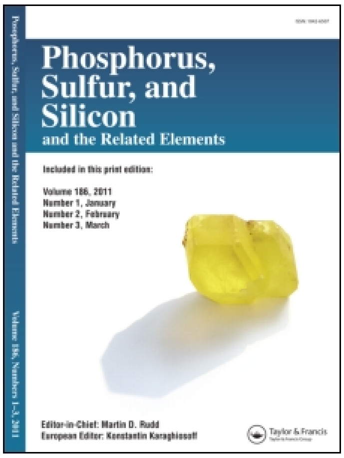

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THE REACTIONS OF PHOSPHAZENES WITH DIFUNCTIONAL AND POLYFUNCTIONAL NUCLEOPHILIC REAGENTS

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THE REACTIONS OF PHOSPHAZENES WITH DIFUNCTIONAL AND POLYFUNCTIONAL NUCLEOPHILIC REAGENTS†

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After a brief introduction of the reaction patterns of $N_3P_3Cl_6$ and $N_4P_4Cl_8$ with monofunctional nucleophilic reagents, the reactions of these two chlorocyclophosphazenes with difunctional, trifunctional and tetrafunctional nucleophilic reagents are surveyed. These reagents contain aliphatic and aromatic hydroxyl and primary and secondary amino groups. Spiro, ansa, dangling and bridging units have been observed as well as a combination of these. The stability of the various ring systems is discussed. Crystal structures and ^1H, ^{13}C and ^{31}P n.m.r. spectroscopic studies are reported.

INTRODUCTION

Monofunctional Nucleophilic Reagents with $N_3P_3Cl_6$ and $N_4P_4Cl_8$

Phosphorus chemistry is predominantly the reactions of phosphorus compounds with nucleophilic reagents. This holds also true for the reactions of phosphazenes. We have for many years explored the reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, (**1**), with monofunctional reagents. These could follow a geminal or a nongeminal replacement pattern or a mixture of both of these (Figure 1).[1–4] Some of the major findings are briefly summarised below.

Secondary amines, NHR_2, follow, in general, a nongeminal pathway, though at the tris-stage $N_3P_3Cl_3(NR_2)_3$, solvent effects become important.[5] Primary amines, NH_2R, depending on their reactivity and the reaction mechanism they follow, give at the bis stage, $N_3P_3Cl_4(NHR)_2$ either nongeminal (e.g. NH_2Et)[6] or geminal products (e.g. NH_2Bu^t).[7] Geminal structures are overwhelmingly preferred at the tetrakis stage, $N_3P_3Cl_2(NHR)_4$.[4,6,7] Ammonia gives exclusively the geminal product, $N_3P_3Cl_4(NH_2)_2$ at the bis stage.[8] Both alcohols, ROH,[9,10] and phenols, ArOH,[2] react almost exclusively by the nongeminal pathway. In contrast, mercaptans, RSH, prefer the geminal pathway with bis $N_3P_3Cl_4(SR)_2$, tetrakis $N_3P_3Cl_2(SR)_4$ and hexakis derivatives, $N_3P_3(SR)_6$, as the major products.[3] The others, $N_3P_3Cl_{6-n}(SR)_n$ ($n = 1$, 3, 5) have been isolated only as minor components.[11] With thiophenol, PhSH, only the bis $N_3P_3Cl_4(SPh)_2$ and the

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† Expanded version of an invited lecture delivered to the 1st Chinese Conference on Phosphorus Chemistry, Beijing, China, 30th May–2nd June 1988.

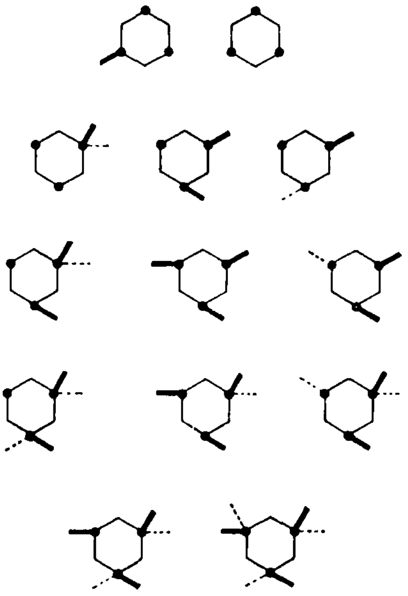
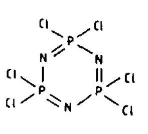


FIGURE 1 Replacement patterns in cyclotriphosphazatrienes.

hexakis $N_3P_3(SPh)_6$ derivatives are major products.[3]



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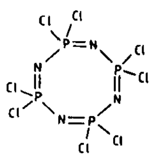
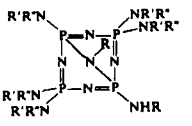


(2)

The reactions of octachlorocyclotetraphosphazatetraene, $N_4P_4Cl_8$, (**2**), have received only fairly recently detailed attention. The potential number of products with a given reagent is much greater (Figure 2) and hence structure determination more difficult. The reactions with secondary amines, NHR_2, are complex. The products are mainly nongeminal, although stoichiometry, reaction temperature and solvent influence the nature of the products and their relative proportions.[12,13]

Primary amines, NH_2R, tend to give quite a lot of resinous material, probably polymeric in nature, due to cross-linking reactions, which in essence make the primary amine difunctional. An excellent example of this difunctionality are the bicyclic cyclotetraphosphazatetraenes (**3**) obtained in the exhaustive aminolysis of the octachloride (**2**).[14–22]



(3)

In partial aminolysis products with primary amines, those which give non-

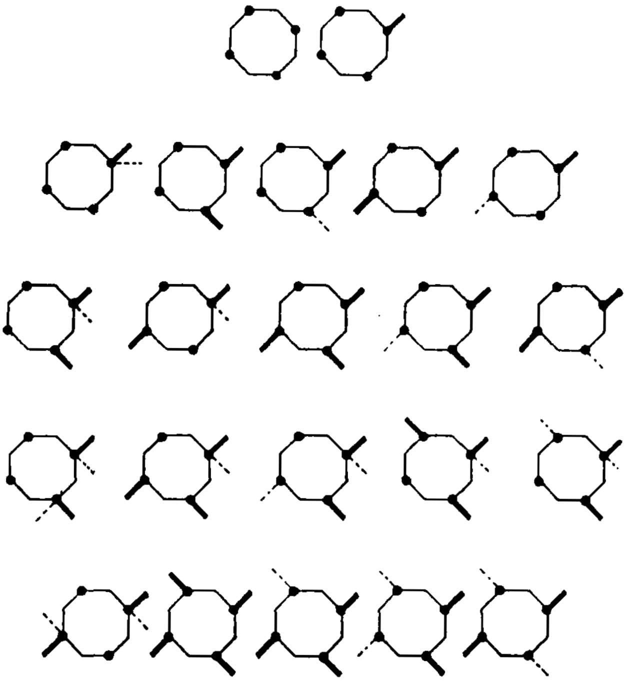
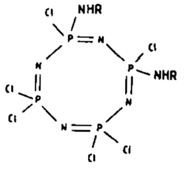


FIGURE 2 Replacement patterns in cyclotetraphosphazatetraenes.

geminal bis derivatives (e.g. NH_2Et) with the trimer (**1**) give only 2,6-bis derivatives, $N_4P_4Cl_6(NHR)_2$ with the tetramer (**2**),[23] whilst those which give geminal bis derivatives with the N_3P_3 system, (e.g. NH_2Bu^t) tend to give both 2,4- (**4**) and 2,6-bis derivatives, (**5**), $N_4P_4Cl_6(NHR)_2$.[24] Geminal products were not observed. In contrast, ammonia, NH_3, gives both geminal (**6**) and nongeminal 2,6-derivatives (**7**) at the bis replacement stage, $N_4P_4Cl_6(NH_2)_2$.[25,26]



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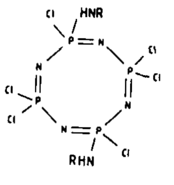

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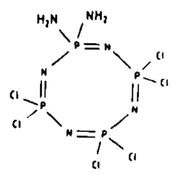

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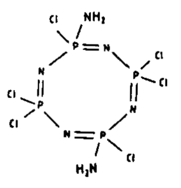
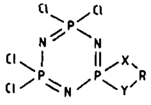


(7)

Alcoholysis[27] and phenolysis[28] reactions are complex. As with the trimer (**1**), reactions with the tetramer (**2**) are predominantly nongeminal. Mercaptolysis is, as with the hexachloride (**1**), mainly geminal with preference for the 2,2,6,6-tetrakis products, $N_4P_4Cl_4(SR)_4$,[29] although again with later, more refined separation techniques, others were isolated in small yields.

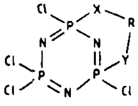
Difunctional Aliphatic Nucleophilic Reagents with $N_3P_3Cl_6$ and $N_4P_4Cl_8$

These reagents have aroused quite intense interest in recent years. Difunctional reagents can, in principle, give rise to four types of products: (i) spiro (both ends attached to same phosphorous atom), (**8**), ansa (the two ends of the reagent attached to different phosphorus atoms in the same molecule), (**9**), bridging (the two ends bonded to phosphorus atoms in different molecules, (**10**) and dangling (only one functional group attached to phosphorus, the other free) (**11**). With propane-1,3-diol, (see below) all four types were observed, although spiro products predominated.[30]



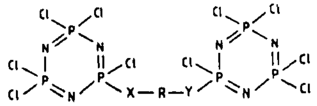
SPIRO

(8)



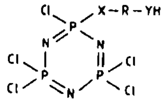
ANSA

(9)



BRIDGING

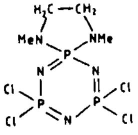
(10)



OPEN CHAIN (DANGLING)

(11)

With di-secondary amines, $HNR(CH_2)_nNRH$, e.g. $HNMe(CH_2)_2NMeH$, mono-, $N_3P_3Cl_4[NMe(CH_2)_2NMe]$, (**12**), bis-, $N_3P_3Cl_2[NMe(CH_2)_2NMe]_2$, (**13**), and tris-spiro derivatives, $N_3P_3[NMe(CH_2)_2NMe]_3$ (**14**), have been isolated, which contained 5-membered spiro rings.[31,32] This contrasts with the analogous di-primary amine, $H_2N(CH_2)_2NH_2$, where only the monospiro derivative, $N_3P_3Cl_4[NH(CH_2)_2NH]$, (**15**) could be isolated (see below).[33]



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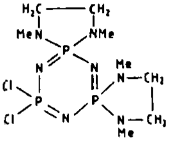

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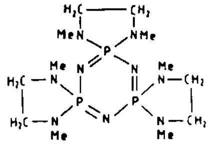

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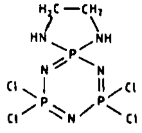
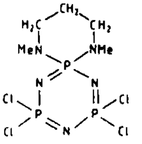


(15)

Now let me turn to the most recent findings. Whilst studying the diamino spiro derivatives of the hexachloride (**1**), we noted that the secondary amino compound, $N_3P_3Cl_4[NMe(CH_2)_3NMe]$, (**16**), had a $^3J(PNCC)$ coupling constant of only 2.3 Hz, whilst its primary amino analogue, $N_3P_3Cl_4[NH(CH_2)_3NH)$, (**17**) has a coupling constant of 6.5 Hz.[34] Comparison of their crystal structures showed that the dihedral angles PNCC were 49° and 62°, respectively.[34]



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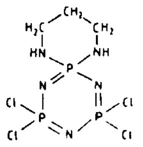
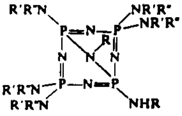


(17)

It is clear that the large decrease of the $^3J(PNCC)$ coupling constant is not mainly due to a change in dihedral angle. Indeed, in all known Karplus relationships[35–39] a dihedral angle of 49° would give rise to a larger coupling constant than would one of 62°. There is, however, no guarantee that the solid state conformations are the only, or even the predominant, ones in solution.

Close inspection of the structures of (**17**) and (**16**) revealed that the sums of the bond angles around the substituent nitrogen atoms are 359.9° and 351° (av) respectively [the N atoms of (**16**) lying 0.26 Å out of the planes of their three bonding partners].

To test the above hypothesis further, we have measured the $^3J(PNCC)$ spin-spin coupling constants of compounds known to contain non-planar nitrogen atoms.[40] Such compounds are the bicyclic systems $N_4P_4(NHMe)_6(NMe)$ (**18**)[41] and $N_4P_4(NMe_2)_5(NHEt)(NEt)$ (**19**)[14,42] in both of which the bridging nitrogen atoms were reported to have a very pronounced pyramidal character [sums of bond angles 337.5(6)° and 336.8(1.3)° respectively]. As there are no $^3J(PNCC)$ coupling constants for (**18**) we have determined these in its ethyl analogue, $N_4P_4(NHEt)_6(NEt)$, (**20**) and found them to be 2.6 Hz for the bridging NEt group and 8.0, 8.4 and 9.0 Hz for the three types of NHEt substituents. We undertook a single crystal X-ray structure determination of (**20**).



(18) R = R' = Me; R'' = H
(19) R = Et; R' = R'' = Me
(20) R = R' = Et; R'' = H

Because of the high thermal vibrations of some of the substituent atoms, it is not possible to comment on the exact stereochemistry of all the substituent nitrogen atoms. However, the bridging nitrogen atom has again a very pronounced pyramidality [sum of bond angles 339.5(5)° (av)], and the NHEt nitrogen atoms are much more planar (sums of bond angles are in the range of 355.6–360.0°).

In compound (**19**) the N–H hydrogen atom was not refined;[14,42] we therefore redetermined its crystal structure. The sums of the bond angles around the nitrogen atom of the bridging NEt and the substituent NHEt groups are 340.5(2) and 359.8(9)° and the relevant $^3J(PNCC)$ values are 2.4 and 7.3 Hz respectively.

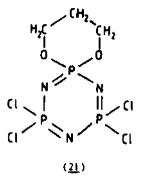
In the two bicyclic compounds (**19**) and (**20**) the ethyl groups can rotate freely and thus there are no constraints on the PNCC dihedral angles, as there are in the spiro derivatives (**16**) and (**17**). These constraints on the dihedral angles in the spiro derivatives account for the apparent (but misleading) similarity in J-values of (**16**) (non-planar N atoms) and (**19**) and (**20**) (planar N atoms).

Concomitant with an increase in the pyramidality of the nitrogen atoms is an increase of the exocyclic P–N bond lengths in question.[34,41,42] Thus for the spiro compounds (**17**) and (**16**) their bonds are 1.618(6) and 1.637(3) Å (av) respectively. In the bicyclic compounds (**18**)[41]–(**20**) the bonds to the bridging nitrogen atoms are in the range 1.699–1.724 Å, those to the bridge-head substituents 1.624–1.636 Å and the others 1.636–1.648 Å.

It is clear from the above that the deviation from planarity of the nitrogen atoms in question, together with the increase in the P–N bond lengths, cause a marked decrease in $^3J(PNCC)$ coupling constants.

Karplus[35–37] has drawn attention to that dihedral angles are not the only parameter determining vicinal coupling constants and *inter alia* referred to hybridisation and bond length. We believe that the PNCC system provides excellent examples of such other effects.

We decided to extend these studies to the POCC system. We therefore investigated P-O bond lengths and $^3J(POCC)$ spin-spin coupling constants in the monospiro propanedioxy derivative, $N_3P_3Cl_4[O(CH_2)_3O]$, **(21)** and its derivatives in which two, *trans*-$N_3P_3Cl_4pyr_2[O(CH_2)_3O]$, **(22)**, respectively four chlorine atoms $N_3P_3pyr_4[O(CH_2)_3O]$, **(23)** were replaced by pyrrolidino groups.[43]



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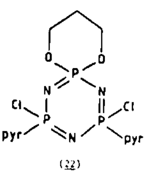
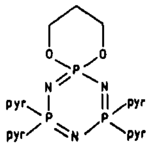


(22)



(23)

The pyrrolidino group is the most electron-donating secondary amino group we have observed in our basicity studies on cyclophosphazenes and we have obtained values of 5.9 and 3.0 for α_{pyr} and γ_{pyr} respectively.[44,45] Whilst these studies measure the electron density (perturbed under the influence of a proton) at a ring nitrogen atom of the cyclotriphosphazatriene ring, X-ray crystallography measures parameters of the unperturbed molecule. Nevertheless, a fairly close relationship has been noted between the effects observed by the two types of measurements.

The electron releasing capacity pyr > NMe_2 > pip > morph (pip = piperidino, morph = morpholino groups) has been established for uncharged π-systems in the ground state, as well as for aminobenzene/trinitrobenzene charge transfer complexes[46] and for enamines.[47]

A priori, one would have expected that replacement of the electron-withdrawing chlorine atoms by the strongly electron-releasing pyrrolidino groups would displace electron density towards, and within, the 6-membered phosphate ring. We indeed note that in the asymmetric segments $(CH_2)_3O_2P—N—PXY$ [X = Y = Cl, **(21)**; X = Cl, Y = pyr, **(22)**; X = Y = pyr **(23)**], the $(CH_2)_3O_2P—N$ bond is the longer one in compound **(21)**, whilst progressive substitution of chlorine atoms by pyrrolidino groups, diminishes the difference in the three atom segments in compound **(22)**, and finally reverses the bond length pattern in compound **(23)**.

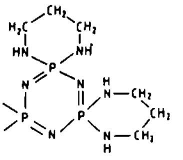
We have called this difference Δ(P—N) (for definitions see refs 8, 48). Δ(P—N) for compounds **(21)**, **(22)** and **(23)** is 0.021(4), 0.012(3) and −0.029(3)Å, respectively. Concomitant with increasing electron-density at the spiro phosphorus atom, the back-donations of the lone pairs of electrons on the oxygen atoms towards the phosphorus atom is decreased, and we observe an increase in P—O bond length on passing from compound **(21)** to **(22)** and then to **(23)** these bond lengths being 1.551(3), 1.571(2) and 1.586(2) Å respectively,[43] in line with increasing electron supply. This is reflected in a decrease in the three bond spin–spin coupling constant, $^3J(POCC)$, which varies from **(21)** 7.35 Hz to **(22)** 6.45 Hz and to **(23)** 5.9 Hz. The average POCC dihedral angles change from **(21)** 54.4° to **(22)** 56.3° and **(23)** 57.2°. If no effects other than dihedral angles affected the vicinal coupling constants, a marginal overall decrease of 0.3 to 0.4 Hz would have been expected. The considerably larger changes observed must be attributed to the P-O bond lengthening with increasing electron supply to the phosphorus atom.

It is well known that lone pairs of electrons on N atoms can back-donate much more effectively than can lone pairs of O atoms. One would therefore, *a priori*, expect to see smaller changes in the POCC system than in the PNCC system and this is what is observed.

The decrease in $^3J(POCC)$ and $^3J(PNCC)$ spin–spin coupling constants with increased P-O and P—N bond lengths, respectively, indicates the importance of Fermi contact. The large Fermi contact contributions to coupling constants in cyclophosphazenes have been established experimentally and theoretically by Thomas, Grossmann and Meyer.[49]

$^3J(POCC)$ spin–spin coupling constants are widely used to obtain information about conformation; this includes molecules of biological importance. Our results show that factors other than dihedral angles affect vicinal coupling constants, and these must be taken into consideration. However, in most other phosphorus systems, changes in electron supply towards the P—O bond will be much less than in phosphazene derivatives, hence changes in P—O bond lengths would be smaller and therefore more difficult to observe.

Whilst the hexachloride (**1**) with ethylene diamine yielded only a mono spiro compound (**15**),[33] 1,3-diaminopropane gave all three spiro-derivatives, $N_3P_3Cl_4[NH(CH_2)_3NH]$, (**17**), $N_3P_3Cl_2[NH(CH_2)_3NH]_2$, (**24**), and $N_3P_3[NH(CH_2)_3NH]_3$, (**25**).[50–52] Somewhat surprisingly the reactions with 1,4-diaminobutane have so far yielded only the mono-, $N_3P_3Cl_4[NH(CH_2)_4NH]$, (**26**) and bis spiro derivative, $N_3P_3Cl_2[NH(CH_2)_4NH]_2$, (**27**).[52–54] Mixed diamino spiro derivatives have also been reported, viz. $N_3P_3Cl_2[NH(CH_2)_2NH][NH(CH_2)_3NH]$, (**28**), $N_3P_3Cl_2[NH(CH_2)_2NH][NH(CH_2)_4NH]$, (**29**), and $N_3P_3Cl_2[NH(CH_2)_3NH]$-$[NH(CH_2)_4NH]$, (**30**).[55]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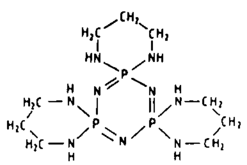
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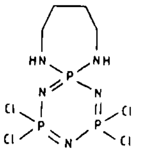
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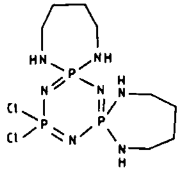
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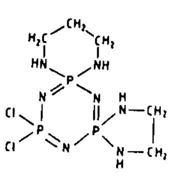
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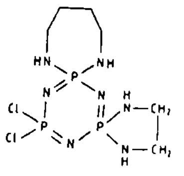
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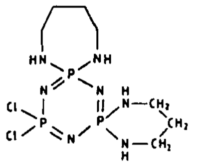
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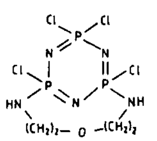
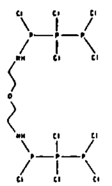

(31)

Quite recently an ansa structure $N_3P_3Cl_4[NH(CH_2)_2O(CH_2)_2NH]$, (**31**) with a chain of seven atoms between the two phosphorus atoms has been isolated. It was prepared from the reaction of the hexachloride (**1**) with 1,5-diamino diethyl ether, $H_2N(CH_2)_2O(CH_2)_2NH_2$.[56]

Before leaving the subject of diamines, we note that when the number of methylene groups between the two amino functions are from five to ten, singly bridged derivatives $N_3P_3Cl_5[NH(CH_2)_nNH]N_3P_3Cl_5$ ($n = 5$–10), (**32**), were the only products isolated.[57] Subsequently these studies were extended to doubly $N_3P_3Cl_4[NH(CH_2)_nNH]_2N_3P_3Cl_4$ ($n = 6$ and 8) (**33**) and triply bridged derivatives, $N_3P_3Cl_3[NH(CH_2)_nNH]_3N_3P_3Cl_3$ ($n = 6$ or 8) (**34**).[58]



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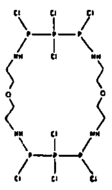

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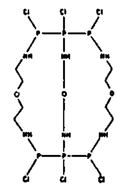
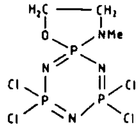


(34)

We now turn our attention to aminoalcohols. When the amino function is secondary, viz. $HO(CH_2)_2NMeH$, mono-, $N_3P_3Cl_4[O(CH_2)_2NMe]$, (**35**), bis-, $N_3P_3Cl_2[O(CH_2)_2NMe]_2$, (**36**) and tris-spiro derivatives, $N_3P_3[O(CH_2)_2NMe]_3$ (**37**) are obtained.[59] *Cis-trans* isomerism is possible for the bis and tris derivatives of aminoalcohols. For structure-property relationships[60] we investigated also the n.m.r., basicity and X-ray crystallographic properties of the primary amino derivatives, $N_3P_3Cl_4[O(CH_2)_2NH]$, (**38**) and $N_3P_3Cl_4[O(CH_2)_3NH]$, (**39**).[61] With ethanolamine, $HO(CH_2)_2NH_2$, only traces of the isomeric *cis* and *trans* bis isomers, $N_3P_3Cl_2[O(CH_2)_2NH]_2$ (**40**) and none of the tris derivatives, $N_3P_3[O(CH_2)_2NH]_3$, (**41**) could be isolated.[33] We also note the synthesis of an ansa $N_3P_3Me[O(CH_2)_3NH]Cl_3$ structure, (**42**), from the reaction of $N_3P_3Cl_5Me$ with propanolamine.[62]



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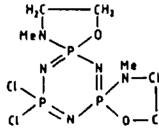

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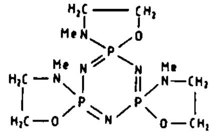

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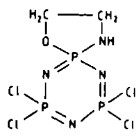

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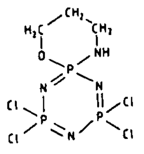

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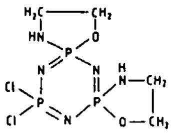

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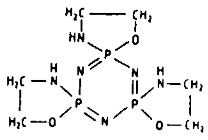

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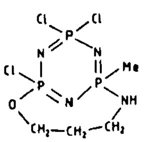


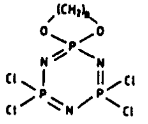
(42)

We now consider the diols. These have probably received the most detailed attention of all the systems reported here.

We subjected the reactions of the hexachloride, (**1**), to a systematic investigation with ethane-, propane-1,3-, and butane-1,4-diols.[30] Preliminary reports of this work have appeared.[63]

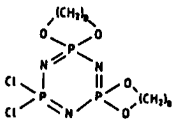
We isolated a total of 15 compounds, which included examples of all 4 structural types: 9 spiro, $N_3P_3[O(CH_2)_nO]_xCl_{6-x}$ ($x = 1$, 2, and 3; $n = 2$, 3, and 4)

(**43**, **44**, **21**, **45–50**); 1 ansa, $N_3P_3[O(CH_2)_3O]Cl_4$ (**51**); 1 spiro-ansa, $N_3P_3[O(CH_2)_3O]_2Cl_2$ (**52**); 2 bridged, $N_3P_3Cl_5[O(CH_2)_nO]N_3P_3Cl_5$ ($n = 3$ and 4), (**53**, **54**) and 2 dangling, $N_3P_3[O(CH_2)_nOH]Cl_5$ ($n = 3$ and 4) (**55**, **56**). In addition, we observed, but did not isolate in a pure form, a bridge $N_3P_3Cl_5[O(CH_2)_2O]N_3P_3Cl_5$, and a dangling derivative, $N_3P_3[O(CH_2)_2OH]Cl_5$, based on ethylene diol. The spiro derivatives are by far the major products, especially for the ethylene and propylene diols. Bridged derivatives assume significant importance with butylene diol. The spiro-ansa compound (**52**) is present in considerably smaller amounts than its dispiro isomer (**46**). The ansa derivative (**51**) is isolated in only trace amounts. Bridged compounds are obtained in better yields than danglers.

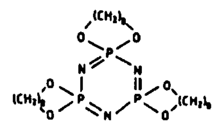


(43) $n = 2$

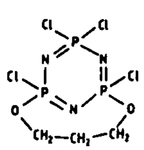
(44) $n = 4$



(45) $n = 2$
(46) $n = 3$
(47) $n = 4$



(48) $n = 2$
(49) $n = 3$
(50) $n = 4$



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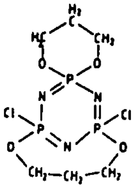

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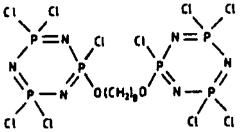
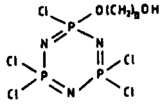


(53) $n = 3$
(54) $n = 4$



(55) $n = 3$
(56) $n = 4$

Crystal structures of 7 of these (**21**, **43–46**, **50**, **52**) have been reported,[48,61,63] as well as the ^{35}Cl n.q.r. measurements of three of these (**21**, **43**, **44**).[64] As with ethylene diamine and ethanolamine, the five-membered ring substituent, the ethylene dioxy group, differed markedly from the six- and seven-membered homologues and from related acyclic compounds.

We had shown earlier that with ethylene diamine only a mono-, $N_3P_3[NH(CH_2)_2NH]Cl_4$, (**15**) with ethanolamine, a mono-, $N_3P_3[O(CH_2)_2NH]Cl_4$ (**38**) and traces of two isomeric bis-derivatives, $N_3P_3[O(CH_2]_2NH]_2Cl_2$ (**40**) could be isolated. More forcing reaction conditions lead to resinous, polymeric glues.[33] We had suggested[65] that the structural moiety P–NH in a *five-membered ring* was responsible for the polymerisation reaction, and this was borne out by subsequent studies with N,N′-dimethylethylene-diamine[31,32] and N-methyl ethanolamine,[59] where mono-, bis-, and tris-derivatives were characterised. Thus, the formation of the three spiro ethanedioxy derivatives follows the same predicted pattern. These three derivatives, especially the tris (**48**), appear, however, to be unstable on storage, probably due to hydrolysis. The unique nature of five-membered ring phosphates has been recognised since the seminal work by Westheimer's group[66] on the kinetics of their hydrolysis.

The chemical uniqueness of the five-membered phosphorus-containing rings is mirrored in their ^{31}P n.m.r. chemical shifts. Attention to this in mononuclear phsophates was drawn some time ago.[67–69] In cyclotriphosphazatriene derivatives, the six- and seven-membered ring spiro-derivatives give well-resolved spectra.[34]

By contrast, those of the ethylene diamine and ethanolamine derivatives gave only a single broad line at medium magnetic field, because of the small chemical shift separation between the $\equiv PCl_2$ and the $\equiv$Pspiro group. We have now been able to analyse these spectra at high field.[30] Similar remarks pertain to the mono- and particularly to the bis-ethylenedioxy derivatives. The ^{31}P chemical shifts for some of these compounds have been related to their exocyclic OPO bond angles.[48]

The ^{31}P n.m.r. spectra at 24.15 MHz of the three monospiro dioxy derivatives, $N_3P_3[O(CH_2)_nO]Cl_4$ ($n = 2$, 3, and 4), are given in Figure 3, those at 162.0 MHz of $N_3P_3[O(CH_2)_2O]Cl_4$, $N_3P_3[O(CH_2)_2NH]Cl_4$ and $N_3P_3[NH(CH_2)_2NH]Cl_4$, in Figure 4. At low or medium field strengths these give rise A_2B spin systems tending to A_3.

The following points are noteworthy: (i) The $\equiv$P spiro nuclei are deshielded in the order 6-membered > 7-membered ≫ 5-membered spiro rings. (ii) The effect of the spiro substituents on the $\equiv$P spiro nuclei shows the same order, giving rise to some of the most deshielded $\equiv PCl_2$ nuclei recorded. (iv) Whilst the chemical shifts of the $\equiv$P spiro nuclei cover a large range (34 p.p.m.), 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 2 ansa compounds to δ30–31. This may be related to the ring compression, which has been observed, and is due to the *trans*-annular link.[63] (v) All two bond coupling constants, $^2J(PP)$, are large and in the range of 57–77 Hz.

We have shown earlier that alkoxyphosphazenes can show virtual coupling effects.[70,71] The methoxy- (as the dimethylamino-) derivatives exhibit hump-like absorption between the outer doublets,[71] whilst the ethoxy-derivatives, gem.-$N_3P_3Ph_4(OEt)_2$, gem.-$N_3P_3Ph_2(OEt)_4$, and $N_3P_3(OEt)_6$, show the expected fine

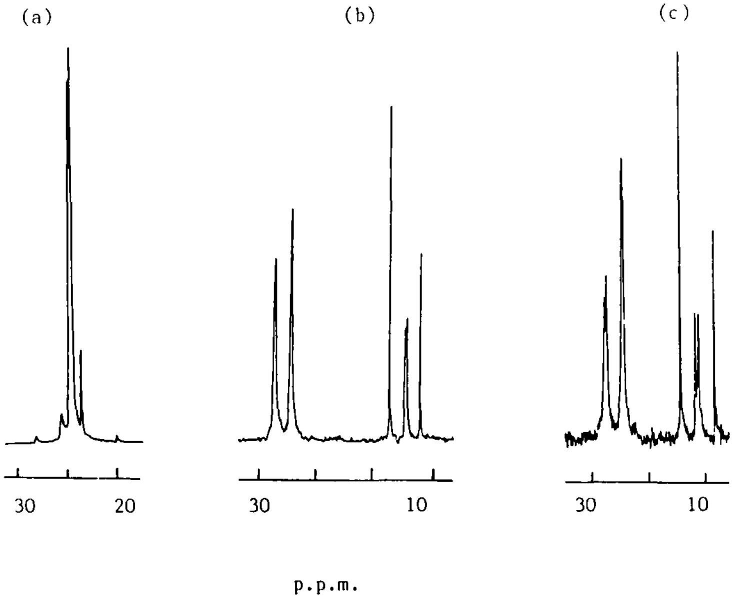


FIGURE 3 ^{31}P N.m.r. spectra of (a) $N_3P_3Cl_4[O(CH_2)_2O]$, (b) $N_3P_3Cl_4[O(CH_2)_3O]$, and (c) $N_3P_3Cl_4[O(CH_2)_4O]$ at 24.15 MHz, solvent $CDCl_3$, referenced to external 85% H_3PO_4.

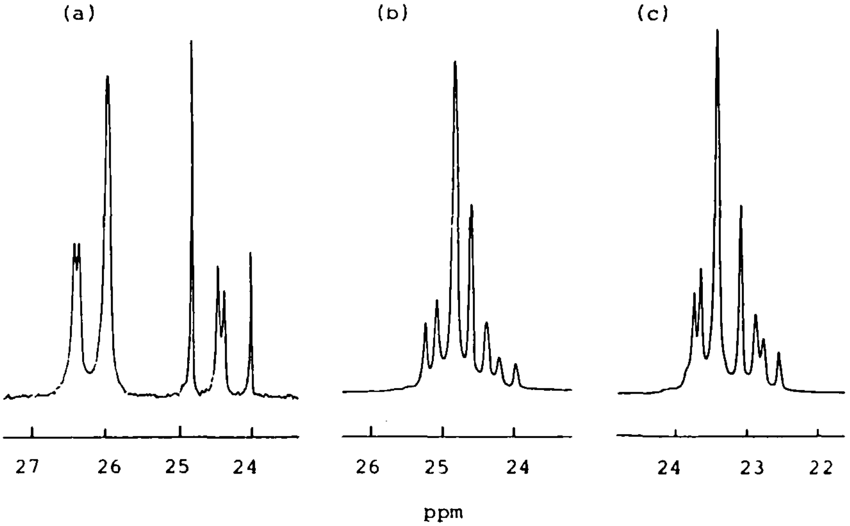


FIGURE 4 ^{31}P N.m.r. spectra of (a) $N_3P_3Cl_4[O(CH_2)_2O]$ (b) $N_3P_3Cl_4[O(CH_2)_2NH]$ and (c) $N_3P_3Cl_4[NH(CH_2)_2NH]$ at 162.0 MHz, solvent $CDCl_3$, referenced to external 85% H_3PO_4.

line splitting.[70] The OCH_2 protons of the alkanedioxy groups appeared to be very suitable to demonstrate virtual coupling. *A priori,* one would have expected the bis- and tris-derivatives to show multiplicities arising from virtual coupling to two, respectively three, phosphorus nuclei. This is observed for the 1,3-propylenedioxy and the 1,4-butylenedioxy derivatives, where there are considerable chemical shift differences between the $\equiv PCl_2$ and the $\equiv$Pspiro absorptions. The situation is more complex for the ethylenedioxy compounds, because of the proximity of the absorption signals of the two chemically different types of ^{31}P nuclei. Similar observations have been made previously.[72]

The mono-1,3-propylenedioxy-, (**21**), and the mono-1,4-butylenedioxy-compounds, (**44**), have relatively simple proton spectra, with some four bond coupling, $^4J(PH)$, observable. That of the mono-ethylenedioxy-derivative, (**43**), is complicated by the above mentioned effect. The spectra of the tris spiro compounds are again relatively simple, additional fine structure being observed due to long range virtual coupling, as the three $\equiv$Pspiro nuclei are equivalent and are strongly coupled. That of the ethylenedioxy derivative, (**48**), gives a beautiful example of this phenomenon, without the need for homonuclear proton-proton decoupling[70] (Figure 5).

The expected quartet structure of the OCH_2 protons becomes also clear in the tris-1,3-propylenedioxy, (**49**), and the tris-1,4-butylenedioxy derivatives, (**50**), on homonuclear decoupling of the CCH_2 protons. The ^{1}H n.m.r. spectra of the bis-derivatives are by far the most complex and also the most interesting. The protons of the OCH_2 and the CCH_2 methylene groups are non-equivalent 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 5-membered ring. Thus, over and above the coupling effects observed for the mono- and tris-derivatives, each methylene

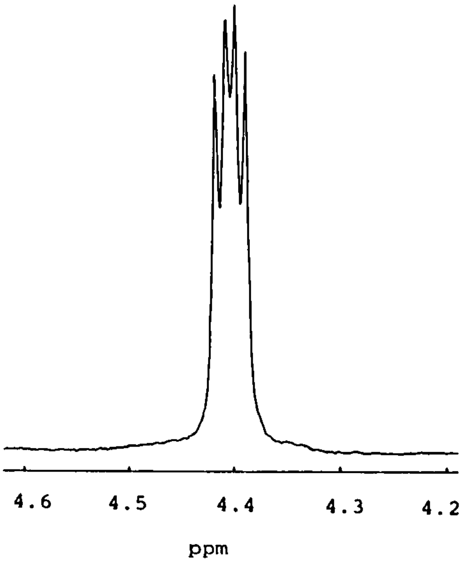


FIGURE 5 ^{1}H N.m.r. spectrum of $N_3P_3[O(CH_2)_2O]_3$ at 400 MHz in $CDCl_3$, TMS as internal reference.

group gives rise to an AB quartet structure. This is demonstrated for the bis-1,3-propylenedioxy-derivative, (**46**), (Figure 6a). Homonuclear decoupling considerably simplifies the spectrum (Figure 6b).

We have noted above that in the reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, (**1**) with ethanediol, propane-1,3-diol, and butane-1,4-diol, spiro derivatives were the most prevalent products. These contained, with the above reagents, 5-, 6-, and 7-membered phosphate rings. In a number of these the OCH_2 protons, and, where appropriate, the CCH_2 protons were in different chemical environments. Differences in chemical shifts of these methylene protons were only pronounced in the 6-membered phosphate rings, and these proved most useful for structural assignments. The very complexity of their ^{1}H n.m.r. spectra required heteronuclear and homonuclear decoupling techniques to extract the relevant parameters. The widths of these signals were, however, in some cases too large for satisfactory homonuclear decoupling, and this applied particularly to the decoupling of the CCH_2 protons.

We have therefore studied the reactions of compound (**1**) with 2,2-dimethylpropane-1,3-diol.[73] Not only are the OCH_2 proton signals much less complicated than those with propane-1,3-diol derivatives, but in addition the CCH_3 groups give rise to singlets, and hence different environments are more readily detected.

Through the inductive effect of the methyl groups the methylated diol should be a somewhat stronger nuceleophile than its unmethylated analogue. As a corollary, the presence of the methylated spiro ring should be somewhat more deactivating than its unmethylated counterpart, towards further S_N2 type of attack. Additionally the effects of the gem-dimethyl groups are well known, viz. the Thorpe-Ingold effect.[74] We therefore wished to examine the effects, if any, of the above structural changes in the diol on the type and quantity of products

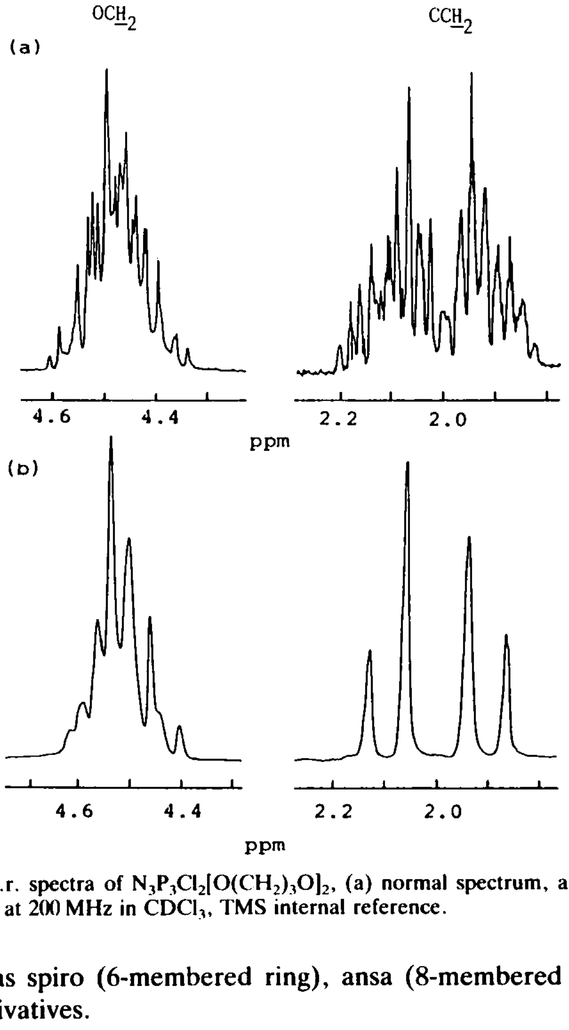


FIGURE 6 ^{1}H n.m.r. spectra of $N_3P_3Cl_2[O(CH_2)_3O]_2$, (a) normal spectrum, and (b) homonuclear decoupled spectrum, at 200 MHz in $CDCl_3$, TMS internal reference.

produced, such as spiro (6-membered ring), ansa (8-membered ring), bridging, and dangling derivatives.

We isolated so far five products from the above reaction system: $N_3P_3Cl_4(OCH_2CMe_2CH_2O)$, (**57**), $N_3P_3Cl_2(OCH_2CMe_2CH_2O)_2$, (**58** and **59**), $N_3P_3(OCH_2CMe_2CH_2O)_3$, (**60**) and $(N_3P_3Cl_4)_2(OCH_2Me_2CH_2O)_2$ (**61**). Their structures were deduced by n.m.r. spectroscopy. Four of these were analogous to the products obtained from propane-1,3-diol. Thus (**57**), (**58**) and (**60**) were respectively the mono-, bis- and tris-spiro derivatives, whilst (**59**) is the spiro-ansa isomer of (**58**). Compound (**61**) is of a novel type. It is a doubly bridged diol derivative. The ^{1}H n.m.r. spectra are worth commenting on. These are greatly simplified compared to the spectra of analogous compounds based on propane-1,3-diol. In the bis spiro derivatives (**46**) and (**58**) the OCH_2 protons and (where appropriate) the CCH_2 and CCH_3 protons observe different environments. The spectra of these two compounds are shown in Figure 7. If we consider the findings pertaining to the reactions of 2,2-dimethylpropane-1,3-diol with the hexachloride and compare these with our earlier ones on propane-1,3-diol,[30] we note resemblances as well as contrasts. The methylated diol gave a considerably

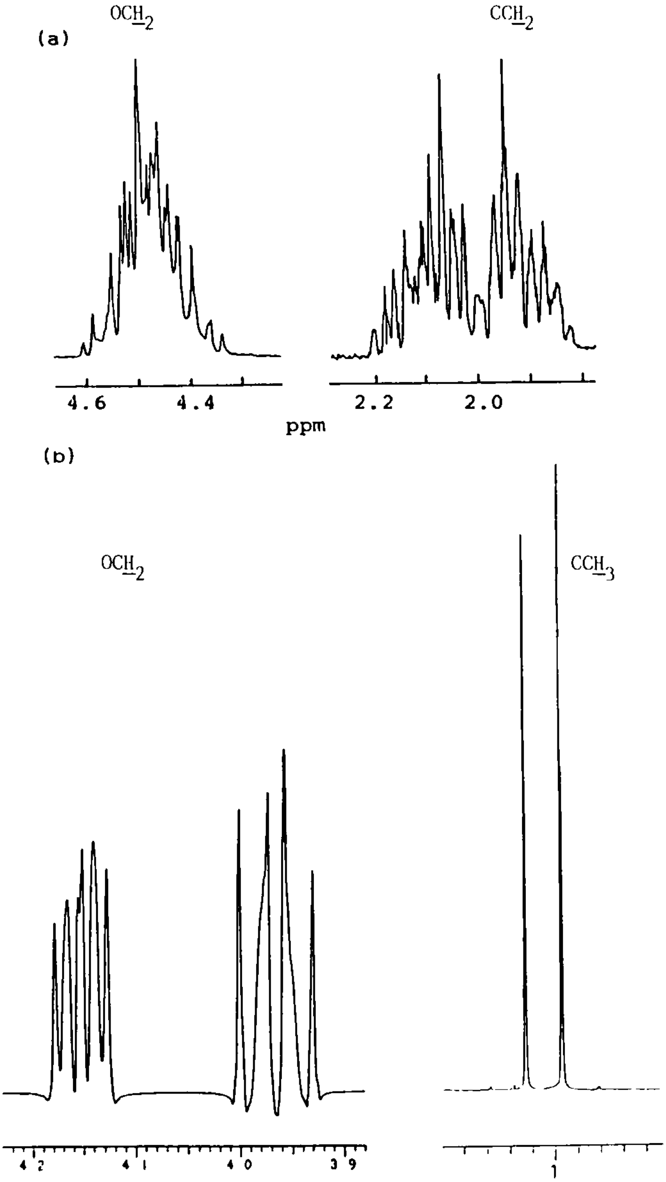
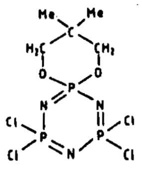


FIGURE 7 Comparison of ^{1}H n.m.r. spectra of (a) $N_3P_3[O(CH_2)_3O]_2Cl_2$ and (b) $N_3P_3[(OCH_2)_2CMe_2]_2Cl_2$.

smaller number of derivatives than its unmethylated analogue. Both gave predominantly spiro derivatives (mono, bis, and tris). The C-methylated diol gave a rather larger ratio of spiro-ansa to dispiro isomer than its unmethylated analogue.

Unlike in our earlier study[30] we did not so far observe any danglers or singly bridged compound. On the other hand we isolated the first example of a doubly bridged diol derivative with a central 16-membered ring. Doubly bridged



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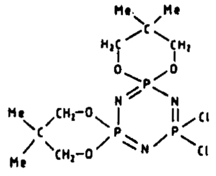

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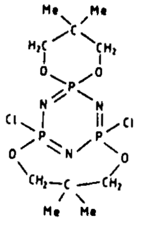

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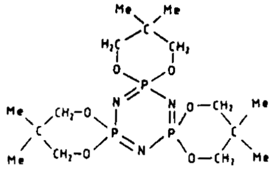

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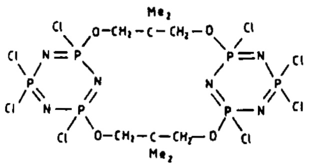
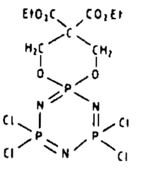


(61)

di(primary amino) derivatives have been reported by Labarre and coworkers.[58] In their examples the chains linking the two phosphazene rings were considerably larger (8 or 10 atoms) than ours (5 atoms).

Having compared the unsubstituted diol with its electron releasing dimethyl analogue, we extended our studies to a diol with electron-withdrawing carboxyethyl groups, i.e. diethyl bis(hydroxymethyl)malonate, $(HOCH_2)_2C(CO_2Et)_2$. The diol itself is somewhat unstable to hydrolysis and hence difficult to purify and to keep pure. The same pertains also probably to its phosphazene derivatives. This was borne out in our study, as we obtained more uncharacterised, probably polymeric, material, than with the other two diols. The only products we isolated were the mono-, $N_3P_3Cl_4[(OCH_2)_2C(CO_2Et)_2]$, (**62**), bis-, $N_3P_3Cl_2[(OCH_2)_2C(CO_2Et)_2]_2$, (**63**), and tris-derivatives, $N_3P_3[(OCH_2)_2C(CO_2Et)_2]_3$ (**64**). All three were shown to have spiro structures. When determining the mass spectra of the three spiro malonate derivatives (**62**–**64**), no molecular ions, M^+, were observed. Instead for compounds (**62**) and (**63**) $(M+1)^+$, and for compound (**64**) $(M+3)^+$ were found. A very recent paper[75] reported that for a very small number of compounds (10 out of 1400 examined), the molecular ion M^+ was generally absent, but the mono-protonated species $(M+H)^+$ was present in excess of 10% of the base peak. The common structural feature in these 14 compounds was the presence of a carbonyl group and the phenomenon was described as self-induced chemical ionisation under electron ionisation conditions. Compounds (**62**–**64**) contain 2, 4 and 6 such groups respectively. We can therefore add two more compounds (**62** and **63**) to the list of those showing $(M+H)^+$ peaks and report, what we believe to be the



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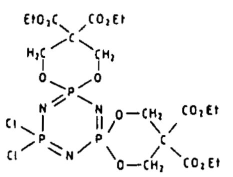

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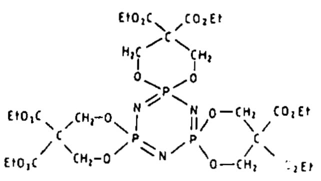
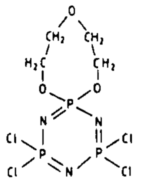


(64)

first example, of a derivative showing an $(M + 3H)^+$ peak. This phenomenon will be subjected to more detailed investigations, which will be reported later on.

Summarising our findings we find that all three diols have a preference for spiro derivative formation. Two diols give singly and doubly bridged derivatives respectively. The same two diols give ansa derivatives, the methylated one apparently giving a somewhat higher proportion of the spiro-ansa isomer. With the simplest diol danglers were also isolated.

We recently began to investigate the reactions of compound (**1**) with 1,5-bishydroxy diethyl ether, $HO(CH_2)_2O(CH_2)_2OH$. So far we have isolated a spiro derivative, $N_3P_3Cl_4[O(CH_2)_2O(CH_2)_2O]$, (**65**), its ansa isomer (**66**), and a bridged compound, $N_3P_3Cl_5[O(CH_2)_2O(CH_2)_2O]N_3P_3Cl_5$, (**67**).[76] This ansa compound (**66**) like its diamino analogue (**31**)[56] contains a 10-membered ring.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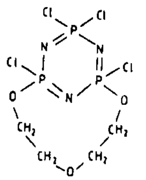
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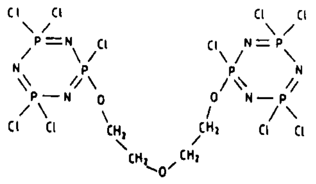
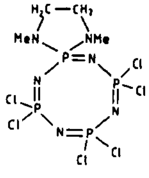
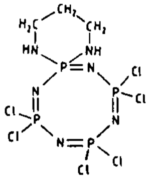

(67)

We have already mentioned that the reactions of the eight-membered ring system, $N_4P_4Cl_8$, (**2**) with monofunctional reagents have received much less attention than those of its lower homologue, $N_3P_3Cl_6$, (**1**). The octachloride, (**2**), is more reactive than the hexachloride (**1**); the former can also, in principle, give rise to a much larger number of products, and hence structure determination is made more difficult. The same pertains, with even greater force to the less investigated difunctional reagents and hitherto little was known about this system. Only two derivatives of (**2**), $N_4P_4Cl_6[NMe(CH_2)_2NMe]$,[31,77] (**68**), and $N_4P_4Cl_6[NH(CH_2)_3NH]$,[77] (**69**), had been isolated as such, two further ones, $N_4P_4(NMe_2)_6[O(CH_2)_2NMe]$,[77] (**70**), and $N_4P_4(OMe)_6[O(CH_2)_3O]$,[77] (**71**), only on derivatisation. Only resinous material was obtained from the reactions with ethylene glycol and diaminoethane.[77]


(68)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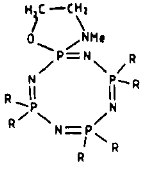
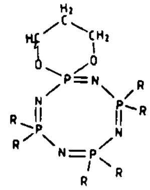
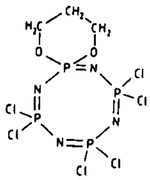

(70) (R = NMe₂)


(R = OMe) (71)

We have described above detailed studies of the reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, (**1**) with ethane diol, 1,3-propanediol, and 1,4-butanediol. Spiro, ansa, bridging and dangling derivatives were characterised.[30] We now describe reactions of the diols with the next higher homologue, octachlorocyclotetraphosphazatetraene, $N_4P_4Cl_8$, (**2**).[78]

In keeping with earlier work,[77] we found the reaction products of the octachloride, (**2**), with ethylene glycol too unstable to be isolated. Indeed, we were unable to identify with certainty, any products in the reaction mixture. This instability was also noticed, although to a lesser extent, with 1,3-propanediol. This too had been noted earlier,[77] but we were able to isolate derivatives. 1,4-Butanediol gave stable derivatives.

From the reactions of 1,3-propanediol, we isolated one mono-, $N_4P_4Cl_6[O(CH_2)_3O]$, (**72**), two isomeric bis-, $N_4P_4Cl_4[O(CH_2)_3O]_2$, (**73** and **74**), and one tris-derivative, $N_4P_4Cl_2[O(CH_2)_3O]_3$, (**75**). In spite of repeated attempts, we failed to obtain the tetrakis-derivative, $N_4P_4[O(CH_2)_3O]_4$, (**76**). The homologous diol, 1,4-butanediol, yielded one mono-, $N_4P_4Cl_6[O(CH_2)_4O]$, (**77**), two isomeric bis-, $N_4P_4Cl_4[O(CH_2)_4O]_2$, (**78** and **79**), one tris-, $N_4P_4Cl_2[O(CH_2)_4O]_3$, (**80**), and a tetrakis-derivative, $N_4P_4[O(CH_2)_4O]_4$, (**81**). Initially, the ^{31}P n.m.r. spectrum of compound (**79**), a single line reminiscent of an A_4 system, suggested misleadingly a bis ansa structure (**79A** or **79B**). A 2,6:4,8 doubly *trans*-annular bridged structure (of type **79A**) is known for a metallocene derivative of octafluorocyclotetraphosphazatetraene.[79] Ansa structures of type (**79B**) are known in the trimer system.[56,62,63,76] However, a detailed comparative analysis of the ^{31}P spectra of the derivatives reported here, as well as of earlier ones together with ^1H and ^{13}C data showed convincingly that this compound had a 2,2,6,6,-bis spiro structure (**79C**). N.m.r. spectroscopy proved to a powerful tool to deduce the structures of the derivatives prepared in this study.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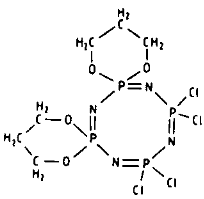
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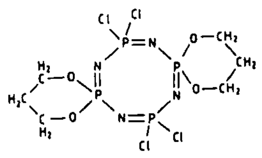
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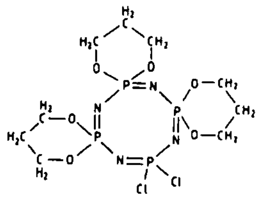
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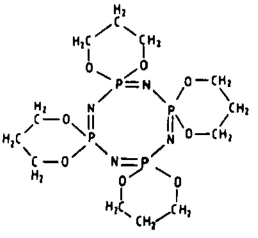
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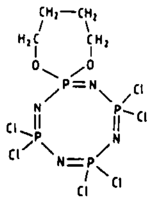
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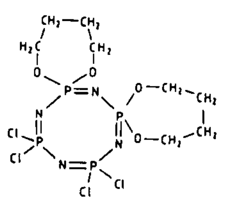
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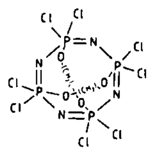
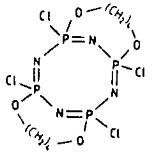
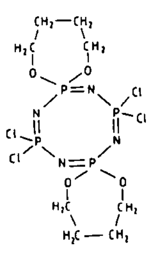

(79A)


(79B)


(79C)

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

The spectra of the derivatives of the tetramer, (**2**), with four spins are obviously more complicated than those of the trimer (**1**) with only three spins. There is also the possibility that, in addition to two-bond $^2J(PP)$, four-bond coupling $^4J(PP)$ might further complicate the spectra. We did not observe any of the latter in our analyses; examples of it are, however, known.[8,80,81] With the above group of compounds we observed spectra of four types: A_2MX (A_2BX), AA'XX' (AA'BB'), A_2X_2 (A_2B_2), and A_4.

Compounds (**72**, **75**, **77**, and **80**) show spectra of the A_2MX (A_2BX) type, establishing that these mono- and tris-derivatives are all spiro compounds. Proton coupled spectra allow unambiguous assignments to ≡Pspiro and ≡ PCl_2 moieties. A spectrum of the A_2MX type, viz. that of compound (**77**) is shown in Figure 8. Compounds (**73** and **78**) are of the AA'XX' (AA'BB') type. This establishes them clearly as 2,2,4,4-bis spiro derivatives. The spectrum of the latter (**78**) is shown in Figure 9. Compound (**74**) exhibiting two triplets is of the A_2X_2 (A_2B_2) type and is thus shown to have a 2,2,6,6-bis-spiro structure.

Compounds (**79** and **81**) show only a singlet, i.e. the A_4 type. This is, what one would have expected of a tetrakis-spiro derivative (**81**). More surprising is its occurrence in the bis-derivative (**79**).

A graphical representation of all the ^{31}P n.m.r. shifts of the compounds discussed here, showed that replacement of a spiro propanedioxy by a spiro butanedioxy group causes a deshielding of the ≡Pspiro nucleus, which brings it into the region of absorption for the ≡ PCl_2 nuclei and thus gives rise to an accidental isochrony. A detailed comparison of the graph suggested that a 2,2,6,6-bis-spiro butanedioxy derivative (**79C**) should have ^{31}P n.m.r. absorptions for both the ≡PCl_2 and the ≡Pspiro nuclei around −1 p.p.m., and these might well be isochronous. Furthermore this graph allows a prediction of chemical shift of also approximately −1 p.p.m. for the, so far unknown, tetrakis-spiro propanedioxy derivative, $N_4P_4[O(CH_2)_3O]_4$. The ^1H and ^{13}C data supported structure (**79C**).

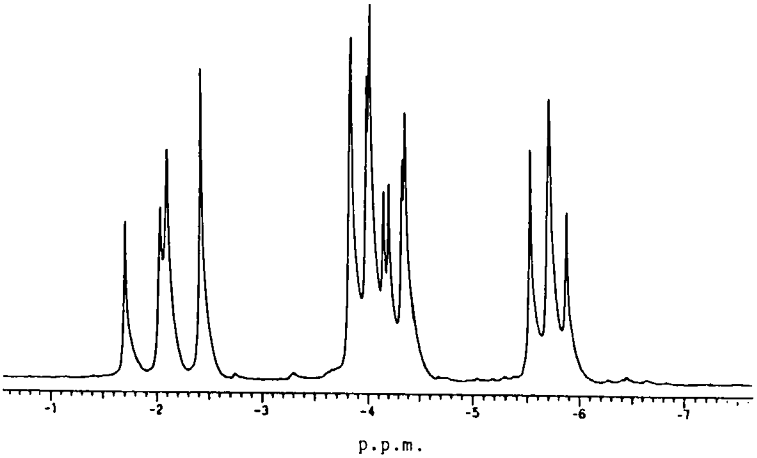


FIGURE 8 $^{31}P\{^1H\}$ N.m.r. spectrum of $N_4P_4Cl_6[O(CH_2)_4O]$ in $CDCl_3$ (85% phosphoric acid external reference) at 162.0 MHz (room temperature).

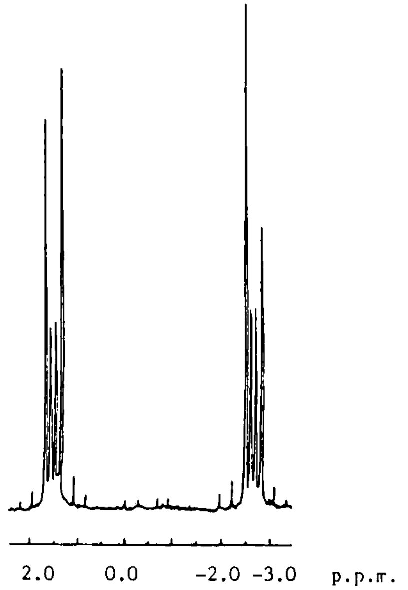


FIGURE 9 $^{31}P\{^1H\}$ N.m.r. spectrum of 2,2,4,4-$N_4P_4Cl_4[O(CH_2]_4O]_2$ in $CDCl_3$ at 162.0 MHz (room temperature).

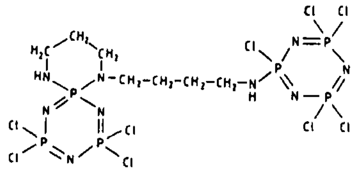
Comparing the results of this study with our earlier one on the lower homologue (**1**), we note that the octachloride (**2**) is more reactive than the hexachloride (**1**) towards the diols investigated. The instability of the products with a given diol is considerably greater for the cyclotetraphosphazatetraene system than for its lower homologue. This is most pronounced for the reaction products with ethylene glycol and least for those with 1,4-butanediol. The five-membered spiro rings are somewhat unstable in the N_3P_3 system. We, in keeping with earlier observations,[77] were unable to isolate any based on N_4P_4 rings. The six-membered spiro rings are stable with the lower homologue (**1**), but rather unstable (when P–Cl bonds are present)[77] in the higher homologue (**2**). The seven-membered spiro derivatives appear to be stable in both systems. In keeping with the above, resin formation is considerably greater for the N_4P_4 than for the N_3P_3 system.

Finally we make the following empirical observations. We have already drawn attention that monofunction nucleophilic reagents, which on disubstitution of the trimer (**1**), give rise to nongeminal products, tend to give in the tetramer system on disubstitution only 2,6-derivatives. Those reagents, which with the trimer give geminal bis derivatives, have a tendency with the tetramer to give 2,4-, as well as 2,6-derivatives. The above diols give predominantly (though not exclusively) spiro derivatives with the N_3P_3 system.[30] In keeping with the above empirical rule, they give rise to 2,2,4,4-, as well as, 2,2,6,6-derivatives in the N_4P_4 system.

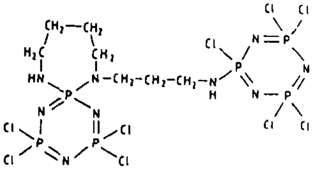
Trifunctional Aliphatic Nucleophilic Reagents with $N_3P_3Cl_6$ and $N_4P_4Cl_8$

Only one study, has been devoted to a trifunctional amine reagent. This is the reaction of compound (**1**) with a triamine, spermidine,

$H_2N(CH_2)_3NH(CH_2)_4NH_2$.[82,83] Only one product, (**82**), was reported from this reaction[82] and this was shown by X-ray crystallography to have a six-membered spiro ring (**82A**), involving one N_3P_3 moiety and a bridge to a second such unit.[83] No evidence was found for the isomeric product (**82B**) containing a seven-membered spiro ring, or for danglers based on (**82A**) or (**82B**), although both, six-membered and seven-membered spiro rings, are well documented in phosphazene chemistry.[30,53,54,81]

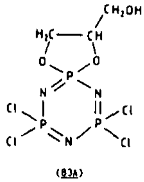


(82A)

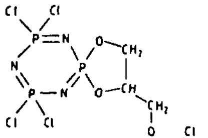


(82B)

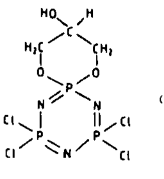
We have studied the behaviour of a tri-ol. From the reaction of the hexachloride (**1**) with glycerol we isolated an oily and a crystalline product.[84,85] Analytical data of the major product from the oily fraction indicated a composition corresponding to $N_3P_3Cl_4(O_2C_3H_6)$. The mass spectrum showed a parent ion peak at 348. It had an isotope pattern characteristic of four chlorine atoms. Hydroxy compounds are known to lose water (−18) and to pick up a proton (+1) under mass spectrometric conditions.[86,87] Adding 17 to 348 gives 365, which corresponds to $N_3P_3{}^{35}Cl_4(O_2C_3H_6)$. Two isomeric structures (**83A** and **83B**) would be in keeping with this. The ^{31}P n.m.r. spectrum of compound (**83**) (Figure 10) was closely similar to that of the five-membered spiro derivative (**43**) and very different from that of its six-membered analogue (**21**). Clearly, the oily derivative must be assigned the five-membered spiro structure (**83A**). In studies of the reaction between benzaldehyde and glycerol the product based on a five-membered ring (oily) predominated over that with a six-membered ring (crystalline).[88]



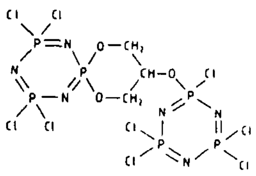
(83A)



(84A)



(83B)



(84B)

The crystalline product (**84**) had a composition corresponding to $N_6P_6(O_2C_3H_5)Cl_9$ and its mass spectrum confirmed this (parent ion at 674). Two isomeric structures (**84A** and **84B**) would fit the above. The ^{31}P n.m.r. spectrum of compound (**84**) (Figure 11) resembles closely the superposition of that of the oily product (**83A**) [and also of that of compound (**43**)] and that of the monethoxy derivative, $N_3P_3Cl_5(OEt)$.[89] This strongly suggests that this derivative too is based on a five-membered spiro ring and this was confirmed by X-ray crystallography.[84]

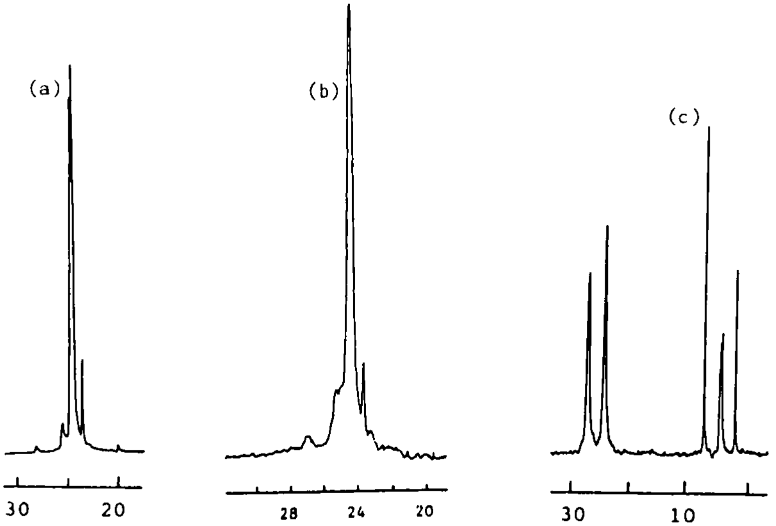
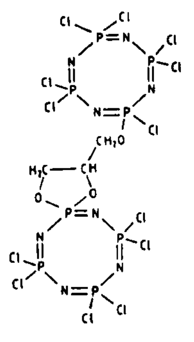
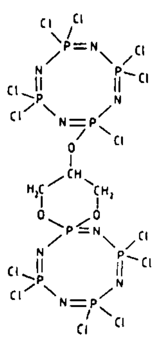


FIGURE 10 ^{31}P N.m.r. spectra of (a) $N_3P_3[O(CH_2)_2O]Cl_4$, (b) $N_3P_3[OCH_2CH(CH_2OH)O]Cl_4$ and (c) $N_3P_3[O(CH_2)_3O]Cl_4$ ($CDCl_3$ solution, room temperature at 24.15 MHz).

Thus the crystalline compound has the structure (**84A**) and like the oily derivative is based on a five-membered spiro ring.

From the reaction of the octachloride, $N_4P_4Cl_8$, (**2**), with glycerol we isolated only one compound, a crystalline one (**85**). Its elemental analysis corresponded to $N_8P_8Cl_{13}O_2C_3H_5$ and its mass spectrum (which showed the presence of 13 chlorine atoms) confirmed this. Again we must consider for this spiro-bridged derivative two isomeric structures (**85A** and **85B**).


(85A)


(85B)

The ^{31}P spectrum is complex, but indicates six groups of absorption signals. One would expect two independent patterns of the AB_2C or AB_2X type. The proton coupled spectrum reveals an additional quartet fine structure at δ7.8 and an additional triplet fine structure at δ −6.4. Thus the former can be assigned to the ≡Pspiro group, the latter to the ≡P(OR)Cl moiety. There are no data available on five-membered spiro-dioxy derivatives of compound (**2**), e.g. $N_4P_4Cl_6[O(CH_2)_2O]$. However, the six-membered analogue, $N_4P_4Cl_6[O(CH_2)_3O]$, (**72**), has its ≡Pspiro absorption at δ −10.5.[78] In the cyclotriphosphazatriene

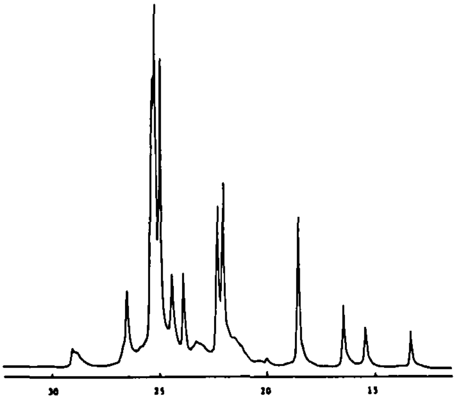


FIGURE 11 ^{31}P N.m.r. spectrum of $N_3P_3Cl_4[OCH_2CH(CH_2O)O]N_3P_3Cl_5$ ($CDCl_3$ solution, room temperature at 24.15 MHz).

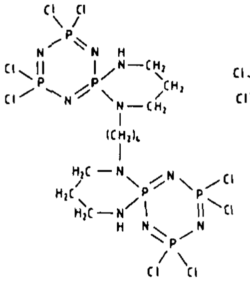
series the ≡Pspiro absorption for the five- and six-membered groupings occur at δ24.5 and 3.4 respectively. The former thus absorbs 21.1 p.p.m. downfield from the latter. In the cyclotetraphosphazatetraene group, compound (**85**) has its ≡Pspiro absorption 18.3 p.p.m. downfield from compound (**72**). The Pspiro absorption for $N_4P_4Cl_6[NMe(CH_2)_2NMe]$, (**68**), was reported to be at 6.1.[77] Clearly the glycerol derivative has the structure (**85A**). The absence of a dangler, under our experimental conditions, is presumably related to the greater reactivity of the tetramer towards nucleophilic attack compared to that of the trimer.

Comparing the reactions of our tri-ol, glycerol, with that of the tri-amine, spermidine, we make the following observations. (i) In reactions with the hexachloride (**1**), we were able to observe and isolate a dangler (**83A**) with the tri-ol, none was reported for the triamine, presumably due to the greater reactivity of the latter. (ii) Having the choice between a five- and a six-membered spiro ring, the tri-ol prefers the former. By contrast, the tri-amine favours the six- over the seven-membered spiro moiety.

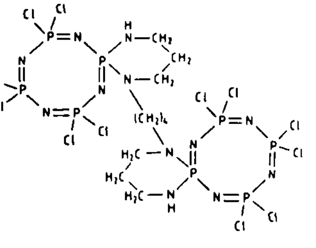
Tetrafunctional Aliphatic Nucleophilic Reagents with $N_3P_3Cl_6$ and $N_4P_4Cl_8$

These reagents had been almost entirely neglected. One study, by Labarre's group in Toulouse, reported the reaction of the tetra-amine, spermine, $H_2N(CH_2)_3NH(CH_2)_4NH(CH_2)_3NH_2$, with the hexachloride (**1**).[82] One product was isolated and its structure shown to be based on two six-membered spiro rings bridged by a tetramethylene chain (**86**).[82] Derivatives have also been reported.[90,91] We have studied the reaction of the same amine with the octachloride, (**2**), and obtained an analogous product (**87**).[92]

We now turn our attention to a tetrafunctional alcohol, pentaerythritol, $(HOCH_2)_4C$. This tetra-ol can, however, also be regarded as a derivative of propane-1,3-diol, $(HOCH_2)_2CR_2$, of which we have already discussed three examples R = H, Me, CO_2Et, whilst for pentaerythritol, R = CH_2OH. From the reactions of this alcohol with hexachlorocyclotriphosphazatriene, (**1**), we isolated three products. The major one is a spirane, $N_3P_3Cl_4[(OCH_2)_2C(CH_2O)_2]N_3P_3Cl_4$, (**88**), whose crystal structure has been determined.[93] The four six-membered rings



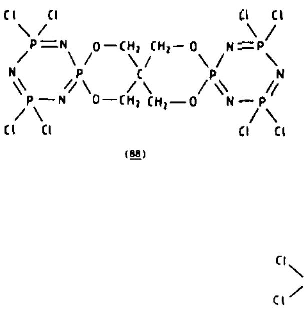
(86)



(87)

are alternatively placed at 90° to each other. This compound (**88**) can also be regarded as two six-membered spiro structures fused at the central carbon atom. With the propane-1,3-diols (R = H, Me) we observed also ansa structures, including isomeric bis propanedioxy derivatives of a dispiro and a spiro-ansa type. With pentaerythritol we also isolated an isomer (**89**) of the spirane (**88**), and this has a spiro ring with one $N_3P_3Cl_4$ moiety, an ansa structural unit with the other. A spiro-dangler, $N_3P_3Cl_4[(OCH_2)_2C(CH_2OH)_2]$ (**90**) was also isolated and characterised.

As with glycerol, the octachloride (**2**) gave only one derivative with pentaerythritol, a tetramer spirane, $N_4P_4Cl_6[(OCH_2)_2C(CH_2O)_2]N_4P_4Cl_6$, (**91**), analogous to the trimer spirane (**88**) above.



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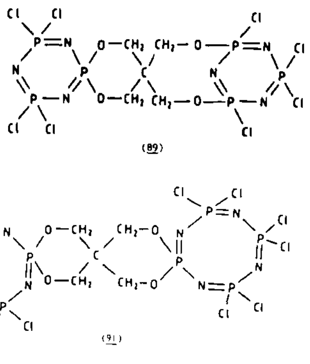

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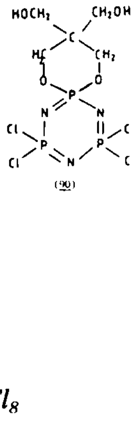

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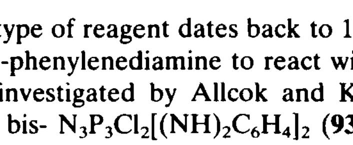
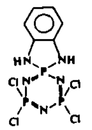


(91)

Difunctional Aromatic Nucleophilic Reagents with $N_3P_3Cl_6$ and $N_4P_4Cl_8$

The first reaction with this type of reagent dates back to 1948, when Bode, Bütow and Lienau[94] allowed *ortho*-phenylenediamine to react with the hexachloride (**1**). The same reaction was reinvestigated by Allcok and Kugel in 1966.[95] Mono-, $N_3P_3Cl_4[(NH)_2C_6H_4]$, (**92**), bis- $N_3P_3Cl_2[(NH)_2C_6H_4]_2$ (**93**), and tris-spiro derivatives, $N_3P_3[(NH)_2C_6H_4]_3$, (**94**) were isolated. By contrast, with *ortho*-aminophenol, no phosphazene derivative was obtained, only the break-down product a phosphorane (**95**).[96,97] With catechol, the tris-spiro derivative $N_3P_3(O_2C_6H_4)_3$ (**96**) has been known for some time.[98] With an excess of reagent it breaks down to a phosphorane (**97**), analogous to the product with *ortho*-aminophenol.[97-99] We have recently reinvestigated the reaction with catechol and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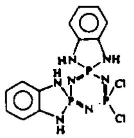
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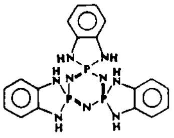
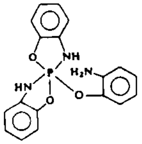

(94)

have isolated in addition to the tris compound (**96**) also the mono-, $N_3P_3Cl_4(O_2C_6H_4)$, (**98**), and bis spiro derivatives, $N_3P_3Cl_2[O_2C_6H_4]_2$ (**99**),[100] which the earlier workers[98] had failed to obtain. Only the phosphorane (**97**) was reported from the reaction of (**2**) with catechol.[99]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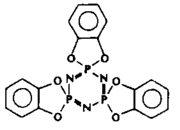
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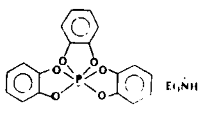

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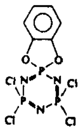
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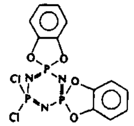
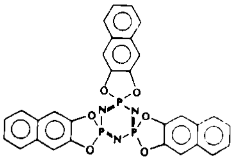

(99)

An analogous compound, (**100**), to (**96**), was reported from the reaction of the hexachloride (**1**) with 2,3-dihydroxynaphthalene.[96] When aromatic diols were chosen, which would give rise to six- and seven-membered spiro rings tris-spiro and tetrakis-spiro derivatives could be obtained from the hexachloride (**1**) and the octachloride (**2**), respectively (compounds **101–104**).[99] A sulphur analogue (**105**) of the catechol derivative (**96**) was also obtained.[96] All of the above aromatic phosphazene derivatives, which contain a 5-membered spiro ring react with *ortho*-aminophenol to give the phosphorane (**95**).[96,97] By contrast, the 6- and 7-membered spiro ring derivatives are stable towards the same reagent.[99]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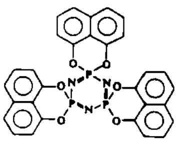
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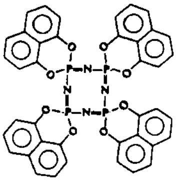
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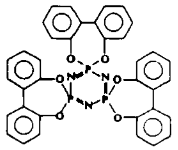
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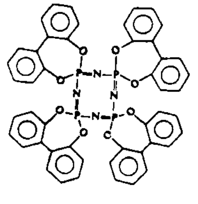
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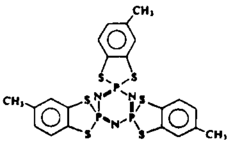
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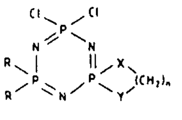
Difunctional Aliphatic and Aromatic Nucleophilic Reagents with gem $N_3P_3Cl_4R_2$ ($R = Ph$ or $NHBu^t$)

We investigated the reactions of the above geminal cyclotriphosphazatriene derivatives for a number of reasons: (i) We wished to see how the reduced reactivity (compared to $N_3P_3Cl_6$) towards nucleophilic reagents affected product type and distribution. (ii) We needed especially the monospiro compounds, $N_3P_3Cl_2R_2[X(CH_2)_nY]$, **(106)**, to evaluate basicity substituent constants, α_R, which, in turn, allowed us to study structure-property relationships.[60] (iii) We wanted to investigate further some n.m.r. spectroscopic phenomena, which had intrigued us.

Comparing the reactivity towards nucleophilic reagents we note that this decreases in the order $N_3P_3Cl_6$ **(1)** > $N_3P_3Cl_4Ph_2$ **(107)** > $N_3P_3Cl_4(NHBu^t)_2$ **(108)**.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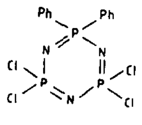
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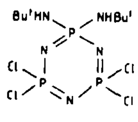
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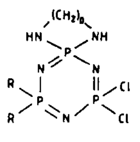
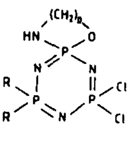
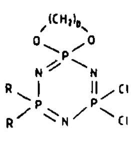
We summarise our extensive results as follows:

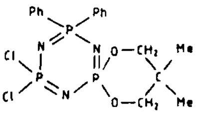
(i) The most important products are the spiro derivatives.[101-103] This applied to diamines, aminoalcohols and diols. A few examples are illustrated below **(109-111)**.


(109) (R = Ph, $NHBu^t$)


(110) (R = Ph, $NHBu^t$)


(111) (R = Ph, $NHBu^t$)

(ii) With the diphenyl derivative, $N_3P_3Cl_4Ph_2$, **(107)**, and 2,2-dimethylpropane-1,3-diol, we obtained both the mono spiro derivative $N_3P_3Cl_2Ph_2[(OCH_2)CMe_2]$ **(112)** and its mono ansa isomer **(113)**.[103]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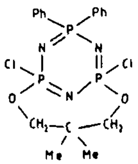
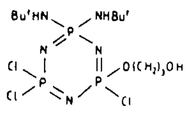

(113)

(iii) With the tert. butylamino compound, $N_3P_3Cl_4(NHBu^t)_2$ **(108)** the reduced reactivity towards S_N2 attack allowed ready observation and isolation of the dangler precursor, $N_3P_3Cl_3(NHBu^t)_2[O(CH_2)_3OH]$ **(114)** of the spiro derivative, $N_3P_3Cl_2(NHBu^t)_2[O(CH_2)_3O]$ **(115)**.[102]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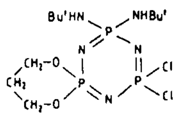
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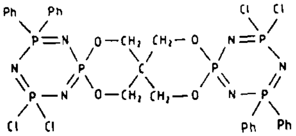
(116)

(iv) Accidental isochrony of ^{31}P n.m.r. chemical shifts in the case of $N_3P_3Cl_4Ph_2$

derivatives could be readily resolved by a change in temperature[101,104] (Figures 12 and 13).

(v) The above isochrony gave rise to interesting second order effects in the ^{13}C n.m.r. spectra of the phenyl groups, which again were affected by temperature.[105] (Figure 14).

(vi) Accidental isochrony of the ^{31}P n.m.r. chemical shifts of the $N_3P_3Cl_4(NHBu^t)_2$ derivatives could be overcome by solvent effects.[102,106] (Figure 15). In the case of compound (**115**), the coincidence of chemical shift values of the $\equiv PO(CH_2)_3O]$ and $\equiv (NHBu^t)_2$ moieties had been so pronounced that both ^{31}P and ^{13}C n.m.r. spectra originally led us to the erroneous conclusion that we had an ansa structure. An X-ray crystallographic study, however, revealed the spiro structure (**115**).[106]

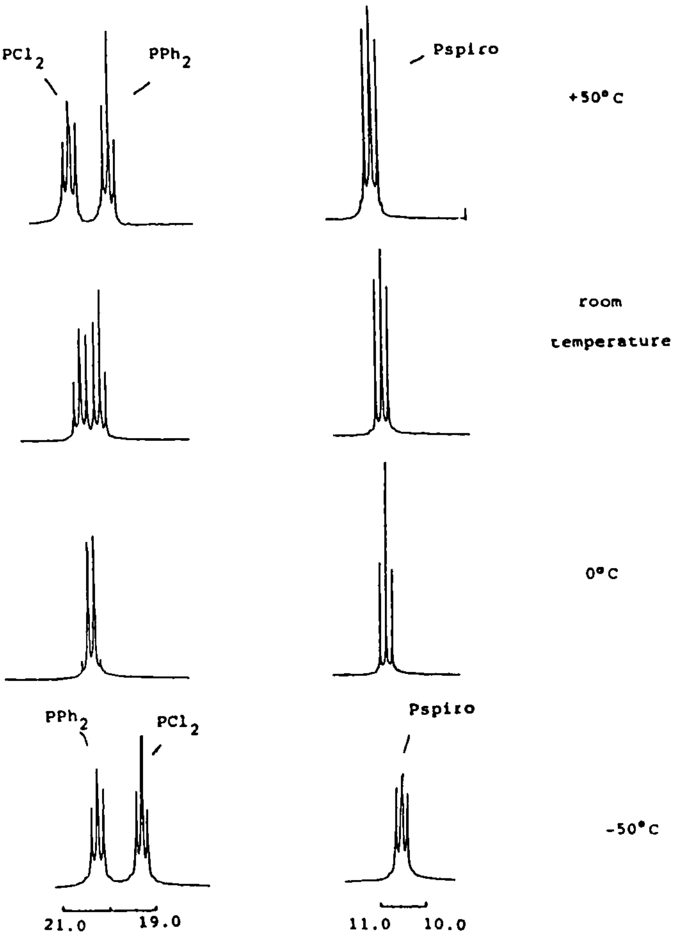

FIGURE 12 Variable temperature $^{31}P\{^1H\}$ n.m.r. spectra of $N_3P_3Ph_2[HN(CH_2)_3NH]Cl_2$ using $CDCl_3$ as lock solvent.

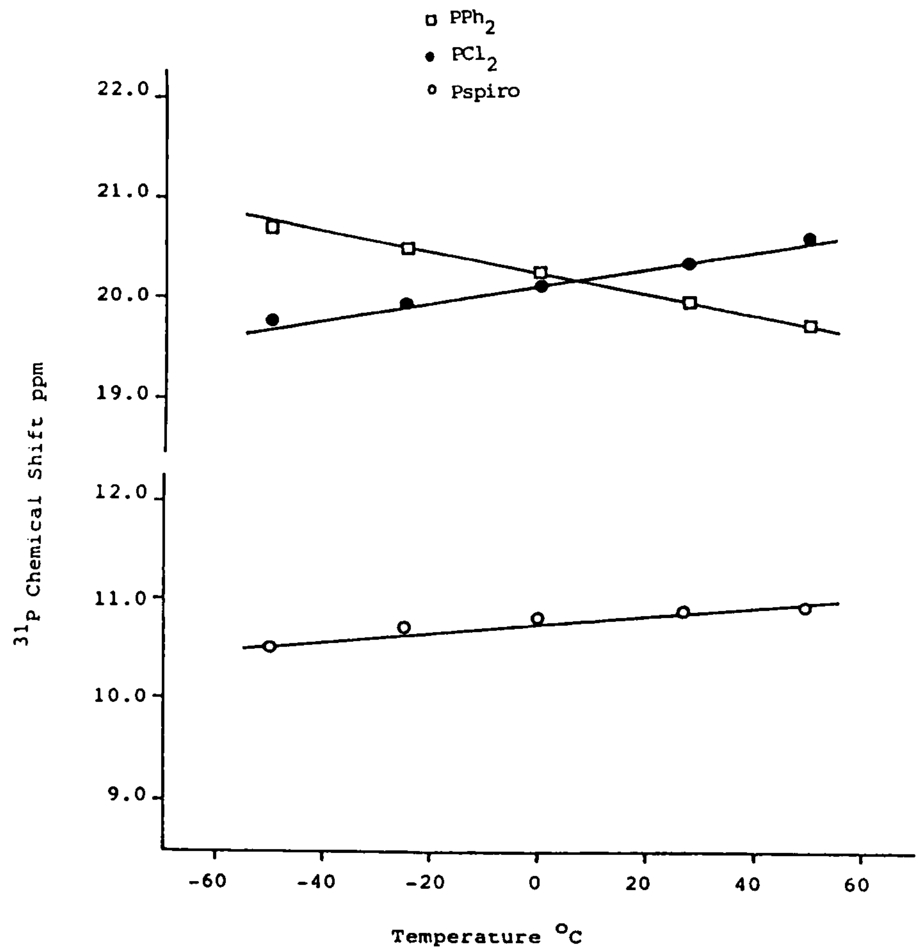

FIGURE 13 Plot of temperature against chemical shift of $N_3P_3Ph_2[HN(CH_2)_3NH]Cl_2$ using $CDCl_3$ as lock solvent.

(vii) Complexities in the ^1H n.m.r. spectra of the spiro portions arising from the non-equivalence of the methylene protons[30,101,107] (Figure 16).

Tetrafunctional Aliphatic Nucleophilic Reagents with $N_3P_3Cl_4Ph_2$

The reaction of $N_3P_3Cl_4Ph_2$ (**108**) with pentaerythritol gave rise to a spirane derivative, $N_3P_3Cl_2Ph_2[O(CH_2)_2C(CH_2O)_2]N_3P_3Cl_2Ph_2$, (**116**).[108] This gave an exceedingly complex ^1H n.m.r. spectrum of the methylene protons (Figure 17a). This is contrasted with that of the parent spirane (**88**). (Figure 17b).

In the latter, (**88**), there is only one proton environment, in the former (**116**) there are four; all of these are clearly resolved at high field. This non-equivalence arises from each proton (in each half of the molecule) seeing a different combination of chlorine atoms and phenyl groups on the near and on the far N_3P_3 rings.

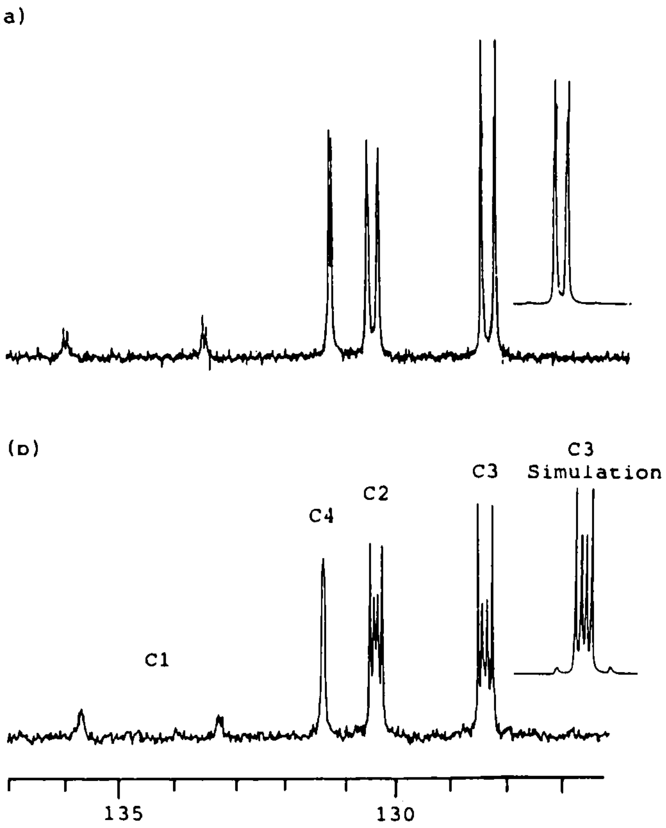

FIGURE 14 $^{13}C\{^1H\}$ N.m.r. spectrum of the phenyl groups of $N_3P_3Ph_2[NH(CH_2)_3NH]Cl_2$ at 50.1 MHz in $CDCl_3$, TMS as internal reference, (a) at room temperature, and (b) at 0°C.

SUMMARY

This review of the reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$ (**1**) and octachlorocyclotetraphosphazatetraene, $N_4P_4Cl_8$, (**2**), has described their behaviour with difunctional, trifunctional and tetrafunctional reagents containing aliphatic and aromatic amino and hydroxyl functions. The diversity of structural types is vast. Some general observations can be made. Spiro derivatives are the most common types, if the linking atoms between the functional groups of the nucleophilic reagents number from 2 to 4. 5-Membered spiro rings exhibit instabilities to varying degrees. The seminal work of Westheimer[66] on 5-membered ring phosphates and their enormous reactivity has clarified the situation in the simpler mononuclear phosphorus group of compounds. With the hexachloride (**1**), the P–NH moiety[65] increases the instability over and above that of other 5-membered ring species. With the octachloride (**2**) this instability is even more pronounced. Only two 5-membered ring derivatives have been reported. Most reagents, which one would expect to lead to 5-membered rings, yield breakdown products instead.

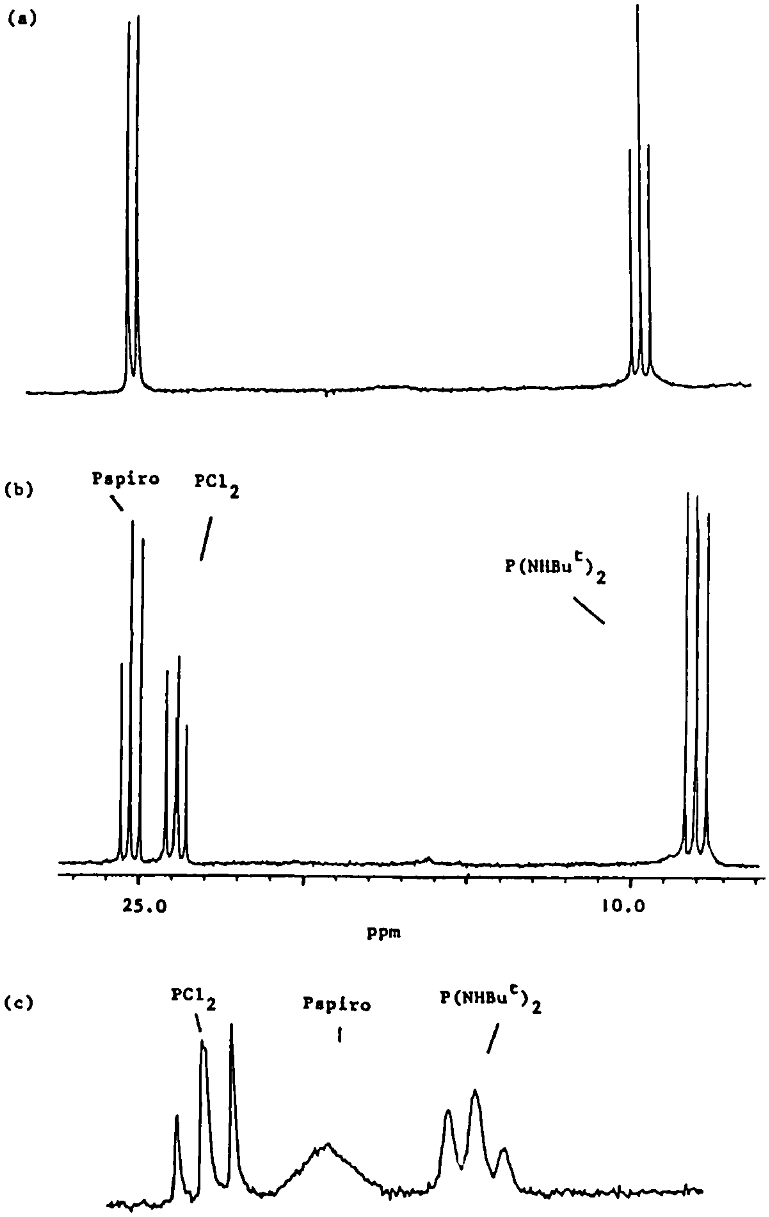

FIGURE 15 $^{31}P\{^1H\}$ N.m.r. spectra at room temperature of $N_3P_3(NHBu^t)_2[HN(CH_2)_2NMe]Cl_2$ (a) 162.0 MHz ($CDCl_3$); (b) 162.0 MHz (benzene); (c) 24.15 MHz [$CDCl_3$, 0.3 equivalents $Pr(fod)_3$].

6-Membered spiro ring derivatives appear to be stable with the hexachloride (**1**), but exhibit some instability in its higher homologue (**2**). 7-Membered spiro derivatives appear to be stable in both systems.

Thus for 5-membered and 6-membered spiro rings the instability appears to be greater for the N_3P_3 than for the N_4P_4 system.

Ansa derivatives are scarce. So far we have a few in the trimer system. The

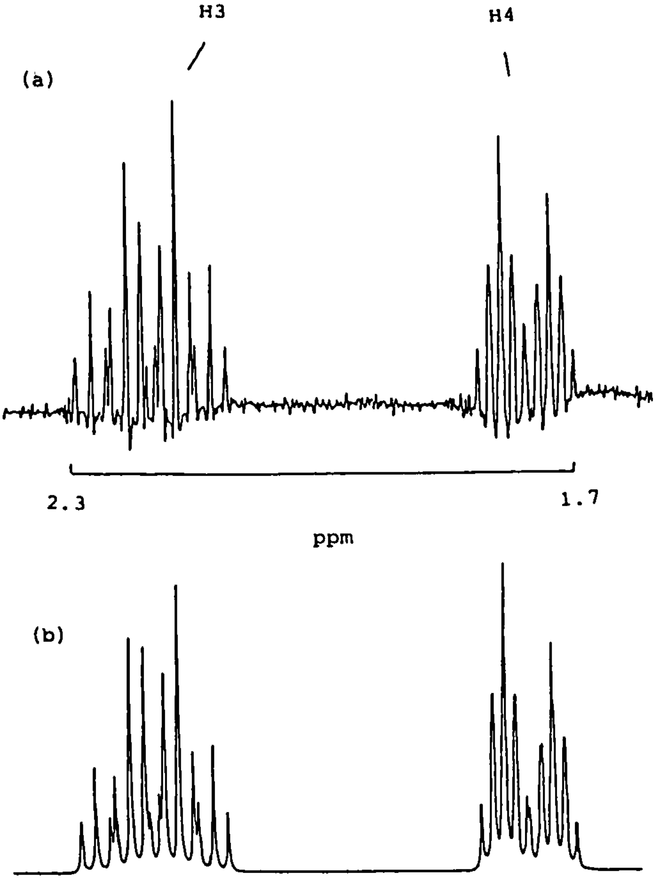

FIGURE 16 $^1H\{^{31}H\}$ N.m.r. spectrum at 250.48 MHz (room temperature) of $N_3P_3Ph_2[O(CH_2)_3O]Cl_2$ showing CCH_2C region: (a) observed spectrum (b) simulated spectrum.

initial examples contained three linking atoms between the functional groups. Quite recently two examples with five linking atoms have been discovered.

Danglers and bridging compounds will provide intermediates for further reactions; in particular, they should be useful as building bricks (or model compounds) for high polymers.

I foresee a rapidly growing interest in this fascinating field of the reactions of polyfunctional phosphorus compounds with polyfunctional organic reagents.

ACKNOWLEDGEMENTS

I would like to thank the organisers of this Symposium for the honour of inviting me to give this Lecture.

I wish to express my gratitude to my co-workers, past and present, on whose skilled work this paper is based. Their names will be found in the references, though it is particularly appropriate to mention those, who are now still active in this collaborative research.

Professor C. S. Sharma, Department of Mathematics, Birkbeck College (University of London), London, UK.
Mathematical Help to "Flatten out" Puckered Rings

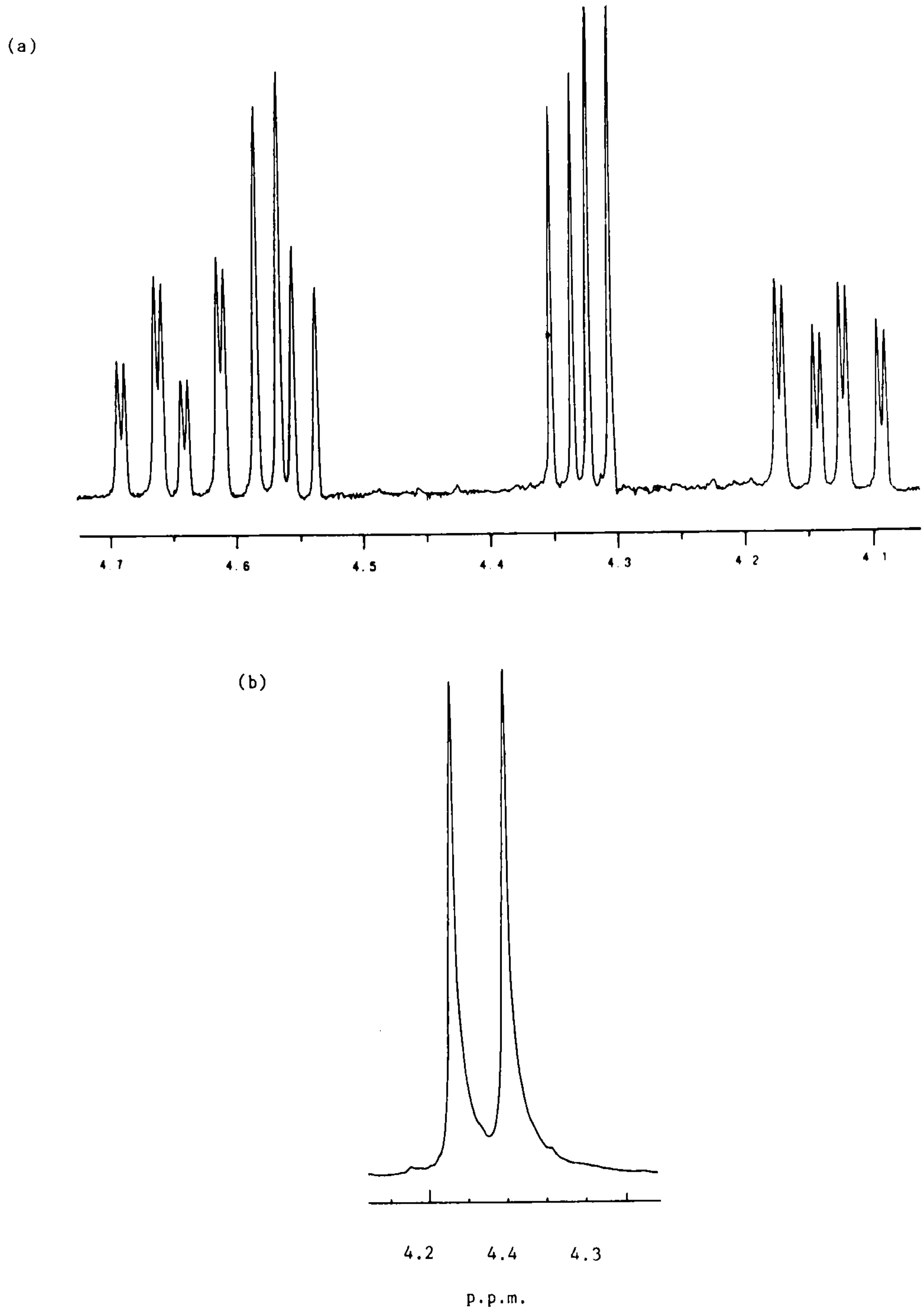

FIGURE 17 ^{1}H N.m.r. spectra of the OCH_2 region of (a) $N_3P_3Ph_2[(OCH_2)_2C(CH_2O)_2]N_3P_3Cl_2Ph_2$ and (b) $N_3P_3Cl_4[(OCH_2)_2C(CH_2O)_2]N_3P_3Cl_4$.

Dr Andrew L. Porte, Department of Chemistry, University of Glasgow, Glasgow, UK.
^{35}Cl N.Q.R. Spectroscopic Studies

Professor Necla Gündüz, Professor Turgut Gündüz, Dr Esma Kilic, Dr Mürside Tüzün, Department of Chemistry, Ankara University, Ankara, Turkey.
Potentiometric and Conductometric Studies in Non-aqueous Media

Dr Harold G. Parkes, Department of Chemistry, Birkbeck College (University of London), London, UK.
N.M.R. Spectroscopic Studies

Dr Abdulla, H. Alkubaisi, Dr Homaid A. Al-Madfa, Dr W. Francis Deutsch, Dr John K. Fincham, Dr Z. Kilic, Dr A. Kilic, Mr S. Ture, Dr David A. Watkins, Department of Chemistry, Birkbeck College (University of London), London, UK.
Synthetic Investigations.

Most of all, however, I wish to pay tribute to my wife, Dr Leylâ S. Shaw, Departments of Chemistry, Birkbeck College and Queen Mary College, (University of London), London, UK, whose skilled and dedicated X-ray crystallographic work and computing, at all sorts of unsociable hours, provided much needed structural evidence for the work described in the present lecture, and who patiently endured endless questioning on details of her own work and of that in the literature, to enable us to deduce relationships between structure and properties.

I am grateful to the Shin Nisso Kako Co. Limited for gifts of $N_3P_3Cl_6$ and $N_4P_4Cl_8$, and to the University of London Intercollegiate Research Service for some n.m.r. and mass spectrometric measurements.

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