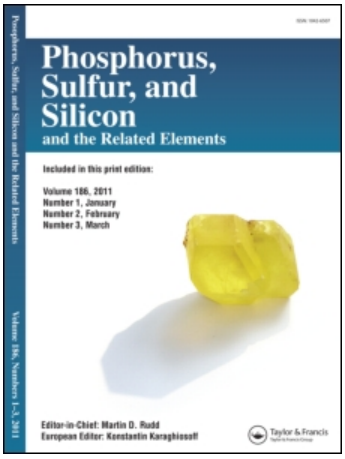

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PHOSPHORUS-NITROGEN COMPOUNDS. PART 69.[1] THE REACTIONS OF GEMINAL TETRACHLORO-1', 3'-PROPANEDIOXYCYCLOTRIPHOSPHAZA-TRIENE WITH PRIMARY AND SECONDARY AMINES. THE USE OF THE METHYLENE PROTONS OF THE 1',3'-PROPANEDIOXY GROUP TO DISTINGUISH POSITIONAL AND GEOMETRIC ISOMERS

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From the reactions of the geminal tetrachloro-1′,3′-propanedioxycyclotriphosphazatriene, $N_3P_3Cl_4[O(CH_2)_3O]$, with primary and secondary amines, the following derivatives have been isolated: $N_3P_3Cl_3R[O(CH_2)_3O]$, R = NHC_3H_5, NC_4H_8, NC_4H_8O, NC_5H_{10}; $N_3P_3Cl_2R_2[O(CH_2)_3O]$, R = NHEt, NHC_3H_5, NHC_6H_{11}, NMe_2, NC_4H_8 (3 isomers), NC_4H_8O, NC_5H_{10}; $N_3P_3R_4[O(CH_2)_3O]$, R = NHEt, NHC_3H_5, NMe_2, NC_4H_8, NC_4H_8O. Their ^1H, ^{13}C and ^{31}P n.m.r. spectra are reported. The non-equivalence of the OCH_2 and/or the CCH_2 protons of the 1′,3′-propanedioxy group is used to distinguish between geminal and nongeminal *cis*- and *trans*-isomers in $N_3P_3Cl_2R_2[O(CH_2)_3O]$. Primary amines give geminal bis-derivatives, secondary amines mainly nongeminal *trans*-isomers in $N_3P_3Cl_2R_2[O(CH_2)_3O]$, but for pyrrolidine *cis*- and geminal isomers were also isolated.

Key words: Hexachlorocyclotriphosphazatriene, 1′,3′-propanedioxy spiro derivatives, amine substitution, n.m.r. studies, non-equivalent methylene protons.

INTRODUCTION

We have shown earlier[2] that the protons of the OCH_2 and the CCH_2 groups of the 1′,3′-propanedioxy substituent in the bis-spiro derivative, $N_3P_3Cl_2[O(CH_2)_3O]_2$, exhibit non-equivalence. We decided to make use of this phenomenon to study the structures of the bis-amino derivatives, $N_3P_3Cl_2R_2[O(CH_2)_3O]$, of the mono-spiro compound, $N_3P_3Cl_4[O(CH_2)_3O]$ (**1**). A single crystal X-ray structure determination of the latter (**1**)[3] confirmed the spirostructure and showed that the two OCH_2 groups above and below the cyclotriphosphazatriene ring to be equivalent, and that the CCH_2 group was lying in the plane of this ring. In solution, however, at ambient temperature, fast interconversion of conformers occurs and removes the distinction between axial and equatorial protons, thus making the two protons of each methylene group equivalent.[2] If we ignore any $^4J(PH)$ coupling for the time being, the

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tetrachloride, $N_3P_3Cl_4[O(CH_2)_3O]$ **(1)**, and the tetra-amide, $N_3P_3R_4[O(CH_2)_3O]$ **(6)**, should both give simple ^1H n.m.r. spectra for the propanedioxy-group, the OCH_2 protons being equivalent and give rise to a doublet of triplets, whilst the CCH_2 protons should give a quintet. Homonuclear proton-proton decoupling would reduce these to a doublet and a singlet respectively. In the mono-amino-derivatives, $N_3P_3Cl_3R[O(CH_2)_3O]$, **(2)**, whose structures are totally unambiguous, the proton spectra have become exceedingly complex. The two $OC\underline{H}_2$ groups are now non-equivalent, with one exhibiting non-equivalent methylene protons. The $CC\underline{H}_2$ protons are also nonequivalent, being in the plane of the ring, one seeing a $\equiv PCl_2$, the other a $\equiv PClR$ group. Homonuclear decoupled ^1H n.m.r. spectra should show an eight-line spectrum (AB quartet split by phosphorus) for the $OC\underline{H}_2$ group on the same side of the cyclotriphosphazatriene ring as the substituent R, and a two-line spectrum for the $OC\underline{H}_2$ group on the opposite side (this analysis assumes that the differences in the chlorine atoms environments of the $\equiv PCl_2$ and the $\equiv PClR$ moieties are not marked enough to make observable differences in the environments of the $OC\underline{H}_2$ protons). The $CC\underline{H}_2$ regions should be a four-line signal. These and similar analyses for the three possible bis amino-derivatives are summarized in Table I.

Table I also shows that examination of both the $OC\underline{H}_2$ and $CC\underline{H}_2$ regions is necessary as, for instance, the 8-line signal of the $OC\underline{H}_2$ region alone fails to distinguish between the geminal and the *trans*-nongeminal bis-derivatives. The above analysis is quite general and is here applied to R being an amino substituent.

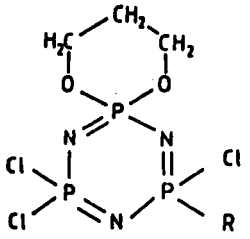
RESULTS AND DISCUSSION

We allowed the spiro-derivative, **(1)**, to react with varying stoichiometries of a number of different primary and secondary amines and isolated mono-amino compounds, $N_3P_3Cl_3R[O(CH_2)_3O]$, (**2**, R = NHC_3H_5, NC_4H_8, NC_4H_8O, NC_5H_{10}), diamino-derivatives, $N_3P_3Cl_2R_2[O(CH_2)_3O]$, (R = NHEt, NHC_3H_5, NHC_6H_{11}, NMe_2, NC_4H_8 (3 isomers), NC_4H_8O, NC_5H_{10}) [whose structures (**3, 4, 5**) will be discussed below] and tetra-amino derivatives, $N_3P_3R_4[O(CH_2)_3O]$, **(6)**. We now report our n.m.r. spectroscopic investigations.

TABLE I

Predicted ^1H n.m.r. splitting pattern (homonuclear decoupled and ignoring any $^4J(PH)$ coupling) of the 1,3-propanedioxy group of $N_3P_3Cl_{4-n}R_n$ $[O(CH_2)_3O]$(R = any substituent other than Cl)

Compound	Structure	Number of lines in $OC\underline{H}_2$ region	$CC\underline{H}_2$ region
$N_3P_3Cl_4[O(CH_2)_3O]$		2	1
$N_3P_3Cl_3R[O(CH_2)_3O]$		8 + 2 = 10	4
$N_3P_3Cl_2R_2[O(CH_2)_3O]$	geminal	8	4
$N_3P_3Cl_2R_2[O(CH_2)_3O]$	*cis*-nongeminal	2 + 2 = 4	1
$N_3P_3Cl_2R_2[O(CH_2)_3O]$	*trans*-nongeminal	8	1
$N_3P_3ClR_3[O(CH_2)_3O]$		8 + 2 = 10	4
$N_3P_3R_4[O(CH_2)_3O]$		2	1



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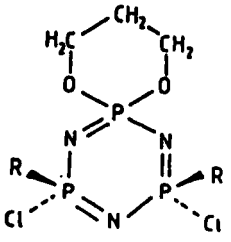

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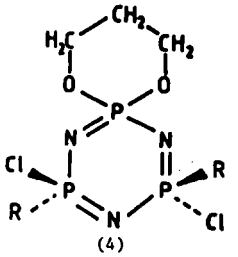

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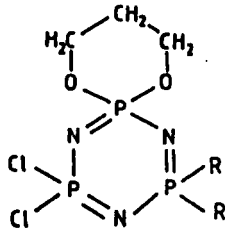

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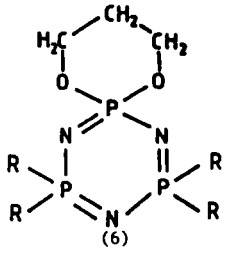

(6)

^1H. N.m.r. investigations

The observation (in a homonuclear decoupled spectrum) of a 10 line signal (8 + 2) in the $OC\underline{H}_2$ and a 4-line signal in the $OC\underline{H}_2$ regions of $N_3P_3Cl_3R[O(CH_2)_3O]$ ($R = NC_4H_8$) assures the accuracy of the analysis given in Table I.

The ^1H n.m.r. spectra of the compounds reported here are in Table II. It can be seen that for the amines studied so far, when R is a primary amino group, the bis-derivatives are geminal, whilst when R is a secondary amino group, the major bis-amino compounds have a *trans*-nongeminal structure. A single crystal X-ray structure analysis of the bis-pyrrolidino derivative, $N_3P_3Cl_2(NC_4H_8)_2[O(CH_2)_3O]$, m.p. 179–180°C, confirms its *trans*-nongeminal structure.[3] The structure of the tetrakis pyrrolidino compound has also been reported.[3]

Table II reveals some $^4J(PH)$ coupling. It also demonstrates long range virtual coupling effects for the amino substituents in the *cis* and *trans*-nongeminal bis- and in the tetrakis derivatives.

A particularly detailed investigation of the pyrrolidine system revealed the existance of three bis-isomers (**3**, **4** and **5**, $R = NC_4H_8$) and the spectra of these, together with the mono(**2**, $R = NC_4H_8$) and the tetrakis-amino derivatives (**6**, $R = NC_4H_8$) will be discussed in some detail.

TABLE II

^{1}H N.m.r. data for the 1′,3′-spiropropylenedioxy-amino derivatives[a]

Compound	δ N—H	δ N—CH	δ C—CH$_2$	δ C—CH$_3$	δ N—CH$_2$	δ O—CH$_2$	δ N—Me$_2$	^3J(P—H)	Propane-1,3-dioxy residue: δ OCH$_2$	δ CCH$_2$	^3J(P—H)
(1)									4.53	2.07	12.9
(3, R = NHEt)	2.31		2.97	1.12				9.1	4.41	2.10	14.3
(6, R = NHEt)	2.11		2.90	1.11				9.8	4.38	1.91	14.7
(2, R = NHC$_3$H$_5$)	2.93	2.43	0.50					[b]	4.44	2.11	14.2
(3, R = NHC$_3$H$_5$)	2.88	2.39	0.58					[b]	4.41	2.10	14.4
(6, R = NHC$_3$H$_5$)	2.80	2.33	0.59					[b]	4.40	2.09	14.5
(3, R = NHC$_6$H$_{11}$)	2.25	3.02	1.73[c] 1.21[c]					[b]	4.40	2.01	14.6
(4, R = NMe$_2$)							2.68	13.6	4.48	2.06	14.4
(6, R = NMe$_2$)							2.61	10.7	4.41	1.91	14.6
(2, R = NC$_4$H$_8$)			1.87		3.22			7.6	4.46	2.17, 1.85	[b]
(5, R = NC$_4$H$_8$)			1.86		3.24			8.65	4.46	1.99	12.6
(4, R = NC$_4$H$_8$)			1.87		3.26			9.15	4.46	1.98	12.7
(3, R = NC$_4$H$_8$)			1.84		3.12			5.9	4.46	2.20, 1.87	[b]
(6, R = NC$_4$H$_8$)			1.77		3.11			2.5	4.39	1.88	12.2
(2, R = NC$_4$H$_8$O)					3.12	3.69		13.9	4.43	2.02	14.3
(4, R = NC$_4$H$_8$O)					3.14	3.67		13.3	4.43	2.01	14.4
(6, R = NC$_4$H$_8$O)					2.97	3.48		10.7	4.21	1.85	14.6
(2, R = NC$_5$H$_{10}$)			1.61		3.11			13.6	4.44	2.00	14.3
(4, R = NC$_5$H$_{10}$)			1.60		3.10			13.7	4.43	2.01	14.3

[a] δ in p.p.m.; *J* in Hz.; Measurements in $CDCl_3$ (internal reference TMS) at room temperature at 200 and 400 MHz.
[b] Too complex to be measured.
[c] Two sets of signals for the α and β protons.

The pyrrolidino derivatives of $N_3P_3Cl_4[O(CH_2)_3O]$ have, in general, four types of proton environments. The protons of the two types of methylene groups in the dioxy-spiro ring and those of the two types of methylene groups in the pyrrolidino rings, NC_4H_8. The substitution patterns of the chlorine atoms by pyrrolidino groups may impose a non-equivalency on the protons among the methylene groups of the six-membered spiro ring.

The proton n.m.r. data of this series measured at 200 and 400 MHz. are shown in Table II.

The replacement of one chlorine atom of compound (**1**) by a pyrrolidino group (**2**, R = NC_4H_8) affects the proton environments of the methylene protons of the spiro ring in such a manner that these protons become both chemically and magnetically non-equivalent. The coupling constant arising from the interaction of one proton with another nucleus is different from the coupling constant arising from interaction of the other proton with the same nucleus (and this difference may be observable) and in addition each methylene proton environment of the spiro ring gives an AB quartet signal.

For the $POC\underline{H}_2$, the AB quartet would couple with the adjacent $OCC\underline{H}_2$ protons to give a total of 12 or 16 lines, depending on the coupling magnitude between the $POC\underline{H}_2$ and $POCC\underline{H}_2$ protons. Further coupling with the phosphorus nucleus would give a total of 24 or 32 line spectrum. At 200 MHz. only 26 lines were observed centered at 4.46 p.p.m. Fewer lines than predicted may be due to accidental coincidence.

The non-equivalent $POCC\underline{H}_2$ protons would give rise to 40 or 48 lines if coupled to the phosphorus nucleus. At 200 MHz. only 14 lines were observed centered at 2.17 p.p.m. In this study it was found that the non-equivalent protons of the $POCC\underline{H}_2$ group in six-membered rings give rise to more lines, but those are subdivided into two subgroups. Therefore, one would predict that in this spectrum of the $POCC\underline{H}_2$ group, the 14 lines observed represent one subgroup, whilst the other was accidentally hidden under the $PNCC\underline{H}_2$ signals of the pyrrolidino group. When this spectrum was measured at 400 MHz., parts of these hidden signals were uncovered. When the $POC\underline{H}_2$ protons were decoupled, 3 lines of the $POCC\underline{H}_2$ protons AB quartet were clearly observed, while the fourth line was still hidden under the $PNCC\underline{H}_2$ group region. No long range coupling with the phosphorus nucleus was detected. When these protons were decoupled by irradiating at the frequency of the $PNCC\underline{H}_2$ protons, the $PNC\underline{H}_2$ spectrum was simplified into a doublet from coupling with the near phosphorus nucleus. The $PNCC\underline{H}_2$ proton spectrum give rise to five lines, which on homonuclear decoupling gave a singlet.

^1H n.m.r. spectroscopy proved to be very useful in distinguishing between the three bis-isomers (**3, 4** and **5**, R = NC_4H_8). If we consider the protons of the $POC\underline{H}_2$ group, the number of lines obtained vary from one isomer to another. If we consider the spectrum of the *trans*-isomer (**4**) one would expect a total of up to 24 lines. At 200 MHz. the $POC\underline{H}_2$ protons displayed a deceptively symmetrical 6 lines spectrum, as if the $POC\underline{H}_2$ protons were equivalent. At 400 MHz., however, a total of 10 lines were observed and centered at 4.46 p.p.m. Fewer lines than predicted may be due to accidental coincidence. (Figure 1a). On homonuclear decoupling the spectrum simplified into a total of 8 lines (splitting of the $POC\underline{H}_2$ AB quartet by coupling with the near phosphorus nucleus). (Figure 2a).

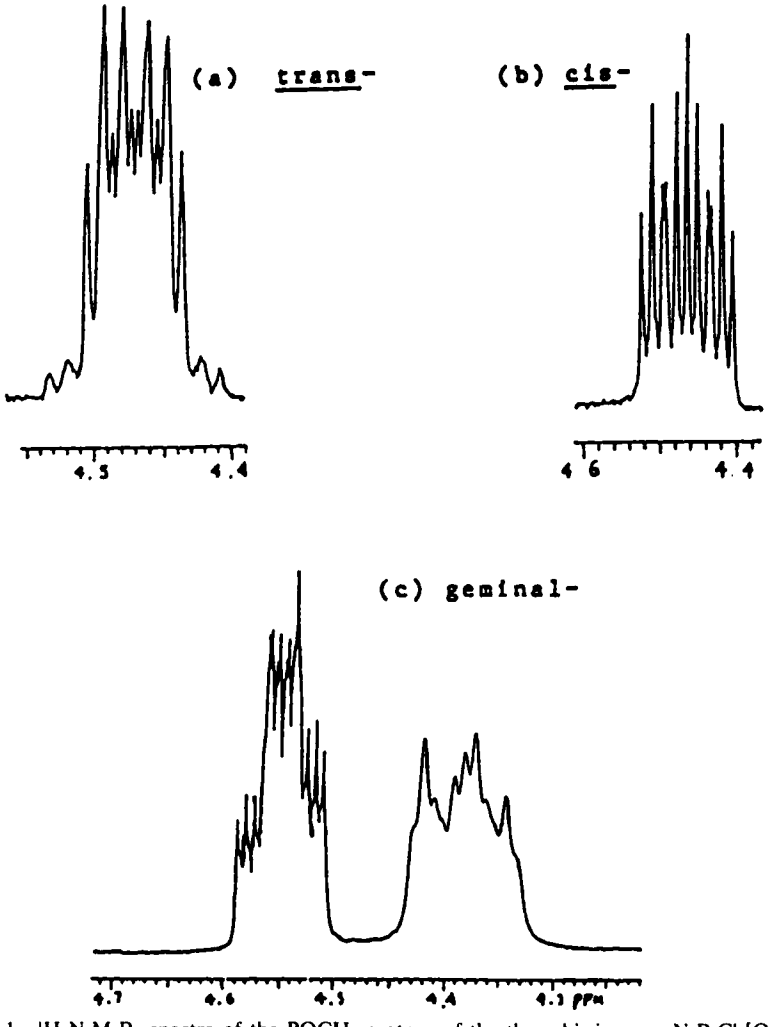

FIGURE 1 ^{1}H N.M.R. spectra of the POC$\underline{H}_2$ protons of the three bis-isomers $N_3P_3Cl_2[O(CH_2)_3O](NC_4H_8)_2$ (**3**), (**4**) and (**5**) in $CDCl_3$ at 400.0 MHz. (Room temperature).

For the *cis*-isomer (**5**, R = NC_4H_8), the methylene groups of the POC$\underline{H}_2$ moieties are not equivalent. One methylene group would observe the pyrrolidino groups, whilst the other methylene would observe preferentially the chlorine atoms. However, the protons within each of the POC$\underline{H}_2$ groups and of the POCC$\underline{H}_2$ group are equivalent. The POC$\underline{H}_2$ n.m.r. spectrum displays 11 lines out of the predicted 12 lines (Figure 1b), which on homonuclear decoupling give rise to two doublets (Figure 2b).

The POC$\underline{H}_2$ proton signals of the geminal isomer, however, are more complex and differ from the above two nongeminal isomers. The two POC$\underline{H}_2$ methylene groups are equivalent, since each group observes one pyrrolidino group and one chlorine atom. However, their protons are non-equivalent, since one proton observes preferentially the two pyrrolidino groups, the other the two chlorine atoms. At 200 and 400 MHz. only 26 lines in a complex band were observed centered at

4.46 p.p.m. (Figure 1c). As we have pointed out earlier[2] the simplification of the $POC\underline{H}_2$ proton spectrum by total decoupling of the adjacent $OC\underline{CH}_2$ protons signal is not feasible, because of the width of $OC\underline{CH}_2$ signal.

The ^1H n.m.r. spectra of the $POCC\underline{H}_2$ groups have also provided help in distinguishing between the three isomers. In the *trans* case, these two protons are equivalent, and 10 lines would be predicted arising from coupling with the neighbouring protons of the $POC\underline{H}_2$ groups and further coupling with the near phosphorus nucleus. At 400 MHz. 8 lines were observed, which collapsed into a doublet on homonuclear decoupling.

The protons of the $OC\underline{CH}_2$ group of the *cis*-isomer behaved similarly except that here 10 lines were observed.

The geminal bis isomer (**3**, R = NC_4H_8) gave the expected complex $POCC\underline{H}_2$ signal (Figure 3a). At 400 MHz. 25 lines could be discerned, which on homonuclear decoupling gave rise to an AB quartet (Figure 3b).

The ^1H n.m.r. spectra of the pyrrolidino groups showed that the methylene protons $PNC\underline{H}_2$ and $PNCC\underline{H}_2$ form part of an AA'XX' system. Extraction of n.m.r. parameters proved difficult, because of the coalescence of large numbers of lines. These protons were further coupled with the phosphorus nuclei directly and, in some cases, through second order "virtual" coupling effects. In the two nongeminal isomers, the signals of $PNC\underline{H}_2$ of the *cis* and *trans* derivatives displayed 11 and 9 lines spectra at 400 MHz., respectively. Decoupling of the $PNCC\underline{H}_2$ protons resulted in triplet structures for both the *cis* and *trans* isomers. These three lines arise from the virtual coupling with the two phosphorus nuclei bearing the pyrrolidino residues. (Figure 4a).

The proton n.m.r. signals of the $PNC\underline{H}_2$ proton of the geminal isomer displayed a five line spectrum at 400 MHz. centered at 3.12 p.p.m., which on decoupling gave rise to a doublet (Figure 4b).

The homonuclear decoupled spectra of the $PNCC\underline{H}_2$ protons gave singlets in all cases, showing the absence of $^4J(PH)$ coupling in the pyrrolidino groups.

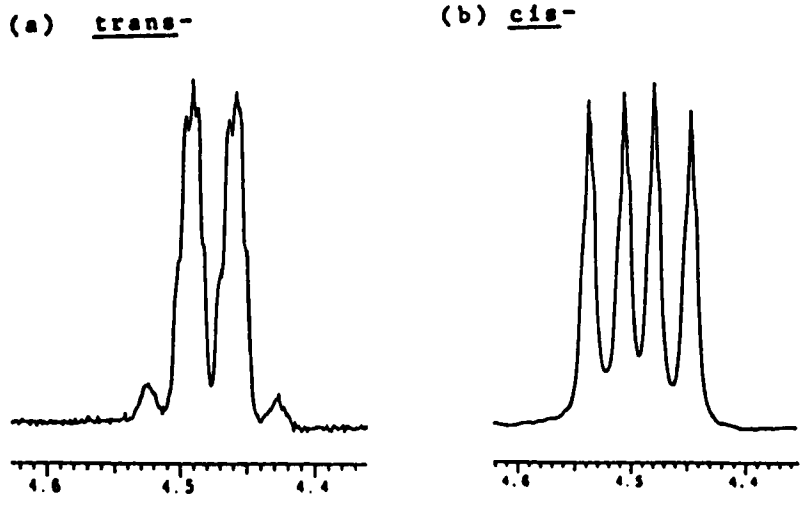

FIGURE 2 ^1H N.M.R. spectra of the $POC\underline{H}_2$ protons ($POCC\underline{H}_2$ decoupled) of the non-geminal bis-isomers $N_3P_3Cl_2[O(CH_2)_3O](NC_4H_8)_2$ (**4**) and (**5**) in $CDCl_3$ at 400.0 MHz.

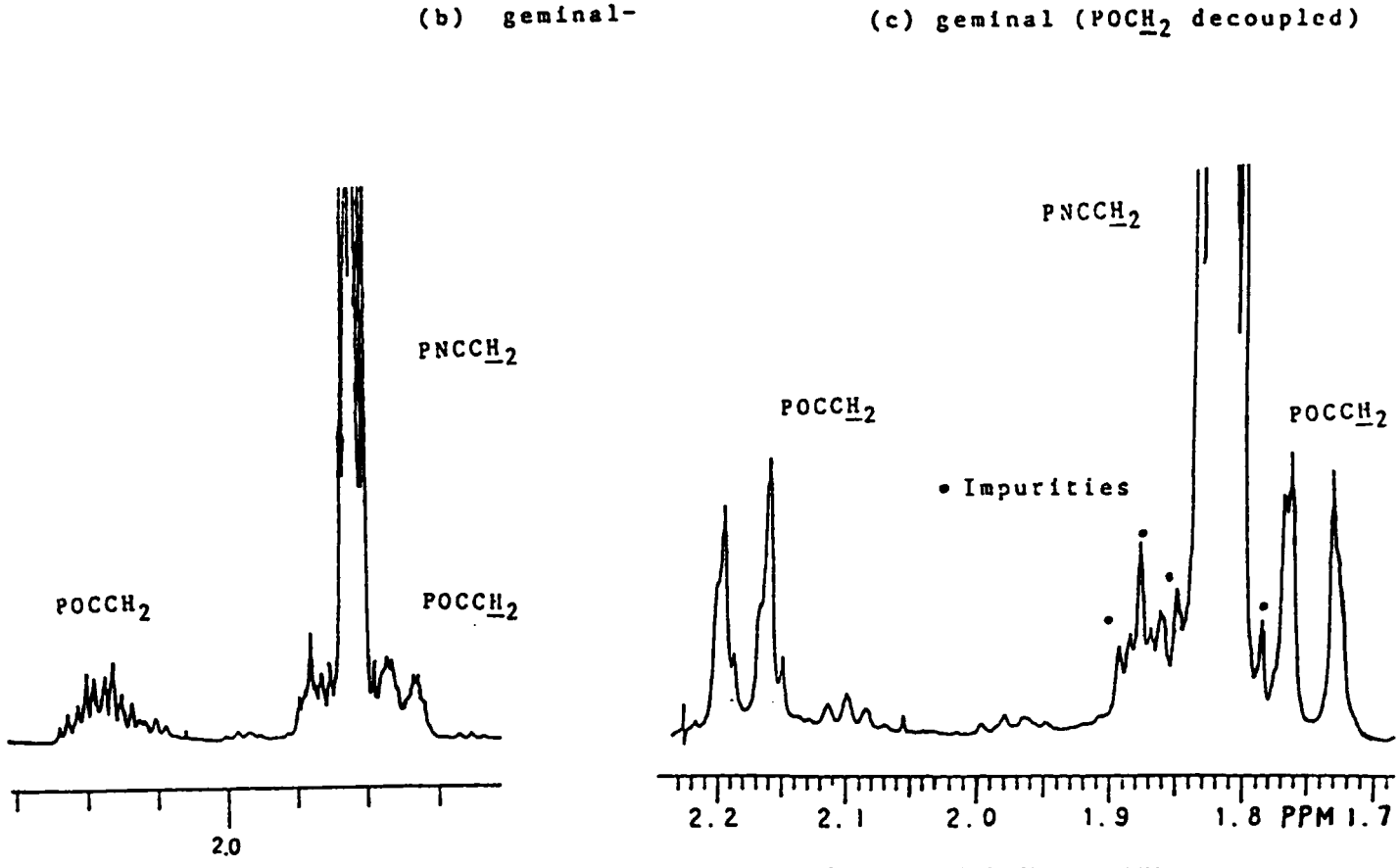

FIGURE 3 ^{1}H N.M.R. spectrum of geminal $N_3P_3Cl_2[O(CH_2)_3O](NC_4H_8)_2$ (**3**) in $CDCl_3$ at 400.0 MHz.

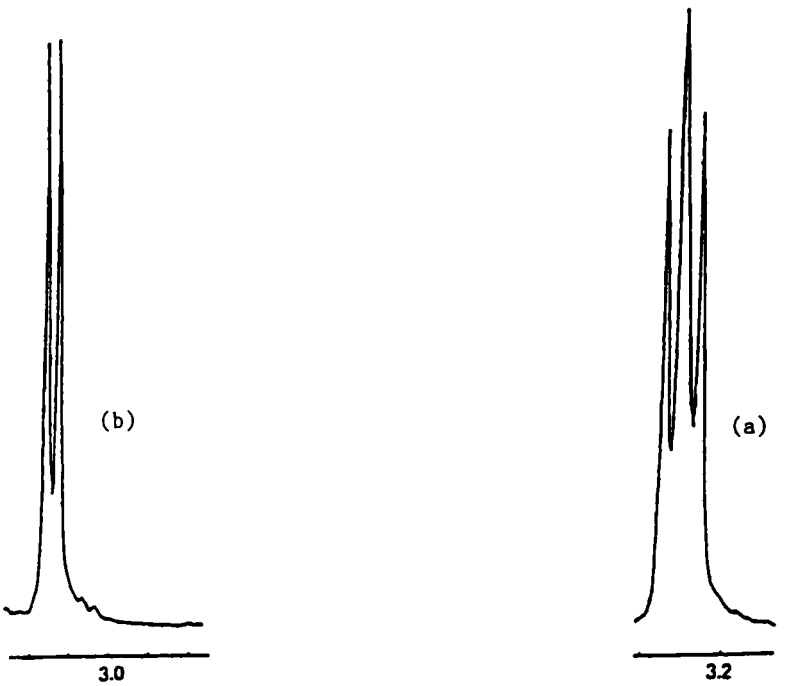

FIGURE 4 ^{1}H N.M.R. spectra of the PNC$\underline{H}_2$ protons (PNCC$\underline{H}_2$ protons decoupled) of the $N_3P_3Cl_2[O(CH_2)_3O](NC_4H_8)_2$ isomers (**3**) (a) and (**4**) (b) in $CDCl_3$ at 199.5 MHz.

The protons of the tetrakis pyrrolidino derivative (**6**) are in symmetric environments and this is reflected in their much simpler n.m.r. spectra. Homonuclear decoupling gave rise to a doublet for the POC$\underline{H}_2$ and a triplet for the PNC$\underline{H}_2$ protons.

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

Table III summarizes the ^{31}P n.m.r. spectra of the compounds described here.

It can be seen that ^{31}P n.m.r. spectroscopy allows a distinction between geminal and nongeminal bis-isomers, as they give rise to ABX (AMX) or AB_2 (AX_2) spectra respectively. ^{31}P N.m.r. spectroscopy does not, however, permit a distinction between the bis *cis* and *trans*-isomeric structures.

^{13}C N.m.r. spectra

These were only obtained for the pyrrolidino derivatives and the data are given in Table IV.

The decrease in ^3J(P$\underline{O}$C$\underline{C}$) with increasing replacement of electron-withdrawing chlorine atoms by electron supplying pyrrolidino groups should be noted. We have drawn attention elsewhere to the relationship between P—O (and P—N) bond length and these three-bond coupling constants. Clearly this successive replacement of chlorine atoms by pyrrolidino groups lessens the electron-withdrawing power of

TABLE III

Phosphorus–31 n.m.r. data for 1,3-spiropropylenedioxy amino derivatives[a]

Compound	δ P(spiro)	δ PCl_2	δ PR_2	δ PRCl	^2J(Pspiro–PR_2)	^2J(Pspiro–PCl_2)	^2J(Pspiro–PClR)	^2J(PCl_2–PR_2)	^2J(PCl_2–PClR)
(1)	3.4	24.1				69.2		33.2	
(3, R = NHEt)	7.3	25.9	16.3		26.7	72.1		33.2	
(6, R = NHEt)	14.9		18.5		67.0				
(2, R = NHC_3H_5)[b]	6.0	24.5		11.7					
(3, R = NHC_3H_5)	6.6	25.1	12.9		25.4	63.2		33.1	
(6, R = NHC_3H_5)	8.9		14.8		63.2				
(3, R = NHC_6H_{11})	8.4	24.6	12.0		27.3	64.7		32.6	
(4, R = NMe_2)	8.4			27.6			60.2		
(6, R = NMe_2)	15.8		27.0		62.3				
(2, R = NC_4H_8)	5.95	24.2		25.3		60.0	63.9		51.3
(5, R = NC_4H_8)	8.6			27.2			56.9		
(4, R = NC_4H_8)	8.7			27.65			56.6		
(3, R = NC_4H_8)	7.45	23.9	16.0		54.9	61.65		44.6	
(6, R = NC_4H_8)	15.5		18.9		62.25				
(2, R = NC_4H_8O)[b]	7.6	27.6		24.8					
(4, R = NC_4H_8O)	8.1			27.3			59.8		
(6, R = NC_4H_8O)	14.6		21.8		63.0				
(2, R = NC_5H_{10})[b]	6.4	24.6		24.1					
(4, R = NC_5H_{10})	8.4			27.8			63.2		

[a] In $CDCl_3$ at room temperature; δ in p.p.m.; J in Hz.
[b] Not all three coupling constants evaluated.

TABLE IV

^{13}C N.m.r. spectroscopic data of the pyrrolidino derivatives of compound (1)[a]

Compound	δ POC	^2J (POC)	δ POCC	^3J (POCC)	δ PNC	^2J (PNC)	δ PNCC	^3J (PNCC)
(1)	68.05	6.65	25.82	7.3				
(2, R = NC_4H_8)	67.49	6.4	25.89	7.0	46.79	3.0	25.83	10.2
(5, R = NC_4H_8)	66.90	6.6	26.07	6.6	46.64	4.1	25.79	11.5
(4, R = NC_4H_8)	67.05	6.2	26.01	6.45	46.91	4.4	25.81	11.6
(3, R = NC_4H_8)	67.05	6.1	26.00	6.7	45.99	4.3	26.20	9.8
(6, R = NC_4H_8)	65.79	6.5	26.40	5.9	46.05	4.2	26.35	9.3

[a] At 50.10 MHz. in $CDCl_3$ at room temperature; δ in p.p.m.; J in Hz.

the phosphazene moiety, which in turn reduces the back-donation of the lone pairs of electrons on the oxygen atoms and thus increases the P—O bond length and reduces the magnitude of the coupling constant ^3J(POCC). We have also noted earlier that this phenomenon is more pronounced with the PNCC system, as the lone pair of electrons on nitrogen is more prone to back-donation than those on oxygen. In keeping with this, we observed for the groupings $\equiv P(NC_4H_8)_2$ and $\equiv PCl(NC_4H_8)$ coupling constants of 9.5 and 11.5 Hz. respectively.

SUMMARY

Apart from definite structural data obtained by single crystal X-ray crystallographic studies, n.m.r. spectroscopy and basicity measurements have been the main tools to determine structure in cyclotriphosphazatriene derivatives. The latter technique does not distinguish between geometric isomers and requires substituents of significantly different base strengthening effect, e.g., amino-groups and chlorine atoms, for other structure determinations. ^{31}P, ^1H and ^{13}C n.m.r. spectroscopy allow, in many cases, reasonably reliable structural assignments to be made. This technique is at its weakest when assigning *cis-* and *trans-* structures to nongeminal derivatives, e.g., $N_3P_3Cl_4R_2$, $N_3P_3Ph_2Cl_2R_2$, etc., when structural assignments are based on small, sometimes very small, chemical shift changes, and of course, is even more difficult to apply, if only one geometric isomer is available. Derivatization, as frequently employed, always carries the risk of inadvertent isomerisation reactions. This probably does not apply to structure determination by ^{19}F n.m.r. spectroscopy on some fluorinated derivatives. The method, described in this paper, allows unambiguous distinctions to be made, if methylene groups with potentially non-equivalent protons are present. It remains to be tested, how sensitive this method is, if the substituent groups R differ only slightly amongst themselves.

EXPERIMENTAL

Chemicals were obtained as follows: benzene, light petroleum (b.p. 40–60°C), anhydrous diethylether, dichloromethane (May and Baker Ltd.), tetrahydrofuran (Fluka-Garantie 99.5%), deuteriated solvents for n.m.r. spectroscopy, cyclopropylamine (Aldrich Chem. Co. Ltd.), propane-1,3-diol, ethylamine, cyclohexylamine, pyrrolidine, morpholine and piperidine (B.D.H. Chemical Ltd.), hexachlorocyclotriphosphazatriene (Shin Nisso Kako Co., Ltd.). Amines and solvents were dried by conventional

methods. Elemental analyses were carried out by the Microanalytical Service of University College, London.

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[4] 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 polarizing microscope.

^{1}H n.m.r. spectra were recorded using a JEOL JNM FX 200 spectrometer (operating at 199.5 MHz.), a Brucker WH400 spectrometer (operating at 400.13 MHz.-Queen Mary College, London) 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 Brucker-HFX90 spectrometer (operating at 36.43 MHz.-Kings College, London), a Varian XL-200 spectrometer (operating at 80.98 MHz.-University College, London), a Brucker WH400 spectrometer (operating at 162 MHz.-Queen Mary College, London) and a Varian VXR 400 spectrometer (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 and on a AE1–MS902 spectrometer by the PCMU service at Harwell.

The reactions of (**1**) with pyrrolidine are described in some detail. Conditions for the rest are found in Table V. Analytical data are collected in Table VI.

Reactions of compound (**1**) *with pyrrolidine. (a) With two equivalents of pyrrolidine.* Anhydrous pyrrolidine (0.79 g, 11.2 mmol) was added dropwise to a well stirred solution of (**1**) (2g, 5.6 mmol) in benzene (100 cm^3) at ca 0°C. On completion of the addition the reaction mixture was allowed to attain room temperature and then refluxed for 1.5 h. Dark brownish pyrrolidine hydrochloride was filtered off and the filtrate was concentrated (15 cm^3). T.l.c. revealed the formation of a major compound,

TABLE V

Experimental details of the reactions of compound (**1**) with various amines

(1) Amount			Amount		Solvent and volume (cm^3)[a]	Time of addition of amine and total reaction time (h)	Products and yields		
g	mmol	Amine	g	mmol			no.	g	%
3	8.50	ethylamine	1.53	34	benzene (150)	0.5 (5)	**(3)**	1.8	58
3	8.50	ethylamine	3.60	68	benzene (150)	[b] (6)	**(6)**	2.1	64
3	8.50	cyclopropylamine	0.96	17	benzene (150)	0.1 (6)	**(2)**	1.4	45
3	8.50	cyclopropylamine	1.93	34	benzene (150)	0.1 (6)	**(3)**	2.1	64
3	8.50	cyclopropylamine (slight excess)	3.87	68	benzene (150)	[b] (6)	**(6)**	1.9	52
3	8.50	cyclohexylamine	3.36	34	benzene (150)	0.5 (5)	**(3)**	2.1	52.5
3	8.50	dimethylamine	1.53	34	benzene (150)	0.5 (5)	**(4)**	1.7	54.5
3	8.50	dimethylmaine (slight excess)	5.81	68	benzene (150)	[b] (8)	**(6)**	2.1	64
3	8.50	morpholine	1.48	17	benzene (150)	0.5 (2.5)	**(2)**	2.0	58
3	8.50	morpholine	2.97	34	benzene (150)	0.5 (2.5)	**(4)**	2.4	62
3	8.50	morpholine (slight excess)	6.00	68	benzene (150)	[b] (7)	**(6)**	2.6	55
							(4)	0.3	9
3	8.50	piperidine	1.45	17	benzene (150)	0.5 (2.5)	**(2)**	2.0	59
3	8.0	piperidine	2.90	34	benzene (150)	0.5 (8)	**(4)**	2.4	62

[a]Reactions carried out at *ca* −2°C.
[b]Amine added at once.

TABLE VI
Analytical Data

Compound	Formula	M.p. (°C)	Elemental Analysis (%) C	H	N	P	Found (Calc.) Cl	Mass M^+ (M)[a]
(**3**, R = NHEt)	$C_7H_{18}N_5Cl_2O_2P_3$	87	23.1 (22.8)	5.4 (4.9)	18.5 (19.8)	24.95 (25.3)	19.0 (19.3)	367 (367)
(**6**, R = NHEt)	$C_{11}H_{30}N_7O_2P_3$	115	33.9 (34.3)	7.3 (7.8)	25.0 (25.45)	23.85 (24.15)		385 (385)
(**2**, R = NHC_3H_5)	$C_6H_{12}N_4Cl_3O_2P_3$	139	19.0 (19.4)	3.3 (3.2)	14.7 (15.1)	25.5 (25.0)	29.0 (28.7)	370 (370)
(**3**, R = NHC_3H_5)	$C_9H_{18}N_5Cl_2O_2P_3$	180	27.3 (27.7)	4.6 (4.6)	17.4 (17.9)	22.6 (23.3)	18.5 (18.2)	391 (391)
(**6**, R = NHC_3H_5)	$C_{15}H_{30}N_7O_2P_3$	192	41.2 (41.6)	6.5 (6.9)	22.3 (22.6)	21.9 (21.5)		433 (433)
(**3**, R = NHC_6H_{11})	$C_{15}H_{30}N_5Cl_2O_2P_3$	184	38.1 (37.8)	6.5 (6.3)	14.7 (14.7)	19.4 (19.5)	14.3 (14.9)	475 (475)
(**4**, R = NMe_2)	$C_7H_{12}N_5Cl_2O_2P_3$	oil	23.4 (22.9)	5.2 (4.9)	18.8 (19.0)	24.9 (25.2)	19.1 (19.3)	367 (367)
(**6**, R = NMe_2)	$C_{11}H_{30}N_7O_2P_3$	102	34.0 (34.3)	7.3 (7.8)	25.65 (25.45)	23.7 (24.15)		385 (385)
(**2**, R = NC_4H_8)	$C_7H_{14}N_4Cl_3O_2P_3$	84	21.5 (21.8)	3.7 (3.6)	14.3 (14.5)			384 (384)
(**5**, R = NC_4H_8)	$C_{11}H_{22}N_5Cl_2O_2P_3$	160	31.5 (31.7)	5.3 (5.2)	16.5 (16.7)			419 (419)
(**4**, R = NC_4H_8)	$C_{11}H_{22}N_5Cl_2O_2P_3$	176	31.4 (31.7)	5.0 (5.2)	16.4 (16.7)			419 (419)
(**3**, R = NC_4H_8)	$C_{11}H_{22}N_5Cl_2O_2P_3$	166	31.4 (31.7)	5.45 (5.2)	16.5 (16.7)			419 (419)
(**6**, R = NC_4H_8)	$C_{19}H_{38}N_7O_2P_3$	139	46.7 (46.6)	7.7 (7.8)	20.2 (20.0)			489 (489)
(**2**, R = NC_4H_8O)	$C_7H_{14}N_4Cl_3O_3P_3$	132	21.1 (20.9)	3.7 (3.5)	14.3 (13.9)	22.7 (23.2)	25.9 (25.9)	400 (400)
(**4**, R = NC_4H_8O)	$C_{11}H_{22}N_5Cl_2O_4P_3$	169	29.6 (29.3)	4.4 (4.9)	15.1 (15.5)	21.0 (20.6)	16.0 (15.7)	451 (451)
(**6**, R = NC_4H_8O)	$C_{19}H_{38}N_7O_6P_3$	188	41.6 (41.6)	6.8 (6.8)	17.4 (17.8)	16.6 (16.8)		553 (553)
(**2**, R = NC_5H_{10})	$C_8H_{16}N_4Cl_3O_2P_3$	124	23.9 (24.0)	3.7 (4.0)	13.7 (14.0)	22.8 (23.3)	27.1 (26.65)	398 (398)
(**4**, R = NC_5H_{10})	$C_{13}H_{26}N_5Cl_2O_2P_3$	143	35.0 (34.8)	5.5 (5.8)	15.2 (15.6)	21.7 (20.75)	16.2 (15.8)	447 (447)

[a] Based on mass of most abundant isotopes.

accompanied by unreacted starting materials. An intense spot was observable on the base line of the t.l.c. plate, presumably due to pyrrolidine hydrochloride and polymeric products. Separation of this compound was achieved by using column chromatography [40 g silica gel, and a solvent system of light petroleum (b.p. 40–60°C): diethyl ether anhydrous (2:3)]. Fractions containing the major compound were collected, brought to dryness, and then the residue recrystallized from light petroleum. This compound was characterized as 2,2-spiro (1′,3′-propanedioxy)-4-pyrrolidino-4,6,6-trichlorocyclotriphosphazatriene, (**2**, R = NC_4H_8), m.p. 84°C, R_f-value = 0.75 (in eluent), (39% yield, 0.78 g).

(b) With four equivalent of pyrrolidine. Anhydrous pyrrolidine (1.58 g, 22.4 mmol) was added dropwise to a stirred solution of (**1**) (2g, 5.6 mmol) in benzene (100 cm^3) at ca 0°C. The reaction mixture was allowed to attain room temperature. The stirring was continued for 2 h. and then the mixture boiled under reflux for a further 2 h. The reaction mixture was allowed to attain room temperature. The dark brownish pyrrolidine hydrochloride was filtered off and the filtrate was concentrated. T.l.c. of the mother-liquor revealed a major spot, which had a figure-of-eight shape and a relatively small spot which had a R_f-value similar to that of the compound obtained from the previous reaction (**a**) and pyrrolidine hydrochloride on the base line. The major component (1.2 g) was isolated by column chromatography [40 g silic gel, and a solvent system of light petroleum (b.p. 40–60°C): diethyl ether anhydrous as eluent (2:1)]. The melting point range of this component (137–178°C) and its ^{31}P n.m.r. spectrum showed that more than one compound was present in this major component. Preliminary tests by HPLC analytical chromatography revealed the presence of three peaks with different retention times (V_r 90, 156, and 186 seconds) associated with this component, which was a strong indication of geometric and positional isomers. Separation of these compounds was achieved by using HPLC (lichroprep 5–2 μm silica), with a solvent system of 40% ethyl acetate in light petroleum (b.p. 40–60°C) as mobile phase (flow rate of 5.0 cm^3/min). Full separation was achieved for each injected sample after three times recycling through the column. This was due to the relatively small differences in retention time of these three components. Fractions of each compound were collected, brought to dryness, and recrystallized from benzene: *n*-hexane (1:2). The first compound was characterized as 2,2-spiro-(1′,3′-propanedioxy)-4-*trans*-6-bispyrrolidino-4,6-dichlorocyclotriphosphazatriene, (**4**, R = NC_4H_8) m.p. 176°C; (46% yield, 0.55 g); (V_r = 90 sec). The second compound was identified as 2,2-spiro(1′,3′-propanedioxy)-4-*cis*-6-bispyrrolidino-4,6-dichlorochlotriphosphazatriene, (**5**, R = NC_4H_8), m.p. 158–160°C; (V_r = 156 sec), (21% yield, 0.25 g). The third compound was 2,2-spiro(1′,3′-propanedioxy)-4,4-bispyrrolidino-6,6-dichlorocyclotriphosphazatriene, (**3**, R = NC_4H_8) m.p. 164–166°C; (12% yield, 0.14 g); (V_r = 186 sec).

(c) With an excess of pyrrolidine. An excess of anhydrous pyrrolidine (11.85 g, 84 mmol) was added to a stirred solution of (**1**) (2 g, 5.6 mmol) in benzene (100 cm^3) at room temperature. The reaction mixture was boiled under reflux for 3 h., filtered, the filtrate concentrated and examined by t.l.c. One component was observed and isolated by crystallization from light petroleum (b.p. 40–60°C). This compound was characterized as 2,2-spiro-(1′,3′-propanedioxy)-4,4,6,6-tetrakispyrrolidinocyclotriphosphazatriene, (**6**, R = NC_4H_8), m.p. 139°C; (53% yield, 1.05 g).

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