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Contributions to the chemistry of phosphazenes—II

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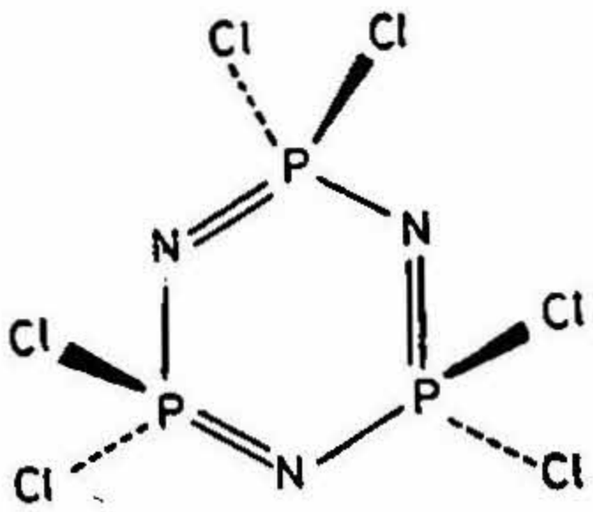
Abstract

In this paper we review our findings on the thermal rearrangement of some methoxycyclophosphazenes ; the tautomeric behaviour of various monohydroxy compounds ; the synthesis of triphenylphosphazenyl and spirocyclic phosphazenes; the reactions of octachlorocyclotetraphosphazene with primary and secondary amines to give chloro(amino)cyclotetraphosphazenes and bicyclic phosphazenes ; and the preparation and characteristion of chloro(phenoxy)cyclotetraphosphazenes and metal complexes of (aminocyclophosphazenes). Structural elucidation of the products of these reactions by NMR spectrospcopy is highlighted. Results of kinetic studies are also described.

Key words: Rearrangement of methoxycyclophosphazenes, tautomerism, triphenylphosphazenyl, spirocyclic and bicyclic phosphazenes, cyclotetraphosphazenes, metal complexes, kinetics, NMR spectroscopy.

1. Introduction

The chemistry of the inorganic heterocyclic compounds, hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ (I), and octachlorocyclotetraphosphazene, $N_4P_4Cl_8$ (II), has been the subject of numerous in-depth studies in recent years[1–4]. The substitution reactions of halogenocyclophosphazenes and the elucidation of the structures of new derivatives by spectroscopy and crystallography continue to occupy a prominent place in these studies. There has also been a burgeoning interest in the technological aspects of phosphazene chemistry as indicated by the steady increase in patent applications[4]. The successful synthesis and characterisation of many linear polyphosphazenes by Allcock and coworkers[3] has undoubtedly inspired the major developments in the applied chemistry of phosphazene polymers.



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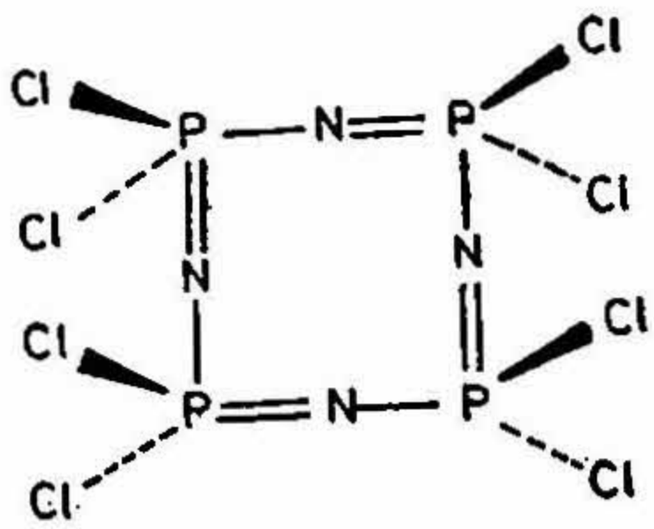


(II)

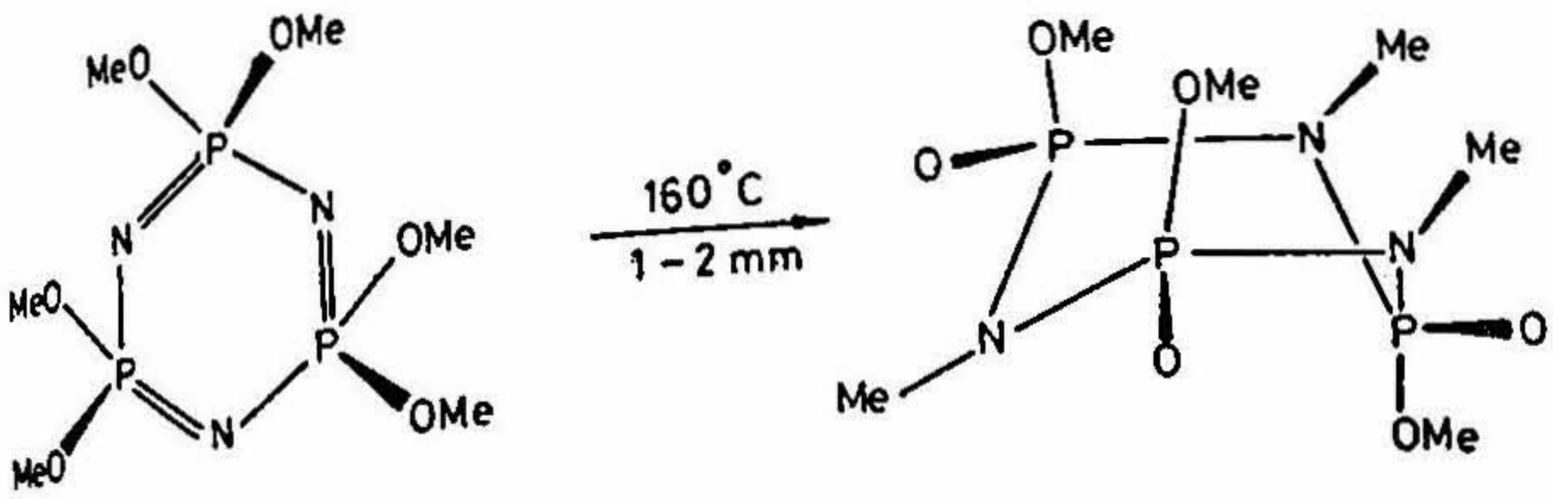
Our fundamental studies of the chemistry of the cyclophosphazenes are the basis of the binaticnal project between the Indian Institute of Science and Birkbeck College, University of London. In an earlier paper[1], we presented an account of our investigations during the first part of this project. The current review summarises our work during 1978–1981.

2. Thermal rearrangement reactions of methoxycyclophosphazenes

Alkoxycyclophosphazenes are excellent flame retardants for viscose rayon and other textiles[2]. The thermal properties of these phosphazenes merit detailed investigations in order to gain an insight into the factors that contribute to their flame retardant behaviour. Our studies have included: (*a*) a reinvestigation of the thermal transformations undergone by the methoxy homologues, $[NP(OMe)_2]_n$, $n = 3$–6, and (*b*) the thermal rearrangement of amino(methoxy)cyclotriphosphazenes[5–7].

The fully substituted methoxy derivatives of chlorocyclophosphazenes are prepared in 60–80% yield by treating the appropriate homologue, $[NPCl_2]_n$, with sodium methoxide in dry benzene. The hexamethoxide, $N_3P_3(OMe)_6$(III), rearranges readily at 150–160° C (1–2 mm Hg) to give the oxocyclophospha*zane*, $N_3Me_3P_3O_3(OMe)_3$(IV) in 70% yield (fig. 1). The 270 MHz proton NMR spectrum[6] of compound (IV) indicates that both –O*Me* and –N*Me* protons are in two environments (each in the ratio 1 : 2). A corresponding non-equivalence is also seen for $-O^{13}CH_3$ and $N^{13}CH_3$ carbon nuclei. These observations suggest that the distorted boat structure found for the solid is retained in solution. A variable temperature proton NMR study of this rearranged product (IV) indicates that the cyclotriphospha*zane* ring is highly rigid[6].

The octamethoxide, $N_4P_4(OMe)_8$, undergoes rearrangement at 160° C (1–2 mm Hg) to give a mixture of two isomeric oxocyclotetraphosphazanes, $N_4Me_4P_4O_4(OMe)_4$[7]. The products are separated by fractional crystallisation. In principle, there are four geometric isomers for an oxocyclotetraphosphazane. The most abundant isomer obtained in the thermal rearrangement has the 2-*trans*-4-*cis*-6-*trans*-8 structure ; the other isomer has the 2-*cis*-4-*trans*-6-*trans*-8 structure[6]. These isomers



III IV

FIG. 1. The methoxyphosphaZENE-N-methyloxophosphaZANE rearrangement.

are also formed in the rearrangement of $N_4P_4(OMe)_8$ catalysed by methyl iodide[8]. The higher homologues, $N_5P_5(OMe)_{10}$ and $N_6P_6(OMe)_{12}$ also undergo complete rearrangement on heating (proton and carbon-13 NMR evidence) but a complex mixture of isomeric cyclophosphazanes is obtained in each case[7].

We have been unable to carry out similar rearrangement reactions using the esters $N_3P_3(OR)_6$ (R = Et, Pr^n)[7]. These alkoxyphosphazenes appear to decompose when they are heated under vacuum; the presence of N-alkylcyclotriphosphazanes could not be detected in any experiment.

The rearrangement of geminal-$N_3P_3R_2(OMe)_4$ could give rise to four products (excluding geometrical and conformational isomers). Three of these products are partially rearranged isomers (fig. 2). The presence of such intermediates in a rearrangement reaction has never been convincingly demonstrated by previous workers. The thermal rearrangement of geminal-$N_3P_3Ph_2(OMe)_4$ and geminal-$N_3P_3(NHBu^t)_2(OMe)_4$ have been investigated in the temperature range 150–200° C *in vacuo*. The thermal transformations are conveniently monitored by 270 MHz proton NMR spectroscopy[7]. This technique shows conclusively that both oxocyclophosphazadienes (fig. 2A, R = Ph or $NHBu^t$; fig. 2B, R = $NHBu^t$) and the fully rearranged products (fig. 2D, R = Ph or $NHBu^t$) are obtained. A typical spectrum is shown in fig. 3.

The nongeminal derivative, *trans*-$N_3P_3(NMe_2)_2(OMe)_4$ (V), undergoes rearrangement very slowly (fig. 4). Even after heating a sample at 150° C (1–2 mm Hg) for seven hours, the bulk of the starting material (V) can be recovered by distillation. The proton NMR spectrum of the oily hygroscopic residue (VI) consists of a broad signal at *ca.* δ 2·6 (NMe) and a doublet at δ 3·48 (OMe); these signals are in the ratio 2:1. Its phosphorus-31 NMR spectrum contains a doublet at δ 9·6 [P (NMe_2) (O)] and a triplet at δ −5·9 [P(O)OMe]. Only a fully rearranged compound is compatible with the NMR data. In contrast, the nongeminal *trans*-derivative, $N_3P_3(NMe_2)_3(OMe)_3$, does not rearrange even when heated at 200° C under reduced pressure[7].

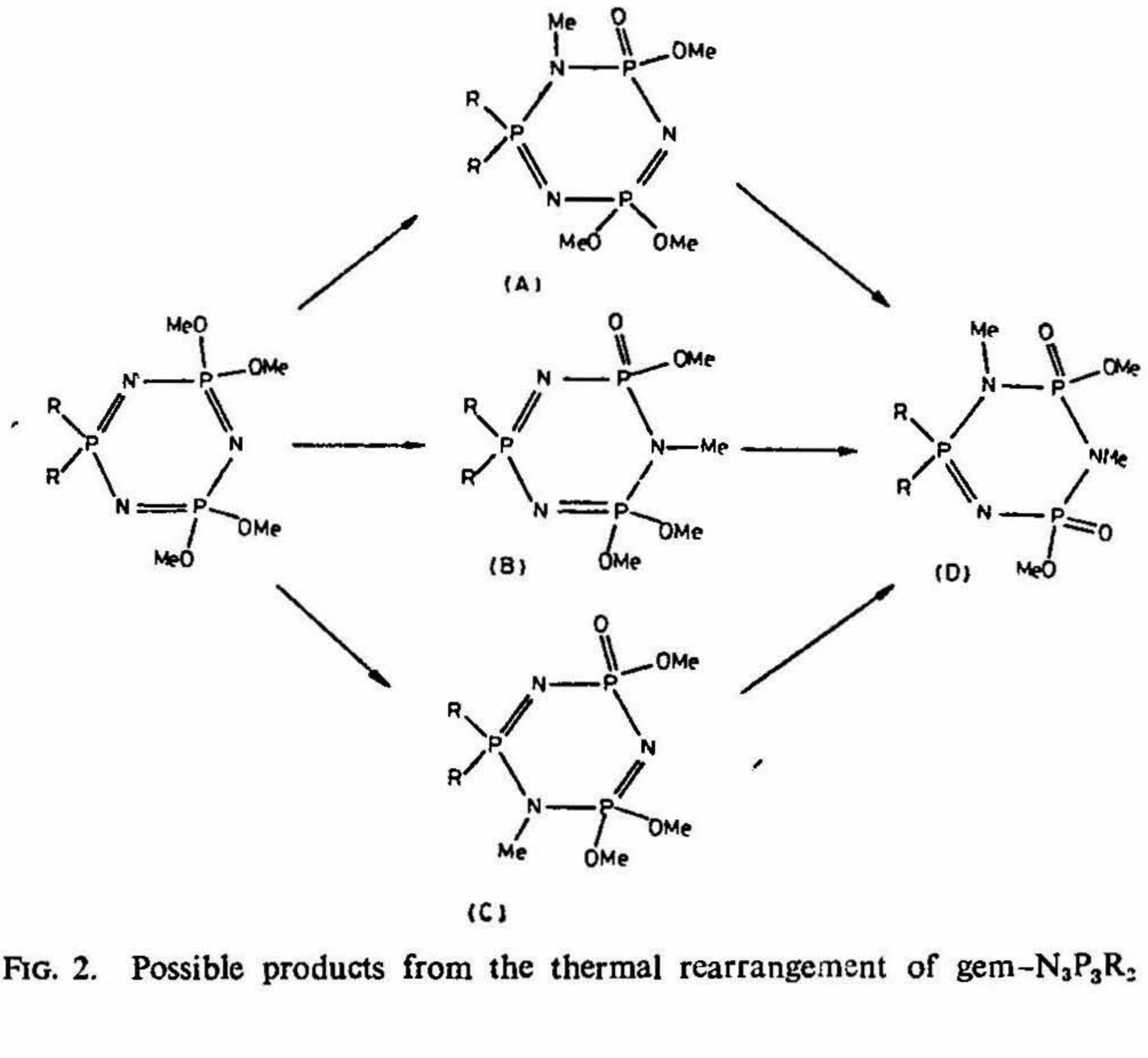


FIG. 2. Possible products from the thermal rearrangement of gem-$N_3P_3R_2(OMe)_4$.

Our results on the thermal rearrangement of methoxycyclophosphazenes suggest that electronic effects and steric factors associated with ring nitrogen atoms control these reactions. The evidence clearly implies that an *inter*molecular pathway is involved in the transformation of cyclophosphaz*ene* to cyclophosphaz*ane*. A recent study by Allcock and coworkers[9] using a mixture of $N_3P_3(OCH_3)_6$ and $N_3P_3(OCD_3)_6$ demonstrates unequivocally that an intermolecular migration of methoxy groups occurs on thermolysis.

3. Tautomeric forms of (hydroxy) cyclotriphosphazenes

The hydrolytic decomposition of the cyclic trimer, $N_3P_3Cl_6$ (I), was first reported at the end of the nineteenth century[2,5]. The initial step is the formation of a (hydroxy) cyclotriphosphazene which then undergoes a rapid tautomeric shift to give a (hydroxy) oxocyclotriphosphaz*ane*, *viz.* $N_3H_3P_3O_3(OH)_3$. In an acidic medium, further hydrolysis leads to ring cleavage and skeletal degradation; the final products are phosphoric acid and ammonia.

We have studied some mono(hydroxy)cyclotriphosphazenes, $N_3P_3R_3R'_2(OH)$, as little attention has been given previously to the structures of these compounds. Four tautomeric forms can be envisaged (fig. 5 ; **1**–**4**) albeit structures **1** and **4** are considered unlikely[10,11]. Dynamic phosphorus-31 NMR spectroscopy is a very useful probe for

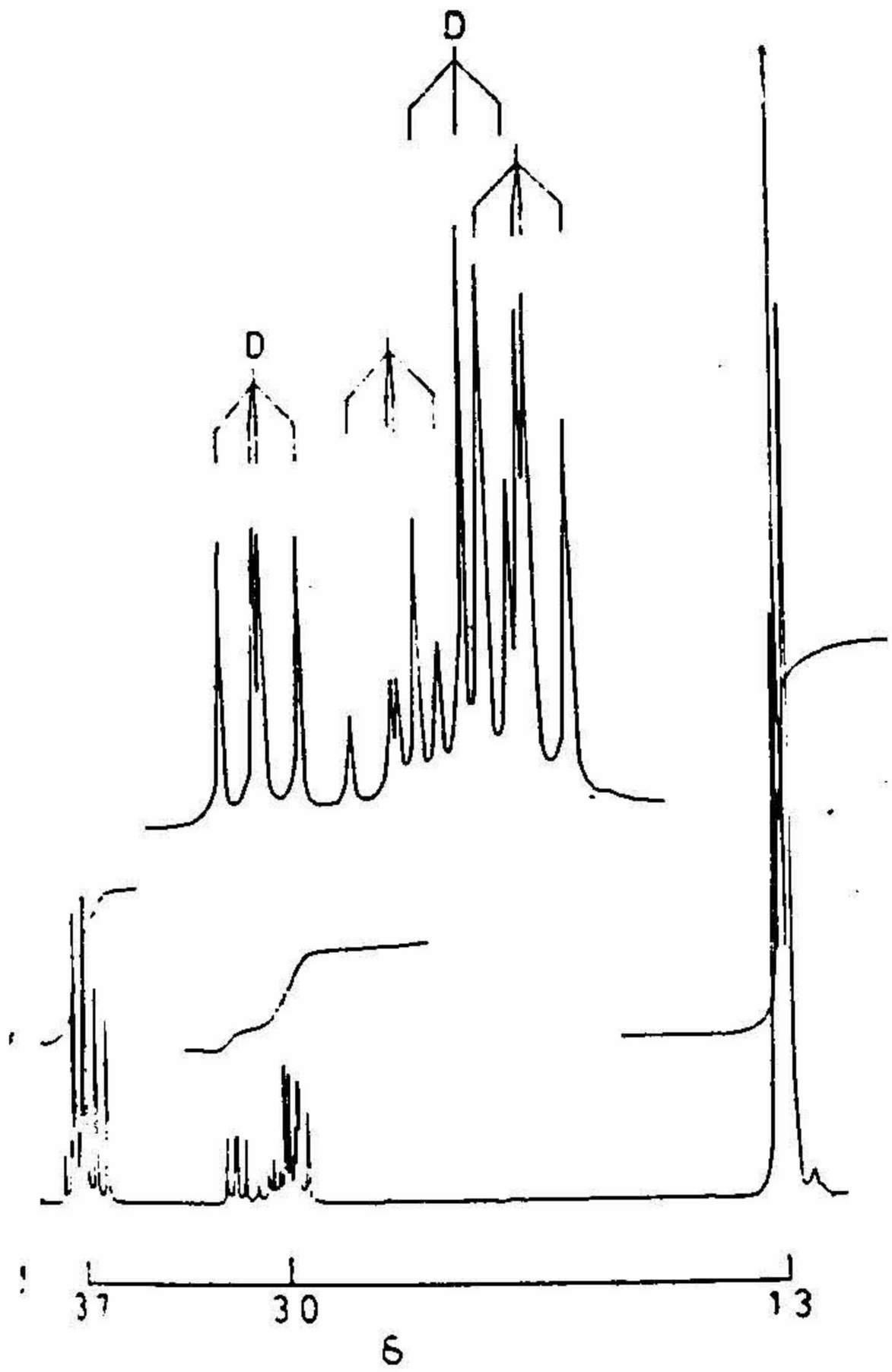
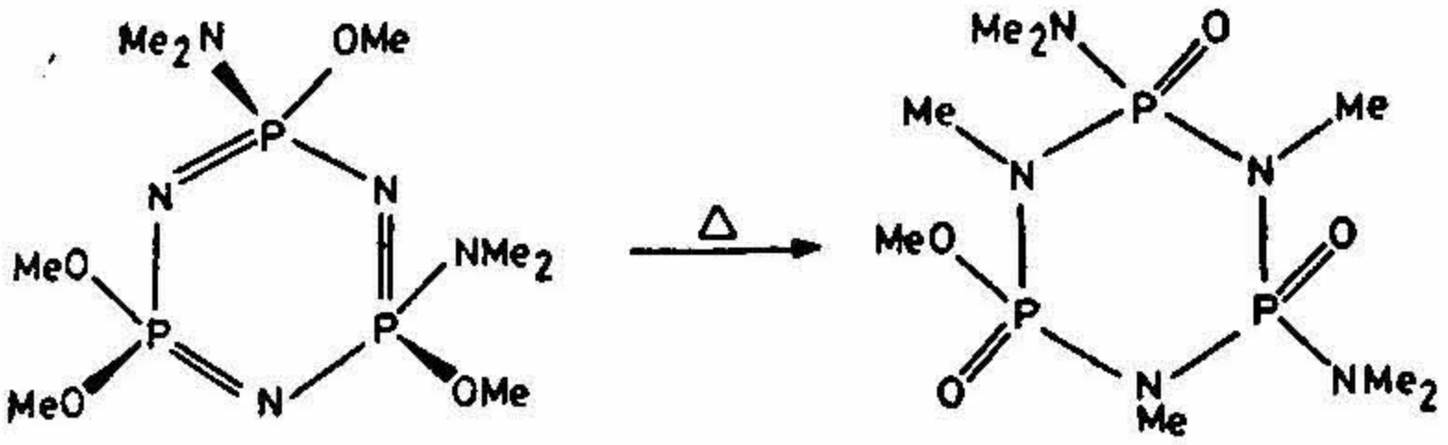


Fig. 3. The ^1H NMR spectrum (270 MHz, $CDCl_3$-D_2O) of a mixture of $N_3MeP_3(NHBu^t)_2(O)(OMe)_3$ (two isomers) and $N_3Me_2P_3(NHBu^t)_2(O)_2(OMe)_2$. The NMe 'triplet' and doublet of doublets marked D are assigned to the fully rearranged dioxophospha-1-ene [Fig. 2D ; R = $NHBu^t$]. [Adapted from Dhathathreyan *et al*[7] by permission of the Chemical Society, London].

studying these tautomers. For example, the $^{31}P\{^1H\}$ NMR spectra of the alkoxy derivatives, $N_3P_3Ph_2(OR)_3(OH)$, vary considerably with temperature. At −40° C, exchange of the proton between two nonequivalent alpha-sites is relatively slow, thus permitting the observation of two distinct tautomeric forms (two overlapping ABX spectra). Exchange becomes more rapid as the temperature is raised (only featureless signals at ambient temperature) and individual tautomers are not distinguished. At 100° C, a single ABX pattern is observed (fast exchange).

The spectrum of $N_3P_3Ph_2(OEt)_3(OH)$ at −40° C and at room temperature is shown in fig. 6 ; values of δ_P and $^2J(P-N-P)$ for each tautomer are also shown. As anticipated from our studies[5-7] of six-membered, cyclic phosphorus-nitrogen compounds containing one or more P-N bonds with phosphaz*ane* character, the value of $^2J(P-P)$

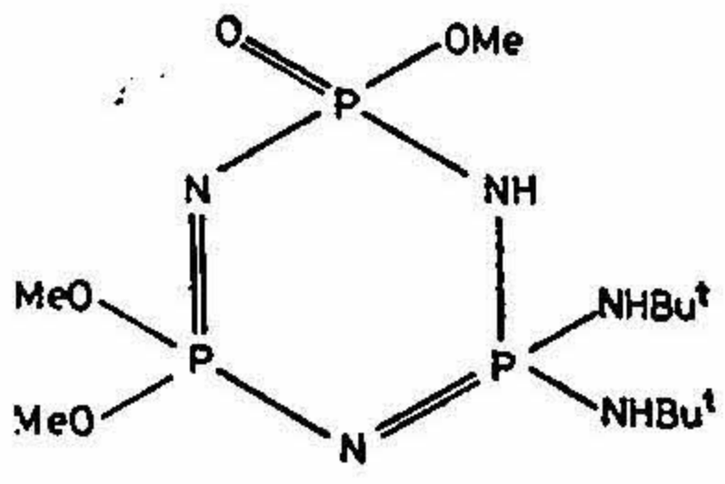


V VI

FIG. 4. The thermal rearrangement of *trans*-$N_3P_3(NMe_2)_2(OMe)_4$ (V).

across the phosphaz*ane* segment [≡ P–NH–P(O)=] is less than that across either of the formal phosphaz*ene* links. The considerable variation in the magnitude of $^2J(P\text{-}P)$ associated with phosphaz*ene* segments may reflect a difference in ring conformation for each ethoxy tautomer (fig. 6)[11].

Other types of prototropic behaviour have been observed for the 'monohydrogen' derivatives, $N_3P_3(NHBu^t)_2(OMe)_3(OH)$ (VII) and $N_3P_3(OMe)_5(OH)$ (VIII). The $^{31}P\{^1H\}$ NMR spectrum of the *t*-butylamino compound (VII) consists of twelve lines (ABX pattern) and does not alter significantly with temperature[11]. This evidence indicates the absence of the exchange phenomenon. The tautomeric form with a proton alpha to ≡P(NHBu^t)$_2$ and =P(O)(OMe) groups is clearly favoured by the NMR parameters. This tautomeric form is also anticipated on electronic grounds : the base strengthening effect of a *t*-butylamino group on an adjacent ring nitrogen atom is considerably greater than that of a methoxy group[11]. Exchange between two equivalent ring nitrogen sites is exhibited by the pentamethoxy derivative (VIII). Its $^{31}P\{^1H\}$ NMR spectrum at −40° C is of the ABX type as the exchange of the proton is 'frozen' thereby conferring nonequivalence on the phosphorus nuclei of the two =P(OMe)$_2$ groups. At ambient temperature, exchange is fast and an AX_2-type spectrum is seen.



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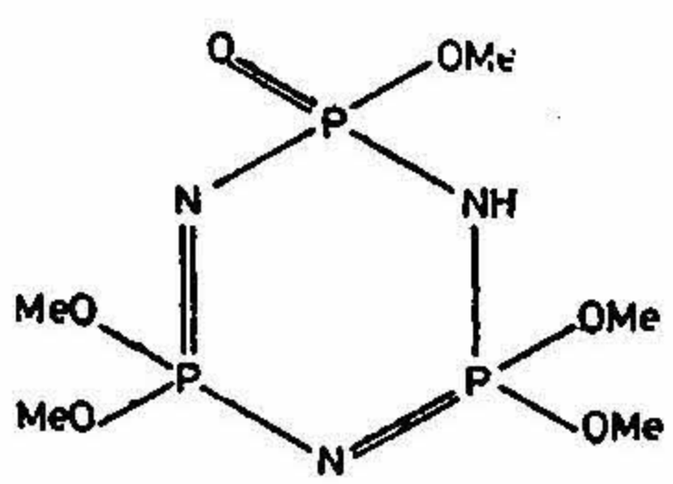

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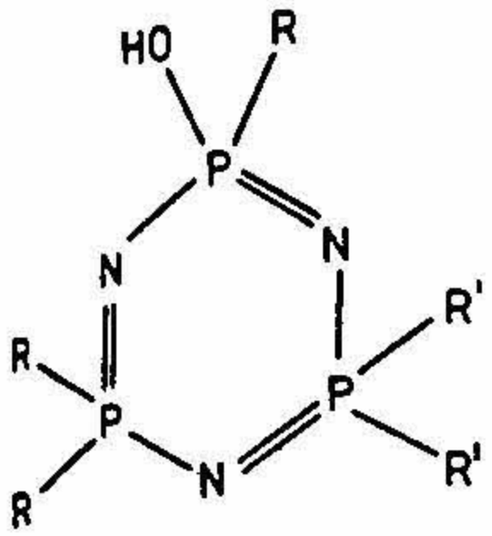

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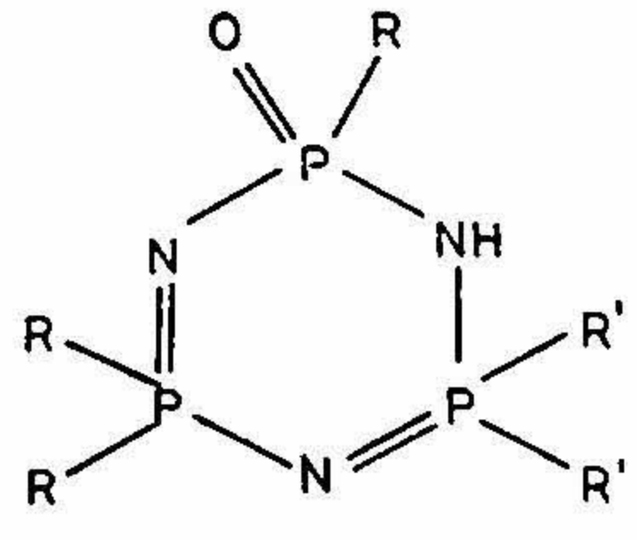

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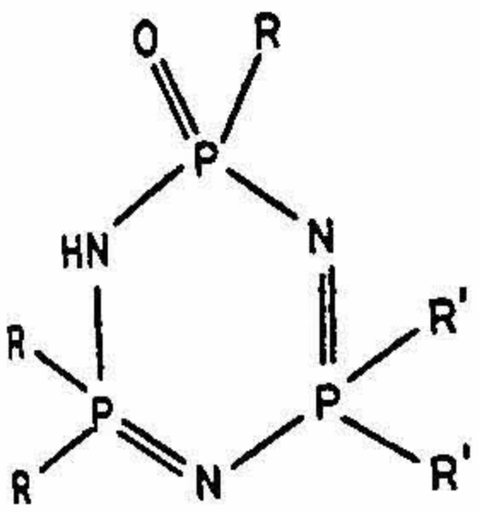

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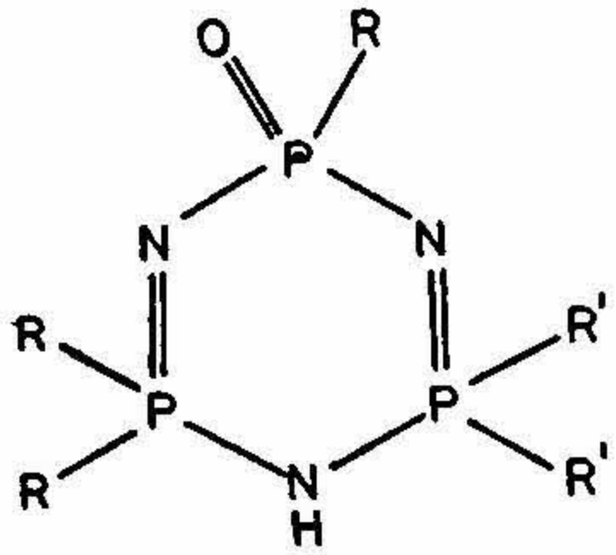


(4)

FIG. 5. Tautomeric forms of $N_3P_3R_3R'OH$.

Our studies on these (hydroxy)cyclophosphazenes and on related compounds[5,11] show that they exist as oxocyclophosphazadienes both in the solid state[10] and in solution. The hydrogen atom is always bonded to a ring nitrogen atom alpha to the phosphoryl group. There is no evidence yet for the existence of the gamma-tautomer (fig. 5 ; structure 4). Although the hydrolysis reactions, of cyclophosphazenes are complex, phosphorus-31 NMR spectroscopy provides a powerful analytical tool for their investigation.

4. Triphenylphosphazenylcyclophosphazenes

Synthetic and kinetic studies suggest that the course of the aminolysis reactions of chlorocyclophosphazenes is influenced more by the nucleophile than by the substituent(s)[2]. For example, secondary amines usually react with the hexachloride (I) to give disubstituted products, $N_3P_3Cl_4R_2$, which have nongeminal structures. Brief reports of the reactions of pentachloro(2′,2′,2′-triphenylphosphazenyl)cyclotriphosphazene, $N_3P_3Cl_5(NPPh_3)$ (IX), with two equivalents of dimethylamine or piperidine in diethyl ether have indicated an apparent exception to the 'normal' behaviour : only geminal products, $N_3P_3Cl_4R(NPPh_3)$, $R = NMe_2$ or NC_5H_{10}, were formed. In contrast, triphenylphosphinimine, $Ph_3P = NH$, reacts with either the monodimethylamino

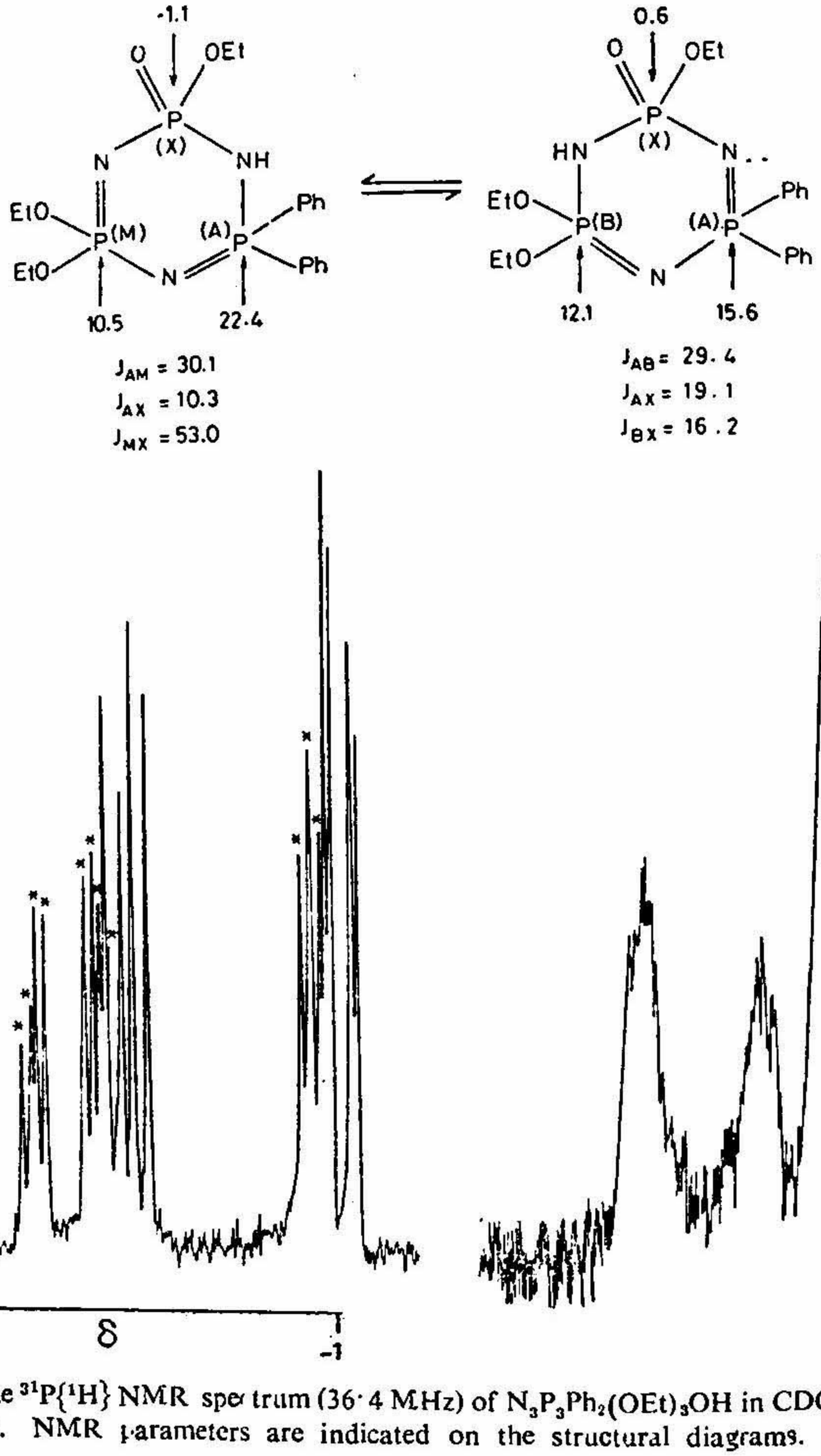


FIG. 6. The $^{31}P\{^{1}H\}$ NMR spectrum (36·4 MHz) of $N_3P_3Ph_2(OEt)_3OH$ in $CDCl_3$ at — 40°C and ambient temperature. NMR parameters are indicated on the structural diagrams.

derivative, $N_3P_3Cl_5(NMe_2)$, or the phosphazenyl compound (IX) to give nongeminal products[12] (fig. 7). This intriguing behaviour of the triphenylphosphazenyl substituent led us to examine the aminolysis reactions of $N_3P_3Cl_5(NPPh_3)$ (IX) in more detail.

The phosphazenyl derivative (IX) is synthesised by a Kirsanov reaction[2] of the geminal bis(amido) compound, $N_3P_3Cl_4(NH_2)_2$ (Eq. 1).

$$N_3P_3Cl_4(NH_2)_2 + Ph_3PCl_2 \rightarrow N_3P_3Cl_5(NPPh_3) + \text{other products.} \quad (1)$$

The secondary amines — dimethylamine, diethylamine and piperidine — react with $N_3P_3Cl_5(NPPh_3)$ (IX) in methyl cyanide to give a mixture of geminal and nongeminal mono(amino) derivatives, $N_3P_3Cl_4R(NPPh_3)$:

$$N_3P_3Cl_5(NPPh_3) + 2RH \rightarrow N_3P_3Cl_4R(NPPh_3) + RH,\ HCl. \quad (2)$$

Nongeminal replacement is favoured[14]. The geminal isomer of $N_3P_3Cl_4R\ (NPPh_3)$ is formed exclusively in a reaction with two mol equivalents of dimethylamine or piperidine in benzene or diethyl ether (Table I).

The derivatives, $N_3P_3Cl_{5-n}R_n\ (NPPh_3)$, R = NMe_2, n = 2,3,5 ; R = NEt_2, NC_5H_{10}, n = 2, have also been identified in reactions using higher stoichiometries of amine. None of these products contain the $\equiv PCl(NPPh_3)$ group (^1H and ^{31}P NMR evidence), an observation which indicates the strong geminal directing influence of the $-NPPh_3$ group[15].

Methylamine reacts with $N_3P_3Cl_5(NPPh_3)$ (IX) in methylcyanide to give *cis*– and *trans*-nongeminal isomers of $N_3P_3Cl_4(NHMe)(NPPh_3)$. Reaction of compound (IX) with *t*-butylamine is extremely slow even in boiling methyl cyanide : the geminal products, $N_3P_3Cl_4(NHBu^t)(NPPh_3)$ (11% yield) and $N_3P_3Cl_2(NHBu^t)_3(NPPh_3)$ (25%) are isolated only when a large excess of *t*-butylamine is used[14].

The geminal and nongeminal triphenylphosphazenyl derivatives, $N_3P_3Cl_4(NEt_2)(NPPh_3)$ are readily distinguished by $^{31}P\{^1H\}$ NMR spectroscopy. Three phosphorus environments are observed for the former structure (δ_{PCl_2} 16·0, δ_{NPPh_3} 12·4, $\delta_{P(NEt_2)(NPPh_3)}$ 1·05) in the ratio 2:1:1. The nongeminal isomer possesses four phosphorus nuclei in different environments and an ABMX-type spectrum is observed[14]. An interesting feature of this spectrum is the coupling of $\equiv PCl_2$ and $\equiv PCl(NEt_2)$ to the exocyclic $-NPPh_3$ [average $^4J(P-P)$ = 4·9Hz]. This four-bond coupling is close to zero for the geminal isomer[14]. This difference in behavoiur may be related to different conformations adopted by the $-NPPh_3$ group. Recently, Manohar and co-workers have reported the X-ray structure of $N_3P_3Cl_5(NPPh_3)$[16a], $N_4P_4Cl_7(NPPh_3)$[16b], gem-$N_3P_3Cl_4(NPPh_3)_2$[17] and gem-$N_3P_3Cl_4(NEt_2)(NPPh_3)$[18], and discussed these conformational aspects at length.

The carbon-13 NMR spectra of several chloro(triphenylphosphazenyl)cyclophosphazenes and their amino derivatives have been recorded using a Bruker WH 270 spectrometer operating at 67·89 MHz. The ^{13}C parameters do not show any significant variations with changes in the conformation of the $-NPPh_3$ substituent nor do they permit a distinction of positional isomers[13]. On the other hand, if phenyl groups are directly attached to the phosphazene ring ($N_3P_3Cl_{6-n}Ph_n$, n = 2, 3, 4, 6), the carbon phosphorus coupling constant, $^1J(C-P)$, can readily distinguish geminal and nongeminal derivatives. In addition, it is possible to differentiate geometric isomers. The ^{13}C shifts for these phenyl substituted cyclophosphazenes follow a regular trend and can

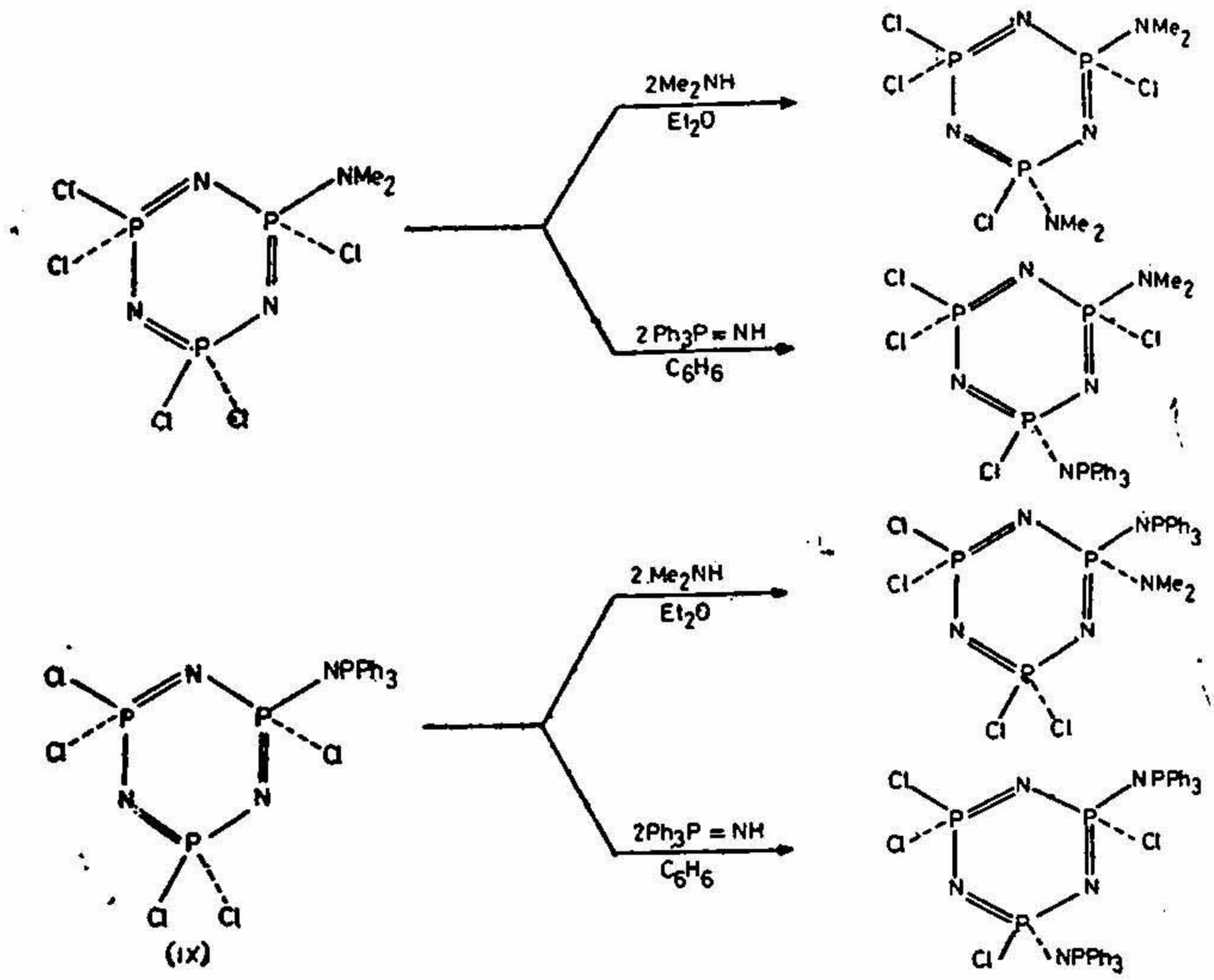


FIG. 7. Formation of geminal and nongeminal isomers of $N_3P_3Cl_4(NMe_2)(NPPh_3)$.

be largely explained on the basis of concomitant mesomeric electron release from the phenyl ring and inductive electron withdrawal by phosphorus[19].

5. Spirocyclic phosphazenes

Four types of products are possible when a chlorocyclophosphazene reacts with a bifunctional reagent[20]: (*i*) replacement of two chlorine atoms from the same phosphorus atom to give a spirocyclic derivative ; (*ii*) replacement of two chlorine atoms from two different phosphorus atoms to give an *ansa*-type compound ; (*iii*) replacement of only one chlorine atom to give an open chain derivative ; and (*iv*) replacement of two (or more) chlorine atoms from different cyclophosphazene rings to give cyclolinear and cyclomatrix polymers by intermolecular condensation. We have demonstrated that the aliphatic diamines (1,2-diaminoethane, 1,3-diaminopropane and 1,4-diaminobutane) react initially with $N_3P_3Cl_6$ (I) in diethyl ether to give the mono-spirocyclic derivatives, $N_3P_3Cl_4[HN(CH_2)_nNH]$, $n = 2$–4. Further reaction of the spiro(ethylenediamino) compound, $N_3P_3Cl_4(HNCH_2CH_2NH)$, with 1,2-diaminoethane gives only non-crystalline, resinous materials which harden and become insoluble in organic solvents on exposure to atmospheric moisture[21]. In contrast, the bis-spirocyclic (1,3-diaminopropane) derivative, $N_3P_3Cl_2[HN(CH_2)_3NH]_2$, is obtained in *ca.* 40% yield from the reaction of $N_3P_3Cl_6$ (I) with an excess of 1,3-diaminopropane in boiling chloro

Table I

Relative yield of isomers of $N_3P_3Cl_4R$ ($NPPh_3$)

Amine (RH)	Reaction solvent [a]	Total yield (%)	Relative yield (%) of gem.-isomer	Relative yield (%) of nongem.-isomer
Me_2NH	Et_2O	66	100	0
	PhH	*b*	100	0
	MeCN	41·5	37	63[c]
Et_2NH[d]	PhH	56·5	66	34
	MeCN	66	36	64
$C_5H_{10}NH$	Et_2O	60·5	100	0
	PhH	37	100	0
	MeCN	65	29	71[c]

a reflux temperature, *b* lit.[12]expt. (25°C), yield not stated, *c cis* and *trans* isomers, *d* no reaction in Et_2O.

form[20]. It would seem that a spirocyclic 1,3-diaminopropane substituent is less able to participate in cross-linking reactions owing to steric inhibition.

Reactions of the hexachloride (I) with ethanolamine[21] and N-methylethanolamine have also been studied[20]. The monospirocyclic (ethanolamino) compound, $N_3P_3Cl_4(HNCH_2CH_2O)$, is obtained in 67% yield from a reaction of equimolar quantities of $N_3P_3Cl_6$ (I) and ethanolamine and two mol. equivalents of triethylamine in tetrahydrofuran. Two crystalline isomers of the bis-spiro(ethanolamino) compound, $N_3P_3Cl_2(HNCH_2CH_2O)_2$, have been isolated in small amounts from a reaction using twice the amount of ethanolamine ; the major product is a sticky resin. Two spirocyclic structures are possible for these isomers depending on whether the exocyclic nitrogen atoms have a '*cis*' or '*trans*' disposition (fig. 8). The reaction of $N_3P_3Cl_6$ (I) with three mol. equivalents of N-methylethanolamine in tetrahydrofuran gives the mono-spirocyclic derivative, $N_3P_3Cl_4(MeNCH_2CH_2O)$, in 70% yield[20]. A bis-spiro(N-methylethanolamino) derivative is obtained in 60% yield from a 1 : 6 reaction in boiling tetrahydrofuran and an X-ray study shows that it has the 'cis' structure[22] (fig. 8 ; R = Me). A mixture of the two tris-spirocyclic isomers of $N_3P_3(MeNCH_2CH_2O)_3$ is obtained in boiling chloroform. Cross-linking processes do

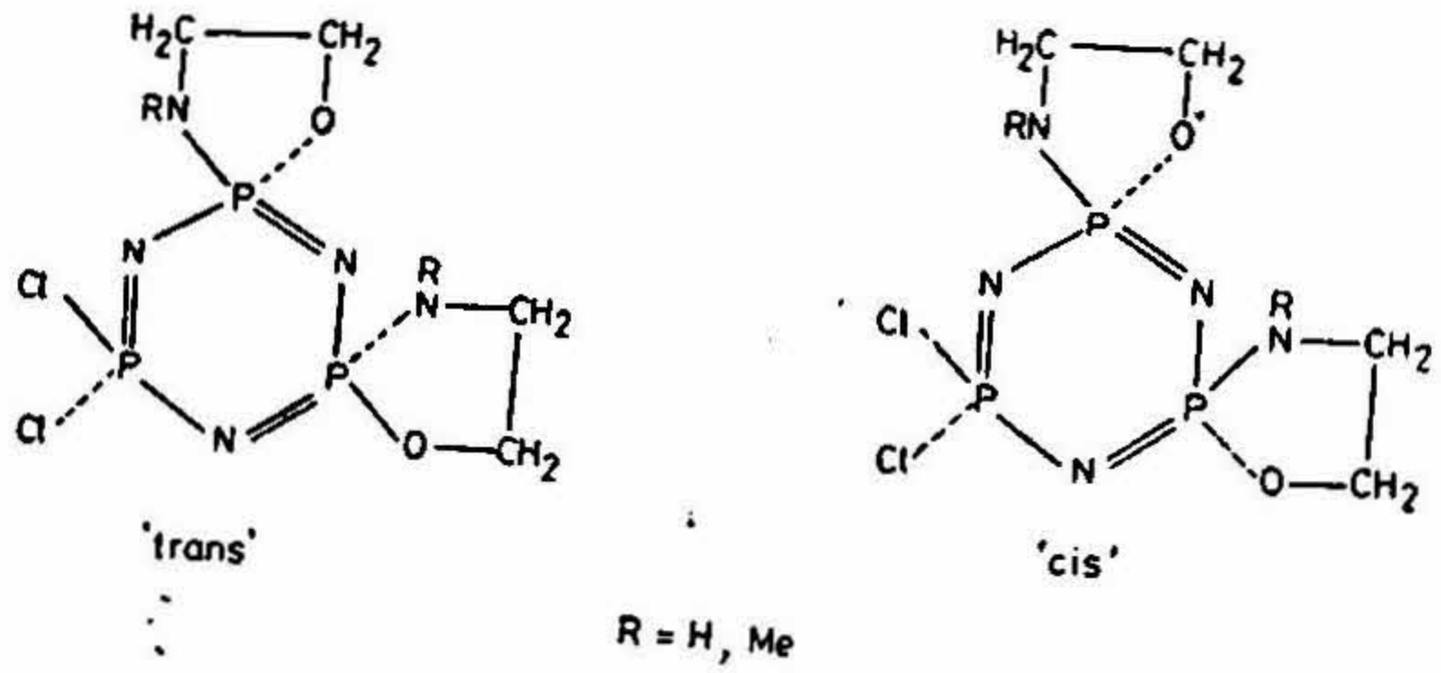


FIG. 8. *Trans*- and *cis*-isomers of $N_3P_3Cl_2(RNCH_2CH_2O)_2$, R = H or Me.

not occur in these reactions with N-methylethanolamine and resinous products are not obtained[20].

The geminal diphenyl compound, $N_3P_3Ph_2Cl_4$, reacts readily with 1,2-diaminoethane or ethanolamine to give the spirocyclic product, $N_3P_3Ph_2Cl_2(HNCH_2CH_2X)$, X = NH or O, in 65–70% yield[21]. The analogous reaction with N-methylethanolamine is somewhat slower and a mixture of products is obtained[20]. Two open chain derivatives $N_3P_3Ph_2Cl_3(MeNCH_2CH_2OH)$ and $N_3P_3Ph_2Cl_2(MeNCH_2CH_2OH)_2$, are formed in addition to the anticipated spirocyclic product, $N_3P_3Ph_2Cl_2(MeNCH_2CH_2O)$.

The spirocyclic structure of the cyclophosphazene derivatives prepared in these studies is readily apparent from a close scrutiny of their proton and phosphorus-31 NMR spectra. Some typical data are given in Table II. In addition, the spirocyclic structure of $N_3P_3(NMe_2)_4(HNCH_2CH_2NH)$, has been confirmed by X-ray crystallography[3].

The cyclic tetramer, $N_4P_4Cl_8$ (II), is considerably more reactive to nucleophilic reagents than its trimeric homologue[2] (see also section 9). Formation of highly unstable products is observed when it reacts with 1,2-diaminoethane and ethylene glycol[20]. Monospiro(spirocyclic)cyclotetraphosphazenes can be prepared from reactions of $N_4P_4Cl_8$ (II) with 1,3-diaminopropane, N-methylethanolamine and 1,3-propanediol. The products are characterised as their dimethylamino or methoxy derivatives, *e.g.*, $N_4P_4(NMe_2)_6[HN(CH_2)_3NH]$ and $N_4P_4(OMe)_6[O(CH_2)_3O]$. Their spirocyclic structure is confirmed in each case by the unsymmetrical appearance of their phopsphorus-31 NMR spectra (AB_2C pattern).

Our studies of the reactions of the cyclic trimer, $N_3P_3Cl_6$ (I), with bifunctional reagents in conjunction with related work reported by other groups[2], indicate that spirocyclic products are the most common. Competition from cross-linking processes is also important in the reactions of $N_3P_3Cl_6$ (I) with small aliphatic reagents that contain one or more $—NH_2$ group. Open chain products are rare and *ansa*-compounds remain elusive.

Table II

Phosphorus-31 NMR data (36.43 MHz) for some spirocyclic derivatives of $N_3P_3Cl_6$[a]

Compound	MP(°C)	$\delta[P(\text{spiro})]$	$\delta(PCl_2)$	$^2J(P\text{–}N\text{–}P)$ Hz.
$N_3P_3Cl_4(HNCH_2CH_2NH)$	198	22·0	22·0[b]	
$N_3P_3Cl_4[HN(CH_2)_3NH]$	164	7·5	21·5	45·5
$N_3P_3Cl_4[HN(CH_2)_4NH]$	187	12·8	21·2	46·0
$N_3P_3Cl_4(HNCH_2CH_2O)$	150	23·3[b]	23·3	
$N_3P_3Cl_4(MeNCH_2CH_2O)$	87	22·4	25·6	53·9
$N_3P_3Cl_2[HN(CH_2)_3NH]_2$	220 (d)	12·3	23·1	43·7
$N_3P_3Cl_2(HNCH_2CH_2O)_2$	200(d)	29·0[b]	29·0[b]	
$N_3P_3Cl_2(MeNCH_2CH_2O)_2$[c]	195–198	28·5	30·7	62·9
$N_3P_3(NMe_2)_4(HNCH_2CH_2NH)$	138	35·5	26·7[d]	40·0
$N_3P_3(NMe_2)_4(HNCH_2CH_2O)$	87	36·5	27·3[d]	46·0

[a] Data from refs. 20–22 ; upfield shifts are negative and the external ref. ($\delta = 0$) is 85% H_3PO_4

[b] Chemical shift separation $< 0{\cdot}5$ ppm.

[c] AB_2 spectrum

[d] $\equiv P(NMe_2)_2$

6. Reactions of $N_4P_4Cl_8$ (II) with primary and secondary amines

(i) *Chloro (amino) cyclotetraphosphazenes,* $N_4P_4Cl_{8-n}(NRR')_n$

The cyclic tetramer (II) reacts with amines in organic solvents to give complex mixtures of chloro(amino)cyclotetraphosphazenes and amine hydrochloride[23,25–27].

$$N_4P_4Cl_8 + 2n\,RR'NH \rightarrow N_4P_4Cl_{8-n}(NRR')_n + n\,RR'NH,HCl \qquad (3)$$

Pure compounds are usually obtained only after chromatography[1] although fractional crystallisation suffices in some cases. Replacement of chlorine atoms is mainly by the nongeminal pathway, *i.e.*, attack at a $\equiv PCl_2$ site is preferred. Substantial amounts of both 2,6- and 2,4-disubstituted products are formed with sluggishly reacting amines such as dibenzylamine[28], N-methylaniline[29], *n*-butylamine[30], *t*-butylamine[31], benzylamine[30] and aniline[30] ; more reactive amines give 2,6-products almost exclusively[30,32,33]. The proposed sturctures of the bis-, tris- and tetra-chloro(amino) derivatives obtained in these studies are shown in fig. 9.

Chloro(primaryamino)cyclotetraphosphazenes containing both $\equiv PCl(NHR)$ and $\equiv P(NHR)_2$ groups have not been identified[31,32]. Attempts to synthesise such derivatives afford only resinous, cross-linked materials[1]. Competitive cross-linking reactions cannot occur with secondary amines. Thus, formation of chloro(secondary amino)cyclotetraphosphazenes, $N_4P_4Cl_{8-n}(NRR')_n$, $n > 4$, is governed largely by the

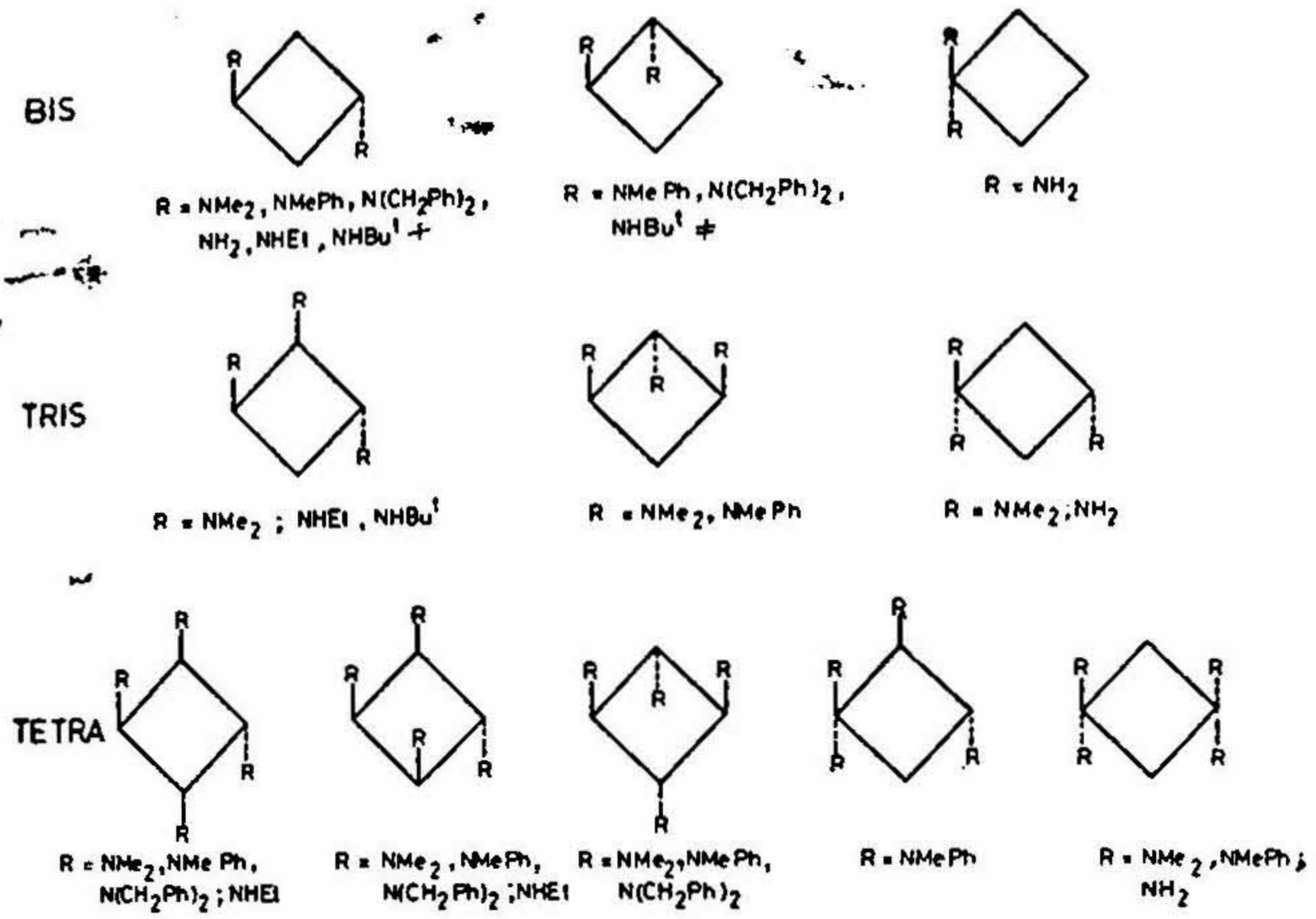


FIG. 9. Proposed structures for $N_4P_4Cl_{8-n}R_n$, $n = 2 - 4$. Phosphorus atoms are represented by corners of the squares ; full or broken lines represent orientations above or below the ring plane. Chlorine and nitrogen atoms are not shown.

† Also R = NHMe, $NHPr^n$, $NHBu^n$, $NHCH_2Ph$, NHPh (Ref. 30).

‡ Also R = $NHBu^n$, $NHCH_2Ph$, NHPh (Ref. 30).

reactivity of the amine. Replacement beyond the tetra stage to give such derivatives is only achieved with difficulty for N-methylaniline[29] and not at all for dibenzylamine[31].

The octachloride (II) reacts with aqueous ammonia (0·88) in diethyl ether in the presence of anhydrous sodium sulphate to give the geminal bis(amido) compound $N_4P_4Cl_6(NH_2)_2$, in 15% yield[34]. This new compound is sensitive to atmospheric moisture ; it is conveniently characterised as its dimethylamino derivative, $N_4P_4(NMe_2)_6(NH_2)_2$. In a much earlier study, de Ficquelmont obtained a different bis(amido) compound from the reaction of $N_4P_4Cl_8$(II) with gaseous ammonia ; a 2,6-nongeminal structure has been assigned to this isomer (fig. 9).

The structures of chloro(amino)cyclotetraphosphazenes can be deduced from the analysis of their phosphorus-31 and proton NMR spectra. In many cases, additional spectroscopic and chemical evidence must also be considered[2]. Some of the structures shown in fig. 9 may require revision in the light of future X-ray evidence, particularly with regard to their cis/trans stereochemistry. Phosphorus-31 NMR data for some amino derivatives of the octachloride (II) are given in Table III. The chemical shifts (δ_P) vary over a range of *ca.* 20 ppm. For compounds containing primary amino substituents, $\delta_{PCl.R}$ is always upfield (more negative shift) from δ_{PCl_2}. The coupling constant, $^2J(P\text{–}N\text{–}P)$, has been determined for some compounds and it is in the range 38–47 Hz and positive in sign.

Table III

Phosphorus-31 NMR data for some chloro(amino)cyclotetraphosphazenes[a]

Compound	MP(°C)	$\delta(PCl_2)$	$\delta(PClR)$	$\delta(PR_2)$	Structure[b]
$N_4P_4Cl_8$	123	—6·7			
$N_4P_4Cl_6(NHMe)_2$	144	—2·2			A
$N_4P_4(NHMe)_8$	206			12·2[c]	
$N_4P_4Cl_6(NHEt)_2$	116	—3·4	—4·9		A
$N_4P_4Cl_4(NHEt)_4$	96		2·3		B
$N_4P_4Cl_4(NHEt)_4$	158		0·9		C
$N_4P_4(NHEt)_8$	118			4·3	
$N_4P_4Cl_6(NHPr^n)_2$	115	—3·4			A
$N_4P_4Cl_6(NHPr^i)_2$	122	—4·0	—7·4		A
$N_4P_4Cl_6(NHBu^n)_2$	114	—3·4	—4·6		A
$N_4P_4Cl_6(NHBu^t)_2$	171	—5·8	—10·6		A
$N_4P_4Cl_6(NHBu^t)_2$	128	—8·7	—7·3		D
$N_4P_4(NHBu^t)_8$	180–200 (d)			—3·1	
$N_4P_4Cl_6(NHCH_2Ph)_2$	150	—2·9	—5·5		A
$N_4P_4Cl_6(NHCH_2Ph)_2$	liq.	—6·1	—0·8		D
$N_4P_4Cl_6(NHPh)_2$	166	—3·0	—12·0		A
$N_4P_4Cl_6(NMe_2)_2$	170	—3·7	—0·2		A*
$N_4P_4Cl_4(NMe_2)_4$	200		5·2		B*
$N_4P_4Cl_2(NMe_2)_6$	168		4·4	9·9	E*
$N_4P_4(NMe_2)_8$	220–238 (d)			9·6	
$N_4P_4Cl_6(NMePh)_2$	145	—5·3			A*
$N_4P_4Cl_6(NMePh)_2$	105	—7·2	—3·2		D*
$N_4P_4Cl_4(NMePh)_4$	162	—11·5		—5·4	F
$N_4P_4Cl_4(NMePh)_4$	128		—2·1		C
$N_4P_4Cl_4(NMePh)_4$	145		—1·4		G
$N_4P_4Cl_4(NMePh)_4$	199		—2·2		B
$N_4P_4Cl_6[N(CH_2Ph)_2]_2$	156–158	—3·9			A
$N_4P_4Cl_6[N(CH_2Ph)_2]_2$	wax	—6·8	—0·2		D
$N_4P_4Cl_4[N(CH_2Ph)_2]_4$	114–115		2·2		B
$N_4P_4Cl_4[N(CH_2Ph)_2]_4$	wax		2·0		C
$N_4P_4Cl_4[N(CH_2Ph)_2]_4$	93–95		2·0		G

a) Spectra measured at 24·3 or 36·4 MHz; CD_2Cl_2 or $CDCl_3$ solution

b) A 2,4,4,6,8,8 : 2-*trans*-6
B 2,4,6,8 : 2-*cis*-4-*trans*-6-*trans*-8
C 2,4,6,8 : 2-*trans*-4-*cis*-6-*trans*-8
D 2,4,6,6,8,8 : 2-*trans*-4
E 2-*trans*-6 : 2,4,4,6,8,8
F 2,2,6,6 : 4,4,8,8
G 2,4,6,8 : 2-*trans*-4-*cis*-6-*trans*-8
Structures marked with an asterisk have been confirmed by X-ray crystallography (Refs. 2,29).
For the nomenclature, see Ref. 2.

c) In D_2O

(ii) *Bicyclic phosphazenes*

Aminolysis reactions of the cyclic tetramer (II) can be rendered even more complex by competitive formation of *trans*-annular-bridged bicyclic phosphazenes. The octachloride (II) reacts with an excess of primary amine[35,36] in chloroform to give moderate yields of the bicyclic phosphazene, $N_4P_4(NHR)_6(NR)$, R = Me (Xa), Et, Pr^n, Pr^i, Bu^n. The octakis(amino)cyclotetraphosphazene, $N_4P_4(NHR)_8$, is also obtained. The bicyclic structure of compound (Xa) is established by NMR and IR spectroscopy[35a]. The proton NMR spectrum (270 MHz) consists of a triplet and three doublets and is shown in fig. 10 along with the assignments. The ^{31}P chemical shifts ($\delta_{P(NHMe)}$ 18·$\delta_{P(NHMe)_2}$ 21·5) lie in the region that is characteristic of bicyclic phosphazenes. An X-ray analysis[37] of compound (Xa) confirms its bicyclic structure. The molecule contains three different types of P–N bond, *viz.*, phosphazene ring P–N (mean 1·594Å), exocyclic P–N(mean 1·637Å) and bridge P–N (mean 1·716Å).

The reactions of hexachloro-2-*trans*-6-bis(alkylamino)cyclotetraphosphazenes, $N_4P_4Cl_6(NHR)_2$ (R = Me, Et, Pr^n, Bu^n, CH_2Ph), with an excess of dimethylamine in chloroform or methyl cyanide give the bicyclic phosphazenes, $N_4P_4(NMe_2)_5(NHR$

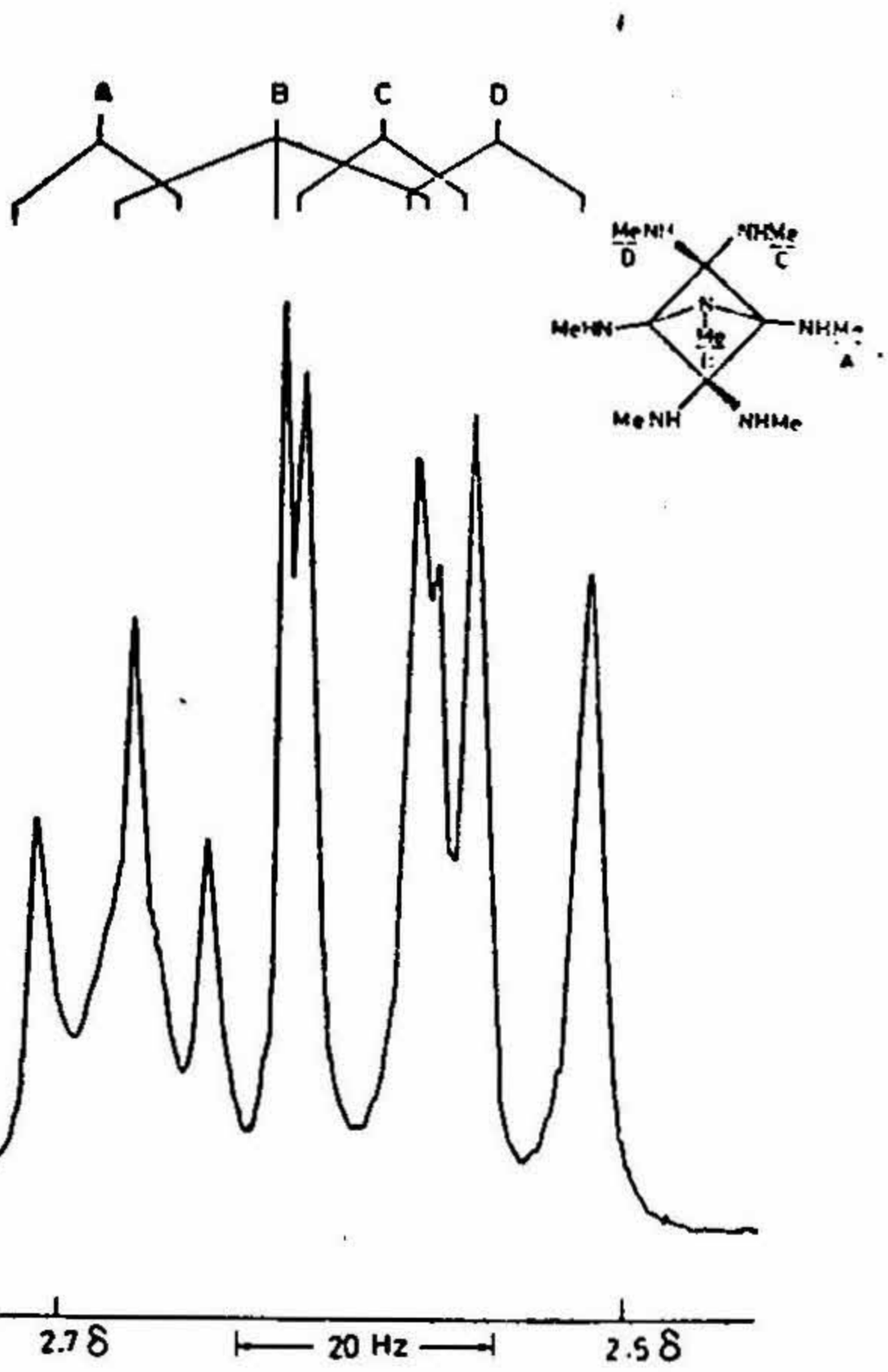


FIG. 10. The ^1H NHR spectrum (270 MHz, $CDCl_3$) of the bicyclic phosphazene, $N_4P_4(NHMe)$ (NMe) (Xa) with assignments. In the structural diagram, corners of the square represent P atoms; other four ring nitrogen atoms not shown.

Table IV

Yields of products formed in reactions of $N_4P_4Cl_6(NHR)_2$ with dimethylamine (R′H)

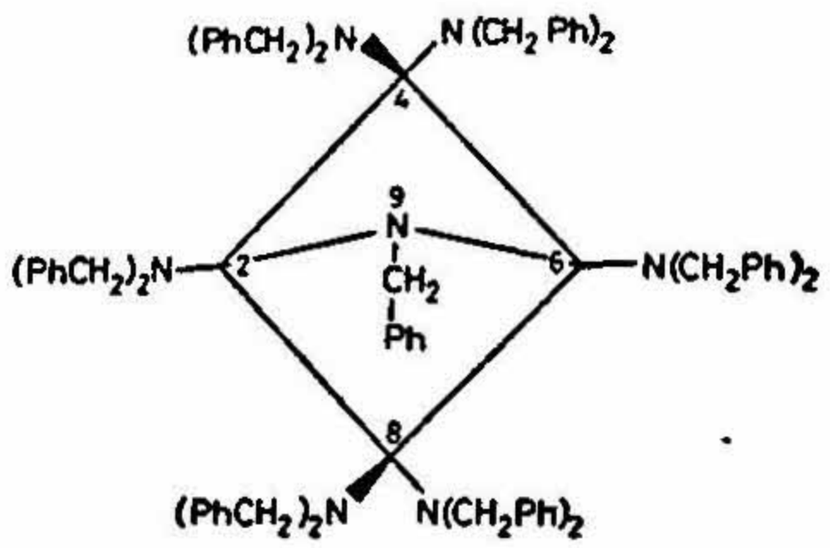
R	Solvent[a]	$N_4P_4R_5'(NHR)(NR)$	$N_4P_4R_6'(NHR)_2$	$N_4P_4R_6'(NHR)_2, xHCl$
Me	$CHCl_3$	30	46	
Et	$CHCl_3$	52	33	3
Et	$CHCl_3/Et_3N$[c]	74	18	
Et	CH_2Cl_2[c]	38	55	
Et	CH_3CN	14	30	35
Pr^n	$CHCl_3$	54	36	
Pr^n	CH_3CN	10[b]	10[b]	68
Bu^n	$CHCl_3$	22	65	
Bu^n	CH_3CN	8	9	64
Bu^t	$CHCl_3$	0	13	65
Bu^t	CH_3CN	0	46	2
CH_2Ph	$CHCl_3$	40	40	
CH_2Ph	CH_3CN	10[b]	70[b]	

a Reflux temperature
b Estimated visually from TLC (± 5%)
c At *ca.* 25°C

NR), and fully aminolysed cyclotetraphosphazenes, $N_4P_4(NMe_2)_6(NHR)_2$, and/or hydrochloride adducts of the latter[38]. Yields of these products are given in Table IV.

A unique bicyclic compound, $N_4P_4[N(CH_2Ph)_2]_6(NCH_2Ph)$ (Xb) has been isolated in 3·5% yield from the reaction of the octachloride(II) with an excess of dibenzylamine in boiling methyl cyanide[28,39]. The mass spectrum of this product exhibits intense peaks at 1460, 1370, 1278 and 639·5 which arise from the ions, $[M-H]^+$, $[M-CH_2Ph]^+$, $[M-(CH_2Ph)_2]^+$ and $[M-(CH_2Ph)_2]^{2+}$. Its proton NMR spectrum (270 MHz) consists of a triplet at δ 4·57 and three doublets at δ 4·38, 3·97, 3·92 in the ratio 1 : 2 : 2 : 2 ; the phosphorus-31 NMR spectrum is a symmetrical triplet centered at δ 21·3 (A_2B_2 tending to A_4). The infrared spectrum of this bicyclic derivative contains an intense band centered at 1180 cm^{-1} which arises from a ring stretching mode [ν (P = N)] and a strong band at 790 cm^{-1} (bridging P – N – P, the phosphaz*ane* part of the bicyclic skeleton). Bands in these regions of the IR spectrum are characteristic of all bicyclic phosphazenes[35,36,38] and some relevant data are presented in Table V.

Formation of bicyclic phosphazenes takes place when cyclotetraphosphazenes bearing primary amino substituents in a *trans* relationship at the 2,6-phosphorus atoms react with strong nucleophiles [35,36,38]. Our proposed mechanism [26,38] for their formation is



(xb)

Corners of the square represent P atoms ring nitrogen atoms not shown.

an intramolecular trans-annular nucleophilic substitution which initially involves proton abstraction (fig. 11). Two limiting cases are considered: (*i*) reversible proton abstraction at P(2) followed by addition of P(6) NHR across P(2)=N and (*ii*) a double proton abstraction at P(2) and P(6) followed by an intramolecular attack. The observation that enhanced yields of bicyclic products are obtained in the presence of a tertiary base provides supporting evidence for a proton abstraction step [38]. The formation of the bicyclic dibenzylamino derivative must obviously involve a dealkylation step prior to or concomitant with the intramolecular nucleophilic attack [28].

Electronic and steric factors associated with the primary amino substituents exert considerable influence on the reaction. The yield of the bicyclic phosphazenes, $N_4P_4(NMe_2)_5(NHR)(NR)$, increases in the order R = Bu^n < Me < CH_2Ph < Et < Pr^i. Bicyclic products are not formed in the dimethylaminolysis reaction when the cyclotetraphosphazene precursor, $N_4P_4Cl_6(NHR)_2$, contains an *a*-branched substituent (*e.g.* R = Pr^i, Bu^t, Ph). The choice of reaction solvent is also important. Chloroform or dichloromethane promotes the formation of bicyclic products (Table IV). The acidic protons of these chlorinated solvents may facilitate the heterolysis of the P–Cl bond at a ≡PCl(NHR) site. Such solvents could also stabilise the species formed after proton abstraction by hydrogen bonding to the electron-rich nitrogen atom involved in the intramolecular attack.

Three major types of reaction can occur in the aminolysis of the octachloride $N_4P_4Cl_8$ (II) : (*a*) intramolecular nucleophilic substitution leading to the formation of bicyclic phosphazenes, (*b*) 'normal' stepwise replacement of chlorine atoms to give nongeminal chloro(amino) cyclotetraphosphazenes, and (*c*) intermolecular condensation processes resulting in the formation of cross-linked products[1]. The competition among these reactions depends on the substituents present on the phosphazene substrate, the nucleophile and the temperature and nature of the reaction medium.

7. Reaction of $N_4P_4Cl_8$ (II) with phenol

Detailed studies of the aminolysis reactions of the tetrameric chloride (II) have revealed significant differences in the chlorine replacement patterns compared to those observed

Table V

Selected IR data for bicyclic phosphazenes and related cyclotetraphosphazenes[a]

Bicyclic phosphazene	ν P=N ring, cm^{-1}	P — N — P bridge, cm^{-1}	Cyclotetraphosphazene	ν P = N ring, cm^{-1}
$N_4P_4(NHMe)_6(NMe)$	1180 vs	790m, 805s, 825 sh	$N_4P_4(N—Me)_8$	1210 vs
$N_4P_4(NHEt)_6$ (NEt)	1195 vs	825s, 840m, sh	$N_4P_4(NHEt)_8$	1250 vs
$N_4P_4(NMe_2)_5(NHMe)(NMe)$	1190 vs	790m, 828s, 840s, sh	$N_4P_4(NMe_2)_6(NHMe)_2$	1265 vs
$N_4P_4(NMe_2)_5(NHEt)(NEt)$	1195 vs	790m, 830s, 838s, sh	$N_4P_4(NMe_2)_6(NHEt)_2$	1270 vs
$N_4P_4(NMe_2)_5(NHPr^n)(NPr^n)$	1190 vs	795m, 822s, 838m, sh	$N_4P_4(NMe_2)_6(NHPr^n)_2$	1265 vs
$N_4P_4(NMe_2)_5(NHCH_2Ph)$ (NCH_2Ph)	1195 vs	800m, 830 s	$N_4P_4(NMe_2)_6(NHCH_2Ph)_2$	1270 vs
$N_4P_4[N(CH_2Ph)_2]_6(NCH_2Ph)$	1180 vs	790s, 820 w	$N_4P_4Cl_4[N(CH_2Ph)_2]_4$[b]	1300 vs

[a] Data from refs. 28, 35, 38

[b] MP 114–115° C, Octakis (dibenzylamino) compound is unknown[28]

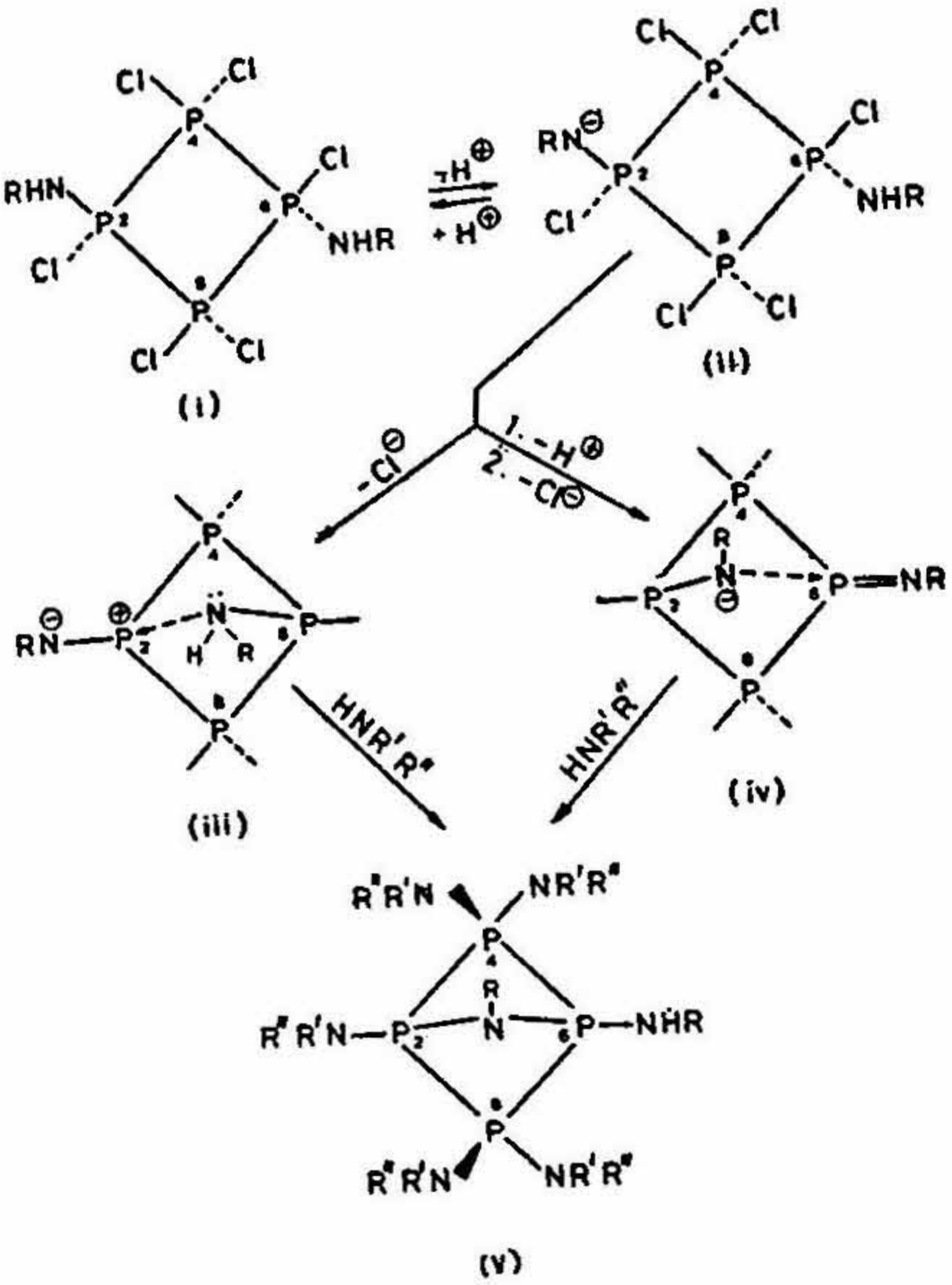


FIG. 11. Possible reaction mechanism for the formation of bicyclic phosphazenes; exocyclic groups are not shown in structures (iii) and (iv) as it is uncertain when the formation of the P-N-P bridge occurs. [Reproduced from Krishnamurthy *et al*[38] by permission of the American Chemical Society].

for analogous reactions of the hexachloride (I)[1,2]. These findings have prompted us to explore the behaviour of $N_4P_4Cl_8$ (II) towards an oxygen-containing nucleophile. Our choice of phenol for this investigation was based on the optimistic anticipation that the products of the reaction would be solids and consequently that purification by fractional cystallisation (even after chromatography) would be relatively straightforward and (*b*) precise structural assignments would often be simplified by synthesising the derivatives, $N_4P_4(OPh)_n$-$(NMe_2)_{8-n}$, and then examining their proton NMR spectra at high field. These hopes were only partially realised.

The phenolysis reaction of $N_4P_4Cl_8$ (II) is exceedingly complex[5,40]. We have obtained the chloro(phenoxy) derivatives,

$$N_4P_4Cl_8 \xrightarrow[PhOH/Et_3N]{NaOPh\ or} N_4P_4Cl_{8-n}(OPh)_n + NaCl\ or\ Et_3N,HCl$$

$N_4P_4Cl_{8-n}(OPh)_n$, [n = 1, 2 (mixture of four nongeminal isomers), 3 (mixture of nongeminal isomers), 4 (mixture of isomers), 5(mixture of isomers), 6 (mixture of five nongeminal isomers) and 8] after extensive use of column chromatography. Geom

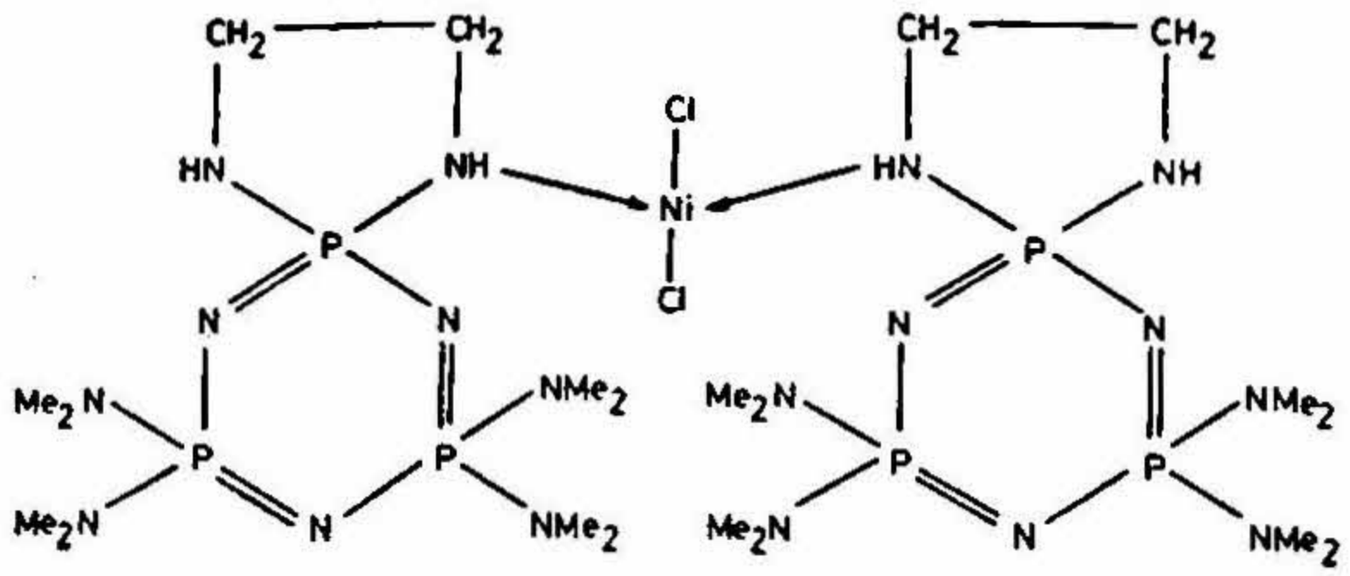
tric isomers could not be separated by this method. Structural elucidation is based on phosphorus-31 NMR data for both chloro (phenoxy) compounds and their dimethyl amino derivatives ; the 270 MHz NMR spectra of the latter are also useful in favourable cases. The replacement pattern is largely nongeminal. At the bis stage of replacement, products with a 2, 4-structure appear to be favoured (at least in diethyl ether or benzene) ; at the hexakis stage, there is a pronounced preference for the isomer 2-*trans*-6 : 2, 4, 4, 6, 8, 8-$N_4P_4Cl_2(OPh)_6$.

8. Metal complexes of cyclophosphazenes

Considerable interest has been shown in the structures of metal complexes of cyclophosphazenes [2,41]. Coordination of a cyclophosphazene ring to a metal ion occurs in numerous ways : *e.g.* (*a*) through antipodal ring nitrogen atoms as in $N_4P_4Me_8$, $PtCl_2$ [42] and $N_6P_6Me_{12}$, $PtCl_2$ [43] ; (*b*) through antipodal ring nitrogen atoms, one of which is protonated, as in $N_4(H)P_4Me_8 \cdot CuCl_3$: (*c*) through a ring nitrogen atom and an exocyclic nitrogen atom, *e.g.*, $N_4P_4(NMe_2)_8$, $W(CO)_4$; (*d*) through exocyclic nitrogen atoms only as in 1-pyrazolylphosphazene complexes of $PdCl_2$ and $PtCl_2$ [44]; or (*e*) through a ring phosphorus atom [45], *e.g.*, $[N_3(H)P_3Ph_4Me]_2$, $PdCl_2$. In some examples a protonated cyclophosphazene can function merely as a counter ion, *e.g* $[N_5(H)_2P_5Me_{10}]^{2+}\ CuCl_4^{2-}$, H_2O. One complex of the sixteen-membered phosphazene ring has a cobalt atom bonded to a bidentate nitrate group and four of the ring nitrogen atoms [46], *viz.* $[N_8P_8Me_{16}\ CoNO_3]^+\ NO_3^-$.

Although metal complexes appear to form most readily with the larger phosphazene rings, we have been able to prepare nickel chloride and cobalt chloride complexes of the spiro-cyclo*tri*phosphazene, $N_3P_3(HNCH_2CH_2NH)(NMe_2)_4$. These complexes are obtained by heating under reflux a solution of the metal chloride and the spirocyclic ligand in methanol (or methyl ethyl ketone) in the presence of dimethoxypropane[47]. The nickel chloride complex (XI) exhibits a low molar conductance in methyl cyanide. It is diamagnetic and a square planar coordination around nickel is indicated. Its IR spectrum contains two split bands [1215 and 1185 cm^{-1} ; $\nu(P=N)$] as compared to a single band at 1195 cm^{-1} for the free ligand[21]. The phosphorus-31 NMR spectra of complex(XI) and of the free ligand are both of the AB_2 type. The phosphorus chemical shifts for compounds (XI) are $\delta_{P(spiro)}$ 25·5 and $\delta_{P(NMe_2)_2}$ 21·9 [$^2J(P\text{-}P.)$ 31.6 Hz]. These shifts are moved upfield compared to the ligand (Table II) ; The spirocyclic phosphorus is most affected. The proton NMR resonances move downfield on complex formation [complex(XI)] : δ_{NCH_2} 3·52, δ_{NH} 4.7 ; ligand : δ_{NCH_2} 3.34, δ_{NH} 2·2]. The results are consistent with the structure shown.

The structure of the cobalt complex, $[N_3P_3(HNCH_2CH_2NH)(NMe_2)_4]_2$, $CoCl_2$ is different from that of the related nickel complex (XI). It has a high molar conductance in methyl cyanide (280 mhos) and a magnetic moment of 4·6 B.M. ; its electronic spectrum is characteristic of a tetrahedral Co (II) complex [λ_{max} (MeCN) 692(895),

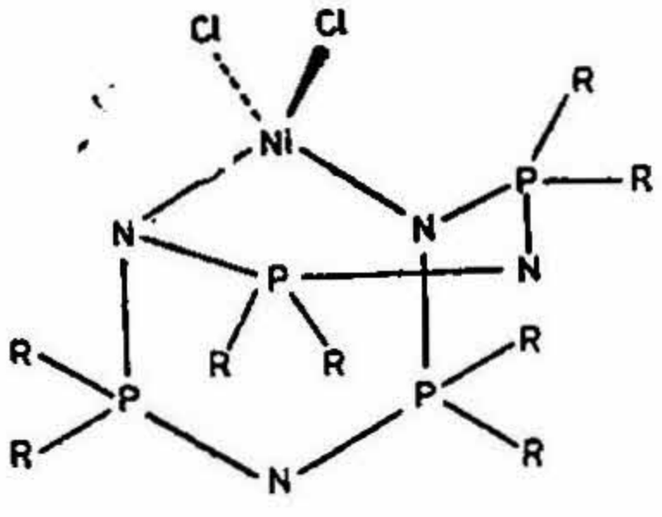


(XI)

635(sh), 590(358)]. It seems likely that one exocyclic and one ring nitrogen from each ligand participates in coordination.

We have also obtained a nickel chloride complex (XII) of the octakismethylamino derivative of the cyclic tetramer (II)[47]. Complex (XII) is paramagnetic (3·3 B.M.) and its phosphorus-31 NMR spectrum is a single line at 8·0δ. A tetrahedral structure has been proposed in which the nickel atom is coordinated to two antipodal nitrogen atoms.

The following complexes with mercuric chloride have also been prepared: $N_3P_3(NHMe)_6$, $2HgCl_2$; $N_4P_4(NHMe)_8$, $2HgCl_2$ and $N_3P_3(HNCH_2CH_2NH)(NMe_2)_4$, $2HgCl_2$. Their high melting points(> 200° C) and insolubility suggest that they are polymeric[22].



(XII) R = NHMe

Multiple bonding within the P-N ring not shown.

9. Kinetic studies

The rates of the reactions of the hexachloride (I) and the octachloride (II) with t-butylamine in methyl cyanide have been determined at three temperatures in the range 0–35° C. Rigorous purification of the chlorocyclophosphazenes and the solvent

is essential to obtain reproducible results. The data are summarised in Table VI. An S_N2 (P) mechanism involving the formation of a pentacoordinated intermediate is in accord with the kinetic data. The enhanced reactivity of $N_4P_4Cl_8$ (II) compared to that of $N_3P_3Cl_6$ (I) arises entirely as a result of the lower enthalpy of activation for the reaction of the octachloride (II). The entropy of activation remains almost unchanged for both the systems[48, 49]. This result can be explained on the basis of the greater skeletal flexibility of the eight-membered ring which facilitates the formation of the pentacoordinated intermediate—a tenet which is supported by the crystal structure analyses of a number of cyclotetraphosphazene derivatives[2]. Table VI also includes kinetic data for the reactions of $N_3P_3Cl_6$ (I) with t-butylamine in tetrahydrofuran (THF) and with dimethylamine in methyl cyanide.

In contrast to the above reactions, the reaction of penta(phenoxy) chlorocyclotriphosphazene, $N_3P_3(OPh)_5Cl$, with methylamine or dimethylamine in methylcyanide follows a first order rate law. The rate of the reaction is independent of the concentration of the nucleophile. The results can be interpreted in terms of an S_N1 (P) mechanism which involves the dissociative formation of a phosphazenium ion in the rate-determining step. Although an S_N1 (P) mechanism has been postulated by earlier works for the replacement of the last chlorine atom in the aminolysis reactions of the hexachloride (I)[2], this is the first time that such a mechanism has been demonstrated experimentally[50].

The above kinetic studies and those reported by Goldschmidt and coworkers[51] have been helpful in gaining a better understanding of the mechanism of this class of reactions than was possible purely from the synthetic studies.

10. Concluding remarks

In this paper, we have reviewed the results of our recent investigations of the synthesis and characterisation of new derivatives of the chlorocyclophosphazenes, $N_3P_3Cl_6$ (I) and $N_4P_4Cl_8$ (II). The pathways observed in the nucleophilic displacement reactions of chlorocyclophosphazenes with some mono- and bi-functional reagents are discussed. The discovery of a *trans*-annular intramolecular reaction that leads to the formation of novel bicyclic phosphazenes is highlighted. The availability of NMR spectrometers operating at high magnetic fields (5–10 Tesla) and access to X-ray diffractometers has greatly facilitated the elucidation of the structures of cyclophosphazene derivatives. Diffraction methods are essential to unravel the diverse bonding modes that are possible in metal complexes of cyclophosphazenes.

The reactions of halogenocyclophosphazenes, particularly their mechanistic aspects, will continue to receive considerable attention as they may be viewed as models for related studies of linear polyphosphazenes[52]. These linear polymers have gained some importance in that they combine several desirable properties for varied practical applications[1,53,54]. Another active area of current research in phosphazene chemistry is the synthesis of cyclic compounds and linear high polymers bonded to transition metals

Table VI*

Kinetic data for the reactions of chlorocyclophosphazenes with t-butylamine and dimethylamine

Cyclo-Phospha-zene	Amine	Solvent	Second order rate constant Temp. T/°C			k_2/dm^{3}mol^{-1} s^{-1}		$\Delta H^{\ddagger}$ kJ mol^{-1}	$\Delta S^{\ddagger}$ J mol^{-1} K^{-1}
			0	10	20	30	35		
I	Bu^tNH_2	MeCN	...	...	$9{\cdot}7 \times 10^{-3}$	$12{\cdot}5 \times 10^{-3}$	$15{\cdot}7 \times 10^{-3}$	$20{\cdot}3 \pm 1{\cdot}7$	$-205{\cdot}7 \pm 12{\cdot}3$
I	Bu^tNH_2	THF	...	...	$1{\cdot}9 \times 10^{-3}$	$3{\cdot}3 \times 10^{-3}$	$5{\cdot}7 \times 10^{-3}$	$47{\cdot}62 \pm 2{\cdot}1$	$-125{\cdot}9 \pm 6{\cdot}0$
I	Me_2NH	MeCN	51·9	84·9	104·2	...	...	$20{\cdot}90 \pm 4{\cdot}6$	$-126{\cdot}1 \pm 1{\cdot}3$
II	Bu^tNH_2	MeCN	1·66	1·89	2·28	...	...	$8{\cdot}2 \pm 2{\cdot}0$	$-201{\cdot}6 \pm 42{\cdot}2$

* Data from Refs. 25 and 49.

or to organic groups of biological interest[55]. The recent reports of anti-tumour activity [56] of some of these compounds will undoubtedly provide an additional impetus to these studies.

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References

1. Krishnamurthy, S. S., Vasudeva Murthy, A. R., Shaw, R. A. and Woods, M. — *J. Indian Inst. Sci.*, 1979, **61 (B)**, 57–83.
2. Krishnamurthy, S. S., Sau, A. C. and Woods, M. — *Adv. Inorg. Radiochem.*, 1978, **21**, 41–112.
3. Allcock, H. R. — *Polymer*, 1980, **21**, 673.
4. Keat, R. — *Spec. Period. Rep., Organophosphorus Chem.*. Chemical Society, (London) 1979–1981, **9–11**.
5. Dhathathreyan, K. S. — Synthetic and spectroscopic studies of alkoxycyclophosphazenes, phosphazadienes and phosphazanes, *Ph.D. Thesis*, Indian Institute of Science, Bangalore, 1981.
6. Dhathathreyan K. S., Krishnamurthy S. S., Vasudeva Murthy, A. R. Shaw, R. A. and Woods, M. — *Inorg. Nucl. Chem, Lett.* 1979, **15**, 109.
7. Dhathathreyan, K. S., Krishnamurthy, S. S., Vasudeva Murthy. A. R., Shaw, R. A. and Woods, M. — *J. Chem. Soc., Dalton Trans.*, 1981, p. 1928.
8. Bullen, G. J., Williams, S. J., Paddock, N. L. and Patmore, D. J., — *Acta Cryst.*, 1981, B37, 607.
9. Ferrar, W. T., Distefano, F. V. and Allcock, H. R — *Macromolecules*, 1980, **13**, 1345.

10. DHATHATHREYAN, K. S., KRISHNAMURTHY S. S. VASUDEVA MURTHY A. R. CAMERON, T. S., CHAN C., SHAW, R. A. AND WOODS, M. — *J. Chem. Soc., Chem. Comm.*, 1980, p. 231.

11. DHATHATHREYAN, K. S., KRISHNAMURTHY, S. S., VASUDEVA MURTHY, A. R., SHAW, R. A. AND WOODS, M. — *J. Chem. Soc., Dalton Trans.*, 1982, p. 1549.

12. BIDDLESTONE, M. AND SHAW, R. A. — *J. Chem. Soc., Dalton Trans.*, 1973, p. 2740.

13. RAMABRAHMAM, P. — Triphenylphosphazenyl cyclophosphazenes and bicyclic phosphazenes, *Ph.D. Thesis*, Indian Institute of Science Bangalore, 19

14. KRISHNAMURTHY, S. S., RAMABRAHMAM, P., VASUDEVA MURTHY, A. R., SHAW, R. A. AND WOODS, M. — *Inorg. Nucl. Chem. Lett.*, 1980, **16**, 215.

15. RAMABRAHMAM, P., KRISHNAMURTHY, S. S., SHAW, R. A., VASUDEVA MURTHY, A. R. AND WOODS, M. — Abstract No. 228, Inter., Conf. Phosphorus Chem. Durz N. Carolina, U.S.A., June 1981.

16. (*a*) BABU, Y. S., MANOHAR, H. AND CAMERON, T. S. — *Acta Cryst.*, 1979, **35B**, 1410.

(*b*) BABU, Y. S. AND MANOHAR, H. — *Acta Cryst.*, 1979, **35B**, 2363.

17. KRISHNAIAH, M., RAMAMURTHY, L., RAMABRAHMAM, P. AND MANOHAR, H. — *Z. Naturforsch.*, 1981, **36B**, 765.

18. BABU, Y. S., MANOHAR, H. AND SHAW, R. A. — *J. Chem. Soc., Dalton Trans.*, 1981, p. 599.

19. KRISHNAMURTHY, S. S., RAMABRAHMAM, P. AND WOODS, M. — *Org. Magn. Reson.*, 1981, **15**, 205.

20. CHANDRASEKHAR, V., KRISHNAMURTHY, S. S., VASUDEVA MURTHY, A. R., SHAW, R. A. AND WOODS, M. — *Inorg. Nucl. Chem. Lett.*, 1981, **17**, 181.

21. KRISHNAMURTHY, S. S., RAMACHANDRAN, K., VASUDEVA MURTHY, A. R., SHAW, R. A. AND WOODS, M. — *J. Chem. Soc., Dalton Trans.*, 1980, p. 840.

22. CHANDRASEKHAR, V. — Spirocyclic phosphazenes and metal complexes of amino(cyclophosphazenes), *Ph.D. Thesis*, Indian Institute of Science, Bangalore, 1982.

23. RAMACHANDRAN, K. — Spirocyclic and bicyclic phosphazenes, *Ph.D. Thesis*, Indian Institute of Science, Bangalore, 1978.

24. BABU, Y. S., MANOHAR, H., RAMACHANDRAN, K. AND KRISHNAMURTHY, S. S. — *Z. Naturforsch.*, 1978, 33B, 588.

25. SUNDARAM, P. M. — Synthetic and kinetic investigations of aminolysis reactions of chlorocylophosphazenes, *Ph.D. Thesis*, Indian Institute of Science, Bangalore, 1980.

26. SAU, A. C. — Aminolysis reactions of octachlorocyclotetraphosphazatetraene, *Ph.D. Thesis*, Indian Institute of Science, Bangalore, 1976.

27. SUDHEENDRA RAO, M. N. — Aminolysis reactions of chloro- and bromo-cyclophosphazenes, *Ph.D. Thesis*, Indian Institute of Science, Bangalore, 1976.

28. KRISHNAMURTHY, S. S., SUNDARAM, P. M. AND WOODS, M. — *Inorg. Chem.*, 1982, **21**, 406.

29. KRISHNAMURTHY, S. S., SUDHEENDRA RAO, M. N., SHAW, R. A., VASUDEVA MURTHY, A. R. AND WOODS, M. — *Inorg. Chem.*, 1978, **17**, 1527.

30. KRISHNAMURTHY, S. S., RAMACHANDRAN, K. AND WOODS, M. — *Phosphorus Sulfur*, 1981, 9, 323.

31. KRISHNAMURTHY, S. S., SAU, A. C., VASUDEVA MURTHY, A. R., KEAT, R., SHAW, R. A. AND WOODS, M. — *J. Chem. Soc., Dalton Trans.*, 1977, p. 1980.

32. KRISHNAMURTHY, S. S., SAU, A. C., VASUDEVA MURTHY, A. R., KEAT, R., SHAW, R. A. AND WOODS, M. — *J. Chem. Soc., Dalton Trans.*, 1976, p. 1405.

33. MILLINGTON, D. AND SOWERBY, D. B. — *J. Chem. Soc., Dalton Trans.*, 1972, p. 2035.

34. RAMABRAHMAM, P., KRISHNAMURTHY, S. S. AND WOODS, M. — *Z. Naturforsch.*, 1981, **36B**, 894.

(*a*) KRISHNAMURTHY, S. S., RAMACHANDRAN, K. AND WOODS, M. — *J. Chem. Res.*, 1979, (S) 92, (M) 1258–1265.

(*b*) KRISHNAMURTHY, S. S., SAU, A. C., VASUDEVA MURTHY, A. R., SHAW, R. A., WOODS, M. AND KEAT, R. — *J. Chem. Res.*, 1977, (S) 70, (M) 0860–0884.