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Contributions to the chemistry of phosphazenes

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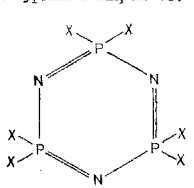
Abstract

Our significant findings on the aminolysis reactions of halogenocyclophosphazenes are summarised with emphasis on the synthesis and characterisation of novel bicyclic phosphazenes and spirocyclic phosphazenes. The use of chromatographic techniques for the separation of cyclophosphazene derivatives and elucidation of their structures by NMR and IR spectroscopy are also reviewed.

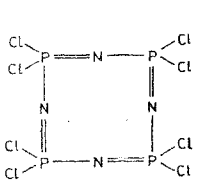
Key words : Halogenocyclophosphazenes, aminolysis reactions, bicyclic phosphazenes, spirocyclic phosphazenes, chromatography, NMR and IR spectroscopy.

1. Introduction

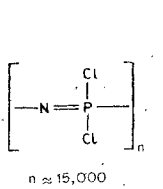
Phosphazenes are inorganic hetero atom compounds with alternate phosphorus and nitrogen atoms in a valence unsaturated skeleton. They can be cyclic or linear and some typical examples are shown below.



I. X = Cl
IV. X = Br
CYCLIC TRIMER



II
CYCLIC TETRAMER



n ≈ 15,000

III
LINEAR HIGH POLYMER

There has been considerable progress in the chemistry of these compounds during the last two decades from both fundamental and technological points of view[1–4]. The fundamental studies are mainly concerned with (*a*) the chemical reactions of the hexachloride(I), (*b*) spectroscopic and crystallographic studies to elucidate the structural chemistry of phosphazenes and (*c*) synthesis and characterisation of linear phosphazene polymers. The development of 'speciality' phosphazene polymers has proceeded rapidly[4] and one material (PNF 200) is now produced commercially[5]. This material is the first rubber to combine the four qualities of oil resistance, durability, resistance to heat and flexibility at low temperature. The development of flame retardant textiles is clearly a 'growth' industry in view of legislative enactments in this connection in many countries. The use of alkoxy (aryloxy) phosphazenes for this purpose is well documented[1,2]. Other potential applications of phosphazene derivatives include the use of (*a*) aziridinocyclophosphazenes as chemosterilants[1,2], (*b*) platinum chloride complexes of (methylamino) phosphazenes as anti-tumour agents[4,6] and (*c*) ammono cyclophosphazenes as sources of plant nutrients[2,3].

We have carried out some extensive investigations of the chemistry of cyclophosphazenes under a binational project on "Phosphazenes—A group of Phosphorus-Nitrogen Compounds" between the Indian Institute of Science and Birkbeck College. This project is designed to train young scientists in research methodology and is sponsored by the University Grants Commission, New Delhi, and the Overseas Development Ministry, London. Our research interest in phosphorus-nitrogen chemistry has been primarily concerned with the fundamental aspects of the subject. The topic provides an interesting and challenging field of research and has aroused a great deal of international interest. A larger number of papers on this subject have been presented at major Conferences* devoted both to phosphorus chemistry and to the chemistry of inorganic heterocyclic compounds. A consolidated account of the results of our investigations during 1973-77 is presented in this review.

2. Aminolysis reactions of $N_4P_4Cl_8$ (II)

Although the substitution reactions of the hexachloride, $N_3P_3Cl_6$ (*I*), have been investigated in great detail, similar reactions of $N_4P_4Cl_8$ (II) have received much less attention. This lack of information may well reflect the considerable difficulties encountered in separating complex mixtures of products and in assigning unambiguous structures to the pure isomers[3]. Fig. 1 shows the positional and geometric isomers that can occur in the tetramer system. Replacement of the chlorine atoms of $N_4P_4Cl_8$ (II) by a substituent group (R) can take place by the geminal or the non-geminal route, *i.e.*, attack at a

* IUPAC Symposium on Inorganic Phosphorus Compounds, Prague, 1974; 1st International Symposium on Inorganic Ring Systems, Besancon, 1975; 1st International Symposium on Inorganic Ring Systems, 2nd meeting, Madrid, 1977; 1st International Congress on Phosphorus Compounds, Rabat, 1977; The Arbuzov Memorial Conference on Organophosphorus Chemistry, Kiev, 1977; 2nd International Symposium on Inorganic Ring Systems, Göttingen, 1978.

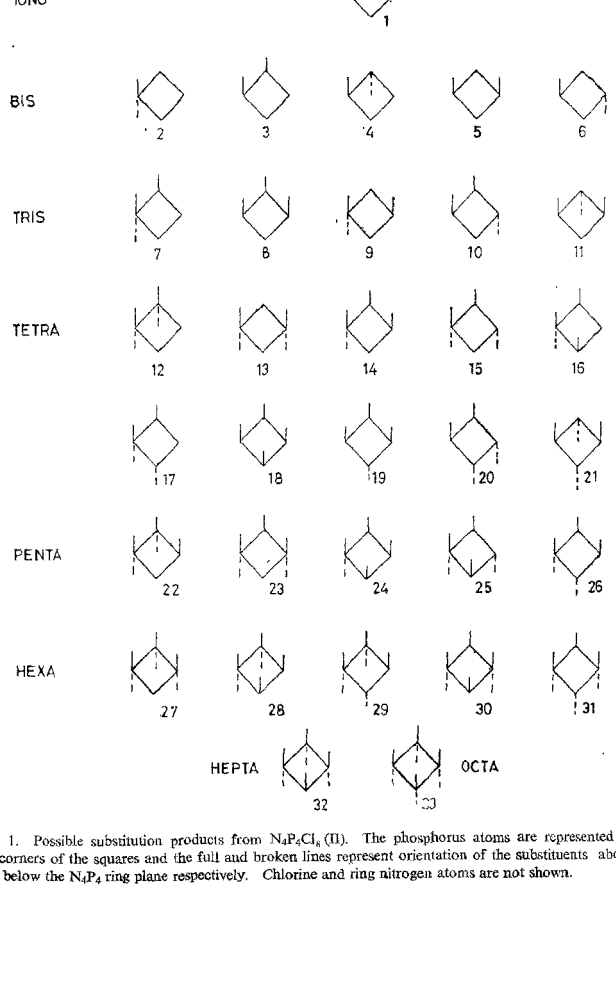


FIG. 1. Possible substitution products from $N_4P_4Cl_8$ (II). The phosphorus atoms are represented by the corners of the squares and the full and broken lines represent orientation of the substituents above and below the N_4P_4 ring plane respectively. Chlorine and ring nitrogen atoms are not shown.

$\equiv PClR$ or a $\equiv PCl_2$ site. Our objectives in a detailed study of the nucleophilic replacement reactions of the octachloride(II) were (*a*) to determine the replacement patterns, (*b*) to compare the results with those for the analogous reactions of $N_3P_3Cl_6$ (I), and (*c*) to ascertain if the mechanisms postulated for the reactions of $N_3P_3Cl_6$ (I) would also be valid for those of the octachloride(II).

The reaction of N-methylaniline with $N_4P_4Cl_8$ (II) was reported in 1960–61 and only two compounds were isolated[7,8]. Our reinvestigation of this reaction has revealed its great complexity and we have obtained ten derivatives, $N_4P_4Cl_{8-n}(NMePh)_n$ [$n = 1$, 2 (two isomers), 3, 4 (five isomers) and 6]. The replacement of chlorine atoms beyond the tetrakis stage is difficult and attempts to prepare the octakis (N-methylanilino) derivative, $N_4P_4(NMePh)_8$, have not been successful. Structures have been assigned to the chloro-N-methylanilino derivatives on the basis of ^1H NMR data (in some cases aided by ^{31}P NMR spectra) and chemical evidence. The methoxy derivatives, $N_4P_4(OMe)_{8-n}(NMePh)_n$ [$n = 2$ (two isomers), 4 (two isomers) and 6] have been prepared to further confirm the structural assignments[9,10]. The chlorine replacement pattern by N-methylanilino groups is predominantly nongeminal as found also for the reaction of $N_4P_4Cl_8$ (II) with dimethylamine[11]. However, in contrast to the dimethylamine reaction where only one bis-derivative, 2-*trans*-6-$N_4P_4(NMe_2)_2Cl_6$ is formed[11], the reaction of $N_4P_4Cl_8$ (II) with N-methylaniline (a much less reactive amine) gives two *bis*-isomers, m.p. 145° C and 105° C, in comparable yields[10,12]. X-ray crystallography establishes 2-*trans*-6 and 2-*trans*-4 structures respectively for these two isomers[13,14]. The isolation of only one tris (N-methylanilino) derivative and the apparent absence of pentakis-derivatives, compared with the isolation of three tris- and two pentakis-chlorodimethylaminocyclotetraphosphazenes, suggests that there is tendency for chloro-(N-methylanilino) cyclotetraphosphazenes containing an odd number of chlorine atoms to react further to give derivatives with an even number of chlorine atoms.

We have also recently completed the first systematic studies of the reaction of $N_4P_4Cl_8$ (II) with primary amines[12,15–17]. The ethylamino- and *t*-butylamino-cyclotetraphosphazenes isolated in these reactions have nongeminal structures and are listed in

$$N_4P_4Cl_8 + 2n\,RNH_2 \rightarrow N_4P_4Cl_{8-n}(NHR)_n + n\,RNH_2, HCl\ (R = Et,\ Bu^t) \qquad (1)$$

Table I. Compounds containing *both* $\equiv PCl(NHR)$ and $\equiv P(NHR)_2$ groups have *not* been obtained. After the tris-stage of replacement of chlorine atoms in the *t*-butylamino system (and after the tetrakis-stage in the ethylamino-system), resinous materials are formed predominantly. However, the octakis (amino)-derivatives, $N_4P_4(NHR)_8$ could be easily prepared by using a two–three fold excess of the amine. These observations have been rationalised by postulating a common "metaphosphorimidate" intermediate (formed by elimination of hydrogen chloride from PCl(NHR) groups) for the formation of resins and the octakis (amino) derivative[16].

The hexachloride (I) reacts with *t*-butylamine only by the geminal mode of replacement; both geminal and non-geminal products are obtained in the analogous

Table I

Ethylamino and t-butylamino derivatives of $N_4P_4Cl_8$ (II)

Compound	MP (° C)	Structure
$N_4P_4Cl_7$ (NHEt)	liq.	
$N_4P_4Cl_6$ $(NHEt)_2$	116	2, 4, 4, 6, 8, 8 : 2-*trans*-6
$N_4P_4Cl_6$ $(NHEt)_2$	124	Nongeminal
$N_4P_4Cl_5$ $(NHEt)_3$	68–70	2, 4, 6, 8, 8 : 2-*cis*-4-*trans*-6
$N_4P_4Cl_4$ $(NHEt)_4$	96	2, 4, 6, 8 : 2-*cis*-4-*trans*-6-*trans*-8
$N_4P_4Cl_4$ $(NHEt)_4$	158	2, 4, 6, 8 : 2-*cis*-4-*cis*-6-*trans*-8
N_4P_4 $(NHEt)_8$	116	
$N_4P_4Cl_7$ $(NHBu^t)$	51–52	
$N_4P_4Cl_6$ $(NHBu^t)_2$	171	2, 4, 4, 6, 8, 8 : 2-*trans*-6
$N_4P_4Cl_6$ $(NHBu^t)_2$	127	2, 4, 6, 6, 8, 8 : 2, 4
$N_4P_4Cl_5$ $(NHBu^t)_3$	163–165	2, 4, 6, 8, 8 : 2, 4, 6
N_4P_4 $(NHBu^t)_8$	180–200 (*d*)	
N_4P_4 $(NHBu^t)_8$, HCl	190–195 (*d*)	

ethylamine reaction[8]. The exclusive nongeminal replacement pattern observed for $N_4P_4Cl_8$(II) with both these primary amines is probably due to the greater reactivity of the octachloride(II). An S_N2 (P) mechanism is compatible with the observations.

Chlorocyclotetraphosphazenes containing both ethylamino and *t*-butylamino groups have also been prepared in order to assess the role of the substituent and the nucleophile in determining the structures of the products. Reactions of the mono-derivatives, $N_4P_4Cl_7$ (NHEt) and $N_4P_4Cl_7$(NHBu^t) with two equivalents of ethylamine and *t*-butylamine are summarized in Fig 2. These results suggest that the nucleophile determines the course of these aminolysis reactions and not the substituent already present[17]. A similar conclusion has been drawn from the aminolysis reactions of $N_3P_3Cl_6$ (I)[1–3].

The most significant highlight of our studies on the aminolysis reactions of the octachloride(II) and its primary amino-derivatives is the isolation and characterisation of novel bicyclic phosphazenes (Fig. 3)[15,18–20]. The expected fully aminolysed cyclotetraphosphazenes are also obtained in these reactions. The relative yield of the two types of product is strongly influenced by the reaction solvent. Bicyclic phosphazenes are formed in highest yield (*ca.* 40–60%) in chloroform or methylene chloride. In diethyl

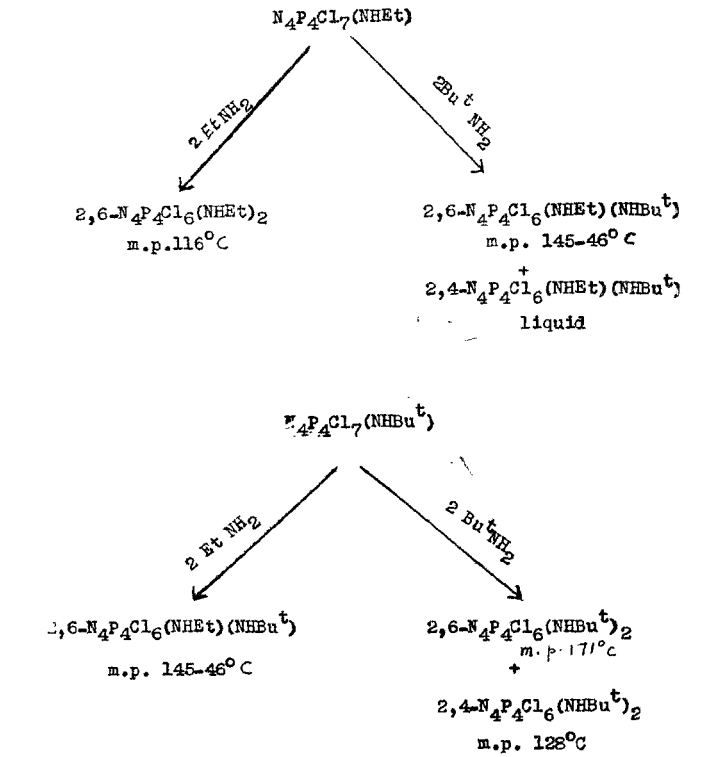


FIG. 2. The effect of the *nucleophile* in the *aminolysis* reactions of (amino) chlorocyclotetraphosphazenes.

ether or carbon tetrachloride, formation of bicyclic phosphazenes $N_4P_4(NMe_2)_5(NHR)(NR)$ has not been observed: only the fully substituted cyclotetraphosphazene derivatives are obtained (*ca.* 75–80%). A proton abstraction mechanism has been proposed for the intramolecular, transannular nucleophilic substitution leading to the formation of bicyclic phosphazenes[15,20]. Crystallographic studies of two bicyclic phosphazenes, $N_4P_4(NHMe)_6(NMe)$[21] and $N_4P_4(NMe_2)_5(NHEt)(NEt)$[22], show that the original 8-membered ring

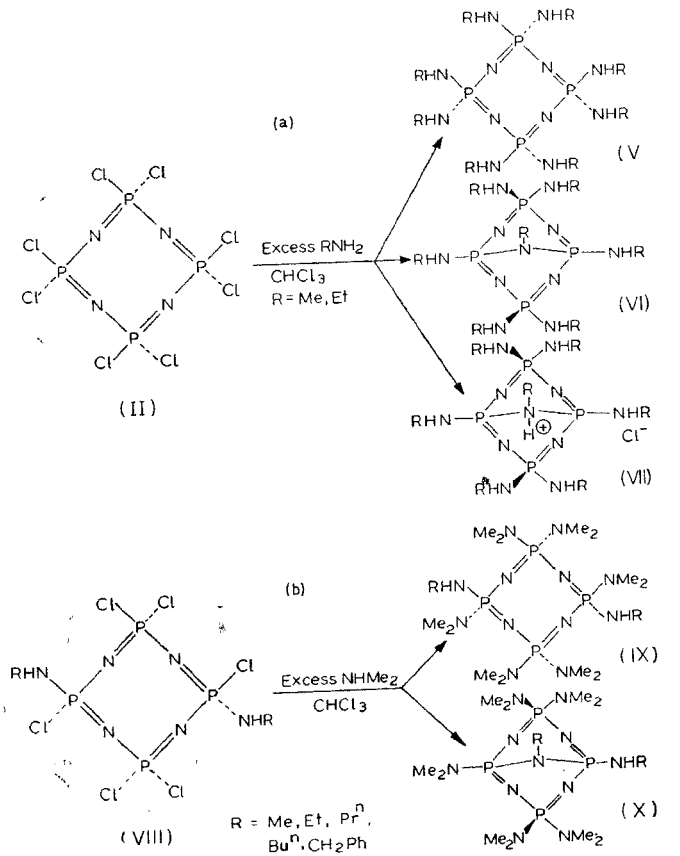
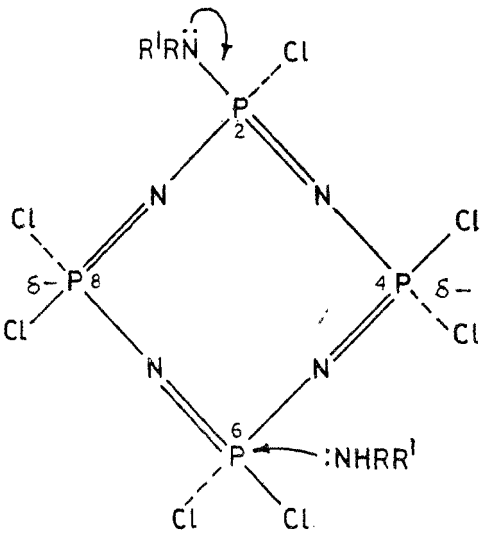


FIG. 3. Formation of bicyclic phosphazenes. The substituents pointing towards the bridgehead nitrogen atom are shown by shaded lines.

retains its phosphaz*ene* character (P–N distances 1·58–1·61 Å) but the bridgehead P–N bond lengths (1·71–1·76 Å) are significantly longer and phosphaz*ane*-like.

Our preliminary conclusions on the aminolysis reactions of $N_4P_4Cl_8$ (II) can be summarised briefly. After the replacement of the first chlorine atom, electron release by the amino substituent at P(2) into the phosphorus-nitrogen ring would preferentially deactivate the adjacent phosphorus atoms, P(4) and P(8) and thereby favour nucleophilic attack at the distant phosphorus atom, P(6). Hence, a reactive amine should



give a 2, 6-product almost exclusively as observed for ethylamine and dimethylamine. Both 2, 6- and 2, 4-bis isomers are obtained in the reaction of $N_4P_4Cl_8$ (II) with less reactive amines, N-methylaniline, dibenzylamine, *t*-butylamine and benzylamine. The ratio of these bis isomers varies markedly with the reaction solvent. As yet, we have no clear rationalisation for these observations although the preferential deactivation at P(4) is likely to diminish with a weaker electron-releasing amino-substituent at P(2) and hence promote substitution at both P(4) and P(6)[9]. The step-wise replacement of chlorine atoms continues in secondary amine reactions[9,11] and compounds with all the possible stages of replacement ($n = 3$–8) are formed, although not necessarily for

all amines. The reactions of the primary amines are more complex. In addition to the step-wise replacement of chlorine atoms to yield chloro (amino)-cyclotetraphosphazenes, intermolecular condensation (resins) and intramolecular displacement (bicyclic phosphazenes) occur. The latter pathway is also found for the reaction of bis (primary amino) cyclotetraphosphazene derivatives with a secondary amine (Me_2NH)[20]. The three pathways discussed above are illustrated in Fig. 4.

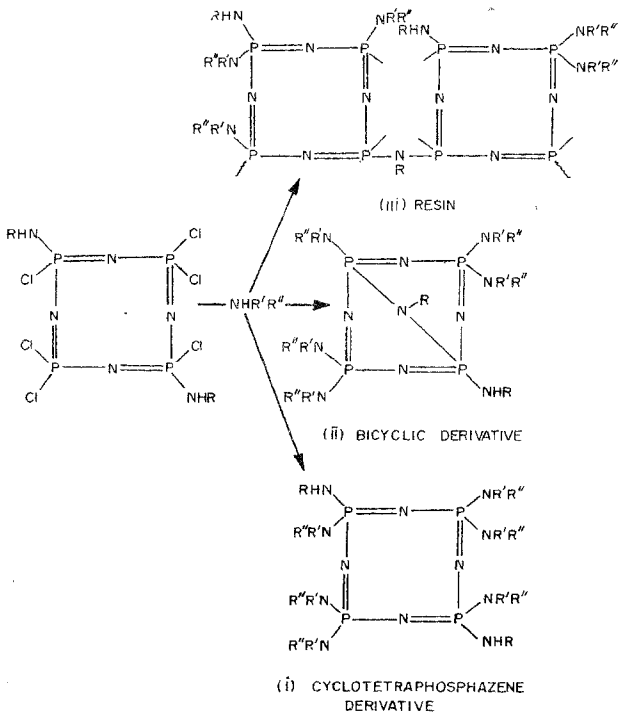


FIG. 4. The three possible pathways in the reactions of $N_4P_4Cl_8$ (II) or $N_4P_4(NHR)_2Cl_6$ (VIII) with amines.

3. Reactions of $N_3P_3Cl_6$ (I) and $N_3P_3Br_6$ (IV)

We have also studied the reaction of N-methylaniline with the hexachloride(1)[23] and isolated the derivatives $N_3P_3Cl_{6-n}(NMePh)_n$, [$n = 1$, 2 (two isomers), 3 (two isomers) and 6]. In addition, a dealkylated product, gem-$N_3P_3Cl_3(NMePh)_2$ (NHPh) has been obtained from a reaction carried out in boiling xylene. The nongeminal bis isomers are obtained in comparable amounts. The tris-isomers have geminal and *cis*- nongeminal structures. The former is the major product formed in all reactions with stoichiometries of 1 : 6 [$N_3P_3Cl_6$ (I): PhNHMe] and above, even in polar solvents such as methyl cyanide. In contrast, the reaction of $N_3P_3Cl_6$ (I) with six equivalents of a more reactive secondary amine (dimethylamine, diethylamine and piperidine) leads to the predominant formation of the *trans*- tris-derivative, $N_3P_3Cl_3R_3$ (particularly in methyl cyanide). The relative proportion of the geminal tris-isomer in these reactions can be enhanced in aromatic reaction media[24]. The reasons for the divergent behaviour of N-methylaniline are uncertain but it is likely that its aromatic and weak basic character are contributing factors.

The preparation of the bromocyclophosphazenes $(NPBr_2)_n$ from phosphorus tribromide, bromine and ammonium bromide is particularly tedious and time-consuming and these factors have undoubtedly contributed to the lack of interest in the chemistry of these compounds. We chose to study the reaction of the hexabromide, $N_3P_3Br_6$ (IV), with ethylamine in order to compare the reactivity of P–Br and P–Cl bonds towards a nucleophilic reagent of this type. The reaction was carried out in diethyl ether at -30 to $-50°$ C and the ethylamino-derivatives, $N_3P_3Br_{6-n}(NHEt)_n$ [$n = 1$, 2 (two isomers), 4 and 6] and the hydrogen bromide adducts, $N_3P_3Br_2(NHEt)_4$, HBr and N_3P_3 $(NHEt_2)_6$, HBr were isolated[25]. Our study of this reaction and a previous report of the dimethylamine reaction[26] suggest that the replacement of the halogen atoms of $N_3P_3Cl_6$ (I) and $N_3P_3Br_6$ (IV) by amino groups is very similar. However, two points of difference are that (*a*) bromo-derivatives are hydrolytically less stable and consequently much more difficult to purify and (*b*) the formation of resins in the reactions of $N_3P_3Br_6$ (IV) with the primary amine is considerably enhanced.

In 1963, the reactions of $N_3P_3Cl_6$ (I) with the diamines, $H_2N(CH_2)_nNH_2$, ($n = 2$, 3 or 4), were reported to give compounds with an *ansa*-structure[27]. The following year, a short paper was published by Italian workers[28] on the ^{31}P NMR spectrum of the propylenediaminoderivative, $N_3P_3Cl_4[NH(CH_2)_3NH]$, which clearly indicated that this compound had a spiro- and not an *ansa*- structure (Fig. 5). This anomaly in the literature apparently escaped the attention of workers in the field of phosphorus-nitrogen chemistry. We have reinvestigated the reaction of $N_3P_3Cl_6$ (I) with ethylenediamine and obtained the derivative $N_3P_3Cl_4[NH(CH_2)_2NH]$ (m.p. 198° C) described previously. We have also synthesised a new *t*-butylamino (ethylenediamino) cyclophosphazene derivative by two different routes (Eqn. 2).

$$\text{gem-}N_3P_3Cl_4(NHBu^t)_2 \xrightarrow{H_2N(CH_2)_2NH_2} N_3P_3Cl_2(NHBu^t)_2[NH(CH_2)_2NH] \quad (2)$$
$$N_3P_3Cl_4[NH(CH_2)_2NH] \xrightarrow{Bu^tNH_2}$$

A small quantity of $N_3P_3Cl_3(NHBu^t)[NH(CH_2)_2NH]$, m.p. 85° C, has also been obtained. This compound appears to be the first geminal cyclotriphosphazene derivative

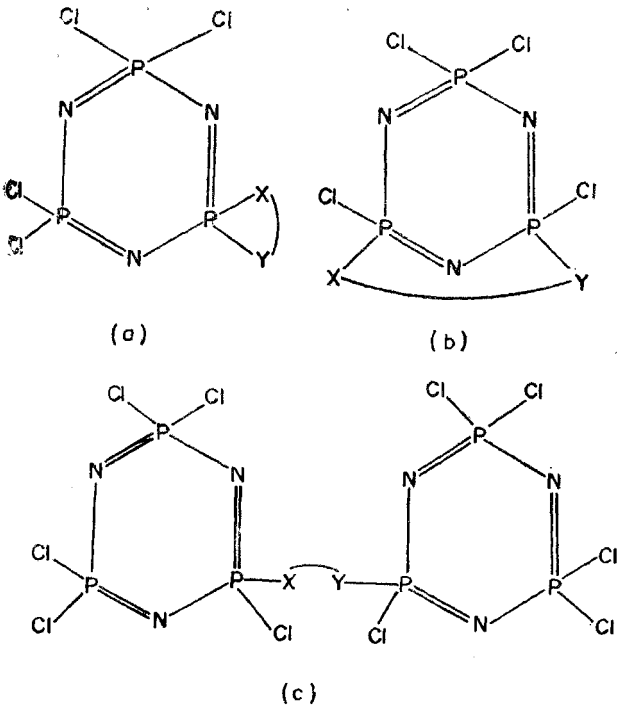


FIG. 5. The possible products of a reaction between $N_3P_3Cl_6$ (I) and a bifunctional reagent HXYH (X and Y need not be directly bonded).

containing three chlorine atoms and three primary alkylamino-substituents. Chemical and NMR spectroscopic evidence show that these ethylenediamino derivatives have spirocyclic structures[20,39]. A recent X-ray structure of the dimethylamino derivative $N_3P_3(NMe_2)_4[NH(CH_2)_2NH]$ has confirmed this conclusion[30].

The reactions of chlorocyclotriphosphazenes with ethanolamine, $NH_2(CH_2)_2OH$, are very similar to those with ethylenediamine and again spirocyclic products are formed. In addition to the mono(ethanolamino) derivative, $N_3P_3Cl_4[NH(CH_2)_2O]$, small quantities of two bis-derivatives, $N_3P_3Cl_2[NH(CH_2)_2O]_2$ have been obtained. Analogous bis (ethylenediamino) cyclotriphosphazenes could not be prepared. After two chlorine atoms of $N_3P_3Cl_6$ (I) have been replaced by ethylenediamino- or ethanolamino- group further replacement of chlorine atoms gives cross-linked products almost exclusively (Fig. 5)[20].

4. Chromatographic techniques

Aminolysis reactions of halogenocyclophosphazenes invariably give a mixture of products with different degrees of halogen replacement which may also include geometric positional isomers. In addition, some unreacted starting material can be present. The amine hydrochloride formed in the reaction can also hinder the purification of the derivatives owing to its considerable solubility in many reaction solvents. A further complication in reactions involving *primary* amines is the formation of resinous materials as a result of side reactions. Hence, the separation of pure cyclophosphazene derivatives from such complex reaction mixtures is very difficult. The "classical" methods of separation—fractional crystallisation and extraction (based on differences in solubility) and fractional distillation and sublimation (differences of volatility)—are often of limited utility. However, the introduction of column, thin-layer and gas-liquid chromatographic techniques has greatly simplified this difficult task[31].

We have used thin-layer chromatography (silica gel adsorbent) for monitoring the course and extent of aminolysis reactions and to identify the components of various fractions collected during column chromatographic separations. TLC can also be used for semi-quantitative estimates of relative yields by visual estimation of the size and intensity of the "spots". The isolation of compounds by preparative TLC is possible but the tediousness of the method and the small quantities of pure compounds obtained are serious limitations. Table II gives the TLC R_f values for some representative aminocyclophosphazenes.

The formation of novel bicyclic phosphazenes, $N_4P_4(NMe_2)_5(NHR)(NR)$, from the reaction of $N_4P_4Cl_6(NHR)_2$ with an excess of dimethylamine in chloroform has been described above. The bicyclic phosphazene has a lower TLC R_f value than the related octakis(amino) cyclotetraphosphazene derivative, $N_4P_4(NMe_2)_6(NHR)_2$, (also formed in the same reaction), thus permitting a ready distinction between the two types of derivatives[20].

Table II

TLC R_f values of selected cyclophosphazene derivatives[a]

Compound	R_f[b]	*Structure*
$N_3P_3Cl_5(NMePh)$	0·85[c]	
$N_3P_3Cl_4(NMePh)_2$	0·81[c]	2, 2, 4, 6: 4-*trans*-6
$N_3P_3Cl_4(NMePh)_2$	0·80[d]	2, 2, 4, 6: 4-*cis*-6
$N_3P_3Cl_3(NMePh)_3$	0·70[e]	2, 4, 6: 2-*cis*-4-*cis*-6
$N_3P_3Cl_3(NMePh)_3$	0·73[c]	2, 2, 4: 4, 6, 6
$N_3P_3(NMePh)_6$	0·66[c]	
$N_3P_3Cl_2(NHPh)(NMePh)_3$	0·28[c]	2, 2: 4: 4, 6, 6
$N_4P_4Cl_7(NMePh)$	0·96[d]	
$N_4P_4Cl_6(NMePh)_2$	0·93[d]	2, 4, 4, 6, 8, 8: 2-*trans*-6
$N_4P_4Cl_6(NMePh)_2$	0·93[d]	2, 4, 6, 6, 8, 8: 2-*trans*-4
$N_4P_4Cl_5(NMePh)_3$	0·84[d]	2, 4, 6, 8, 8: 2-*trans*-4-*cis*-6
$N_4P_4Cl_4(NMePh)_4$	0·80[d]	2, 2, 6, 6: 4, 4, 8, 8
$N_4P_4Cl_4(NMePh)_4$	0·75[d]	2, 2, 6, 8: 4, 4, 6-*trans*-8
$N_4P_4Cl_4(NMePh)_4$	0·70[d]	2, 4, 6, 8: 2-*cis*-4-*trans*-6-*trans*-8
$N_4P_4Cl_4(NMePh)_4$	0·56[d]	2, 4, 6, 8: 2-*trans*-4-*cis*-6-*trans*-8
$N_4P_4Cl_4(NMePh)_4$	0·66[d]	2, 4, 6, 8: 2-*cis*-4-*cis*-6-*trans*-8
$N_4P_4Cl_2(NMePh)_6$	0·68[d]	2-*trans*-6: 2, 4, 4, 6, 8, 8
$N_4P_4Cl_7(NHEt)$	0·71[e]	
$N_4P_4Cl_6(NHEt)_2$	0·58[e]	2, 4, 4, 6, 8, 8: 2-*trans*-6
$N_4P_4Cl_6(NHEt)_2$	0·53[e]	Nongeminal
$N_4P_4Cl_5(NHEt)_3$	0·18[e], 0·74[f]	2, 4, 6, 8, 8: 2-*cis*-4-*trans*-8
$N_4P_4Cl_4(NHEt)_4$	0·65[f]	2, 4, 6, 8: 2-*cis*-4-*trans*-6-*trans*-8
$N_4P_4Cl_4(NHEt)_4$	0·58[f]	2, 4, 6, 8: 2-*cis*-4-*cis*-6-*trans*-8
$N_4P_4Cl_7(NHBu^t)$	0·87[d]	
$N_4P_4Cl_6(NHBu^t)_2$	0·74[d]	2, 4, 4, 6, 8, 8: 2, 6
$N_4P_4Cl_6(NHBu^t)_2$	0·65[d]	2, 4, 4, 6, 8, 8: 2, 4
$N_4P_4Cl_5(NHBu^t)_3$	0·40[d]	2, 4, 6, 6, 8: 2, 4, 6
$N_4P_4Cl_6(NHBu^t)(NHEt)$	0·72[d]	2, 4, 4, 6, 8, 8: 2: 6
$N_4P_4Cl_6(NHBu^t)(NHEt)$	0·55[d]	2, 4, 4, 6, 8, 8: 2: 4

a Data from Refs. 9, 16, 17 and 23.

b Adsorbent: silica gel.

c Eluent: benzene.

d Eluent: benzene-petrol (60–80°) (1 : 1).

e Eluent: benzene-petrol (40–60°) (1 : 1).

f Eluent: benzene-ethyl acetate (9 : 1).

Column chromatography over silica gel is essential to obtain many of the chloro (N-methylanilino)-cyclophosphazene derivatives formed in the reactions of N-methylaniline with $N_3P_3Cl_6$ (I)[23] and $N_4P_4Cl_8$ (II)[9]. In some cases, fractional crystallisation of the reaction mixtures affords crystalline crops enriched in a particular derivative. After further purification by fractional crystallisation, the residual mixture is chromatographed.

The usefulness of column chromatography for the separation of chloro(primary amino) cyclotetraphosphazenes is limited because of considerable loss of material owing to irreversible adsorption or decomposition on the column. This problem is accentuated with increasing number of primary amino groups. For example, the tetrakis(ethylamino isomers of $N_4P_4(NHEt)_4Cl_4$ cannot be eluted from the column even with very polar solvents (ethyl acetate)[15].

Gas-liquid chromatography (GLC) is often much more efficient than column or thin-layer chromatographic technique for the separation of (amino) chlorocyclophosphazenes besides serving as a powerful analytical tool for estimating the relative yields of products. The separation of the two bis (N-methylanilino) tetrachlorocyclotriphosphazene isomers, $N_3P_3(NMePh)_2Cl_4$ has been achieved by GLC[23]. The *cis*-isomer has a larger retention time than the *trans*-analogue. The relative yields of the N-methylanilino derivatives in many reactions have been determined by this technique. Fig. 6. shows the GLC trace of a typical reaction mixture.

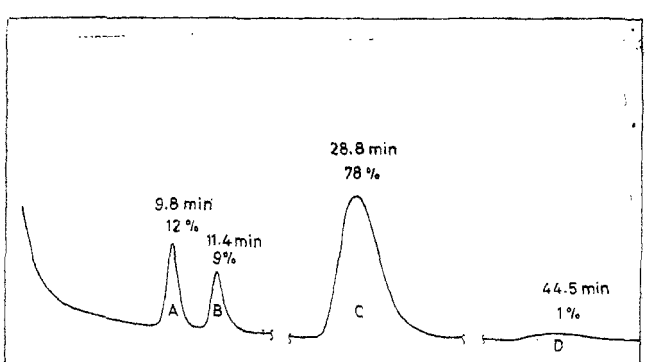


FIG. 6. The GLC trace of the mixture obtained in the reaction of $N_3P_3Cl_6$(I) with N-methylaniline (mol ratio 1 : 6) in boiling methyl cyanide (10 h) using a steel column (15′ × 1/8″) containing 7% Dexil 300 GC liquid phase in chromosil W-HP at 265° C. The percentages refer to relative yield of the chloro (N-methylanilino) derivatives (A) 2-*trans*-4-$N_3P_3(NMePh)_2Cl_4$, (B) 2-*cis*-4-$N_3P_3(NMePh)_2Cl_4$, (C) 2, 2, 4-$N_3P_3(NMePh)_3Cl_3$ and (D) 2-*cis*-4-*cis*-6-$N_3P_3(NMePh)_3Cl_3$. The retention times are also shown.

The reaction of $N_3P_3Cl_6$ (*I*) with isopropylamine was reported in 1966 and one *bis*(isopropylamino) derivative, $N_3P_3Cl_4(NHPr^i)_2$, was isolated[32]. We have reinvestigated this reaction and obtained an oily substance by column chromatography. The oil shows a single spot on TLC and its mass spectrum has a parent ion corresponding to the formula, $N_3P_3Cl_4(NHPr^i)_2$. Attempts to crystallise the oil were unsuccessful. GLC examination of the oil revealed the presence of all three $N_3P_3Cl_4(NHPr^i)_2$ isomers. These isomers have been separated by preparative scale GLC and characterised by NMR spectroscopy. The GLC retention times follow the trend *gem* < *trans* < *cis*[33].

5. Proton magnetic resonance spectroscopy

Nuclear magnetic resonance spectroscopy has proved extremely useful for determining the disposition of substituents in many cyclophosphazene derivatives. Three criteria are of general use for this purpose: (*a*) the number of proton environments, (*b*) the value of $^3J^*(P\text{–}H)$ and (*c*) the relative chemical shifts (geminal/nongeminal and *cis*/*trans*). However, unambiguous assignments are not always possible (particularly for cyclotetraphosphazenes) as it is often possible to interpret the data on the basis of more than one isomeric configuration. In many cases, the different proton environments are poorly resolved but some simplification is possible by recording the spectrum at higher field strength (*i.e.*, 220 MHz)[3]. Fig. 7 illustrates the $-NCH_2$ region of the 220 MHz spectrum of the tris-ethylamino derivative, $N_3P_3Cl_3(NHEt)_3$. Each methylene group is coupled to the neighbouring methyl protons and also to the adjacent phosphorus nucleus. The multiplicity of the signals clearly indicates that there are three $-NCH_2$ environments in this molecule. The magnitude of $^3J^*(P\text{–}H)$ (14·0 Hz) indicates a nongeminal structure[16]. Three such structures are possible (Fig. 8) but only one of them can give rise to three distinct $-NCH_2$ environments [Fig. 8 (*a*)].

The assignment of structures to the chloro (N-methyl-anilino) cyclotri-[23] and cyclotetra-[9] phosphazenes is largely based on their proton NMR spectra. The ^1H NMR data for the five tetrakis (N-methylanilino) cyclotetraphosphazene isomers of $N_4P_4Cl_4(NMePh)_4$, along with their spectra and structures are shown in Fig. 9. The spectra provide good examples of the three criteria mentioned above. For example, the magnitude of $^3J^*(P\text{–}H)$ for $\equiv PCl(NMePh)$ groups are $\sim$4–5 Hz higher than that for $\equiv P(NMePh)_2$ groups. Another notable feature of the spectra is the appearance of additional lines or broad humps among the sharp doublets expected from first-order considerations. This phenomenon is referred to as "virtual coupling". The presence (or absence) of "virtual coupling" can sometimes be useful for assigning structures to isomeric derivatives. The 2, 2, 6, 6-structure of $N_4P_4Cl_4(NMePh)_4$, m.p. 162°C, follows from the absence of "virtual coupling" in its proton NMR spectrum [Fig. 9 (*a*)]. We have also distinguished the geminal 2, 2, 6, 6- and 2, 2, 4, 4- $N_4P_4Ph_4(NMe_2)_4$ isomers as the spectrum of the latter contains a dimethylamino doublet with pronounced "virtual coupling"[34]. The strength of "virtual coupling" is closely related to the differences in chemical shifts of the phosphorus nuclei involved. Consequently, in some cases the above criterion is

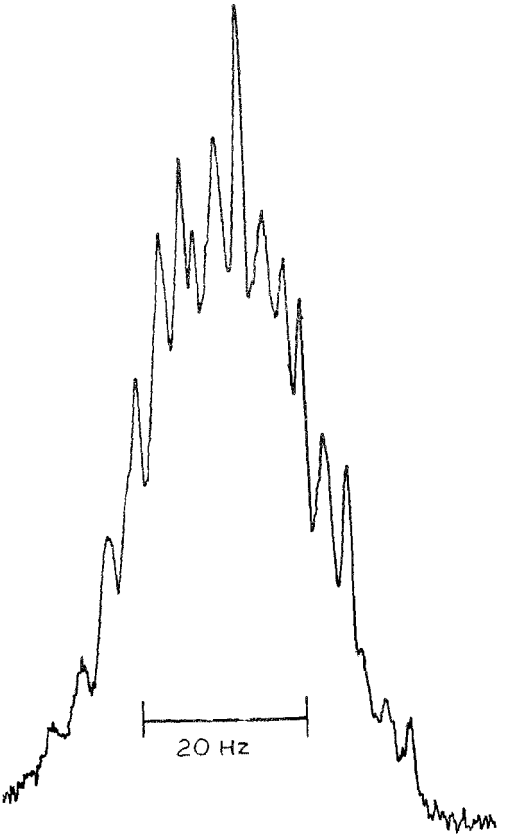


FIG. 7. The ^1H NMR spectrum (220 MHz, $CDCl_3$) of $N_4P_4Cl_6(NHEt)_2$ (the $-NCH_2$ region only).

not useful for differentiating isomers [*e.g.*, the proton spectra (N*Me* signals) of both 2-*trans*-4 and 2-*trans*-6-$N_4P_4Cl_6(NMePh)_2$ exhibit "virtual coupling"[9]].

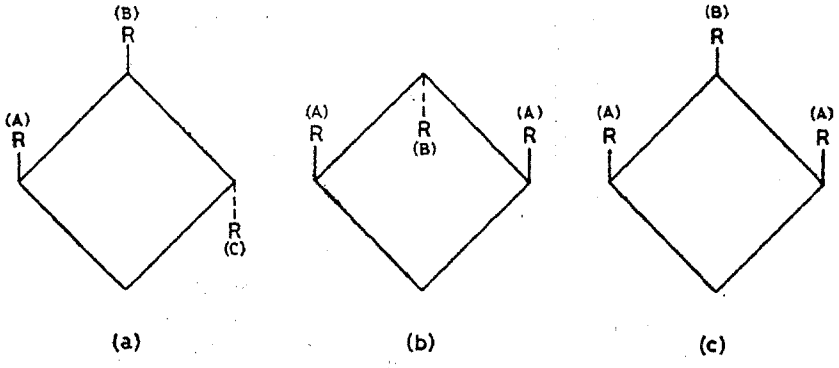


FIG. 8. The three possible nongeminal isomers of $N_4P_4Cl_5R_3$.

The 100 MHz ^1H NMR spectra of bicyclic phosphazenes are generally too complex to yield structural information. However, the spectra are considerably simplified when they are recorded at higher field strength (220 MHz)[19,20]. Complete analysis of the spectrum is then possible in most cases and confirms the bicyclic structure. A typical spectrum is shown in Fig. 10 along with the assignments. The protons of the groups attached to the junction phosphorus atoms, P(2) and P(6) are considerably deshielded. The two amino substituents at P(4) [or P(8)] are non-equivalent. An analysis of the shifts observed on the addition of $Eu(fod)_3$ indicates that the protons of the group pointing to the bridgehead nitrogen atom resonate at a higher field[19].

6. ^{31}P NMR Spectroscopy

The commercial availability of Fourier Transform (FT) NMR spectrometers and the application of broad-band proton decoupling have improved the quality of phosphorus NMR spectra dramatically in recent years and good spectra can now be obtained with relatively small quantities of samples. Phosphorus NMR spectroscopy often confirms the structure assigned by an interpretation of proton NMR data. In some cases, it can provide independent evidence where proton NMR spectra may be uninformative. Many cyclophosphazene derivatives provide examples of multi-spin systems and their ^{31}P spectra cannot usually be analysed by a first order approach.

Our studies of the reactions of $N_3P_3Cl_6$ (I) with ethanolamine and ethylenediamine have greatly benefited from phosphorus NMR data[20]. The technique conclusively demonstrates that these reagents react by the spirocyclic route (see section 2). The spirocyclic derivatives, $N_3P_3Cl_2(NHCH_2CH_2X)$ (X = O or NH; R = Ph or $NHBu^t$) each, contain three chemically different phosphorus nuclei. The $^{31}P\{^1H\}$ spectra of these compounds are of the ABX type and a typical example is shown in Fig. 11. Such spectra are exceedingly rare in cyclotriphosphazene chemistry.

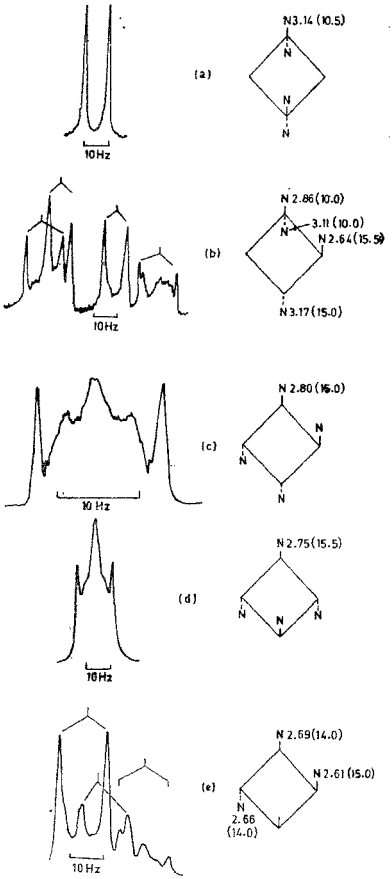
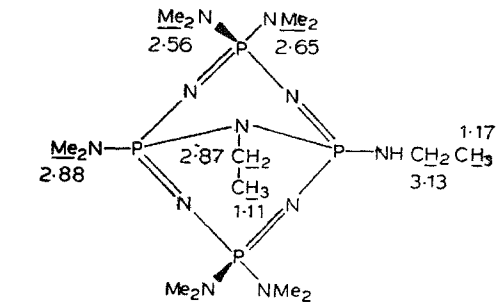


FIG. 9. The $\{^1H\}$ NMR spectra (–NMe region only) of five isomers of $N_4P_4Cl_4(NMePh)_4$ along with their structures. The values shown are the chemical shifts of N-methyl protons with $^3J^*(P–H)$ in parentheses. Spectrum (*e*) was measured in C_6D_6 at 220 MHz; the other spectra were recorded at 100 MHz in $CDCl_3$.



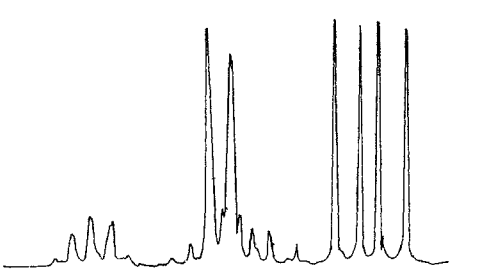


FIG. 10. The $-NCH_2$ and $-NCH_3$ region of the ^1H NMR (220 MHz, $CDCl_3$), spectrum of the bicyclic phosphazene, $N_4P_4(NMe_2)_5(NHEt)(NEt)$ with assignments.

The geminal structure of the *bis* (isopropylamino) derivative, $N_3P_3Cl_4(NHPr^i)_2$ m.p. 114°, is deduced from its $^{31}P\{^1H\}$ NMR spectrum which consists of a doublet (19·8 δ) and a triplet (6·2 δ) (relative intensities 2:1). The ^{31}P NMR spectra of the non-geminal isomers are of the AB_2 type (*trans*: δ_{PCl_2} 21·3, $\delta_{PCl\,(NHR)}$ 19·1; *cis*: δ_{PCl_2} 21·9, $\delta_{PCl\,(NHR)}$ 19·0)[33].

The $^{31}P\{^1H\}$ NMR spectra of cyclotetraphosphazenes with different substituents and bicyclic phosphazenes are particularly interesting as they can provide examples of different types of a four spin system. Derivatives of the general formula, $N_4P_4Cl_6(NRR')_2$ with amino groups in 2, 4 or 2, 6 positions can be distinguished by their AA' BB' and A_2B_2 ^{31}P spectra respectively. The analysis of A_2B_2 spectra is usually straightforward but that of AA' BB' spectra requires computer simulation[35]. The spectra of the bicyclic phosphazenes, $N_4P_4(NHR)_6(NR)$ (R = Me or Et) [Fig. 3 (*a*)] are also of the A_2B_2 type. Unsymmetrically substituted bicyclic phosphazenes [Fig. 3 (*b*)] provide examples

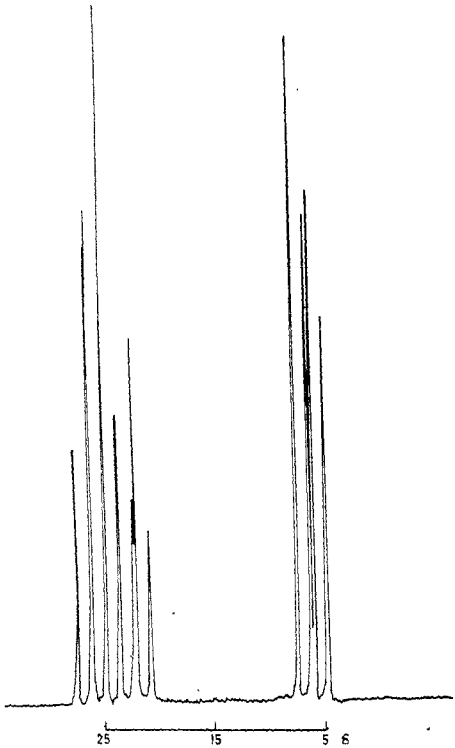


FIG. 11. The $^{31}P\{^{1}H\}$ FT NMR spectrum (36·4 MHz, $CDCl_3$) of $N_3P_3Cl_2(NHCH_2CH_2NH)(NHBut\text{-})_2$.

of an A_2BC spin system. The ^{31}P chemical shifts of bicyclic phosphazenes lie in the region 15–22 δ which is well separated from the region characteristic of fully-aminolysed cyclotetraphosphazenes (4–10 δ). Phosphorus NMR spectroscopy can thus be used as an analytical tool to estimate the yields of bicyclic phosphazenes and fully aminolysed cyclotetraphosphazenes formed in the same reaction[20] (Section 2). The spectrum of one such mixture is illustrated in Fig. 12.

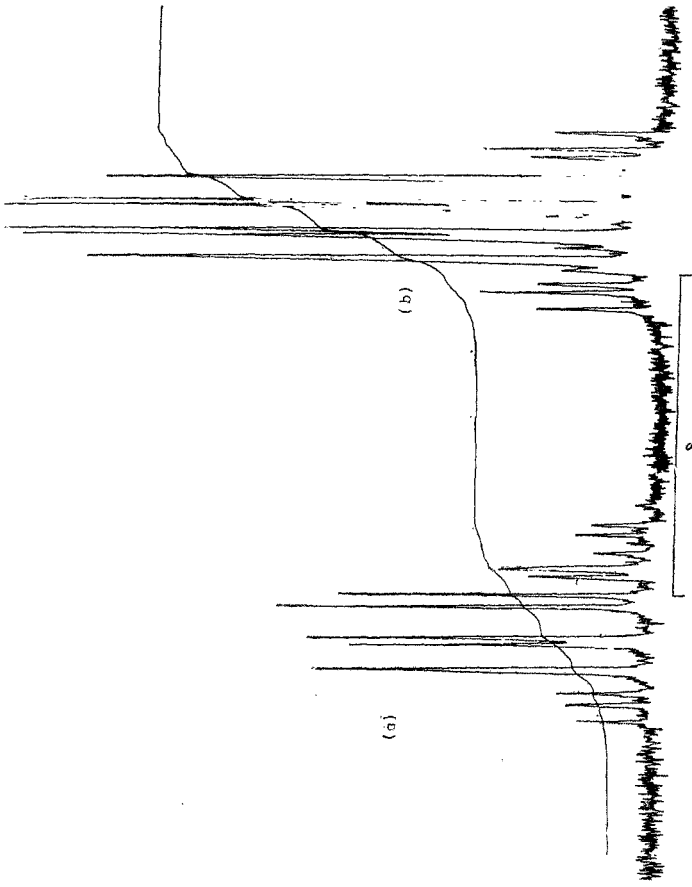


FIG. 12. The ^{31}P $\{^1H\}$ FT NMR spectrum (36·4 MHz, $CDCl_3$) of a mixture of (*a*) $N_3P_3(NMe_2)_5(NHEt)(NEt)$ and (*b*) $N_4P_4(NMe_2)_6(NHEt)_2$.

7. Infrared spectroscopy

The infrared spectra of cyclophosphazenes are valuable for "finger-printing" and thereby ascertaining the identity and purity of products in synthetic reactions. The spectra are characterised by a dominant vibration at 1150–1350 cm^{-1} which is attributed to a ring stretching frequency, $\nu(P{=}N)$. For (amino)cyclotriphosphazenes, the above vibration occurs at 1210–1175 cm^{-1} whereas for (amino)cyclotetraphosphazenes, this band is observed at 1300–1250 cm^{-1}. The (P=N) band is usually broad and often split. A precise measurement of $\nu(P{=}N)$ is hampered by bands arising from the vibrations of the exocyclic amino substituents which also occur in this region[3].

Infrared spectroscopy is particularly useful to distinguish hydrochloride adducts of (amino)cyclophosphazenes from their free bases. It also indicates that protonation occurs at a ring nitrogen atom. The ring stretching vibration, $\nu(P{=}N)$ undergoes an upward shift of ca. 40–60 cm^{-1} in the adduct. New absorption bands are observed at 915–930 and 2400–2650 cm^{-1} attributable to $-P{-}\overset{+}{N}(H){-}P-$ linkage. The infrared spectra of the new bicyclic phosphazenes discovered by us have distinctive features compared to those of their related fully aminolysed cyclotetraphosphazene derivatives. The P=N stretching frequency appears at 1185–1200 cm^{-1}. A new band at 820–830 cm^{-1} is observed which has been assigned to the bridgehead P–N–P unit—the phosphazane part of the bicyclic skeleton. Fig. 13 shows some typical spectra which illustrate the above points[20].

8. Other studies

The Faraday effect of some (amino) chloro cyclotriphosphazenes[36] and nuclear quadrupole resonance of chloro- and bromo- cyclophosphazenes have been studied[37]. The crystal structures of triphenylphosphazenyl ($NPPh_3$) substituted cyclophosphazenes, $N_3P_3Cl_5(NPPh_3)$[38], $N_4P_4Cl_7(NPPh_3)$[39] and $N_6P_3Cl_4(NEt_2)(NPPh_3)$[40] have been determined. The observed changes in the conformations of the phosphazenyl side chain with respect to the local ring NPN segment are correlated with the conclusions drawn from basicity measurements[24].

Pot culture studies on the use of hexaammonocyclotriphosphazene, $N_3P_3(NH_2)_6$, as a fertilizer for *Purna Ragi* crop have been carried out in collaboration with the University of Agricultural Sciences, Bangalore. Enhanced yields of grain compared to control experiments (no fertilizer) are obtained. The yields are almost the same as those obtained with conventional treatments (ammonium sulphate + superphosphate or urea + superphosphate) on equal nutrient (N and P) basis at the recommended levels[41]. On a weight to weight basis, the quantities of the phosphazene compound required to produce the same effect as the two conventional treatments are ten- and six-fold less respectively.

9. Concluding remarks

In this review we have attempted to summarise the significant results of our fundamental investigations on (*a*) the replacement reactions of the octachloride, $N_4P_4Cl_8$(II), with

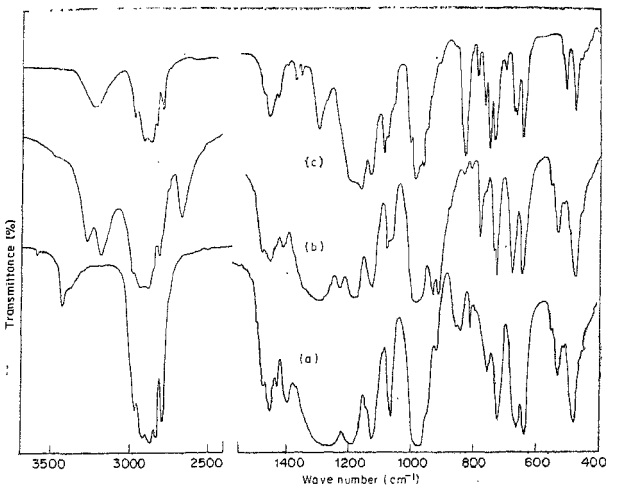


FIG. 13. Infrared spectra of (*a*) $N_4P_4(NMe_2)_6(NHEt)_2$, (*b*) $N_4P_4(NMe_2)_6(NHEt)_2$, 2HCl and (*c*) $N_4P_4(NMe_2)_5(NHEt)(NEt)$.

various amines, (*b*) the isolation and characterization of bicyclic phosphazenes, a novel class of phosphorus-nitrogen compounds and (*c*) the formation of spirocyclic phosphazenes. We are now expanding our studies to other areas, *viz.*, (*a*) alcoholysis reactions of chlorocyclophosphazenes, (*b*) thermal rearrangement reactions of alkoxycyclophosphazenes, (*c*) tautomeric forms of hydroxycyclophosphazenes, (*d*) reactions of phosphazenyl substituted cyclophosphazene derivatives, (*e*) kinetic studies and (*f*) metal complexes of phosphazenes. Our approach to these topics will again reflect our belief that many aspects of modern science require resources that are not always available in a particular laboratory. By complementing the resources of our respective laboratories, we are able to investigate a larger range of problems in greater detail and thereby make a more substantial contribution to the subject. We hope that this article will demonstrate how successful collaboration can help the participants to pursue their scientific interests to their mutual benefit.

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