PHOSPHAZENES : A GROUP OF PHOSPHORUS–NITROGEN COMPOUNDS

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THE reaction of ammonium chloride and phosphorus pentachloride is complex[1] and gives rise to oligomeric chlorocyclophosphazenes (phosphonitrilic chlorides), $(NPCl_2)_n$, and also several linear species containing $(NPCl_2)$ units end-stopped

$$n\,NH_4Cl + n\,PCl_5 \longrightarrow (NPCl_2)_n + 4n\,HCl \qquad (1)$$

by the elements of HCl and/or PCl_5. Although the first member of the homologous series, hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, was isolated by Liebig[2] in 1834, characterisation of higher homologues, (n = 4 to 7) was only achieved in the latter part of the nineteenth century[3]. The fundamental studies of Stokes on chlorocyclophosphazenes and their ammonolysis and hydrolysis reactions[4] provided the basis for the modern development of the subject.

In the last two decades, there has been considerable progress in many aspects of phosphazene chemistry. In particular, a great deal of attention has been paid to the chemical reactions of the hexachloride, $N_3P_3Cl_6$, to spectroscopic studies and molecular structure, to the nature of bonding in cyclic phosphazenes and to the technological development of cyclic oligomers and open-chain polyphosphazenes. There are several excellent reviews on these and other aspects of phosphazene chemistry[5-12]. In this article, a brief introduction to some of the significant features of the subject is given as well as an account of developments in Bangalore and other laboratories in the last few years. Actual and potential applications of cyclophosphazenes and phosphazene polymers are noted.

Basic Chemistry

(a) *Aminolysis Reactions*

The reaction of the hexachloride $N_3P_3Cl_6$ with primary, secondary and tertiary amines has received a great deal of attention[1,8,9]. Replacement of the chlorine atoms of $N_3P_3Cl_6$ by amino groups may proceed by two different routes—geminal and nongeminal (Fig. 1). The nongeminal mode of replacement permits the possibility of *cis-trans* isomerism at the bis, tris and tetrakis stages of replacement. This type of isomerism depends on the disposition of groups with respect to the plane of the ring. In most reactions, both geminal and nongeminal replacement patterns are found although usually one of them predominates. Table I summarises the results obtained for a number of amines.

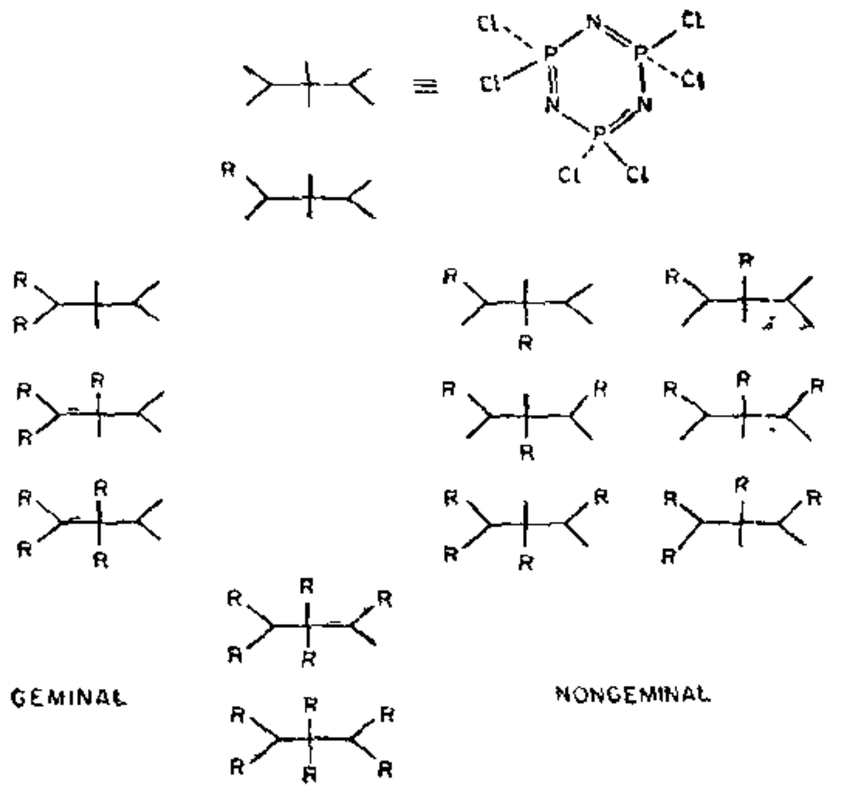


FIG. 1. The geminal and nongeminal pathways in the replacement of chlorine atoms from $N_3P_3Cl_6$ (R groups are attached to P atoms; chlorine and ring nitrogen atoms are not shown).

Secondary amines react predominantly by the nongeminal mode of replacement although significant quantities of geminal tris-compounds can be isolated in aromatic reaction media[13]. The relative proportion of *cis*- and *trans*- nongeminal isomers varies. The major *bis*- and *tris*-aminocyclophosphazenes formed usually have *trans*-structures whereas the structure of the tetrakisamino derivatives appears to be dominated by steric considerations [$N_3P_3Cl_2(NMe_2)_4$ and $N_3P_3Cl_2(NEt_2)_4$ have *cis*[14]- and *trans*[15]- structures respectively and only minor quantities of their stereo-isomers are obtained]. A "cis" effect[16] was proposed to account for the product distribution observed for the reactions of the hexachloride with dimethylamine[14] and piperidine[16]. Recent kinetic data[17] suggest that a substituent solvating effect may also contribute to the preponderance of *trans*- nongeminal *bis* isomers in secondary amine reactions.

TABLE I

Chlorine atom replacement patterns in the reactions of $N_3P_3Cl_6$ with amines

Amine	Replacement pattern
Ammonia	Geminal
Methylamine	Mainly nongeminal + geminal
Ethylamine	Mainly nongeminal + geminal
Isopropylamine	Nongeminal + geminal
tert-Butylamine	Geminal
Benzylamine	Nongeminal + geminal
Aniline	Mainly geminal + nongeminal
Dimethylamine	Mainly nongeminal + geminal
Diethylamine	Mainly nongeminal + geminal
Pyrrolidine	Mainly nongeminal + geminal
Piperidine	Mainly nongeminal + geminal
Aziridine	Geminal
N-Methylaniline	Nongeminal + geminal

Whereas reactions of $N_3P_3Cl_6$ with secondary amines can be rationalised by the assumption of an S_N2 (P) mechanism, analogous reactions with primary amines are more complex and additional mechanistic features assume importance. Ammonia[18] and *t*-butylamine[19] react with the hexachloride, $N_3P_3Cl_6$, to give only products with geminal structures. A proton abstraction mechanism has been suggested to account for this observation (Fig 2).

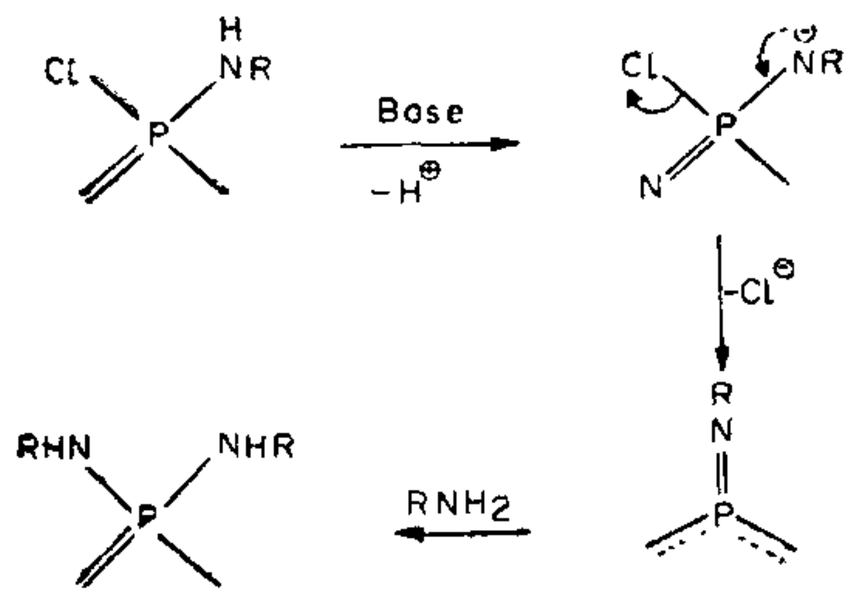


FIG. 2. Proton abstraction mechanism

Such a mechanism is rendered plausible by the recent isolation[20] of a three-coordinate phosphorous (V) compound, $(Me_3Si)_2NP\ (=NSiMe_3)_2$. Ethylamine[21] and isopropylamine[22] react initially by the nongeminal mode of replpacement and then by the geminal one (Equation 2). The geminal *tris* and nongeminal tetrakis derivaties have not been isolated

$$N_3P_3Cl_6 \xrightarrow{4NH_2R} \text{nongem-}N_3P_3Cl_1(NHR)_5 \xrightarrow{4NH_2R} \text{gem-}N_3P_3Cl_2(NHR)_4 \quad (2)$$

although substantial amounts of the former would be expected as intermediates in the formation of geminal tetrakis compounds. In addition to the proton abstraction mechanism, the geminal mode of replacement is probably promoted by the formation of six-membered, cyclic hydrogen-bonded complexes[21] (Fig. 3).

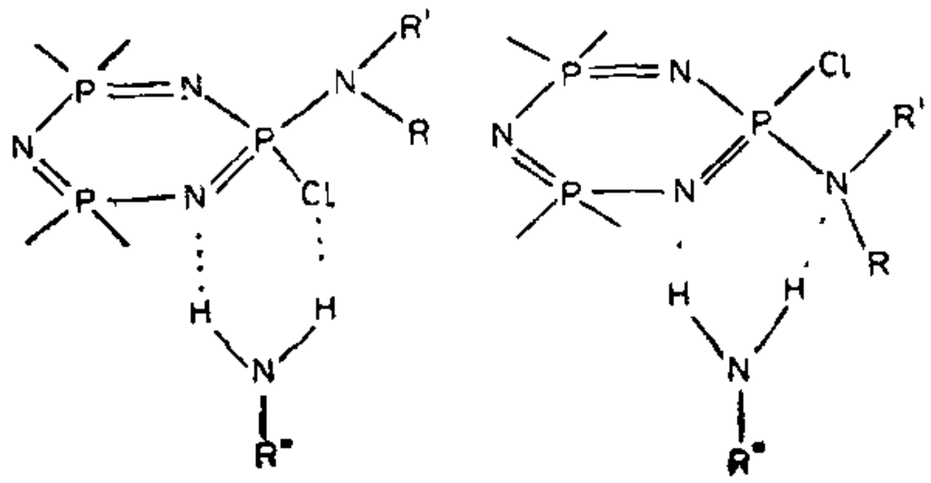


FIG. 3. Possible hydrogen bonded complexes in the reactions of $N_3P_3Cl_6$ with primary amines.

Considerable difficulty is encountered in the isolation[19] of pentakisaminochlorocyclotriphosphazatrienes, $N_3P_3Cl(NRR')_5$. The strong electron supply from amino substituents may cause a changeover to a relatively facile heterolysis of the P–Cl bond in an S_N1 type process. Clare and Sowerby[23] have isolated the monochloropentakisdimethylaminocyclotriphosphazatriene, $N_3P_3Cl(NMe_2)_5$, and noted its ready hydrolysis by atmospheric moisture. A stable monochloropentakisamino compound, $N_3P_3Cl(NMe_2)_4[N(CH_2Ph)_2]$, has been reported recently; its stability may be due to steric shielding by the bulky dibenzylamino group[24].

The aminolysis reactions of fluoro- and bromocyclotriphosphazatrienes have not been studied systematically. Some reactions of $N_3P_3F_6$ with ammonia[25] and primray and secondary amines have been reported[26,27]. Fluorodimethylaminocyclotriphosphazatrienes can be prepared by fluorination of the corresponding chloro derivatives[28,29] or by the reaction of the hexakisdimethylamino compound, $N_3P_3(NMe_2)_6$, with antimony trifluoride[23]. The reaction of $N_3P_3Br_6$ with dimethylamine[30] gives the mono, three *bis* and two *tris* derivatives (gem and nongem *trans*). The *cis*-isomer, $N_3P_3Br_3(NMe_2)_3$, has been obtained only from the reaction of $N_3P_3(NMe_2)_6$ and hydrogen bromide in boiling xylene[31]. Formation of a tertrakis derivative was detected (tlc)[30,31] but pure compounds could not be obtained. A preliminary investigation of the

reaction of $N_3P_3Br_6$ with ethylamine shows that the general features of the system are similar to those found in the analogous reactions[21] of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$ (M. N. Sudheendra Rao, Unpublished results).

Aminolysis reactions of the octachloride, $N_4P_4Cl_8$, and the higher homologues $(NPCl_2)_n$ have received little attention ; the experimental problems associated with the separation of complex mixtures of products and the subsequent difficulties in assigning structures to pure isomers are considerable (there are 33 possible dirivatives of the tetramer). Millington and Sowerby have isolated thirteen products from the reaction[32] of $N_4P_4Cl_8$ with dimethlamine in diethyl ether at — 78° C. The reaction proceeds *via* the non-geminal path ; geminal products were obtained only in poor yields. These workers have also prepared many nongeminal fluorodimethylamino compounds, $N_4P_4F_{8-n}(NMe_2)_n$, by the reaction of $N_4P_4(NMe_2)_8$ with antimony fluoride[33] and by similar reactions using *tris*- and tetrakis-chlorodimethylamino precursors[34].

We have recently investigated the reactions of $N_4P_4Cl_8$ with ethylamine[35], *t*-butylamine[36] and N-methylaniline[36]. The reactions of the primary amines have similar features ; mono, bis, tris, tetrakis (ethylamine only) and octakis derivatives can be obtained. Reactions involving higher stoichiometries (particularly 1 : 10 and 1 : 12, $N_4P_4Cl_8$: amine) give only copious quantities of sticky, resinous materials and chloroaminocyclotetraphosphazatetraenes could not be detected[35]. The resins appear to contain tetrameric units and probably arise by cross-linking reactions. The chloroethylamino derivatives isolated have nongeminal structures (Fig. 4). N-Methylaniline reacts with $N_4P_4Cl_8$ to give the derivatives, $N_4P_4Cl_{8-n}(NMePh)_n$ [n = 1, 2 (two isomers, 3, 4 (five isomers), 6] (S. S. Krishnamurthy, R. A. Shaw, M. N. Sudheendra Rao, A. R. Vasudeva Murthy and M. Woods, unpublished results). In contrast to the dimethylamine reaction where only one major *bis*-isomer (2-*trans*-6) is found[32], reaction of $N_4P_4Cl_8$ with N-methylaniline (a much less reactive amine) gives two *bis*-isomers in roughly equal amounts. Crystallographic evidence confirms that one isomer has a 2-*trans*-6 structure and ^{31}P NMR spectroscopy suggests that the other has a 2, 4-structure[36].

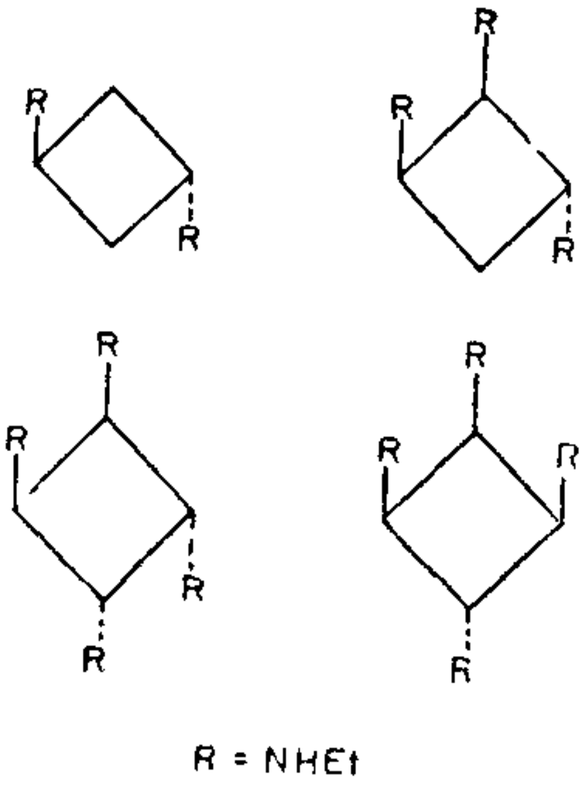


Fig. 4. Structures of $N_4P_4Cl_{8-n}(NHEt)_n$ (n = 2, 3, 4).

The role of the reaction solvent in cyclophosphazene chemistry is not entirely clear at the moment. Recent work shows that solvents can exert a considerable influence on cyclophosphazene reactions. One of the highlights of a current study has been the isolation of bicyclic phosphazenes from the aminolysis reactions of $N_4P_4Cl_8$ in chloroform. These compounds are probably formed by an intramolecular *trans*-annular nucleophilic replacement reaction (Fig. 5). The crystal structure of

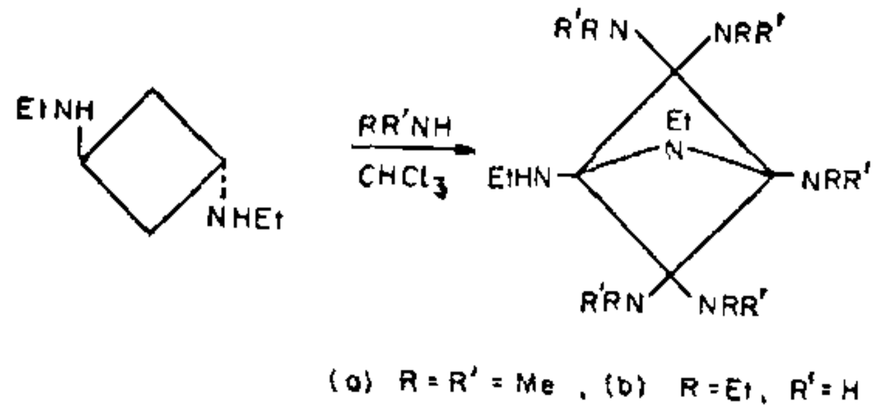
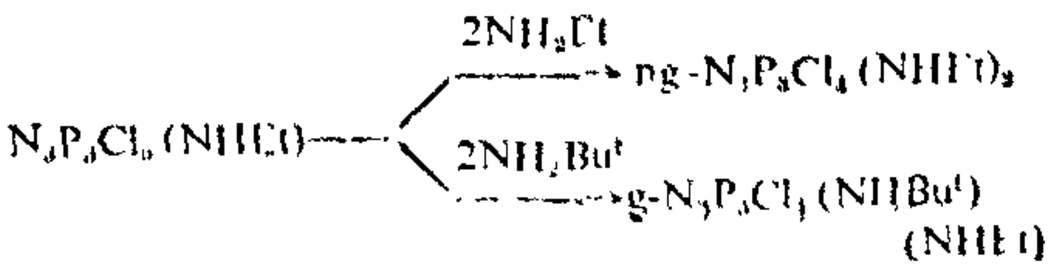


Fig. 5. Formation of bicyclic phosphazenes.

$N_4P_4(NMe_2)_5(NHEt)(NEt)$ shows that the original P–N heterocycle retains its phosphazene character but that the P–N bonds at the bridgehead are longer and more phosphazane-like[37]. If these reactions are carried out in diethyl ether[35], the fully substituted cyclophosphazatetraene derivatives, $N_4P_4(NHEt)_2(NRR')_6$ are isolated in good yields (~ 80%).

Chlorocyclophosphazenes containing two different amino substituents have also been prepared in order to evaluate the role of substituent and nucleophile in determining the structures of the products[13]. The reactions of $N_3P_3Cl_5(NHEt)$ and $N_3P_3Cl_5(NHBu^t)$ with two equivalents of *t*-butylamine and ethylamine are shown in Scheme 1. The structures



$$N_3P_3Cl_5(NHBu^t) \begin{cases} \xrightarrow{2NH_2Et} ng\text{-}N_3P_3Cl_3(NHBu^t)(NHEt) \\ \xrightarrow{2NH_2Bu^t} g\text{-}N_3P_3Cl_4(NHBu^t)_2 \end{cases}$$

g—geminal ng-nongeminal

of the products obtained from the reactions indicate that the attacking nucleophile dominates the course of these aminolysis reactions[38]. It appears that reactions of the octachloride, $N_4P_4Cl_8$, with primary amines[39], are similarly influenced by the nucleophile. The important role of the nucleophile in many cyclophosphazene reactions has also been confirmed by the recent kinetic studies of Goldschmidt and Licht[17]. Chlorocyclophosphazenes containing both primary and secondary amino substituents have also been prepared and similar conclusions can be drawn[9,24].

It appears that in some reactions the substituent already present in the cyclophosphazene ring can counteract the influence of the incoming nucleophile. At present, the only example of this type is provided by the triphenylphosphazenyl ($NPPh_3$) substituent. Dimethylamine[14] and piperidine[16] react with monosubstituted derivatives, $N_3P_3Cl_5R$, to give nongeminal products $N_3P_3Cl_4R_2$ ($R = NMe_2$, pip) but with $N_3P_3Cl_5(NPPh_3)$ to give the geminal product, $N_3P_3Cl_4R(NPPh_3)$[10,47].

(*b*) *Alcoholysis and Thioalcoholysis*

The reactions of chlorocyclophosphazenes with alcohols, phenols and thiols have also been studied in some detail[9]. Alcohols and phenols react mainly by nongeminal replacement of chlorine atoms. The separation of pure chloroalkoxy (aryloxy) isomers is not easy, particularly when small, straight-chain alcohols are employed. Recently, Schmutz and Allcock[42] have prepared and separated nine trifluoroethoxy derivatives, $N_3P_3Cl_{6-n}(OCH_2CF_3)_n$ ($n = 1$-6) by gas liquid chromatography. Several *n*-butoxy derivatives, $N_3P_3Cl_{6-n}(OBu_n)_n$ ($n = 1, 2, 3, 6$) have also been reported[43].

Thiols react exclusively by a geminal mechanism which has been rationalised in terms of 'hard' and 'soft' acid/base interactions[44,45]. Chlorothioalkoxycyclophosphazenes are obtained by using a large excess of a sodium thiolate and usually only an even number of chlorine atoms is replaced (Equation 3).

$$N_3P_3Cl_6 + NaSR \xrightarrow{\text{organic solvent}} N_3P_3Cl_{6-n}(SR)_n \quad n = 2,4,6 \qquad (3)$$

$$N_3P_3F_6 + NaSEt \longrightarrow N_3P_3F_{6-n}(SEt)_n \quad n = 1\text{–}5 \qquad (4)$$

The hexafluoride reacts with sodium ethanethiolate to give mono, *bis*, *tris*, tetrakis and pentakis ethylthio derivatives but again only compounds with geminal structures are obtained (Equation 4). Derivatives containing -SAr groups in nongeminal dispositions can be obtained by an alternative route[47] (Equation 5).

$$cis\text{-}N_3P_3Cl_2(NMe_2)_4 + NaSR \longrightarrow cis\text{-}N_3P_3(SR)_2(NMe_2)_4 \qquad (5)$$
$$R = p\text{-}C_6H_4Me, Ph$$

Although fully substituted thio-esters, $N_3P_3(SR)_6$, can be prepared[44], the analogous compounds in the tetramer series were not obtained : the only reaction products were geminal tetra-substituted derivatives, $N_4P_4Cl_4(SR)_4$, and organic disulphides, R_2S_2. Cleavage of the tetrameric ring occurred under more forcing reaction conditions[45].

An interesting feature of the chemistry of alkoxycyclophosphazenes $[NP(OR)_2]_{3,4}$ is their ability to rearrange when heated alone[48] (Fig. 6) or in the presence of an alkyl halide[49]. Thio-analogues do not undergo this reaction.

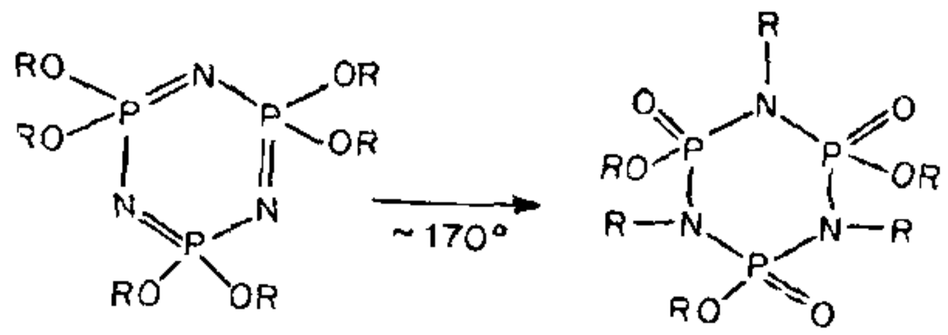


FIG. 6. Alkoxyphosphazene-oxophosphazene rearrangement.

(*c*) *Reactions with Organometallic Reagents*

The hexachloride, $N_3P_3Cl_6$, reacts with phenyl magnesium bromide in diethyl ether to give small quantities of the cyclic hexaphenyl derivative, $N_3P_3Ph_6$ and acyclic phenylated phosphazenyl magnesium complexes from which hydrogen halide derivatives, *e.g.*, $Ph_3P{=}N{-}PPh_2{=}NH{\cdot}HX$, ($X = Cl$, Br) can be isolated[50]. Similar reaction with the octachloride, $N_4P_4Cl_8$, gives two cyclic products[51a], $N_4P_4Cl_4Ph_4$, which have the structures shown in Fig. 7. The ring contraction can

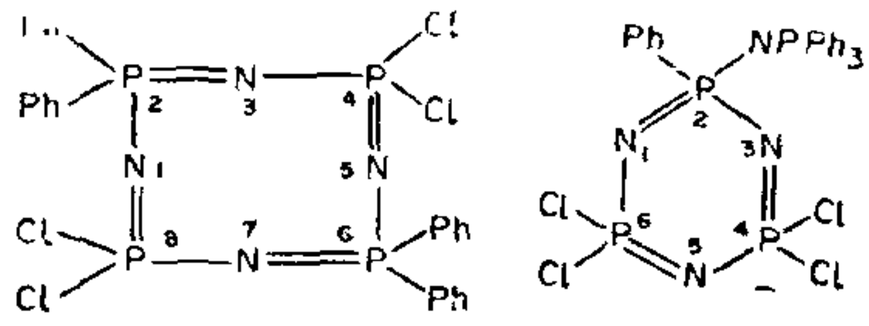


FIG. 7. Products of the reaction of $N_4P_4Cl_8$ with PhMgBr.

be explained by a mechanism involving cleavage of the tetrameric ring followed by cyclisation of

the phenylated acyclic species, $Ph_3P=N-P(PhCl)[=N-PPh_2]_2=N\text{–}Mg\text{–}Br$.

Phenyl lithium reacts with the hexachloride, $N_3P_3Cl_6$ in diethyl ether to give soluble acyclic polymers of low molecular weight[51b]. The latter possess unreacted phosphorus chlorine bonds and chain branching is evident. The analogous reaction[52] with the hexafluoride, $N_3P_3F_6$, gives the cyclic products, $N_3P_3F_{6-n}Ph_n$, $n = 1, 2$ (three isomers); nongeminal structures are predominant. The reaction of the octafluoride, $N_4P_4F_8$, with methyl lithium gives methyl, dimethyl, trimethyl, tetramethyl and octamethyl derivatives. The replacement pattern observed is predominantly geminal and has been interpreted in terms of a π-inductive effect[53].

Non-geminal phenylated chlorocyclophosphazenes can be prepared by a cyclisation reaction[54] (Equation 6). Stereoisomers have been obtained for both trimer and tetramer in this reaction.

$$n\,PhPCl_4 + n\,NH_4Cl \xrightarrow[HCl]{} (PhNPCl)_n + 4n\,HCl \qquad n=3,4 \qquad (5)$$

Bromophenyl derivatives can be prepared similarly[55].

The Friedel Crafts reaction[56] of the hexachloride, $N_3P_3Cl_6$, with boiling benzene in the presence of aluminium chloride gives the geminal diphenyl derivative, $N_3P_3Cl_4Ph_2$. The tetra- and hexa-phenyl derivatives can be obtained under more forcing conditions. Similar reactions with aminochlorocyclophosphazenes, $N_3P_3Cl_{6-n}R_n$ ($R = NMe_2$[57], Pip[58]) indicate that phenylation proceeds most readily at a $\equiv PClR$ group (Fig. 8).

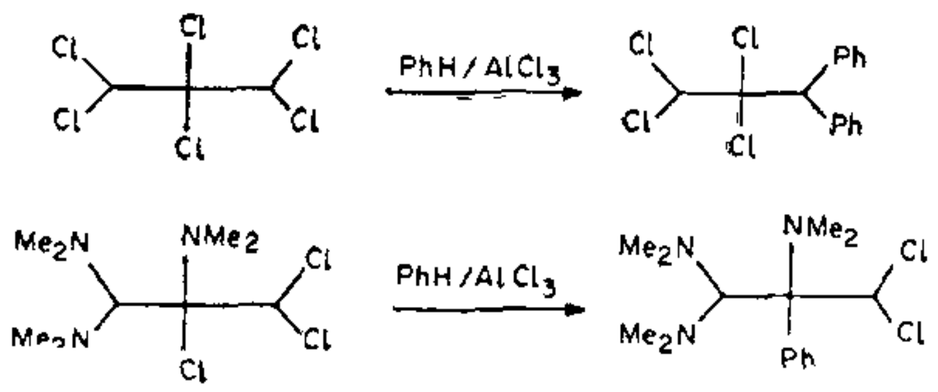


FIG. 8. Friedel Crafts reactions of chlorocyclotriphosphazatrienes.

(d) Complex and Adduct Formation

Cyclophosphazenes form many coordination complexes, Lewis acid-base adducts and crystalline inclusion compounds. Allcock[1,8] has reviewed these aspects in detail and two recent papers[59] summarise the subsequent work.

PHYSICAL METHODS OF STRUCTURE DETERMINATION

(a) Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance spectroscopy has emerged as the most powerful tool for elucidating the molecular structures of cyclophosphazene derivatives in solution. The ^1H nmr spectra of some aminochlorocyclophosphazenes illustrate this aspect very clearly. Keat, Ray and Shaw found that *cis-*, *trans-* and geminal-$N_3P_3Cl_3(NMe_2)_3$ isomers can be distinguished by the observation of one, two and three dimethylamino doublets (coupling to phosphorus) respectively in their proton nmr spectra[60]. In addition, the magnitude of the apparent proton-phosphorus coupling constant $^3J^*$ (P–H) helps to distinguish a geminally substituted group ($\equiv PR_2$) from a nongeminal one ($\equiv PClR$) (R = NHMe, NHEt, NMe_2 NMePh). In general, the magnitude of the geminal coupling constant is 3–5 Hz smaller than that of the non geminal one.

In many of the proton spectra of cyclophosphazene derivatives, additional lines or broad humps appear amongst the signals expected from first-order considerations. This phenomenon has usually been termed long range "virtual coupling" and its origin has been discussed elsewhere[61]. Although "virtual coupling" can create problems in the interpretation of many spectra, the extent of "virtual coupling" (or its absence) can sometimes yield structural information (*viz.*, geminal-$N_4P_4Ph_4(NMe_2)_4$ isomers)[62].

The spectra of three chloro-N-methylanilinocyclotetraphosphazatetraenes are shown in Fig. 9 (N-methyl signals only) and illustrate the general points noted above.

The development of sophisticated instrumental facilities and the application of broad band ^1H decoupling have greatly improved the quality and usefulness of the ^{31}P NMR spectra of cyclophosphazenes. The spectra of the three isomers (I, II and III) (Fig. 10) would be of the types AB_2C, $AA'BB'$ and A_2B_2 respectively and are readily identified although if $J/\Delta\nu$ becomes relatively small, it may not be easy to differentiate $AA'BB'$ and A_2B_2 spin systems. The two bis-*t*-butylaminohexachlorocyclotetraphosphazatetraenes, $N_4P_4(NHBu^t)_2Cl_6$, mp 171° and 128°, give rise to symmetrical A_2B_2 and $AA'BB'$ ^{31}P spectra indicating that these isomers have a 2, 6- and 2, 4-disposition of *t*-butylamino groups[39]. The ^{31}P spectra of many amino-derivatives of $N_3P_3Cl_6$ and some selected tetrameric derivatives have been analysed recently and some trends in ^{31}P chemical shifts and P–N–P coupling constants have been discerned[63].

(b) Infrared Spectroscopy

Infrared studies of cyclophosphazene derivatives have not proved to be as useful as NMR spectroscopy in determining the disposition of substituent groups, although in some cases it is possible to distinguish geminal and non-geminal isomers in the trimeric system[64]. IR spectroscopy can provide

some information on the nature of skeletal bonding. The spectra of cyclophosphazene derivatives exhibit a broad absorption band in the range 1150–1450 cm^{-1} which has been attributed[65] to a degenerate ring *stretching vibration*, $\nu(P=N)$. Typical values are shown in Table II and illustrate the importance of ring size, electronegativity, steric effects, etc.

sequent to protonation). It is believed[13] that in Type I compounds, the N–P bond of the triphenylphosphazenyl group is more or less parallel to the local NPN ring segment whereas in Type II compounds, *it is approximately perpendicular*. Two recent crystallographic studies[67,68] provide examples of Type I and Type II conformations.

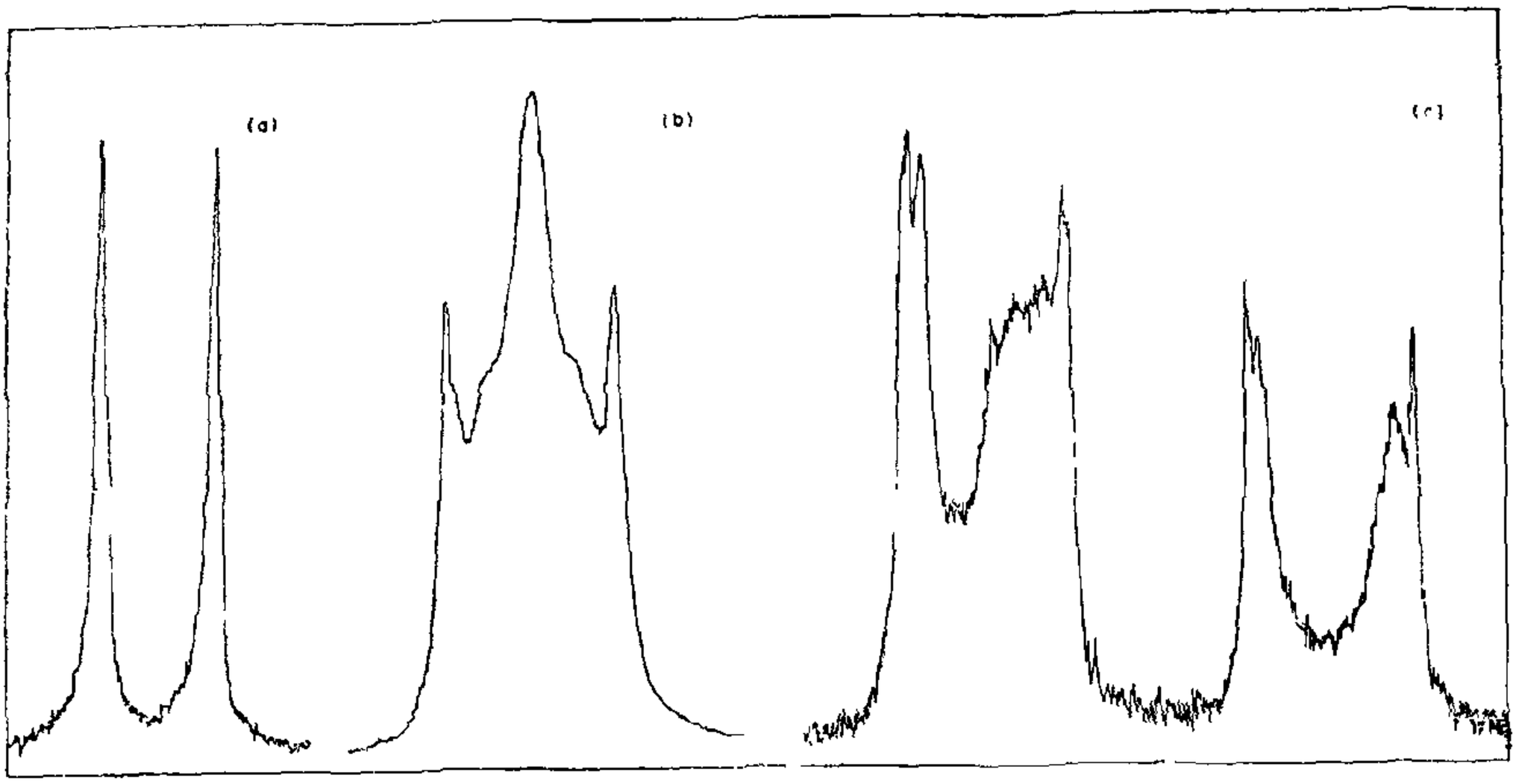
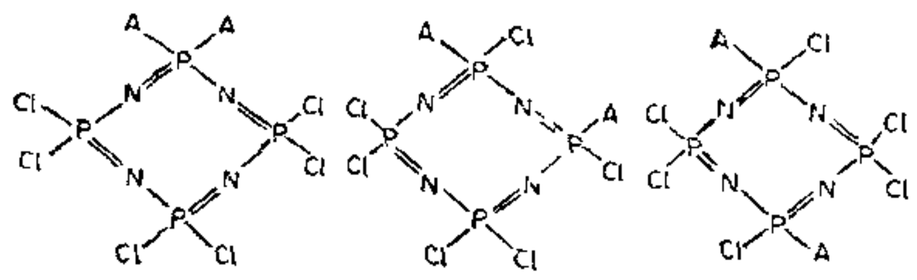


FIG. 9. ^1H NMR spectra ($CDCl_3$, 100 MHz) of (*a*) 2, 2, 6, 6,-$N_4P_4Cl_4(NMePh)_4$. (*b*) 2, 4, 6, 8,-$N_4P_4Cl_4(NMePh)_4$. (*c*) 2, 2, 4, 6, 8-$N_4P_4Cl_5(NMePh)_3$ (Frequency separations on the same scale); (NMe signals only).



I II III

FIG. 10. Isomeric configurations of $N_4P_4Cl_6A_2$.

(c) *Basicity Measurements*

The technique of basicity measurements[9,13] developed by Feakins, Shaw and coworkers can be used to distinguish *geminal* and *nongeminal* tris- and tetrakis-amino isomers. There is now considerable evidence (including X-ray structures of two protonated compounds)[66] for protonation at a ring nitrogen atom in most cyclophosphazenes. Basicity measurements of cyclophosphazenes containing a triphenylphosphazenyl substituent[41] indicate that protonation can take place *either* at a ring nitrogen atom (Type I) or at the nitrogen atom of the phosphazenyl substituent (Type II), probably because of a difference in conformation of the *triphenylphosphazenyl group* (*prior/or* sub-

TABLE II

Ring P = N vibrational frequencies in cyclophosphazene (cm^{-1})[a]

R	$N_3P_3R_6$	$N_4P_4R_8$
F	1297	1435
Cl	1218	1315
Br	1175	1275
Me	1180	1220[c]
Ph	1190	1213
NH_2	1170	1240
NHEt	1180[b]	1250[b]
$NHBu^n$	1195	1260
$NHC_2H_{11}^n$	1190	1265
NMe_2	1195	1265

a Reference 6, p. 197.
b Reference 39, *c* Reference 110.

(d) X-ray Crystallography

The structures of a large number of cyclophosphazene derivatives have been determined by X-ray diffraction. Corbridge has reviwed this work recently[68]. The equality of ring P–N bond lengths in homogeneously substituted cyclophosphazene derivatives and the shortness of these bonds compared with the accepted value (1·77 Å) for P–N single bond have provided good evidence for some kind of π–interaction involving nitrogen and phosphorous atoms. The X-ray crystallographic data have also provided strong evidence for the presence of π–bonding between phosphorus and exocyclic groups such as $-NMe_2$ or $-OR$. It has been pointed out that the ring P–N bond lengths in a derivative $N_3P_3X_6$ decrease with increasing electronegativity of X. This is also accompanied by a decrease in the angle subtended by the exocyclic substituents at phosphorus, an increase in the ring NPN angle and a decrease in the ring PNP angle. In a heterogeneously substituted compound, the ring P–N bonds are of different lengths. Thus in the geminal diphenyl compound, $N_3P_3Cl_4Ph_2$, there are three different P–N bond lengths[70] with mean values 1·555, 1·578 and 1·615 Å. The analogous fluoro compound[71] and the geminal tetraphenyl[72] compound, $N_3P_3Cl_2Ph_4$, also show three types of ring P–N bonds. These differences can be attributed to greater *d*-orbital contractions at the phosphorus atom bearing the most electronegative substituents leading to a strrengthening of the skeletal π–bonding. The X-ray crystal structures of cyclotetraphosphazatetraenes show that the eight membered P–N ring can adopt one of several different conformations (Table III).

(e) Other Techniques

Nuclear Quardrupole Resonance spectra (^{35}Cl) of some chlorocyclophosphazene derivatives have been reported. A linear relationship has been observed between NQR frequency and P–Cl bond length[73]. Positional isomers may be distinguished by this technique but unambiguous structural assignments to geometrical isomers are not generally possible[74].

It should be possible, in principle, to distinguish geometrical isomers from dipole moment measurements as demonstrated for the *cis* and *trans* isomers of $N_3P_3Ph_3Br_3$[56], $N_3P_3Cl_4(NMe_2)_2$ and $N_3P_3Cl_3(NMe_2)_3$[75]. Such measurements are unsuitable for the identification of chloro (trifluroethoxy) cyclotriphosphazene isomers. This difficulty is presumably due to the neglect of the atom polarizability term and the possible deviations of the ring from planarity[42].

Bonding in Cyclophosphazenes

Bonding in cyclophosphazenes (characterised by a formally unsaturated system) has intrigued a number of investigators. Craig and Paddock have proposed a $d\pi - p\pi$ model in which extensive delocalization of π electrons occurs over the entire ring[76]. The same authors also postulated[77] a π-bonding interaction in the ring plane involving the lone pair of electrons on the skeletal nitrogen atom (π'-bonding). Dewar *et al.* have put forward an alternative model in which π-electron interaction is confined to three-centre P–N–P islands[78]. Detailed quantum mechanical calculations[79] and Faraday effect studies[80] on cyclophosphazenes tend to support the latter model. Doggett[81] has suggested that the two models do not differ fundamentally but only in the choice of parameters. Labarre, Perkins and their respèctive coworkers have pointed out that *trans*-annular phosphorus—phosphorus bonding may contribute significantly to the stability of the six-membered P–N ring system[82].

Phosphazene High-Polymers

(a) Cyclolinear and Cyclomatrix Polymers

There are three basic approaches to the synthesis of phosphazene based polymers leading to the formation of cyclolinear, cross-linked cyclomatrix and linear type polyphosphazenes[1,8,11,12,83]. The first two types utilize the high thermal stability of cyclotri- and cyclotetraphosphazene rings by linking them through bifunctional organic groups. The formation of cyclolinear polymers is illustrated in Fig. 11.

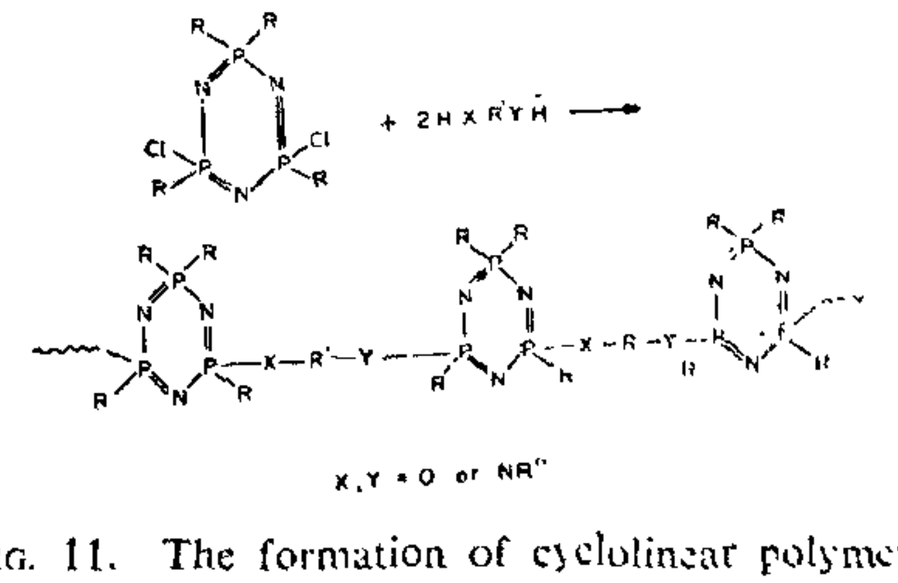


Fig. 11. The formation of cyclolinear polymers.

Cyclophosphazene substrates with more than two active groups (usually halogen) may also react with diols or diamines to give cyclomatrix polymers (Fig. 12). The extensive cross-linking usually found in such polymers is responsible for their insolubility and high melting points.

(b) Linear Polymers

Chlorocyclophosphazenes, $(NPCl_2)_{3,4}$, on heating in the bulk state under non-rigorous experimental

TABLE III

X-ray structural data for cyclotetraphosphazatetraenes

Compound	Ring shape	Mean ring P–N bond length (Å)	Mean ring P–N–P angle (°)	Mean ring N–P–N angle (°)	Ref
$N_4P_4F_8$	Planar	1·51	120·3	119·4	91
$N_4P_4Cl_8$ (K)	Intermediate Boat-saddle	1·57	131·3	121·2	92
$N_4P_4Cl_8$ (T)	Chair	1·56	135·6	120·5	93
$N_4P_4Br_8$	Intermediate Boat-saddle	1·575	131 0	120·1	94
$N_4P_4F_6Me_2$ (2, 2, 4, 4, 6, 6 : 8, 8)	Saddle	1·525	145·0	121·5	95
$N_4P_4F_4Me_4$ (2, 2, 4, 4 : 6, 6, 8, 8)	Saddle	1·56	134·6	121·7	96
$N_4P_4F_4(NMe_2)_4$ 2-*cis*-4-*trans*-6-*trans*-8	Chair	1·55	139 5	121·3	97
$N_4P_4F_4(NMe_2)_4$ 2-*trans*-4-*cis*-6-*trans*-8	Saddle	1·557	134·7	122 0	98
$N_4P_4Cl_4Ph_4$ (2, 2, 4, 4 : 6, 6, 8, 8)	Saddle	1·553, 1·591	128·8–135·4	120 0	99
$N_4P_4Cl_4Ph_4$ 2-*cis*-4-*cis*-6-*cis*-8	Irregular crown	1·57	137 5	121 0	100
$N_4P_4Cl_4Ph_4$ 2-*cis*-4-*trans*-6-*trans*-8	Chair	1·57	135 4	120 0	101
$N_4P_4Cl_6(NMe)_2$ 2-*trans*-6	Chair	1·569	134·2	120 6	102
$N_4P_4Cl_4(NMe_2)_4$ 2-*cis*-4-*trans*-6-*trans*-8	Hybrid crown-saddle	1·556	136 8	121·1	103
$N_4P_4Cl_2(NMe_2)_6$ 2-*trans*-6	Chair	1·57	135 4	120 7	104
$N_4P_4Me_8$	Hybrid boat-saddle	1·60	131 9	119 8	105
$N_4P_4Ph_8$	Hybrid boat-saddle	1·59	127·8	119·8	106
$N_4P_4(OMe)_8$	Saddle	1·57	132 0	121·0	107
$N_4P_4(NMe_2)_8$	Hybrid boat-saddle	1·58	133·0	120·0	108
$N_4P_4(NCS)_8$	Chair	1·543	140 0	120·2	109

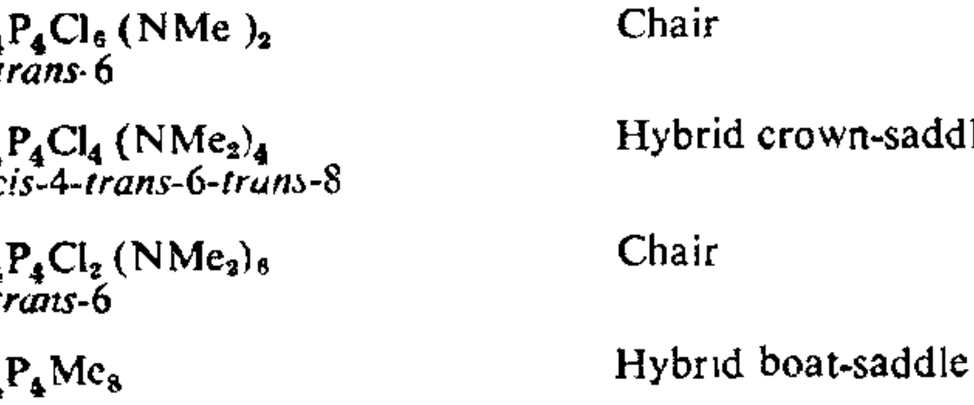


FIG. 12. A phosphazene cyclomatrix polymer.

conditions give an elastomeric polymer called "inorganic rubber" which is highly cross-linked and insoluble in organic solvents. This polymer is hydrolytically unstable and becomes brittle on prolonged exposure to moist air Efforts to overcome this problem by replacement of chlorine atoms with hydrolytically stable organic groups have been unsuccessful because the reactions are very slow and complete replacement of chlorine atoms inside the cross-linked matrix is virtually

impossible. Allcock and coworkers[84] have shown that "poly (dichlorophosphazene)" free from cross-links can be obtained by carrying out the polymerization of $N_3P_3Cl_6$ under carefully controlled conditions and by limiting the conversion to ~ 70%. They have recently established that traces of water, function as a powerful catalyst whereas PCl_5 is a powerful inhibitor for the polymerization reaction[85]. The mechanism of the polymerization reaction is not yet fully understood.

Poly (dichlorophosphazene), free from cross-linking[1,85], is soluble in organic solvents and reacts readily and completely with a wide variety of nucleophilic reagents (Fig. 13). Copolymers and terpolymers

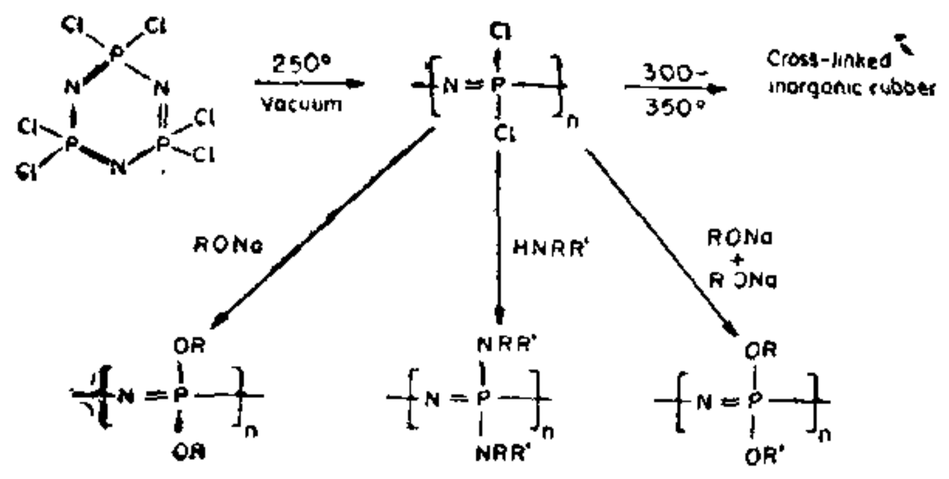


FIG. 13. The reactions of poly (dichlorophosphazene).

containing different substituents can be prepared[11]. Generally the homopolymers are flexible film-forming thermoplastics whereas the copolymers are elastomeric in nature. Polymers with different physical characteristics can be obtained by varying the substituents. Table IV summarises the properties of some selected linear polyphosphazenes. One of the most attractive features of the phosphazene linear polymeric system is the prospect of designing polymers for specific applications by the judicious choice of suitable substituent groups.

Potential Applications

Hexa-ammonocyclotriphosphazatriene, $N_3P_3(NH_2)_6$, is found to be a good fertilizer for certain crops as it can supply both nitrogen and phosphorus in a concentrated form[86]. The aziridinocyclophosphazenes have been used as chemosterilant insecticides (under the trade name "apholate")[87]. The alkoxycyclophosphazenes, in particular the *n*-propoxy derivatives, are excellent flame retardants for viscose rayon[88]. Phosphazene cyclomatrix polymers are amenable to conventional "curing" processes. In has been suggested that they may find use in high temperature aerospace applications and as heat-resistant coatings for electrical components[89]. Linear polyphosphazenes containing fluoroalkoxy groups are resistant to acids, alkales, and hydrocarbon fuels and retain their flexibility over a wide temperature range. They are being developed for fabricating lip seals, gaskets and fuel hoses serviceable at low temperatures (— 40° C)[11]. Poly (alkoxyphosphazene) derivatives have good flame retarding properties and may find extensive use as textile impregnating agents and fire resistant foams. Polyphosphazenes also show promise as body implantation plastics[90].

TABLE IV

Properties of some linear polyphosphazenes[1,11]

Compound	Molecular weight	Intrinsic viscosity dl/g	T_g (° C)[c]	Solubility[d]
$(NPCl_2)_n$	$1–2 \times 10^6$ [a,e]	2·40	—63	Benzene
$[NP(OMe)_2]_n$	6,40,000[a]	1·22	—76	Methanol
$[NP(OCH_2CF_3)]_n$	1,700,000[a]	2·70	—66	Ketones
$[NP(OCH_2CF_3)(OCH_2C_3F_7)]_n$	$>6 \times 10^6$ [a]	2·40	—77	Freons
$[NP(OPh)_2]_n$	3,700,000[a]	2·70	5·5	THF
$[NP(OC_6H_4Cl\text{-}m)]_n$	$3·89 \times 10^6$ [a]	..	—21	Chloroform
$[NP(NHPh)_2]_n$	1,650,000[a]	1·44	91	Benzene
$[NP(NEt_2)(NHMe)]_n$	230,000[b]	1·41	8	THF

a Light scattering.
b Ultracentrifugation.
c By differential thermal analysis or differential scanning calorimetry.
d At room temperature.
e Not very accurate owing to slow cross-linking in solution.

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1. Allcock, H. R., *Phosphorus-Nitrogen Compounds*, Academic Press, New York, 1972.
2. Liebig, J., *Ann. Chem.*, 1834, 11, 139.
3. Stokes, H. N., *Amer. Chem. J.*, 1897, 19, 782.
4. Stokes, H. N., *Ibid*, 1895, 17, 275; *Ibid*, 1896, 18, 629.
5. Shaw, R. A., Fitzsimmons, B. W. and Smith, B. C., *Chem. Rev.*, 1962, 62, 247.
6. Paddock, N. L., *Quart. Rev., Chem. Soc.*, 1964, 18, 168.
7. Sowerby, D. B., "Phosphonitriles", In: *MTP International Review of Science*, Inorganic Chemistry Series, I, 1972, 2, 117.
8. Allcock, H. R., *Chem. Rev.*, 1972, 72, 315.
9. Keat, R. and Shaw, R. A., In: *Organic Phosphorus Compounds*, Kosolapoff, G. M. and Maier, L (Ed.), Interscience, New York, 1973, Vol. 6, 833.
10. Goldschmidt, J. M. E., "The Cyclophosphazenes", In: *Analytical Chemistry of Phosphorus Compounds*, Halmann, M., (Ed.), Wiley—Interscience, New York, 1972, 13, 523.
11. Singler, R. E., Schneider, N. S. and Hagnauer, G. L., *Polymer Eng. and Sci.*, 1975, 15, 321.
12. Kireev, V. V., Kolesnikov, G. S. and Raigorodskii, I. M., *Russ. Chem. Rev.* (Eng. Transl.), 1969, 38, 667.
13. Shaw, R. A., *Z. Naturforsch.* (In press).
14. Keat, R. and Shaw, R. A., *J. Chem. Soc.*, 1965, p. 2215.
15. Lehr, W. and Rosswag, N., *Z. anorg. Chem.*, 1974, 406, 221.
16. Keat, R. and Shaw, R. A., *J. Chem. Soc.* (*A*), 1966, p. 908.
17. Goldschmidt, J. M. E. and Licht, E., *J. Chem. Soc. Dalton*, 1972, p. 728; *Ibid.*, 1972, p. 732.
18. Feistel, G. R. and Moeller, T., *J. Inorg. Nucl. Chem.*, 1967, 29, 2731; Lehr, W., *Z. anorg. Chem.*, 1967, 356, 18.
19. Das, S. K., Keat, R., Shaw, R. A. and Smith, B. C., *J. Chem. Soc.*, 1965, p. 5032.
20. Scherer, O. J. and Kuhn, N., *Chem. Ber.*, 1974, 107, 2123; Niecke, E. and Flick, W., *Angew. Chem. Internat. Edn.* 1974, 13, 134; Pohl, S., Niecke, E. and Krebs, B., *Angew. Chem. Internat. Edn.*, 1975, 14, 261.
21. Das, R., Shaw, R. A., Smith, B. C. and Woods, M., *J. Chem. Soc. Dalton*, 1973, p. 709.
22. Das, S. K., Keat, R., Shaw, R. A. and Smith, B. C., *J. Chem. Soc.* (*A*), 1966, p. 1677.
23. Clare, P. and Sowerby, D. B., *J. Inorg. Nucl. Chem.*, 1974, 36, 729.
24. Hasan, M., Shaw, R. A. and Woods, M., *J. Chem. Soc. Dalton*, 1975, p. 2202.
25. Roesky, H. W. and Niecke, E., *Inorg. Nucl. Chem. Letters*, 1968, 4, 463.
26. Glemser, O., Niecke, E. and Roesky, H. W., *J. Chem. Soc. Chem. Comm.*, 1969, p. 282.
27. Chivers, T., Oakley, R. T. and Paddock, N. L., *J. Chem. Soc.* (*A*), 1970, p. 2324.
28. Green, B. and Sowerby, D. B., *J. Chem Soc.* (*A*), 1970, p. 987.
29. —, — and Clare, P., *Ibid.*, 1971, p. 3487.
30. Stahlberg, R. and Steger, E., *J. Inorg. Nucl. Chem.*, 1966, 28, 684; *Ibid.*, 1967, 29, 961.
31. Nabi, S. N., Shaw, R. A. and Stratton, C., *J. Chem. Soc. Dalton*, 1975, p. 588.
32. Millington, D. and Sowerby, D. B., *Ibid*, 1972, p. 2035.
33. — and —, *Ibid.*, 1974, p. 1070.
34. — and —, *Ibid.*, 1973, p. 2649.
35. Keat, R., Krishnamurthy, S. S., Sau, A. C., Shaw, R. A., Vasudeva Murthy, A. R. and Woods, M., *Ibid.* (In press).
36. —, —, —, —, Sudheendra Rao, M. N., Vasudeva Murthy, A. R. and Woods, M., *Z. Naturforsch.*, 1974, 29 B, 701.
37. Cameron T. S., Mannan, Kh., Krishnamurthy, S. S., Sau, A. C., Shaw, R. A., Vasudeva Murthy, A. R. and Woods, M., *J. Chem. Soc. Chem. Comm*, 1975, p. 975.
38. Keat, R. and Shaw, R. A., *Angew. Chem. Internat. Edn.*, 1968, 7, 212.
39. Sau, A. C., *Ph.D. Thesis*, I.I.Sc., Bangalore, 1976.
40. Biddlestone, M. and Shaw, R. A., *J. Chem. Soc. Dalton*, 1973, p. 2740.
41. —, Nabi, S. N. and Shaw, R. A., *Ibid.*, 1975, p. 2634.
42. Schmutz, J. L. and Allcock, H. R., *Inorg. Chem.*, 1975, 10, 2433.
43. Zeleneva, T. P., Antonov, I. V. and Stepanov, H. I., *J. Gen. Chem.* (U.S.S.R.), 1973, 43, 1000.
44. Carroll, A. P. and Shaw, R. A., *J. Chem. Soc.* (*A*), 1966, p. 914.
45. —, —, and Woods, M., *J. Chem. Soc. Dalton*, 1973, p. 2736.
46. Niecke, E., Glemser, O. and Roesky, H. W., *Z. Naturforsch.*, 1969, 24 B, 1187.
47. Woods, M., *Ph.D. Thesis*, London University, 1969.
48. Fitzsimmons, B. W., Hewlett, C. and Shaw, R. A., *J. Chem. Soc.*, 1964, p. 4459.
49 —, — and —. *Ibid.*, 1965, p. 7432.
50. Biddlestone, M. and Shaw, R. A., *J. Chem. Soc* (*A*), 1969, p. 178; *J. Chem. Soc. Dalton*, 1975, p. 2527.
51. (*a*) — and —, *Ibid.*, 1970, p. 1750;
(*b*) — and —, *Phosphorus*, 1973, 3, 95.
52. Allen, C. W. and Moeller, T., *Inorg. Chem.*, 1968, 7, 2177.
53. Ranganathan, T. N., Todd, S. M. and Paddock, N. L., *Ibid.*, 1973, 12, 317.
54. Grushkin, B., Sanchez, M. G. and Rice, R. G., *Ibid.*, 1964, 3, 623; Humiec, F. S. and Bezman, I. I., *J. Amer. Chem. Soc.*, 1961, 83, 2210; Shaw, R. A. and Stratton, C., *J. Chem. Soc.*, 1962, p. 5004.

55. Moeller, T. and Nannelli, P., *Inorg. Chem.*, 1963, 2, 659 ; *Ibid.*, 1963, 2, 896.
56. Acock, K. G., Shaw, R. A. and Wells, F. B. G., *J. Chem. Soc.*, 1964, p. 121 ; McBee, E. T., Okishara, K. and Morton, C. J., *Inorg. Chem.*, 1965, 4, 1672.
57. Das, S. K., Shaw, R. A. and Smith, B. C., *J. Chem. Soc. Dalton*, 1973, p. 1883.
58. —, — and —, *Ibid.*, 1974, p. 1610.
59 Searle, H. T., Dyson, J., Ranganathan, T. N. and Paddock, N. L., *Ibid.*, 1975, p. 203 ; Calhoun, H. P., Paddock, N. L. and Wingfield, J. N., *Can. J. Chem.*, 1975, 53, 1765.
60. Keat, R., Ray, S. K. and Shaw, R. A., *J. Chem. Soc.*, 1965, p. 7193.
61. Finer, E. G., Harris, R. K., Bond. M. R., Keat, R. and Shaw, R. A., *J. Molecular Spectroscopy*, 1970, 33, 72 ; Finer, E. G., *Ibid.*, 1967, 23, 104.
62. Biddlestone, M., Bullen, G. J., Dann, P. E., Krishnamurthy, S. S., Shaw, R. A. and Woods, M., *Phosphorus*, 1973, 3, 179.
63. Keat, R., Shaw, R. A. and Woods, M., *J. Chem. Soc. Dalton* (In press).
64. Chapman, A. C., Paine, D. H., Searle, H. T., Smith, D. R. and White, R. F. M., *J. Chem. Soc.*, 1961, p. 1768 ; Stahlberg, R. and Steger, E., *Spectrochim. Acta*, 1967, 23 A, 2005.
65. —, and Paddock, N. L., *J. Chem. Soc.*, 1962, p. 635.
66. Mani, N. V. and Wagner, A. J., *Acta Cryst.*, 1971, 27 B, 51 ; Allcock, H. R., Bissell, E. and Shawl, E. T., *Inorg. Chem.*, 1973, 12, 2963.
67. Biddlestone, M., Bullen, G. J., Dann, P. E. and Shaw, R. A., *J. Chem. Soc. Chem. Comm.*, 1974, p. 56.
68. Babu, S., Cameron, T. S., Krishnamurthy, S. S., Manohar, H. and Shaw, R. A., *Z. Naturforsch.* (In press).
69. Corbridge, D. E. C., *The Structural Chemistry of Phosphorus*, Elsevier, Amsterdam, 1974, p. 333.
70. Mani, N. V., Ahmed, F. R. and Barnes, W. H., *Acta Cryst.*, 1965, 19, 693.
71. Allen, C. W., Paul, I. C. and Moeller, T., *J. Amer. Chem. Soc.*, 1967, 89, 6361.
72. Mani, N. V., Ahmed, F. R. and Barnes, W. H., *Acta Cryst.*, 1966, 21, 375.
73. Keat, R., Porte. A. L., Tong, D. A. and Shaw, R. A., *J. Chem. Soc. Dalton*, 1972, p. 1648.
74. Dalgleish, W H, Keat. R., Porte. A. L., Tong, D. A., Hasan, M. and Shaw, R. A., *Ibid.*, 1975, p. 309.
75. Koopman, H., Spruit, F. J., Van Deursen, F. and Backkers, J., *Rec. Trav. Chim.*, 1965, 84, 341.
76. Craig. D. P. and Paddock, N. L., *Nature*, 1958, 181. 1052.
77. — and —, *J. Chem. Soc.*, 1962, p. 4118.
78. Dewar, M. J. S., Lucken, E. A. C. and Whitehead, M. A., *Ibid.*, 1960, p. 2423.
79. Faucher, J.-P., Devanneaux, J., Leibovici, C. and Labarre, J. F., *J. Molecular Struct.*, 1971, 10, 439 ; Faucher, J.-P., Labarre, J. F. and Shaw, R. A., *Ibid.*, 1975, 25, 109.
80. Faucher, J. P., Glemser, O., Labarre, J.-F. and Shaw. R. A., *CR Acad. Sci. Paris*, 1974, 279 C, 441.
81. Doggett, G., *J. Chem. Soc., Faradey* II, 1972, p. 2075.
82. Armstrong, D. R., Longmuir, G. H. and Perkins, P. G., *J. Chem. Soc. Chem. Comm.*, 1972, p. 464 ; Faucher, J.-P. and Labarre, J.-F., *Phosphorus*, 1974, 3, 265.
83. Allcock, H. R., *Chem. in Britain*, 1974, p. 118.
84. — and Kugel, R. L., *J. Amer. Chem. Soc.*, 1965, 87, 4216 ; Allcock, H. R., Kugel, R. L. and Valan, K. J., *Inorg. Chem.*, 1966, 5, 1709.
85. —, Gardner, J. E. and Smeltz, K. M., *Macromolecules*, 1975, 8, 36.
86. Wakefield, Z. T., Allen, S. E., McCullough, J. F., Sheridan, R. C. and Kohle, J. J., *J. Agr. Food Chem.*, 1971, 19, 99.
87. *Chem. Week*, 1963, Dec. 14, 83.
88. Godfrey, L. E. A. and Schappel, J. W., *Ind. Eng. Chem. Prod. Res. Develop.*, 1970, 9, 426.
89. *Reference*, 1, p. 377.
90. *Chem. and Eng. News*, 1975, June 16, 22.
91. McGeachin, H. M. and Tromans, F. R., *J. Chem. Soc.*, 1961, p. 4777.
92. Hazekamp, R., Migchelsen. T. and Vos, A., *Acta Cryst.*, 1962, 15, 539.
93. Wagner, A. J. and Vos, A., *Ibid.*, 1968, 24 B, 707.
94. Zoer, H. and Wagner, A. J., *Ibid.*, 1972, 28 B, 252.
95. Marsch, W. C. and Trotter, J., *J. Chem. Soc. (A)*, 1971, p. 573.
96. Marsh, W. C. and Trotter, J., *Ibid.*, 1971, p. 569.
97. Millington, D., King, T. J. and Sowerby, D. B., *J. Chem. Soc. Dalton*, 1973, p. 396.
98. Begley, M. J., Millington, D., King, T. J. and Sowerby, D. B., *Ibid.*, 1974, p. 1162.
99. Bullen, G. J. and Dann, P. E., *Acta Cryst.*, 1974, 30 B, 2861.
100. — and Tucker, P. E., *J. Chem. Soc. Dalton*, 1972, p. 1651.
101. Burr, A. H., Carlise, C. H. and Bullen, G. J., *Ibid.*, 1974, p. 1659.
102. Bullen, G. J. and Dann, P. E., *Ibid.*, 1973, p. 1453.
103. — and Tucker. P. A., *Ibid.*, 1972, p. 2437.
104. — and Dann, P. E., *Ibid.*, 1974, p. 705.
105. Dougill, M. W., *J. Chem. Soc.*, 1961, p. 5471.
106. Begley, M. J., Sowerby, D. B. and Tillet, R. J., *J. Chem. Soc. Dalton*, 1974, p. 2527.
107. Ansell, G. B. and Bullen, G. J., *J. Chem. Soc. (A)*, 1971, p. 2498.
108. Bullen. G. J., *J. Chem. Soc.*, 1962, p. 3193.
109. Faught, J. B., *Can. J. Chem.*, 1972. 50, 1315.
110. Searle, H. T., *Proc. Chem. Soc.*, 1959, p. 7.