled under reflux (24 h) and then was left stirring at room temperature for a further 24 h. T.l.c. showed (CH_2Cl_2 eluent) the presence of two components, which could not be separated by this method. When a mixture of diethyl ether and light petroleum (b.p. 40–60°C) (1:2) was used as eluent, however, the second compound did not move from the base line. Therefore two stages were used to separate these products by column chromatography. Both products isolated were recrystallised from benzene. The mass spectra of both had intense parent ion peaks at m/e 682 ($C_5H_8O_4N_6P_6Cl_8$ requires 682), and hence were identified as (**a**) the spirane compound, (**8**), and (**b**) the spiro-ansa isomer, (**9**), m.p. 188°C, yield 0.36 g (6%) [Found: C, 9.05; H, 1.2; N, 11.8%; $\underline{M}^+$ 682. $C_5H_8O_4N_6P_6Cl_8$ requires, C, 8.8; H, 1.2; N, 12.3%. $\underline{M}$, 682].

3) The procedures given in (2) were repeated [4-dimethylaminopyridine, $Me_2N_2C_5H_5$ (4.4 g, 36.07 mmol) was used as tertiary base]. Two compounds were isolated by column chromatography using CH_2Cl_2/THF (2:4) eluent. The major product was identified as the spiro-open-chain derivative (**10**), $N_3P_3Cl_4[(OCH_2)_2C(CH_2OH)_2]$, m.p. 142°C, yield 1.0 g (17%), [Found: C, 14.7; H, 2.5; N, 10.3%; $(\underline{M} + \underline{H})^+$, 410. $C_5H_{10}O_4N_3P_3Cl_4$, requires C, 14.6; H, 2.45; N, 10.3; $\underline{M}$, 409).

4) Pentaerythritol (0.74 g, 5.44 mmol) was added to a stirred solution of the octachloride, (**2**), (5g, 10.78 mmol) and pyridine (7g, 88.61 mmol) in dioxane (300 cm^3). The mixture was boiled under reflux for about 38 h. Only one compound, (**11**) was isolated, which was recrystallised from a mixture of benzene and dichloromethane (1:1), m.p. 238°C, yield 0.45 g (9%). [Found: C, 6.6; H, 0.9; N, 12.0%; $(M—Cl)^+$ 877. $C_5H_8O_4N_8P_8Cl_{12}$ requires C, 6.55; H, 0.9; N, 12.2%; $\underline{M}$, 912].

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