CYCLOPHOSPHAZENES

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I. Introduction

Cyclophosphazenes occupy a prominent place among inorganic heterocyclic compounds. They contain an $+N{=}PX_2+$ repeating unit

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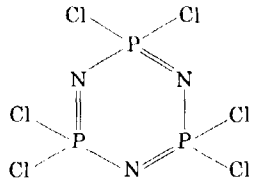
in a valence-unsaturated skeleton. Two typical members are the cyclic trimer (**1**) and the cyclic tetramer (**2**). The chlorocyclophosphazene, $N_3P_3Cl_6$ (**1**), was first isolated by Liebig (*285*) in 1834. The cyclic structure for this compound was originally suggested by Stokes (*426*) who also identified the higher homologs, $(NPCl_2)_{4-7}$ (*429*) in the closing years of the nineteenth century. Research activity in the chemistry of cyclophosphazenes remained quiescent until the mid-1950s, but recently various aspects of this topic have received considerable attention. The major developments are largely due to the advent of new and improved synthetic techniques and powerful instrumental methods of structure determination, the emergence and evolution of quantum theory of chemical binding, and the growing interest in the potential of inorganic polymers.



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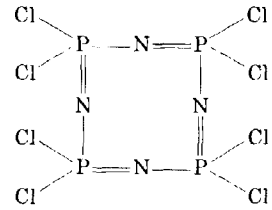

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Early comprehensive reviews of phosphazene chemistry by Audrieth, Steinman, and Toy (*43*), Gribova and Ban-Yuan' (*214*), Paddock and Searle (*337*), Shaw, Fitzsimmons, and Smith (*401*), and Schmulbach (*388*) were followed by reviews on specific aspects, such as preparative methods (*402*), structure and bonding (*336*, *407*), and high polymers (*254*). Some excellent books dealing with the chemistry of cyclophosphazenes (*13*, *21*, *216*) have also appeared. The recent reviews of Allcock (*22*), Sowerby (*418*), and Keat and Shaw (*249*) describe the developments up to 1970–1971. Several short articles on this topic have also appeared from time to time (*264*, *403*, *404*, *408*). Phosphazene chemistry is now reviewed annually (*251*).

During the past 5 years considerable progress has occurred in the structural chemistry of phosphazenes, substitution reactions, reaction mechanisms, synthetic procedures, and phosphazene high polymers. In this review, a broad outline of cyclophosphazene chemistry will be presented with an emphasis on the most recent work. The chemistry of phosphazene high polymers has been reviewed comprehensively in recent years (*21*, *22*, *24*, *412*), and this topic will be mentioned only briefly. Cyclophosphazanes (*21*, *216*) and phosphorines containing skeletal heteroatoms other than nitrogen and phosphorus (*21*, *249*) are outside the scope of this review.

There has not been any general agreement on the nomenclature of phosphorus–nitrogen ring systems (*21*), but there is a discernible trend in recent literature toward adopting the more systematic "phosphazene" notation [originally proposed by Shaw, Fitzsimmons, and Smith (*401*)] in place of the older "phosphonitrilic" terminology. The phosphazene notation will be employed in this chapter. The full systematic name for cyclophosphazene derivatives is often very lengthy and suitable abbreviations will be used unless an exact description is essential. Compounds **1** and **2** will be referred to as the trimeric chloride and the tetrameric chloride, respectively, and their substituted derivatives will be described as cyclotriphosphazenes and cyclotetraphosphazenes, respectively.

II. Synthetic Routes to Cyclophosphazenes

There are a number of methods for the direct synthesis of chloro- and bromocyclophosphazenes and their alkyl and aryl derivatives. Other derivatives have invariably been prepared by replacement reactions of the halogenocyclophosphazene precursors. In this section, ring-forming reactions will be discussed and the following section will deal with the substitution reactions.

A. Reaction of Ammonium Halides with Halophosphoranes

Cyclophosphazenes are conveniently prepared by the reaction of halophosphoranes with ammonium halides,

$$n\mathrm{R'RPX_3} + n\mathrm{NH_4X} \rightarrow (\mathrm{NPRR'})_n + 4n\mathrm{HX} \qquad (1)$$

(R,R' = Cl, Br, or organic group; X = Cl, Br)

usually in boiling organic solvents such as *sym*-tetrachloroethane or chlorobenzene (*21*, *71*, *126*, *331*, *345*, *350*, *352*). In general, the cyclic trimer and tetramer are formed in greatest yields, although small amounts of higher oligomeric species can be isolated from the reactions of PCl_5 and PBr_5 with their corresponding ammonium halides. Mixed chlorobromocyclophosphazene derivatives are obtained by the use of an appropriate mixture of phosphorus halide and ammonium halide (*129*, *361*, *370*):

$$3\mathrm{PCl_3} + 3\mathrm{Br_2} + 3\mathrm{NH_4Br} \xrightarrow[110°]{sym\text{-}\mathrm{C_2H_2Cl_4}} \mathrm{N_3P_3Cl_2Br_4} + 12\mathrm{HX} \qquad (2)$$

The reaction of phosphorus pentachloride with ammonium chloride is tantalizingly complex and has been the subject of numerous investigations (*21*). Cyclic oligomers and linear products are formed, and

these can be separated by exploiting the poor solubility of the latter in petroleum. The separation of individual cyclic compounds, $(NPCl_2)_{3-8}$, can be accomplished by a combination of selective extraction with sulfuric acid, fractional crystallization, and fractional distillation techniques (*286*). The yields of cyclic products can be maximized by carrying out the reaction under high dilution and by the use of finely divided ammonium chloride (*52*, *53*, *165*, *257*) and surfactants (*288*). Various metal halides are found to catalyze the reaction (*208*, *232*, *339*, *340*, *351*, *457*). Addition of phosphoryl chloride not only reduces the reaction time but also affords improved yields of cyclic compounds (*162*, *165*). The reaction can also be carried out in the solid state (*423*, *456*, *457*). In the presence of 4 moles of pyridine, the reaction is reported to terminate within minutes and produce cyclic products in 65% yield (*458*).

The mechanism of ammonolysis of phosphorus pentachloride is not completely understood. It has been shown (*164*) that it proceeds in two steps. Initially, the intermediate $[Cl_3PNPCl_3]^+[PCl_6]^-$ is formed, probably via PCl_4NH_2 and PCl_3NH (*48*, *380*). In the second step, this intermediate reacts with NH_4Cl to produce cationic phosphazene chains that undergo cyclization by the elimination of $[PCl_4]^+$ (*164*, *256*).

For the preparation of bromocyclophosphazenes the use of a mixture of PBr_3 and bromine in place of PBr_5 and addition of bromine to the reaction mixture at frequent intervals leads to improved yields of $(NPBr_2)_{3,4}$ (*128*, *130*, *236*, *451*). 1,2-Dibromoethane is preferred as the reaction solvent because tiny quantities of chlorobromocyclophosphazenes are formed in *sym*-tetrachloroethane (*130*). The preparation of bromocyclophosphazenes is difficult and tedious, and as yet no effective catalyst has been found to reduce the lengthy reaction periods (15–20 days). Fluorocyclophosphazenes cannot be prepared by this route but are obtained by metathetical reactions (Section III,D). Attempts to prepare iodophosphazenes have been unsuccessful (*249*).

B. Other Ring-Forming Reactions

1. Thermal Decomposition of Azidophosphines

The reaction of organohalophosphine with sodium or lithium azide

$$R_2PCl + MN_3 \rightarrow [R_2PN_3] \rightarrow (R_2PN)_3 + N_2 \quad (M = Na, Li, Me_3Si) \tag{3}$$

or Me_3SiN_3 gives organoazidophosphine which on heating eliminates nitrogen to form cyclo- or poly-phosphazenes (*21*). The azidophosphine

intermediates are often highly explosive and careful handling is required (*431*). In many cases it is not necessary to isolate the intermediate (*226*). An equimolar mixture of Ph_2PCl and $PhPCl_2$ yields a nongeminal hexaphenylcyclotetraphosphazenederivative, $N_4P_4Ph_6Cl_2$ (*226*). This synthetic route has not found widespread use because the reactions often lead to high yields of polymeric materials.

2. *Cyclization of Linear Phosphazenes*

The air-stable linear phosphazene (**3**) prepared from the reaction of Ph_2PCl_3 with ammonia in chloroform (*57*, *225*) has proved a useful intermediate for cyclization reactions (Fig. 1) (*379*). A noteworthy feature of this approach is the synthesis of cyclophosphazenes in which hydrogen is attached to phosphorus (*56*, *378*, *382*). The only other route (*383*) reported for the preparation of a hydridocyclophosphazene derivative is

$$3(Me_2N)_2PCl + 3NH_3 \xrightarrow[72^\circ]{Et_2O} N_3P_3H_3(NMe_2)_3 + 3Me_2NH_2Cl \qquad (4)$$

An optically active cyclotriphosphazene has been synthesized by the treatment of the optically active phosphazene salt $[(Ph)(C_6H_4Me)(NH_2)P{\cdots}N{\cdots}P(NH_2)(C_6H_4Me)(Ph)]^+Cl^-$ with PCl_5 (*391*).

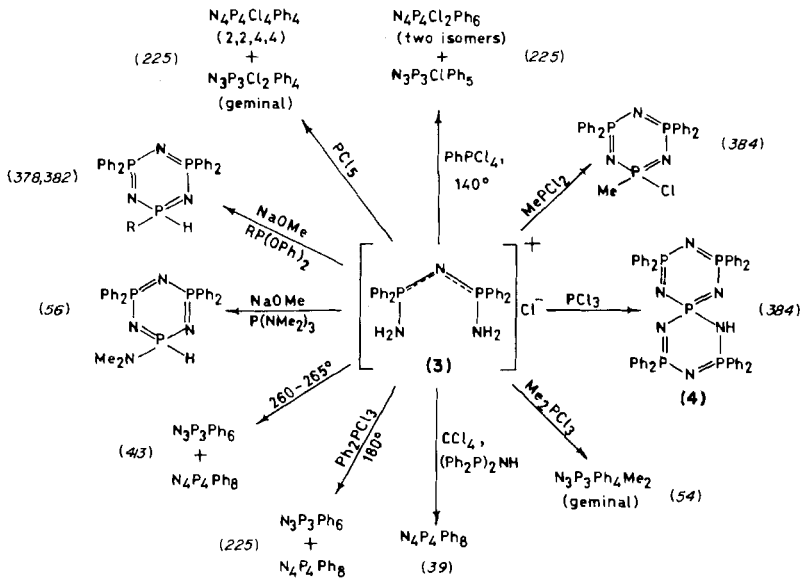


FIG. 1. Formation of cyclophosphazenes from the linear intermediate (**3**).

3. *Miscellaneous Syntheses*

Aminodichlorophosphoranes undergo dehydrohalogenation in the presence of a tertiary amine (*21*, *435*) to yield cyclophosphazenes:

$$R_2PCl_2NH_2 \xrightarrow[Et_3N]{2HCl} (R_2PN)_n \tag{5}$$

Diarylchlorophosphines can be transformed to cyclophosphazenes by treatment with chloramine (*194*) or with ammonia and chloramine (*413*). Fully substituted cyclotriphosphazenes result from the cyclocondensation of bis(diphenylphosphino)amine and aminoiminodiorganylphosphoranes or their hydrohalides with CCl_4 in the presence of triethylamine (*39*). Dehydrohalogenation of fluorocyclodiphosphazanes in the presence of CsF leads to the formation of cyclotriphosphazene derivatives (*393*). An anomalous Kirsanov reaction [Eq. (6)] giving rise to $(NPCl_2)_{3,4}$ has been reported (*198*):

$$[PhCH_2NH_3]^+Cl^- + PCl_5 \rightarrow \tfrac{1}{n}(NPCl_2)_n + PhCH_2Cl + 3HCl \quad (n = 3, 4) \tag{6}$$

Fluorocyclophosphazenes can be directly prepared by the reaction of NF_3 or of CF_3SF_5 with N_5P_3 (*293*) or by the reaction of NF_3 with P_4S_3 and P_4S_{10} (*430*) at elevated temperatures, but these routes are unsuitable for routine synthesis.

III. Halogen Replacement Reactions of Cyclophosphazenes

Halogenocyclophosphazenes undergo nucleophilic and electrophilic reactions that involve the replacement of halogen atoms by a variety of groups. In these reactions the ring is retained in most but not in all cases. Aminolysis reactions, particularly those of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ (**1**), constitute a major area of investigation in cyclophosphazene chemistry. Alcoholysis, phenolysis, thioalcoholysis, metathetical replacement, and many other reactions have been studied to a lesser extent. The halogen replacement reactions of cyclophosphazenes normally give rise to complex mixture of products. The detection, isolation, and purification of derivatives with different degrees of halogen replacement and of different isomers have been greatly facilitated by the advent and adaptation of column, thin-layer and gas-liquid chromatographic techniques. Goldschmidt (*203*) has critically reviewed the various separation techniques commonly employed in cyclophosphazene chemistry.

A. Aminolysis Reactions

1. Reaction Pattern and Mechanism

Halogenocyclophosphazenes react with ammonia and primary and secondary amines to form an ammono- or amino-substituted cyclophosphazene:

$$N_3P_3X_6 + 2n\text{NHR}_2 \rightarrow N_3P_3X_{6-n}(\text{NR}_2)_n + n\text{R}_2\text{NH.HX} \quad (7)$$

(X = F, Cl, Br; R = H, alkyl, aryl)

Two equivalents of amine or ammonia are needed to replace one halogen atom: the amine also functions as the hydrogen halide acceptor. In some cases the aminophosphazene formed in the reaction has a base strength comparable to that of the parent amine, and it is subsequently isolated as a hydrohalide adduct (see Section IV, A,2). A tertiary base, such as triethylamine or pyridine, can also be employed as a hydrogen halide acceptor.

The halogen replacement may proceed either by a geminal or a nongeminal pathway. Figure 2 illustrates these two patterns with

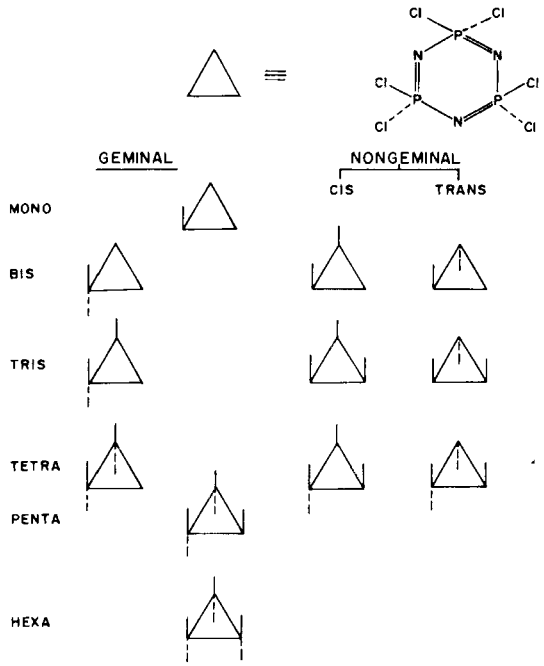


FIG. 2. Geminal and nongeminal modes of replacement of chlorine atoms from $N_3P_3Cl_6$ (1). (The corners of the triangle represent phosphorus atoms; the full and broken lines denote the orientation of the substituents above and below the N_3P_3 ring plane, respectively; chlorine and ring nitrogen atoms are not shown.)

respect to the trimeric (six-membered ring) system. In the nongeminal mode of replacement, the possibility of cis–trans isomerism at the bis, tris, and tetrakis stages of replacement must be considered. This type of isomerism depends on the orientation of the substituents with respect to the P –N ring plane. Similar replacement patterns can be envisaged for the cyclotetraphosphazene system and the possible products containing chlorine and another substituent are shown in Fig. 3.

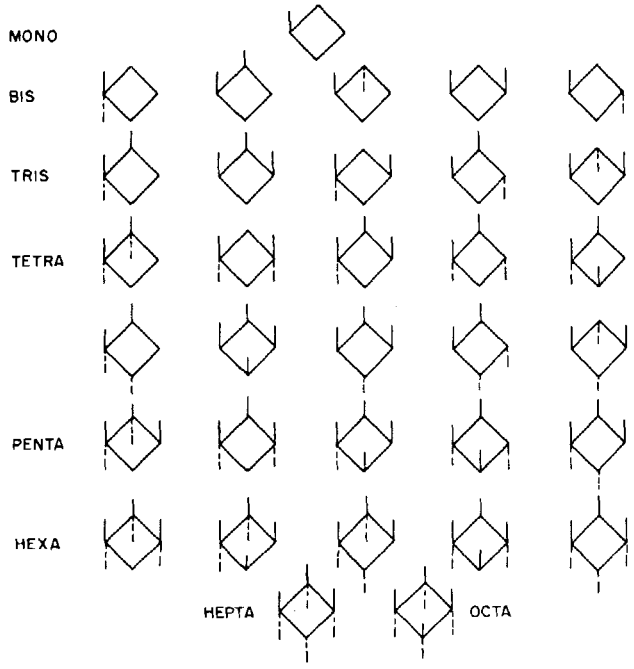


FIG. 3. Possible substitution products from $N_4P_4Cl_8$ (**2**). (The corners of the square represent phosphorus atoms; the full and broken lines denote the orientation of substituents above and below the N_4P_4 ring plane, respectively; chlorine and ring nitrogen atoms are not shown.)

The wealth of data available on the aminolysis reactions of $N_3P_3Cl_6$ (**1**) presents a complex picture (Table I). A comprehensive mechanistic theory explaining all the observations has not yet emerged. Some of the variations in the aminolysis patterns are undoubtedly due to a lack of awareness on the part of earlier investigators of the importance of reaction variables, such as temperature, solvent, and stoichiometry of reagents in determining the relative proportions of isomers formed.

TABLE I

PRODUCTS OF THE REACTIONS OF $N_3P_3Cl_6$ WITH VARIOUS AMINES[a,b]

Amine	$N_3P_3Cl_4R_2$			$N_3P_3Cl_3R_3$			$N_3P_3Cl_2R_4$			Ref.
	gem	*cis*	*trans*	*gem*	*cis*	*trans*	*gem*	*cis*	*trans*	
Ammonia[c]	+	–	–		–	–	–	–	–	*181, 278, 426*
Methylamine	+	+	+	–	–	–	–	–	–	*201, 279, 312, 317*
Ethylamine		(+)[g]	+	–	~~(+)~~		+	–	–	*139*
Isopropylamine	+	+	+	–	–	–	+	–	–	*139, 142, 285a*
t-Butylamine	+	–	–	–	–	–	+	–	–	*140*
Aniline	+	~~(+)~~		(+)	–	–	+	–	–	*74, 153, 277*
Benzylamine	+	–	+	–	–	–	+	–	–	*221*
Dimethylamine[d]	(+)	+	+	+	(+)	+	–	+	(+)	*47, 121, 201, 211, 214, 240, 358*
Diethylamine	–	+	+	+	+	+	–	(+)	+	*283, 453*
N-Methylaniline[e]	–	+	+	+	+	–	–	–	–	*266*
Aziridine[d]	+	–	–	+	–	–	+	–	–	*259, 268, 334, 357*
Piperidine[f]	–	+	+	+	(+)[g]	+	–	+	–	*244, 267, 272*
Pyrrolidine[f]	–	+	+	+	+	+	–	+	+	*270, 271*
Morpholine[f]	–	+	+	–	~~ + ~~		–	~~	+ ~~	*269, 319*

[a] Isolated in good/modest yield, +; isolated in trace quantities, (+); the structure of the geometrical isomer (cis or trans) is not known with certainty, ~~ + ~~ and ~~(+)~~; not isolated, –.

[b] In all cases mono-($N_3P_3Cl_5R$) and hexakis derivative ($N_3P_3R_6$) were isolated.

[c] The mono compound ($N_3P_3Cl_5NH_2$) is isolated by the reaction of $N_3P_3Cl_4(NH_2)_2$ with hydrogen chloride.

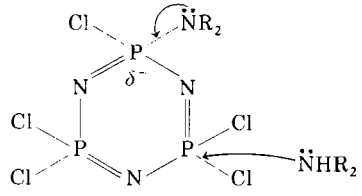
[d] Pentakis derivative ($N_3P_3ClR_5$) isolated.

[e] A mixed derivative, $N_3P_3Cl_2(NHPh)(NMePh)_3$, is also isolated.

[f] Pentakis derivative ($N_3P_3ClR_5$) reported but not authenticated.

[g] Obtained by the isomerization of the geometrical isomer.

Most secondary amines react predominantly by the nongeminal mode of replacement. Assumption of an $S_N2(P)$ mechanism (*228*) would be consistent with this observation. The phosphorus atom carrying the amino substituent acquires a partial negative charge because of



(5)

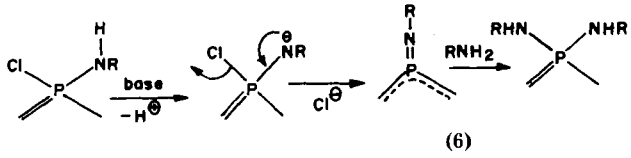
the flow of lone pair of electrons on the adjacent exocyclic nitrogen atom (**5**) and, thus, nucleophilic attack at the same phosphorus atom

is retarded. In the reactions of dimethylamine, diethylamine and piperidine, the trans-bis isomer is always formed in greater yield than the cis isomer. A "cis effect" has been postulated to explain this observation (*244*). An alternative hypothesis considers a substituent solvating effect and has been suggested on the basis of kinetic data (*204*, *205*). A notable feature of the *N*-methylaniline system is the formation of both *cis*- and *trans*-bis-*N*-methylanilino isomers, $N_3P_3Cl_4(NMePh)_2$, in comparable amounts (*266*). In the diethylamine system, the proportion of the cis-bis isomer relative to the trans compound is higher than in the dimethylamine system even though diethylamine is bulkier than dimethylamine (*453*). It appears that at the bis stage of chlorine replacement, the steric effect of the nucleophile exerts only a minor role in determining the structure of the products. The nucleophilic displacement reactions of tetracoordinate phosphorus(V) compounds by an S_N2-type process are accompanied by both retention and inversion of configuration (*228*). With the weaker nucleophiles, such as *N*-methylaniline and possibly dibenzylamine (*221*), the cis effect may be of little significance and there is no preferential formation of the trans isomer.

At the tris stage of chlorine replacement, the trans-nongeminal isomer predominates, although the relative proportion of the geminal compound can be significantly enhanced in aromatic reaction media (*408*). The use of methyl cyanide as solvent for the secondary amine reactions results in almost exclusive formation of nongeminal tris compounds: the trans isomer usually predominates over the cis isomer. However, in the *N*-methylaniline–$N_3P_3Cl_6$ system, the geminal tris compound is the major product even in methyl cyanide. This reaction is considerably retarded after the bis stage of chlorine replacement and unreacted amine is invariably present in the reaction medium. The unreacted *N*-methylaniline could fulfill the role of an aromatic reaction medium, and thereby favor the formation of the geminal tris compound even in methyl cyanide (*266*). It is believed that aromatic solvents preferentially solvate a $\equiv PCl_2$ group rather than a $\equiv PClR$ group and thus facilitate attack at the latter (*408*).

At the tetra stage of chlorine replacement, the structure of the nongeminal derivatives appears to be dominated by steric considerations. In the dimethylamine and diethylamine systems, the major tetrakis isomer has a cis and a trans structure, respectively, and only minor quantities of the other stereoisomer are obtained in each case (*211*, *240*, *283*, *453*). The exceptional behavior of aziridine in yielding exclusively geminal compounds (*259*, *268*, *334*, *357*) is difficult to explain, but its small size and weak nucleophilic and basic character may be contributing factors (*21*, *408*).

The reactions of $N_3P_3Cl_6$ with bulky secondary amines [dicyclohexylamine (*358*) and dibenzylamine (*221*)] as well as with the nitrogenous base 2,2,2-triphenylmonophosphazene, $HN{=}PPh_3$ (*66*), terminate at the bis stage of chlorine replacement. The increasing difficulty of substitution has been attributed mainly to steric factors (*358*), although strong electron supply from the $NPPh_3$ group could deactivate the ring (*66*).

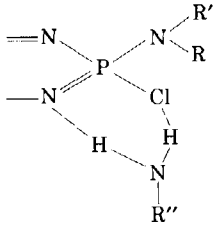


(6)

FIG. 4. Proton abstraction mechanism.

The reactions of $N_3P_3Cl_6$ (**1**) with ammonia and primary amines reveal additional features of interest. Reactive primary amines [methylamine (*279*) and ethylamine (*139*)] afford mainly nongeminal products at the bis stage of chlorine replacement and presumably an $S_N2(P)$ mechanism is involved. The geminal mode is predominant at all stages of the reactions with primary amines that react slowly whether for steric [e.g., *t*-butylamine (*140*)] or for polar reasons [e.g., aniline (*153*)]. Ammonia gives exclusively the geminal bis derivative (*181*, *278*). The geminal replacement occurs also at the later stages of the reactions with the more reactive ethylamine (*139*) and isopropylamine (*142*). The geminal tris* and nongeminal tetrakis derivatives have not been isolated, although substantial amounts of the former must be present as reactive intermediates in the formation of the geminal tetrakisalkylamino derivatives. A proton abstraction mechanism (Fig. 4) has been invoked to explain the geminal pattern observed for ammonia and *t*-butylamine (*140*). This mechanism appears plausible after the recent isolation of a three-coordinate phosphorus(V) compound, $(Me_3Si)_2NP(=NSiMe_3)_2$ (*329*, *348*, *376*), which is clearly of the same type as the "metaphosphorimidate" intermediate (**6**). Shaw and co-workers (*139*) have attempted to rationalize the experimental observations in the reaction of $N_3P_3Cl_6$ with primary amines on the basis of chelated hydrogen bonding. These reactions could involve six-membered, cyclic, hydrogen-bonded complexes (**7**–**9**). The intermediate (**7**), in which a ring nitrogen (most basic site) and a nongeminal

* A notable exception is the isolation of the geminal trisanilino derivative, $N_3P_3Cl_3(NHPh)_3$ (Table I).



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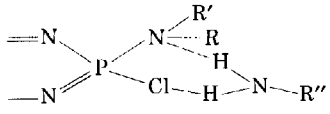

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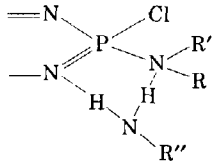


(9)

chlorine atom (most ionic in character) are the sites for chelated hydrogen bonds, is most likely (*408*).

Authentic pentakisaminomonochlorocyclotriphosphazene derivatives, $N_3P_3(NRR')_5Cl$, are rare and derivatives containing only primary amino groups have not been isolated. The strong electron supply from amino groups probably causes a changeover to a relatively facile ionization of the P—Cl bond in an S_N1-type process, with the result that the remaining chlorine atom is replaced rapidly. However, Sowerby and co-workers (*121*, *211*) have isolated the pentakisdimethylaminomonochloro derivative, $N_3P_3(NMe_2)_5Cl$. It is formed in low yield and is readily hydrolyzed by atmospheric moisture. The pentakisaziridino derivative, $N_3P_3(NC_2H_4)_5Cl$ (*259*, *334*), and the mixed amino derivatives, $N_3P_3Cl(NHR)(NMe_2)_4$ (*410*), have also been satisfactorily characterized. A stable monochloropentakisamino compound, $N_3P_3Cl(NMe_2)_4[N(CH_2Ph)_2]$, has been reported recently, and probably steric shielding by the bulky dibenzylamino group contributes to its hydrolytic stability (*221*).

The aminolysis reactions of fluoro- and bromocyclotriphosphazenes have not been investigated systematically. Compound $N_3P_3F_6$ reacts with ammonia (*362*) and with primary (*196*, *327*) and secondary amines (*114*, *196*, *327*, *328*) to give the monoaminopentafluoro derivatives, $N_3P_3RF_5$. Some examples of nongeminal bis- and trisamino derivatives, $N_3P_3R_2F_4$ and $N_3P_3R_3F_3$, are also known (*114*, *197*, *328*). Aminofluoro derivatives are usually prepared by indirect methods (Section III,D). The reaction of $N_3P_3Br_6$ with ammonia has been reported and only the geminal bisammono derivative, $N_3P_3Br_4(NH_2)_2$, has been obtained (*156*). The reaction of $N_3P_3Br_6$ with dimethylamine in diethyl ether (*419*, *421*) gives the derivatives $N_3P_3Br_{6-n}(NMe_2)_n$ [$n = 1$, 2 (three isomers), 3 (gem and trans)]. It has not been possible to isolate a tetrakisdimethylamino derivative $N_3P_3Br_2(NMe_2)_4$, although thin-layer chromatography indicates its presence. The cis-tris derivative, $N_3P_3Br_3(NMe_2)_3$, has been obtained only from a deaminolysis reaction of $N_3P_3(NMe_2)_6$ with hydrogen bromide in boiling xylene (*322*). The halogen replacement pattern observed in the reaction of $N_3P_3Br_6$

with ethylamine is essentially similar to that found in the analogous reaction of $N_3P_3Cl_6$ (*355*).

The aminolysis reactions of halogenocyclotetraphosphazenes, $N_4P_4X_8$, and the higher homologs, $(NPX_2)_n$, have received little attention and only the reactions of the octachloride, $N_4P_4Cl_8$ (**2**), have been investigated in some detail. The paucity of information can be attributed to the practical problems associated with the separation of complex mixture of products and the subsequent difficulties in making unambiguous structural assignments to the pure isomers. The number of isomers that can arise in the tetrameric system is much larger than in the corresponding trimeric system (Figs. 2 and 3). Millington and Sowerby (*304*) have investigated the reaction of $N_4P_4Cl_8$ with dimethylamine in diethyl ether at $-78°$ and isolated the derivatives, $N_4P_4Cl_{8-n}(NMe_2)_n$ [n = 2, 3 (three isomers), 4 (four isomers), 5 (two isomers), 6 and 8]. The reaction proceeds via the nongeminal path; geminal products are formed in poor yields. Evidence is presented for the presence of $N_4P_4Cl(NMe_2)_7$ but the pure compound could not be obtained. $N_4P_4Cl_8$ (**2**) reacts with *N*-methylaniline to yield the partially substituted derivatives, $N_4P_4Cl_{8-n}(NMePh)_n$ [n = 1, 2 (two isomers), 3, 4 (five isomers) and 6]. A notable feature is the isolation of five tetrakis, $N_4P_4Cl_4(NMePh)_4$, and two bis, $N_4P_4Cl_6(NMePh)_2$, derivatives (*355*). The complexity of the system was not apparent to earlier workers (*233*, *235*).

The reactions of $N_4P_4Cl_8$ (**2**) with ethylamine (*265*) and *t*-butylamine (*373*) have many features in common. In the former system, the mono, two bis, a tris, two tetrakis, and the octakis derivatives have been isolated. The *t*-butylamine system gives the mono, two bis, a tris, and the octakis derivatives. In addition, the hydrochloride adduct, $N_4P_4(NHBu^t)_8 \cdot HCl$ has been obtained. The isolation of two distinct bis-*t*-butylaminohexachloro derivatives, $N_4P_4Cl_6(NHBu^t)_2$, m.p. = 171° and 128° [which have been assigned a 2,6- and 2,4-structure, respectively (*373*)] reconciles some of the earlier observations (*359*, *233*). All the chloroamino derivatives have nongeminal structures. This observation may be contrasted with the exclusive formation of geminal products in the reaction of $N_3P_3Cl_6$ with *t*-butylamine (*140*) and the isolation of a geminal tetrakis derivative, $N_3P_3Cl_2(NHEt)_4$, with ethylamine (*139*). The difference in the behavior between the trimeric and tetrameric systems is probably due to the greater reactivity of the tetrameric chloride, $N_4P_4Cl_8$ (**2**) toward nucleophilic reagents (Section III,A,4). Reactions involving higher stoichiometries (particularly 1:10 and 1:12, $N_4P_4Cl_8$/amine) give only copious quantities of sticky resinous materials, and chloroaminocyclotetraphosphazenes could not be detected (*265*). These resins appear to contain cross-linked

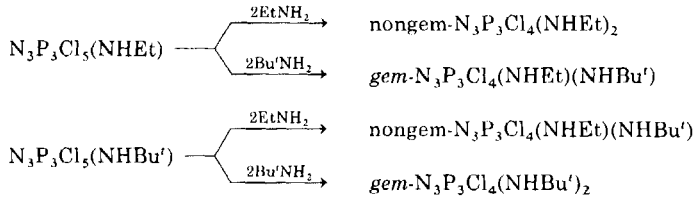
tetrameric units. Resin formation is also a prominent feature of the reactions of primary amines with $N_3P_3Cl_6$ (**1**) (*139*).

The reactions of halogenocyclophosphazenes with diamines is less well-documented. Hydrazine (*335*) and phenylhydrazine (*375*) react with $N_3P_3Cl_6$ (**1**) to yield the hexakis compounds, $N_3P_3(NHNHR)_6$ (R = H,Ph). *o*-Phenylenediamine (*11*) and *N,N'*-dimethylethylenediamine (*117*) form spirocyclic derivatives. The reactions of $N_3P_3Cl_6$ (**1**) with many aliphatic diamines (*49*, *102*, *103*) and amino alcohols (*102*, *450*) have been reported, but the structures of the products have not been established with certainty. With *meta*- and *para*-aromatic diamines (and probably with aliphatic diamines also), ring-coupling reactions occur (*21*). *o*-Aminophenol brings about an unusually rapid degradation of the ring in halogenocyclophosphazenes and certain organocyclophosphazenes (see Section IV,D).

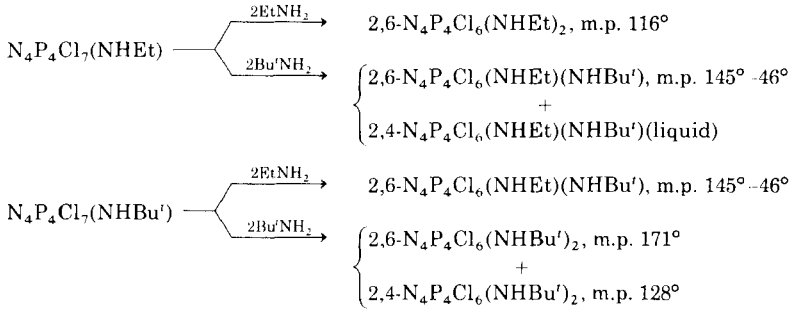
2. *Mixed Amino Derivatives*

A number of mixed aminochloro derivatives of cyclotri- (*221*, *249*, *408*) and cyclotetraphosphazene (*371*) have been prepared in order to assess the roles of substituent and nucleophile in determining the structure of products. The reactions of $N_3P_3Cl_5(NHEt)$ and $N_3P_3Cl_5(NHBu^t)$ with two equivalents of ethylamine yield nongeminal derivatives in both cases, whereas geminal products are obtained in the analogous reactions with two equivalents of *t*-butylamine (Scheme 1) (*247*). The results indicate that the attacking nucleophile determines the course of these aminolysis reactions and not the substituent already present.

There are many examples of this kind of behavior in the trimeric system (*152*, *153*, *249*). It appears that the reactions of the octachloride, $N_4P_4Cl_8$ (**2**), with primary amines are similarly influenced by the nucleophile (Scheme 2) (*373*). The substituent already present in the cyclophosphazene ring can sometimes counteract the influence of the entering nucleophile. At present, the only example of this type is provided by the triphenylphosphazenyl ($-N{=}PPh_3$) substituent in the trimeric system (Scheme 3) (*66*, *323*).

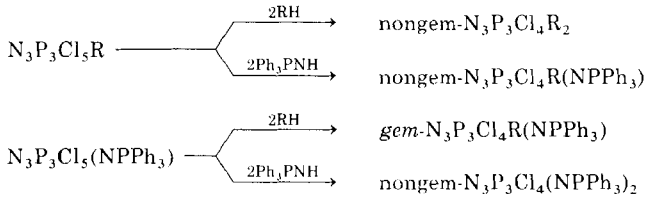


SCHEME 1



The numbers alongside each compound refer to the disposition of amino substituents.

SCHEME 2



[R = NMe_2, NC_5H_{10} (piperidino)]

SCHEME 3

3. *Cis-Trans Isomerizations*

Many nongeminal chlorocyclophosphazenes undergo cis–trans isomerization under a variety of conditions. Amine hydrochlorides (*239*, *242*), aluminum chloride (*241*), hydrogen halides (*320*, *322*), and bases [408] have been used as inverting agents. Isomerization can also be brought about by purely thermal methods (*289*, *408*). Generally, isomerization takes place in boiling chloroform, methyl cyanide, or pyridine. Isomerization apparently does not occur in petroleum ether, benzene, or diethyl ether: the poor solubility of amine hydrochlorides and other inverting agents in these solvents may be a contributing factor. Several mechanisms have been advanced to explain the isomerization (*21*, *289*). It must be emphasized that not all nongeminal compounds undergo isomerization (*241*, *242*, *403*); the reasons for this remain obscure.

Amine hydrochloride is one of the products of aminolysis reactions of chlorocyclophosphazenes and, hence, cis—trans isomerization may occur during aminolysis. Consequently, generalizations on the distribution of nongeminal isomeric products in an aminolysis reaction

(particularly carried out at elevated temperature) and assignment of structures to aminochlorocyclophosphazenes by subsequent substitution steps must be made with caution.

There does not appear to be any reliable information on the isomerization reactions of chloroaminocyclotetraphosphazenes. Lehr (*281*) claims to have observed the isomerization of 2-*trans*-6- and 2-*trans*-4-$N_4P_4(NMe_2)_2Cl_6$ derivatives to the corresponding cis compounds in the presence of pyridinium hydrochloride in chloroform. Details of the experimental procedures and the evidence for the structural assignments have not been stated.

4. *Kinetic Studies*

Studies on the kinetics of aminolysis reactions of halogenocyclophosphazenes are limited (*45*, *101*, *202*, *204*, *205*, *314*). The rate of aminolysis by *n*-propylamine (*314*) follows the order $N_3P_3F_6 < N_3P_3Cl_6 \approx N_4P_4F_8 < N_3P_3Br_6 \approx N_4P_4Cl_8 < N_4P_4Br_8$. Capon *et al.* (*101*) have found that during replacement of the first chlorine atom by diethylamine, $N_4P_4Cl_8$ reacts faster than $N_3P_3Cl_6$ by a factor of 10^2 to 10^3. Several explanations have been suggested for the observed trends in reactivity (*21*, *101*, *314*).

Recently, Goldschmidt and Licht have reported detailed investigations of the kinetics of the reactions of cyclotriphosphazenes with dimethylamine (*202*) and methylamine (*204*) in tetrahydrofuran (THF). A mechanism involving the participation of a solvent (THF) molecule in the transition state has been suggested (*202*). The same authors have also studied the kinetics of the reactions of $N_3P_3Cl_5(NHMe)$ with dimethylamine and that of $N_3P_3Cl_5(NMe_2)$ with methylamine forming the same nongeminal product, $N_3P_3Cl_4(NHMe)(NMe_2)$ (*205*). The rate of the former reaction is almost equal to that of the reaction of $N_3P_3Cl_5(NMe_2)$ with dimethylamine and the rate of the latter reaction roughly equals that of the reaction of $N_3P_3Cl_5(NHMe)$ with methylamine. These results reveal the dominant role of the nucleophile in determining the nature of products of the aminolysis reactions (Section III,A,2).

More extensive kinetic studies on different systems are needed for a better understanding of the mechanism of aminolysis reactions.

5. *Solvent Effects*

The precise role of the solvent in the reactions of halogenocyclophosphazenes with nitrogenous bases is not clearly understood. However, it has been recognized that the yields of specific isomers can be significantly altered in certain reaction media. Some examples in the aminolysis reactions of $N_3P_3Cl_6$ have been mentioned in Section

III,A,1. In the reaction of the octachloride, $N_4P_4Cl_8$, with *t*-butylamine (1:4 stoichiometry), 2,6- and 2,4-$N_4P_4(NHBu^t)_2Cl_6$ are obtained in comparable amounts in benzene as solvent. The 2,4-isomer is formed almost exclusively in chloroform, whereas in methyl cyanide the 2,6-isomer is the major product (*373*). Similar effects are observed in the reactions of $N_4P_4Cl_8$ with *N*-methylaniline (*355*) and benzylamine (*353*). In the tetrameric system, the choice of solvent not only influences the relative yields of isomeric products but sometimes gives rise to an entirely different class of compounds (Fig. 5). Thus, the 2-*trans*-6-bisethylaminohexachloro derivative, $N_4P_4(NHEt)_2Cl_6$, reacts with an excess of dimethylamine or ethylamine in diethyl ether to give the fully substituted cyclotetraphosphazene derivatives, $N_4P_4(NHEt)_2(NRR')_6$ (**10** and **11**) in very high yield (80%). If the reactions are carried out in chloroform, bicyclic compounds, $N_4P_4(NRR')_5(NHEt)(NEt)$ (**12** and **13**) are formed as the major products in addition to the expected compounds (**10** and **11**) (*100*, *372*). A mechanism involving an intramolecular transannular nucleophilic substitution reaction has been suggested for the formation of bicyclic compounds (*371*).

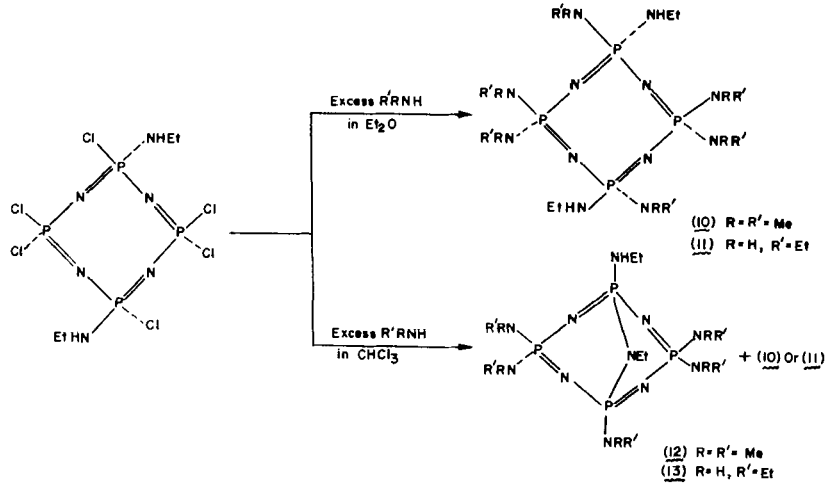


FIG. 5. Formation of bicyclic phosphazenes.

B. HYDROLYSIS

Hydrolysis of halogenocyclophosphazenes occurs rapidly in acidic, basic, and neutral solution. The ease of hydrolysis increases in the order F < Cl < Br. The initial step is the formation of a hydroxyphosphazene that undergoes tautomeric shift to give a hydroxyoxophosphazane (**14**). In an acidic medium, the formation of the hydroxyoxophosphazane (**14**) is quickly followed by ring cleavage and skeletal

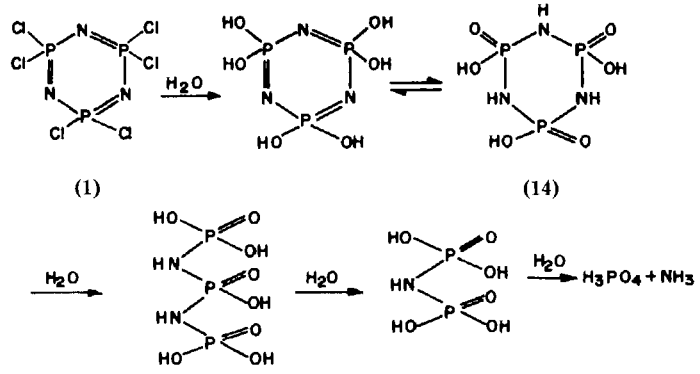
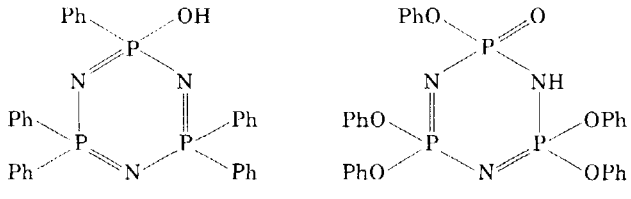


FIG. 6. Hydrolysis of $N_3P_3Cl_6$ (1).

degradation (*427*, *452*) (Fig. 6). In alkaline media, salts of the hydroxyoxophosphazane (**14**) can be isolated (*427*). The octachloride is hydrolyzed (*428*) much more rapidly than $N_3P_3Cl_6$, but the hydroxyoxophosphazane derivative, $(NH)_4P_4P_4(OH)_4$, is much more stable to hydrolysis than **14**. The greater stability of the tetrameric ring is also evident in the different hydrolytic behavior of $N_3P_3(NH_2)_6$ (*159*, *258*) and $N_4P_4(NH_2)_8$ (*159*). The tetrameric fluoride, $N_4P_4F_8$, reacts with methanolic alkali at room temperature, whereas the trimeric fluoride, $N_3P_3F_6$, requires heating in a sealed tube at 100° for comparable hydrolysis (*398*).

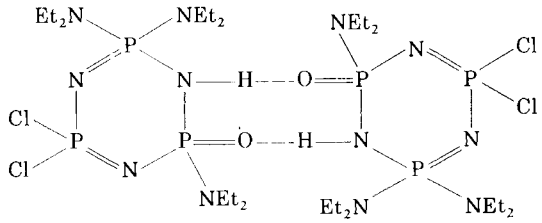
Chlorocyclophosphazenes are rapidly hydrolyzed by aqueous pyridine to give labile pyridine salts (*374*, *424*), and this reaction forms the basis of an analytical method for the determination of chlorine in chlorocyclophosphazenes (*424*).

Hydrolytic degradation of chlorocyclophosphazenes containing phenyl substituents provides valuable structural information (*1*, *62*, *73*, *226*). Pentaphenylchlorocyclotriphosphazene, $N_3P_3ClPh_5$, is hydrolyzed by aqueous pyridine to the hydroxyphosphazene (**15**) which, on treatment with $N_3P_3ClPh_5$ in the presence of pyridine, gives the oxygen-bridged compound $Ph_5N_3P_3—O—P_3N_3Ph_5$ (*389*). By contrast, the hydrolysis of pentaphenoxy derivative, $N_3P_3Cl(OPh)_5$ (*190*),



(15) (16)

yields a phosphaza*diene* (**16**). Recently, a cyclophosphazadiene, $HN_3P_3OCl_2(NEt_2)_3$, has been isolated from the reaction of $N_3P_3Cl_6$ with diethylamine in aqueous benzene (*91*). The compound exists as a hydrogen-bonded dimer (**17**) in the solid state.



(17)

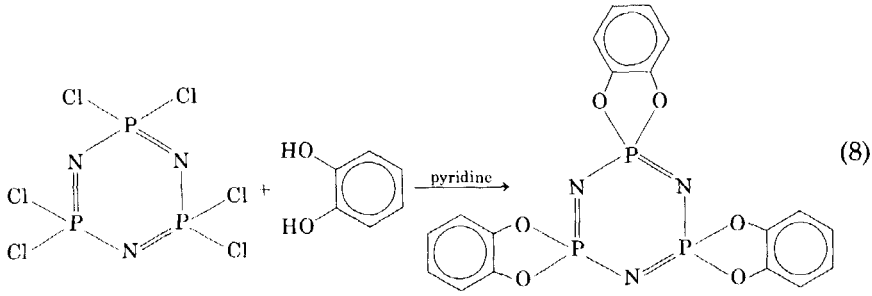
The alkaline hydrolysis of fluoroalkoxy- (*19*), aryloxy-, and spiroarylenedioxycyclophosphazenes (*20*) proceeds by the initial cleavage of the P—O bond. The removal of trifluoroethoxy groups from $[NP(OCH_2CF_3)_2]_3$ occurs by a nongeminal pathway (*19*). Cyclic tetramers undergo hydrolysis 2–4 times faster than the corresponding trimers. An S_N2-type mechanism involving a pentacoordinate trigonal bipyramidal transition state has been postulated. The hydrolysis rate is markedly accelerated by the presence of a five-membered exocyclic ring at phosphorus, probably as a result of release of steric strain (*20*).

C. Reactions with Alkoxides, Aryloxides, and Thiolates

Alkoxy(aryloxy)cyclophosphazene derivatives are usually prepared by the reaction of halogenocyclophosphazenes with alcohols (phenols) in organic solvents in the presence of a hydrogen halide acceptor (pyridine or triethylamine) or by reaction with a metal alkoxide(aryloxide) (*189*). A large number of fully substituted alkoxy(aryloxy)cyclophosphazenes (*21*, *249*) have been prepared by these methods. Only a few mixed halogenoalkoxy(aryloxy) derivatives have been characterized because of difficulties encountered in separation and purification procedures. The *n*-butoxy derivatives, $N_3P_3Cl_{6-n}(OBu^n)_n$ (n = 1, 2, 3, 5) (*416*, *454*, *455*), nongem-$N_3P_3Cl_3(OMe)_3$ (*77*, *185*), $N_3P_3(OMe)_5Cl$ (*77*), and the fluoro derivatives, $N_3P_3F_5(OR)$ (R = Me, Et, Ph) (*326*) have been reported. Recently, Schmutz and Allcock (*392*) have prepared and separated nine trifluoroethoxy derivatives, $N_3P_3Cl_{6-n}(OCH_2CF_3)_n$ (n = 1–6) by gas-liquid chromatography. It has been shown that the replacement of chlorine atoms by fluoroalkoxy (*392*, *399*), phenoxy (*148*), and *p*-bromophenoxy groups (*147*) proceeds

by the nongeminal pathway. This substitution pattern is consistent with an $S_N2(P)$-type mechanism.

The reaction of $N_3P_3Cl_6$ with catechol (*8*), 2,3-dihydroxynaphthalene (*11*), 1,8-dihydroxynaphthalene (*17*), 2,2-dihydroxybiphenyl (*11*), and several aliphatic diols (*21, 399*) gives spirocyclic derivatives. A typical example is

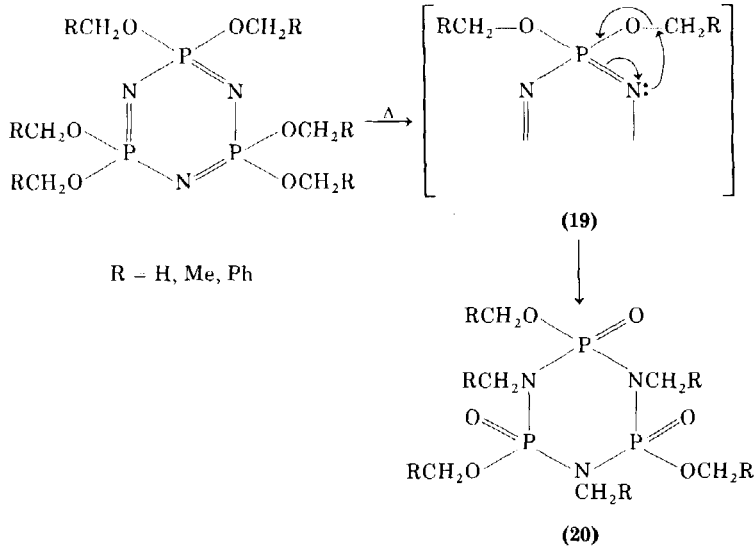


(8)

(1) (18)

The reaction of catechol with $N_4P_4Cl_8$ does not give the tetrameric analog of **18** but leads to the degradation of the phosphazene skeleton (*17*). With diols, such as hydroquinone or resorcinol, cyclolinear and cyclomatrix polymers are formed (*21*).

A notable feature of the chemistry of alkoxycyclophosphazenes is their ability to rearrange to oxocyclophosphazanes (**20**) when heated alone or in the presence of an alkyl halide (*187*). The rearrangement



(19) (20)

reaction is believed to proceed by an inter- or intramolecular attack of a ring nitrogen atom on the α-carbon atom of the alkoxy group (**19**). This mechanism is supported by the observation that phenoxy and trifluoroethoxy derivatives do not undergo this rearrangement.

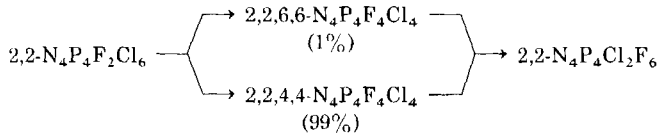
Chlorothioalkoxy(aryloxy)cyclophosphazenes are prepared from the interaction of a chlorocyclophosphazene with an excess of sodium thiolate (*104*, *105*) in an anhydrous organic solvent; the reactions are apparently heterogeneous. The degree of chlorine atom replacement obtained is governed by the steric requirements of the thiolate and by the choice of the reaction solvent. The alkanethio derivatives, $N_3P_3Cl_4(SR)_2$ (R = Et, Pr^n, Bu^n), are prepared in diethyl ether at room temperature, whereas boiling benzene is needed to obtain the isopropylthio derivative, $N_3P_3Cl_4(SPr^i)_2$. The hexa-alkanethio compounds, $N_3P_3(SR)_6$ (R = Et, Pr^n, Bu^n), are obtained in boiling tetrahydrofuran, but the isopropanethiolate reaction terminates at the tetra stage of chlorine replacement (*104*). Recently, the preparation of methanethiolate derivatives, $N_3P_3Cl_{6-n}(SMe)_n$ (n = 1, 2, 3, 4, 6) has been reported (*438*). The replacement of chlorine (*104*, *438*) or fluorine atoms (*324*) by thiolate groups gives rise to products with geminal structures, and compounds containing two, four, or six substituents predominate.

The reactions of the octachloride, $N_4P_4Cl_8$, with sodium thiolates in diethyl ether give only the geminal 2,2,6,6-derivative, $N_4P_4Cl_4(SR)_4$, and organic disulfides (*105*). Attempts to prepare the fully substituted compounds, $N_4P_4(SR)_8$, by utilizing higher reaction temperature were unsuccessful: cleavage of the P—N ring occurred to give phosphorotrithioites, $P(SR)_3$. The exclusive geminal replacement pattern observed for thioalcoholysis reactions of the trimeric and tetrameric chlorides may be a consequence of the high polarizability of a $\equiv$PCl.SR group compared to that of a $\equiv PCl_2$ group (*104*, *105*).

D. Metathetical Exchange Reactions

The most extensively studied metathetical exchange reaction in cyclophosphazene chemistry is the replacement of chlorine by fluorine. A variety of fluorinating agents—sodium fluoride, antimony trifluoride, potassium fluorosulfite, lead fluoride, and silver monofluoride—have been used (*21*, *22*). Fluorocyclophosphazenes, $(NPF_2)_{3-9}$, are conveniently prepared by the reaction of the corresponding chlorocyclophosphazenes with NaF suspended in acetonitrile (*394*) or KSO_2F in nitrobenzene (*107*, *398*). The mixed chloride fluorides, $N_3P_3F_nCl_{6-n}$ (n = 1–3) are formed when $N_3P_3Cl_6$ (**1**) is fluorinated with NaF in nitromethane; higher fluorinated derivatives are obtained in

nitrobenzene (*163*). Tetrameric fluoride chlorides are prepared by the reaction of $N_4P_4Cl_8$ with KSO_2F in the absence of a solvent (*163*). Fluorination of $(NPCl_2)_{3,4}$ by KSO_2F follows a geminal pathway. In the tetrameric system fluorination can take place by two geminal routes, but proceeds almost exclusively by attack on the phosphorus atom closest to that already fluorinated (*163*):



(9)

The reaction of the pentameric chloride, $N_5P_5Cl_{10}$, with KSO_2F has been studied (*343*). The chloride fluorides, $N_5P_5Cl_{10-n}F_n$ (n = 1–9) have been identified mainly by gas-liquid chromatography. Nuclear magnetic resonance spectroscopic data indicate that compounds containing more than one $\equiv$PClF group are not formed. The preferential fluorination of a $\equiv$PFCl group rather than a $\equiv PCl_2$ group indicates that the electron withdrawal by fluorine considerably enhances the electrophilicity of the phosphorus atom to which it is bonded (*163*). The ratio of the rate of replacement of the first fluorine (k_1) to the rate of replacement of a second fluorine (k_2) is ca. 8 for $N_3P_3Cl_6$, ca. 100 for $N_4P_4Cl_8$, and ca. 7 for $N_5P_5Cl_{10}$. This result indicates that the π-inductive effect may also be important in determining the replacement pattern (*163*, *343*).

Compounds $N_3P_3Cl_6$ and $N_3P_3Cl_5(NMe_2)$ do not undergo fluorination with antimony trifluoride in boiling 1,1,2,2-tetrachloroethane (*210*), but the latter can be fluorinated at 200° if no solvent is used and traces of $SbCl_5$ are present (*213*). Paddock and Patmore (*344*) have shown that fluorination of the cyclic chlorophosphazenes, $(NPCl_2)_{3-6}$, with a mixture of SbF_3 and $SbCl_5$ gives reasonable yields of the monofluoro compounds. Mixtures of nongeminal chloride fluorides can also be obtained by this route. A small amount of geminal substitution occurs with $N_6P_6Cl_{12}$.

Fluorination of dimethylaminochlorocyclophosphazenes has been studied by Sowerby and co-workers. Reaction of *cis*- and *trans*-$N_3P_3Cl_4(NMe_2)_2$ with KSO_2F takes place at the $\equiv PCl_2$ site rather that at the $\equiv$PCl(NMe_2) site (*209*). In contrast, the tetrameric derivatives, $N_4P_4Cl_6(NMe_2)_2$ and $N_4P_4Cl_5(NMe_2)_3$, undergo complete fluorination with this reagent to yield pairs of isomeric hexa- and pentafluoro compounds (*309*). Fluorination with SbF_3 proceeds preferentially (although not exclusively) at a $\equiv$PCl(NMe_2) group (*209*, *210*, *307*).

Antimony trifluoride not only replaces chlorine by fluorine in dimethylaminochlorocyclophosphazenes but also brings about deamination (*119*, *213*, *307*, *308*). The reaction of SbF_3 with $N_4P_4(NMe_2)_8$ yields fourteen compounds, $N_4P_4F_n(NMe_2)_{8-n}$ [n = 1, 2 (four isomers), 3 (three isomers), 4 (three isomers), and 5 (three isomers)]. The reaction follows a nongeminal path (*308*). The analogous reaction with $N_3P_3(NMe_2)_6$ takes place much less rapidly (*119*) and provides a route to the pentaaminofluoro derivative, $N_3P_3(NMe_2)_5F$ (*121*). The reactions of SbF_3 are believed to proceed via the initial formation of an adduct by coordination of SbF_3 to the most basic, ring nitrogen atom (*209*, *308*). Replacement of dimethylamino groups by chlorine and bromine can be effected by anhydrous hydrogen chloride and bromide (*114*, *120*, *181*, *197*, *322*). Deamination is not observed with hydrogen iodide but adducts, $N_3P_3(NMe_2)_6 \cdot HI$ and $N_3P_3(NMe_2)_6 \cdot HI_3$, are obtained (*322*).

Chlorocyclophosphazenes, $(NPCl_2)_{3-6}$, undergo exchange reactions with chloride ion. The reaction has been followed by using tetraethylammonium chloride containing radioactive chlorine (*417*). The rate of exchange varies in the order $N_4P_4Cl_8 > N_5P_5Cl_{10} > N_6P_6Cl_{12} > N_3P_3Cl_6$. The overall second-order kinetics suggest a bimolecular mechanism. The slower exchange rate of the trimer is probably a consequence of the considerable restraint on its skeletal flexibility which hinders the formation of the pentacoordinate transition state.

Other inorganic metathetical exchange reactions studied include the replacement of bromine by fluorine and chlorine in $N_3P_3Br_6$ and the preparation of azido-, cyano-, and isothiocyanatocyclophosphazenes (*21*, *22*, *249*). In the reactions of $N_3P_3Cl_6$ with KF and KSCN, addition of [18-Crown-6]ether considerably enhances the yields of substituted cyclophosphazenes, $N_3P_3R_6$ (R = F, NCS) (*449*).

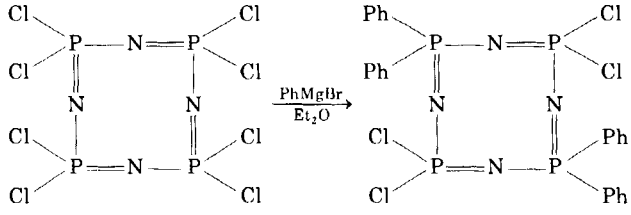
Exchange reactions in which an organic group at phosphorus is replaced by a related anion are also known. For example, the fluoroalkoxycyclophosphazenes, $[NP(OCH_2CF_3)_2]_{3,4}$, undergo ligand exchange with phenoxide or ethoxide ions. In general, a particular group is displaced by a less electron-withdrawing group (*15*).

E. Reactions with Organometallic Reagents

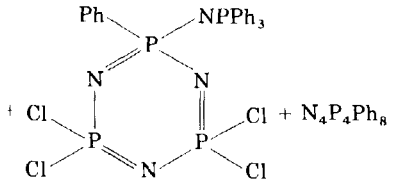
The alkylation and arylation reactions of halogenocyclophosphazenes are often very complex, and ring cleavage and/or polymerization occurs in many cases. The cleavage of the phosphazene ring appears to increase in the order F < Cl < Br. Cyclic products have not been isolated from the reactions of $N_3P_3Br_6$ with Grignard reagents (*21*).

Alkylation is found to proceed smoothly when an amino group is present at the phosphorus atom undergoing the reaction (*402*, *432*).

The reaction of phenylmagnesium bromide with $N_3P_3Cl_6$ in diethyl ether (*61*, *73*) gives a small quantity of the cyclic hexaphenyl compound, $N_3P_3Ph_6$. The main reaction products are acyclic phenylated magnesium complexes (*61*) from which the hydrogen halide derivatives, $Ph_3P{=}NPPh_2{=}NH{\cdot}HX$ (X = Cl, Br), have recently been characterized (*68*). With $N_4P_4Cl_8$, the reaction is somewhat slower (*62*), and two isomeric products, $N_4P_4Cl_4Ph_4$, which have structures (**21**) and (**22**), have been obtained together with small quantities of $N_4P_4Ph_8$. The reaction mixture also contains acyclic phosphazenyl magnesium complexes.



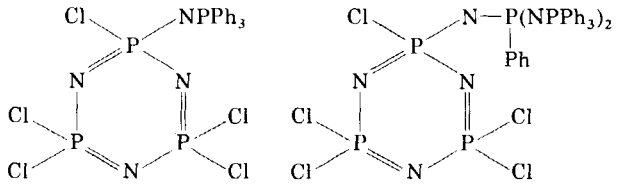
(2) (21)



(22)

Cleavage of the tetrameric ring followed by cyclization of the phenylated acyclic species, $Ph_3P{=}N{-}PPhCl{=}(NPCl_2)_2{=}NMgBr$, would give the ring-contracted derivative (**22**).

The reaction of $N_3P_3Cl_6$ with diphenylmagnesium in 1,4-dioxane (*60*, *63*, *69*) follows an unusual course. Cyclic compounds ($N_3P_3Ph_6$,



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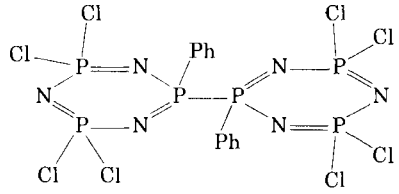


(25)

23, **24**, and **25**) as well as linear phosphazenylmagnesium products are formed. Compound (**24**) is the major product. Because the products obtained from this reaction differ from those formed in the corresponding reaction with phenylmagnesium bromide in diethyl ether, some of the phosphazenylmagnesium intermediates involved must also be different. Formation of products (**23**) and (**24**) suggests that the species $Ph_3P{=}N{-}Mg$ and $(Ph_3P{=}N)_2P(Ph){=}N{-}Mg$, play an important role. Phenyllithium (*64*), *n*-butyllithium (*402*) and R_3SnLi (*349*) behave similarly to phenylmagnesium bromide and bring about extensive ring cleavage of the trimer (**1**). The nongeminal trisdimethylamino derivative, $N_3P_3Cl_3(NMe_2)_3$, reacts with methylmagnesium iodide to give $N_3P_3Me_3(NMe_2)_3$ in 81% yield (*432*).

The reaction of $N_3P_3F_6$ with phenylmagnesium bromide (*34*) gives the mono and the geminal diphenyl derivatives, $N_3P_3F_5Ph$ and $N_3P_3F_4Ph_2$, in modest yields. The analogous reaction with phenyllithium (*32*, *311*) affords the mono compound ($N_3P_3F_5Ph$) and the three bis isomers ($N_3P_3F_4Ph_2$); nongeminal derivatives predominate. The reaction of *gem*-$N_3P_3F_4Ph_2$ with phenyllithium gives the geminal tris derivative, $N_3P_3F_3Ph_3$ (*33*). Methyllithium reacts with $N_3P_3F_6$ (*341*) to give the geminal derivative, $N_3P_3F_4Me_2$. The hexamethyl compound has been isolated as the quaternary salt, $N_3P_3Me_7I$ (*341*). The corresponding reaction with $N_4P_4F_8$ gives the derivatives, $N_4P_4F_{8-n}Me_n$ (n = 1, 2, 3, 4, 8). Fluorine atoms are replaced in a predominantly geminal sequence and the tetra derivative, $N_4P_4F_4Me_4$, has a 2,2,6,6-structure. This replacement pattern has been interpreted in terms of a π-inductive effect of the substituents (*354*). The preparation of $N_5P_5Me_{10}$ by this route has also been reported (*341*).

F. Friedel–Crafts Reactions

Although the reaction of $N_3P_3Cl_6$ with boiling benzene in the presence of aluminum chloride is slow, the geminal derivatives, $N_3P_3Cl_4Ph_2$ and $N_3P_3Cl_2Ph_4$, have been isolated (*1*, *73*). The yield of the diphenyl derivative, $N_3P_3Cl_4Ph_2$, can be improved by the addition

of triethylamine (*301*). The addition of the base also reduces the lengthy reaction times (*332*). Only very small quantities of the hexaphenyl compound, $N_3P_3Ph_6$, have been isolated from this reaction and drastic conditions (150°, stainless steel autoclave) are necessary to obtain modest yields (*1*). Chlorobenzene reacts with $N_3P_3Cl_6$ more readily than either benzene or toluene to give the geminal derivatives, $N_3P_3(p\text{-}C_6H_4Cl)_nCl_{6-n}$ ($n = 2, 4, 6$), and also the mono compound, $N_3P_3Cl_5(p\text{-}C_6H_4Cl)$ (*1*). Phenylation of 2-*trans*-4,6-$N_3P_3Cl_3Ph_3$ in the presence of aluminum chloride yields the cis and trans isomers, 2,2,4,6-$N_3P_3Ph_4Cl_2$, and the pentaphenyl derivative, $N_3P_3Ph_5Cl$ (*215*). Analogous reactions of $N_3P_3F_5Ph$ and $N_3P_3F_4Ph_2$ (mixture of three isomers) provide a route for the preparation of the geminal derivatives, $N_3P_3F_4Ph_2$ and $N_3P_3F_2Ph_4$, respectively (*33*). The octachloride, $N_4P_4Cl_8$, reacts with boiling benzene in the presence of aluminum chloride (*151*) to give the ring-contracted derivative, 2,2,4,4:6:6-$N_3P_3Cl_4Ph(NPPh_3)$ (**22**) in 0.6% yield. The formation of a pentaphenylcyclotetraphosphazene compound in this reaction has been indicated by the isolation of its dimethylamino derivative, $N_4P_4Ph_5Cl_2(NMe_2)$ (0.6% yield).

The Friedel–Crafts reaction probably proceeds by the initial formation of an ionic complex (e.g., $[N_3P_3Cl_5]^{\oplus}[AlCl_4]^{\ominus}$) followed by electrophilic attack on the aromatic molecule by the phosphazenium cation. The observed geminal replacement pattern can be rationalized because the heterolysis of a P—Cl bond is more likely to occur at the $=PClPh$ group than at the $=PCl_2$ group. The postulated mechanism is also in agreement with the observation that phenylation of the amino derivatives, $N_3P_3Cl_5R$ (R = NMe_2, piperidino, $NPPh_3$), proceeds preferentially at a $=PClR$ site rather than at a $=PCl_2$ group (*58, 144, 145, 191, 245*).

IV. Other Reactions of Cyclophosphazenes

A. Complexes, Salts, and Adducts

The skeletal nitrogen atoms in cyclophosphazenes possess a lone pair of electrons and, hence, they have long been viewed as potential donor sites to bind a proton or to form complexes with electron-acceptor molecules. The possibility of formation of anion–cation complexes by release of a halogen ion to a Lewis acid and charge-transfer complexes has also been studied. In addition, some cyclophosphazene derivatives form crystalline inclusion clathrates with a variety of guest molecules. Allcock (*21, 22*) has reviewed these aspects in detail.

1. Metal Complexes

Halogenocyclophosphazenes appear to form two types of complexes with metal halides. The first category is typified by the complex, $N_3P_3Cl_6 \cdot AlCl_3$, which is believed to have the cation–anion structure, $[N_3P_3Cl_5]^{\oplus}[AlCl_4]^{\ominus}$ and is presumably an intermediate in Friedel–Crafts arylation of cyclophosphazenes (*73*). Similar anion–cation complexes with other metal chlorides have been reported (*22*). A non-ionic fluorine-bridged structure has been proposed for complexes of the type $(NPF_2)_n \cdot 2SbF_5$ ($n = 3$ to 6) (*112*). The second category of complexes comprises those which are formed by coordination of the metal to a ring nitrogen atom as in $N_3P_3Br_6 \cdot nAlBr_3$ ($n = 1, 2$) and $N_3P_3Cl_6 \cdot AlBr_3$ (*133*).

The availability of the lone pair of electrons on skeletal nitrogen atoms of cyclophosphazenes can be greatly enhanced by replacing halogen atoms by less electronegative groups (e.g., Me) or by substituents capable of conjugative electron release (e.g., NRR′). The transition metal complexes of methyl- and dimethylaminocyclophosphazenes have been described (*98, 274, 342, 397*), and in a few cases the structures have been determined by X-ray crystallography (*94–96, 127, 217, 296, 300, 439, 440*). Cupric chloride reacts with $N_4P_4Me_8$ to give the complex, $[N_4P_4Me_8H]^{\oplus}[CuCl_3]^{\ominus}$, in which a proton and a $[CuCl_3]^{\ominus}$ group are *bonded* to opposite nitrogen atoms of the eight-membered phosphazene ring. The phosphazene ring has a "tub" conformation. The geometry around copper is distorted square planar (*439*). The cobalt chloride complex of the same ligand has the composition $[N_4P_4Me_8H]_2^{\oplus}[CoCl_4]^{2-}$ and contains two protonated phosphazene rings with tub and "saddle" conformations and a $[CoCl_4]^{2-}$ ion. The association is ionic and there is no evidence of cobalt–nitrogen bonding (*440*). Complex $[N_5P_5Me_{10}H_2]^{2+}[CuCl_4]^{2-} \cdot H_2O$ consists of a distorted tetrahedral $[CuCl_4]^{2-}$ ion and a ten-membered P—N ring with 2 protonated nitrogen atoms (*96*). The interaction of $N_6P_6(NMe_2)_{12}$ (L) with $CuCl_2$, CuCl, or an equimolar mixture of the two halides yields the same complex, $[LCu(II)Cl]^{\oplus}[Cu(I)Cl_2]^{\ominus}$ (*300*). The cobalt chloride complex formed with the same ligand has been isolated as the chloroform solvate, $[(LCoCl)^{\oplus}]_2[Co_2Cl_6]^{2-} \cdot 2CHCl_3$ (*217*). In both the complexes, the metal ion is coordinated to 4 of the 6 ring nitrogen atoms and a chlorine atom in a distorted trigonal bipyramidal geometry (Fig. 7).

Complexes of $N_6P_6(NMe_2)_{12}$ with other metal chlorides and nitrates have essentially similar structures as indicated by infrared and electronic spectroscopic data (*98*). Compounds $N_4P_4Me_8$ and $N_5P_5Me_{10}$(L′) react with molybdenum and tungsten hexacarbonyls

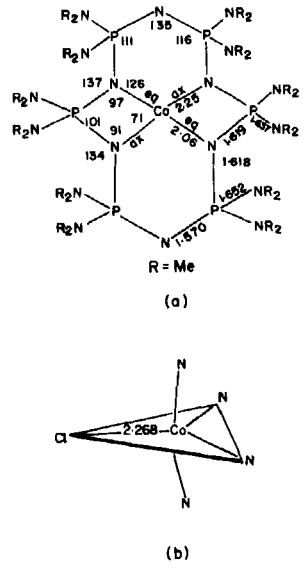


FIG. 7. Metal atom coordination in $[N_6P_6(NMe_2)_{12}CoCl]^{\oplus}$. [Reproduced from Harrison and Trotter (*217*) by permission of The Chemical Society, London.]

to give $L'M(CO)_3$ (M = Mo and W) (*342*); $N_4P_4(NMe_2)_8$ forms a tetracarbonyl, $N_4P_4(NMe_2)_8 \cdot W(CO)_4$, in which the phosphazene ligand is coordinated to tungsten through a ring nitrogen atom and an exocyclic nitrogen atom (Fig. 8). The geometry around the metal is distorted octahedral with the nitrogen atoms occupying cis positions (*94*). The bond length and bond angle variations in the phosphazene rings caused by coordination can be explained in terms of π-bonding theory (Section VI). The quaternary iodide, $[N_4P_4Me_9]^{\oplus}I^{\ominus}$, reacts with $M(CO)_6$ (M = Cr, Mo) to give the crystalline compounds, $[N_4P_4Me_9]^{\oplus}[M(CO)_5I]^{\ominus}$ (*342*). The crystal structure of the chromium complex has been reported (*95*). The hexachloride reacts with

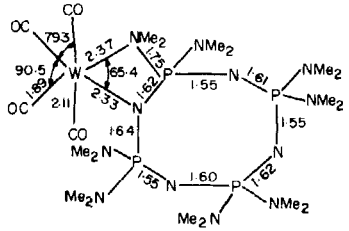


FIG. 8. The structure of $[N_4P_4(NMe_2)_8 \cdot W(CO)_4]$. [Adapted from Calhoun *et al.* (*94*) by permission of The Chemical Society, London.]

$Cr(CO)_3(CH_3CN)_3$ to give $[N_3P_3Cl_6][Cr(CO)_3]$, which is believed to be a π-complex (*227*).

There are also other reports of metal complexes of cyclophosphazene derivatives, but in most cases the structures of the complexes have not been established with certainty (*21*, *150*, *229*, *231*, *357*, *386*).

2. *Salts and Adducts*

Halogenocyclophosphazenes form salts with perchloric acid (*74*) and hydrofluoric acid (*387*). Alkyl- and alkylaminocyclophosphazenes are much more basic than halogenocyclophosphazenes, and their hydrogen chloride adducts have been well-characterized. The adducts are prepared by the direct reaction of the phosphazene derivatives with the acid in an organic solvent (*149*, *220*, *322*, *397*, *410*). Many aminocyclophosphazenes have base strengths comparable to or greater than that of the parent amine from which they are derived and, hence, a hydrohalide adduct of the aminophosphazene may be formed in the aminolysis reactions of halogenocyclophosphazenes (*140*, *142*, *149*, *192*, *313*, *355*, *371*). It appears that in the aminolysis reactions, the (primaryamino)cyclophosphazene derivatives have a much more pronounced tendency to form hydrochloride adducts than secondary amino derivatives (*140*, *142*, *355*, *371*). Hydrogen halide adducts of aminocyclotetraphosphazenes have been isolated only recently (e.g., $N_4P_4(NMe_2)_6(NHEt)_2 \cdot 2HCl$; $N_4P_4(NHBu^t)_8 \cdot HCl$; $N_4P_4(NMe_2)_6(NHBu^t)_2 \cdot HCl$ (two isomers)) (*371*). The free phosphazene base can be generated from the adducts by treating the latter with a strong tertiary base (e.g., triethylamine, pyridine) in an organic solvent.

Basicity measurements and infrared and NMR spectroscopic data (Section V) show that the site of protonation for most cyclophosphazenes is a ring nitrogen atom rather than an exocyclic nitrogen atom (for aminocyclophosphazenes). X-Ray crystal structure analyses of $N_3P_3Cl_2(NHPr^i)_4 \cdot HCl$ (*292*), $N_4P_4Et_2Me_6 \cdot 2HCl$(2-*trans*-6) (*99*), $[HN_3P_3(NMe_2)_6]_2^{\oplus}[Mo_6O_{19}]^{2-}$ (*23*), $[HN_3P_3(NMe_2)_6]^{\oplus}[CoCl_4]^{\ominus}$ (*287*), and some metal derivatives of cyclophosphazenes containing protonated species (Section IV,A,1) confirm that protonation occurs at the skeletal nitrogen atom(s). Recent basicity measurements suggest that for cyclophosphazene derivatives bearing a triphenylphosphazenyl ($-N{=}PPh_3$) substituent, protonation may occur either at a ring nitrogen atom or at the exocyclic phosphazenyl nitrogen atom (*323*). The bicyclic phosphazene (**13**) forms a hydrochloride adduct, and spectroscopic data suggest that the proton is probably attached to the bridgehead nitrogen atom (*372*). It is known that the bridgehead nitrogen atom of the base (**12**) has considerable sp^3 character (*100*).

Methylcyclophosphazenes react with alkyl iodides to form *N*-alkylphosphazenium iodides (*397*). The iodide can be exchanged for other anions, such as Cl^- or HgI_3^-. Dimethylaminocyclotriphosphazene derivatives react with trimethyloxonium tetrafluoroborate ($Me_3O^+BF_4^-$) to give onium ions in which methylation takes place at the exocyclic nitrogen atom(s). However, ring alkylation occurs under similar conditions with *gem*-$N_3P_3Cl_2(NHPr^i)_4$ and $N_3P_3Ph_6$ (*356*).

The reaction of $N_3P_3Me_6$ with iodine results in the formation of a 1:1 adduct in which charge transfer interaction takes place by the donation of nitrogen lone pair of electrons into an antibonding orbital of the iodine molecule (*295*). Recently, the formation of 1:3 adduct of $N_3P_3F_6$ and PF_3 has been reported from the reaction of $[Cl_3P{=}N{-}PCl_3][BCl_4]$ with AsF_3 (*72*). Molecular addition compounds between cyclophosphazene derivatives [e.g., $N_3P_3Cl_4(NHPr^i)_2$: $N_3P_3Cl_2(NHPr^i)_4$ and $N_4P_4Cl_4(NHEt)_4$:$N_4P_4(NHEt)_8$] (*141*, *143*, *265*) are also known.

3. Inclusion Clathrates

When some cyclotriphosphazenes are recrystallized from organic solvents, they often tend to hold the solvent molecules tenaciously in their crystal lattice to form molecular inclusion clathrates. The clathrates of tris(*o*-phenylenedioxy)- (**18**) (*9*), tris(2,3-dioxynaphthyl)- (*11*), and tris(1,8-naphthalenedioxy)cyclotriphosphazenes (*17*) have been investigated in some detail. X-Ray crystallographic analysis (*9*, *25*, *411*) indicates that the guest molecules are trapped in channels that exist between the bulky substituent side groups in the host lattice. This behavior may be contrasted with that of tris(2,2′-dioxydiphenyl)-cyclotriphosphazene which does not form an inclusion clathrate, presumably because the greater bulkiness of the side groups prevents the formation of channels (*16*). The clathration process can be used to separate the components of a mixture of organic solvents (*9*). Tris-(*o*-phenylenediamino)cyclotriphosphazene specifically retains esters and ketones, and it is suggested that hydrogen bonding is responsible for the specificity (*11*). Other cyclophosphazenes also form inclusion adducts (*21*, *56*) and particular mention may be made of the triphenylphosphazenylcyclotriphosphazene derivatives, $N_3P_3Cl_5$-$[N{=}P(Ph)(N{=}PPh_3)_2]$ (**24**) (*63*) and nongeminal $N_3P_3Cl_4(NPPh_3)_2$ (*66*).

B. Reactions At Side Chains

There are many reactions of cyclophosphazene derivatives involving substitution or transformations at side chains that do not affect the

ring skeleton. The Kirsanov reaction of ammonocyclophosphazenes,

$$\begin{gathered} RNH_2 + X'_3PX_2 \rightarrow RN{=}PX'_3 + 2HX \\ (R = \text{cyclophosphazenyl unit};\ X' = Cl, Br, Ph;\ X = Cl, Br) \end{gathered} \tag{10}$$

belongs to this category and has been investigated in some detail (*55*, *181*, *245*, *278*, *282*, *363*, *415*, *442*). The side chain in $N_3P_3F_5(NPX_3)$ (X = F, Cl) can be lengthened by treating these compounds alternately with hexamethyldisilazane and PCl_5 (*364*).

The ammono derivatives react with $COCl_2$ (*434*), $SOCl_2$ (*325*, *368*), and oxalyl dichloride [436], and add to isocyanates and isothiocyanates (*366*, *433*). Compound $N_4P_4F_6(NSO)_2$ eliminates SO_2 in the presence of pyridine to give a bicyclic phosphazene containing a sulfur diimido bridging group (*368*). Under similar conditions, $N_3P_3F_5(NSO)$ gives the derivative, $N_3P_3F_5{-}N{=}S{=}N{-}N_3P_3F_5$ (*325*).

Treatment of $N_4P_4Me_8$ with methyllithium gives the anion $N_4P_4Me_4(CH_2^-)_4$, which reacts with MeI and Me_3XCl (X = Si, Ge, Sn) to give $N_4P_4Me_4(CH_2R)_4$ (R = Me, XMe_3) [*96a*].

Ring closure occurs in the reaction of *gem*-$N_3P_3Cl_4(NPCl_3)_2$ with heptamethyldisilazane (*280*) and of *gem*-$N_3P_3(NH_2)_2(OCH_2CF_3)_4$ with $MeSiHCl_2$ (*237*). Trans-esterification reactions take place between alkoxycyclophosphazenes and R_3SiCl (*21*). The reaction of 2,6-bis-(azido)hexaphenylcyclotetraphosphazene, $N_4P_4(N_3)_2Ph_6$, with Ph_3P yields a bis(triphenylphosphazenyl)hexaphenyl derivative; with *cis*-1,4-bis(diphosphino)butane, cage-type compounds can be obtained (*400*). Cleavage of the aziridine ring occurs when hexakisaziridinocyclotriphosphazene reacts with protic species (*357*). Photochemical chlorination, addition of bromine to double bonds, polymerization of olefinic units, and reduction of nitro groups have also been observed with organic side chains in cyclophosphazene derivatives (*21*).

Brief reports of many other reactions involving side chains are scattered in the literature (*115*, *182*, *327*, *364*, *367*, *414*).

C. Thermal Polymerization Of Cyclophosphazenes

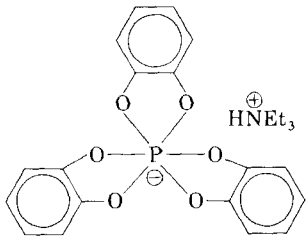
The thermal polymerization of chlorocyclophosphazenes to give an "inorganic rubber" of high molecular weight was discovered by Stokes (*429*) in 1897. Allcock and co-workers (*10*, *12*) have shown that poly(dichlorophosphazene) free from cross-links can be obtained by careful control of the reaction conditions employed in the polymerization of $N_3P_3Cl_6$. Poly(dichlorophosphazene) is a key intermediate in the preparation of high molecular weight poly(organophosphazenes) (*18*, *21*, *22*, *24*, *37*, *412*). The mechanism of the polymerization of halogenocyclophosphazenes is very complex and has not yet been

completely unraveled. Recently, Allcock and co-workers (*29*) have established that traces of water function as a powerful catalyst, whereas PCl_5 is a powerful inhibitor for the polymerization of $N_3P_3Cl_6$. The polymerization and copolymerization of phenylhalogenocyclotriphosphazenes have been studied (*28*). Attempts to polymerize fully substituted organocyclotri- and tetraphosphazenes have been unsuccessful. Poly(bisorganophosphazenes), prepared indirectly by the nucleophilic displacement of chlorine atoms from poly(dichlorophosphazene), depolymerize on heating to organocyclophosphazene oligomers. This behavior has been rationalized in terms of the thermodynamic stability of cyclic oligomers and the kinetic stability of poly(bisorganophosphazenes) at ambient temperatures (*21*, *22*, *24*, *26*, *27*).

The ammonocyclophosphazenes, $[NP(NH_2)_2]_{3,4}$ and $N_4P_4Cl_4(NH_2)_4$ pyrolyze to phosphams, $(PN_2H)_n$, by elimination of NH_3 or HCl, respectively (*146*, *303*). Anilinocyclophosphazenes, $[NP(NHPh)_2]_{3,4}$, can also be converted to phosphams on heating by the elimination of aniline (*75*). It is believed that the phosphams contain six or eight-membered P—N rings linked by N—H or N—Ph bridges (*303*). The formation of resins in the reaction of halogenocyclophosphazenes with primary amines is well authenticated, although their exact nature is not clear (*139*, *221*, *265*, *355*, *371*). It is possible that these resins may have a structure similar to that of phosphams (*265*). The thermal stability of several spirocyclophosphazenes toward ring-opening polymerization seems to depend on the steric strain of the exocyclic rings (*21*).

D. Ring Degradation Reactions

Several reactions of cyclophosphazenes that involve cleavage of the phosphorus–nitrogen skeleton have been described. The formation of ring-degraded products in the hydrolysis (Section III,B) and Friedel–Crafts reactions (Section III,F) and also in the reactions with organometallic reagents (Section III,E) has already been mentioned. Compound **1** reacts with catechol in the presence of tertiary amines to give the spirophosphorane (**26**) in addition to the spirocyclophosphazene (**18**) (*7*, *8*). A similar ring-degradation occurs in the reactions of *o*-aminophenol with fluoro-, chloro-, and bromocyclophosphazenes to yield the phosphorane (**27**), but in contrast to the reactions of catechol, the spirocyclophosphazene intermediate has not been isolated (*14*). *o*-Aminophenol also reacts with spirocyclophosphazenes that contain a five-membered arylenedioxy, arylenedithio, or arylenediamino group at phosphorus to give the same phosphorane (**27**).



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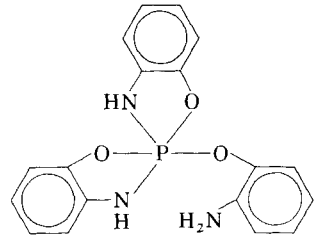


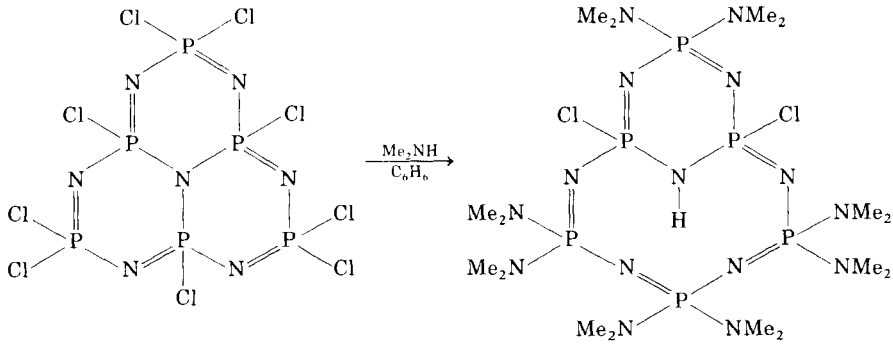
(27)

Recently, Allcock and co-workers have discussed the mechanism of these reactions (*30*).

Chlorocyclophosphazenes react with organic acids or their salts (*21*, *346*, *448*), acid amides (*206*), and acid halides (*207*) to yield the nitrile of the acid; the phosphazene ring is degraded. The reaction of benzoyl chloride with $[NP(OEt)_2]_{3,4}$ gives ethyl chloride, ethyl phosphenates, and triphenyl-*s*-triazine (*188*). The trifluoroethoxy derivatives, $[NP(OCH_2CF_3)_2]_{3,4}$, react with diphenyl ketone to afford the acid, $(CF_3CH_2O)_2P(O)(OH)$, and organic imines (*405*, *406*).

A novel reaction of quaternary *N*-methylphosphazenium iodides, $[N_nP_nMe_{2n+1}]^{\oplus}I^{\ominus}(n = 3, 4)$, with sodium bis(trimethylsilyl)amide has been reported. Phosphorines with exocyclic methylamino groups are formed as a result of phosphazene ring cleavage. Similar cleavage occurs in the reaction of quaternary phosphazenium iodides with potassium-*t*-butoxide (*97*).

The reaction of the tricyclic compound $N_7P_6Cl_9$ (**28**) with dimethylamine involves the rupture of one of the central bonds leading to the formation of a bridged-ring imide (**29**) (*330*).



(28) (29)

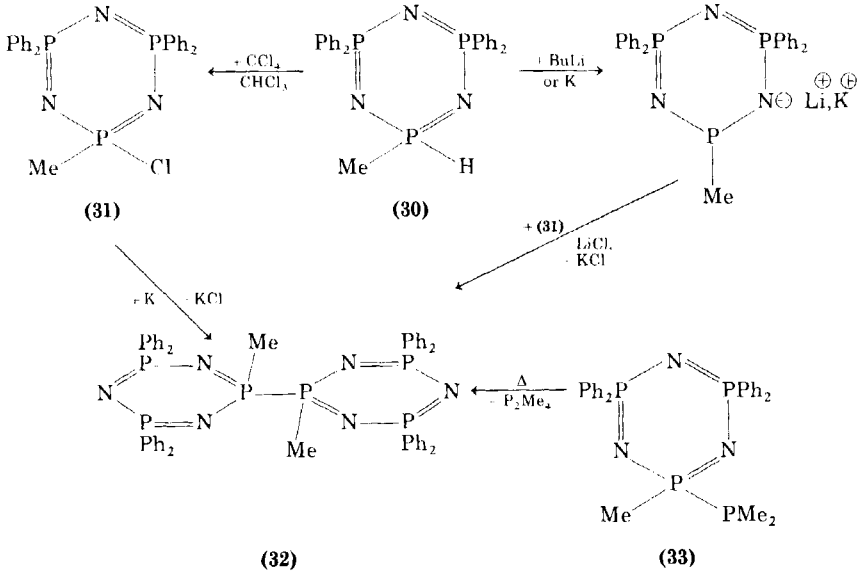
Ring degradation is also reported to occur in the reactions of $N_3P_3Cl_6$ with formamide and thioformamide (*230*), potassium bromide in the presence of [18-Crown-6]ether (*449*), dimethylsulfoxide (*447*), and metal hydrides (*262*).

E. Miscellaneous Reactions

Trimethylamine reacts with $(NPCl_2)_{3,4}$ at room temperature to give chlorodimethylaminocyclophosphazenes. Similar dealkylation does not occur with triethylamine (*92*).

Dealkylation of aromatic secondary and tertiary amines has also been reported (*106*, *266*). The reaction of fluorocyclophosphazenes with (dimethylamino)trimethylsilane affords dimethylamino-substituted derivatives (*113*). A similar approach has been followed to prepare spirocyclic aminohydrazino- and dihydrazinocyclotriphosphazenes by the reactions of $N_3P_3Cl_6$ with cyclic silicon–nitrogen compounds (*200*). Hexamethyldisilylazane undergoes a very slow reaction with $N_3P_3Cl_6$ to give the geminal product, $N_3P_3Cl_4(NHSiMe_3)_2$ (*183*). Epoxides undergo ring opening on treatment with $(NPCl_2)_{3,4}$ to yield chloroalkoxy derivatives (*275*, *276*). The reaction of $N_3P_3Cl_6$ with aldoximes is a useful route to nitriles (*369*). A novel cyclophosphazene-substituted Sn-N ring compound has been isolated from the reaction of $N_3P_3F_5[N(SnMe_3)_2]$ and $(CF_3CO)_2O$ (*365*).

Reaction of *P*-hydridocyclophosphazenes (e.g., **30**) with CCl_4 results in the replacement of hydrogen by chlorine (*383-385*). Metalation of the hydridocyclophosphazene (**30**) and subsequent treatment with the chlorocyclophosphazene (**31**) leads to the formation of the two-ring assembly phosphazene (**32**), which can also be prepared by the direct reduction of **31** with potassium or by thermal disproportionation of the phosphinocyclophosphazene (**33**) (*385*).



Chlorocyclophosphazenes function as peptide coupling agents, aromatic coupling reagents, and substrates for photochemical and electron-induced alkylation and arylation (*21*). The reaction of $N_3P_3Cl_6$ with sodium salt of *O,O*-diethyl-*N*-methylamido-phosphate (*193*) gives the derivatives $N_3P_3Cl_{6-n}[NMeP(O)(OEt)_2]_n$ ($n = 1, 2, 3$). The bis compound is nongeminally substituted, whereas the tris derivative possesses a geminal structure (*437*). The reaction of chlorocyclophosphazenes with dimethylformamide (*425*) gives "onium"-type salts.

V. Physical Methods

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. Proton NMR spectroscopy has been widely used because of its easy accessibility. The recent development of sophisticated instrumental facilities and the application of broad-band proton decoupling have greatly improved the quality and usefulness of the ^{31}P spectra (*252*) of cyclophosphazenes, and it is likely that this technique will become increasingly popular in the future. Fluorine NMR studies are useful for deducing the structures of fluorocyclophosphazenes, and the potential of this technique has been demonstrated in recent years (*209, 210, 213, 307, 308, 343*).

1. Proton Magnetic Resonance

Proton NMR spectroscopy is particularly useful for determining the disposition of substituents in aminohalogenocyclophosphazenes. Four criteria are utilized for this purpose: (*a*) the number of proton environments, (*b*) the value of $^3J^*$(P—H),* (c) the relative chemical shifts (geminal versus nongeminal and cis versus trans), and (*d*) the presence or absence of "virtual coupling" (see detailed discussion in the following).

The three isomeric trisdimethylaminotrischlorocyclotriphosphazenes, *cis-*, *trans-*, and *gem*-$N_3P_3Cl_3(NMe_2)_3$, have been identified by the observation of one, two, and three dimethylamino doublets (coupling to ^{31}P), respectively, in their proton NMR spectra. In addition, the magnitude of $^3J^*$(P—H) in $\equiv PCl(NMe_2)$ and $\equiv P(NMe_2)_2$

* The value of P—H coupling constant determined from the spectrum is slightly different from the true value of ^3J(P – H) because of second-order effects (see later) and, hence, is designated as the apparent P – H coupling constant, $^3J^*$(P—H).

groupings lies in the range 16–17 and 11–13 Hz, respectively (*240, 243*). Similar trends in $^3J^*$(P—H) help distinguish a geminally substituted group, $\equiv PR_2$, from a nongeminal one, $\equiv PXR$ [X = Cl and R = —NHMe (*192, 279*), —NHEt (*139, 265*), —NMePh (*266, 355*), —NEt_2 (*283, 453*); X = Br and R = —NMe_2 (*166, 246*), —NHEt (*355*)]. In general, the geminal coupling constant is 3–4 Hz lower than the nongeminal one.

The chemical shifts of N—H protons can often provide a diagnostic test for geminal and nongeminal structures in cyclophosphazene derivatives with primary amino substituents (*139, 221, 265, 355, 371*). The N—H resonances for the nongeminal compounds occur at 6.1–6.4τ, whereas the geminal compounds display resonances at 7.1–7.8τ. The proton NMR spectra of *cis-* and *trans*-bisaminotetrahalogeno derivatives, $N_3P_3R_2X_4$, (X = Cl, Br) are essentially similar, but a distinction is possible because of the greater shielding of protons (three bonds away from phosphorus) in the cis isomer [R = —NMe_2 (*166, 240, 246*), —NEt_2 (*283, 453*), —NMePh (*266*), —NHMe (*279*), and NHEt (*139, 355*)].

Unambiguous structural assignments for cyclotetraphosphazene derivatives by proton NMR spectroscopy are difficult because it is often possible to interpret the data on the basis of more than one isomeric configuration. In a number of cases, the spectra are poorly resolved but the problem can be overcome to some extent by recording the spectra at higher field strength (220 MHz) (*265, 304, 355*). Figure 9 shows the spectrum of 2-*trans*-6-$N_4P_4Cl_2(NMePh)_6$ recorded at 100 and 220 MHz and illustrates the effect of field strength in simplifying the spectrum. Recent crystallographic studies of chloro- and fluorodimethylaminocyclotetraphosphazene derivatives (*51, 86, 87, 89, 306*) confirm the structures proposed on the basis of the proton NMR data except in the case of $N_4P_4Cl_3(NMe_2)_5$, m.p. = 154° (*46*).

The proton NMR spectra of many cyclophosphazenes are complicated by second-order effects characteristic of multispin systems. These second-order effects give rise to additional lines or a broad hump among the signals expected on the basis of first-order considerations and are referred to as "virtual coupling." One of the essential conditions for the occurrence of virtual coupling is that the chemical shift between the ^{31}P nuclei involved in these effects is small or zero (*184, 185, 252*). Unfortunately, reliable guidelines for predicting the trends in the chemical shifts of ^{31}P nuclei of cyclophosphazene derivatives containing different substituents have not yet been established (see Section V,A,2). However, the strength of virtual coupling effects or their absence can sometimes yield structural information on isomeric compounds (*65, 88, 142, 355, 371*). For example, the geminal 2,2,6,6-isomer of $N_4P_4Ph_4(NMe_2)_4$ is distinguished from the 2,2,4,4-isomer by

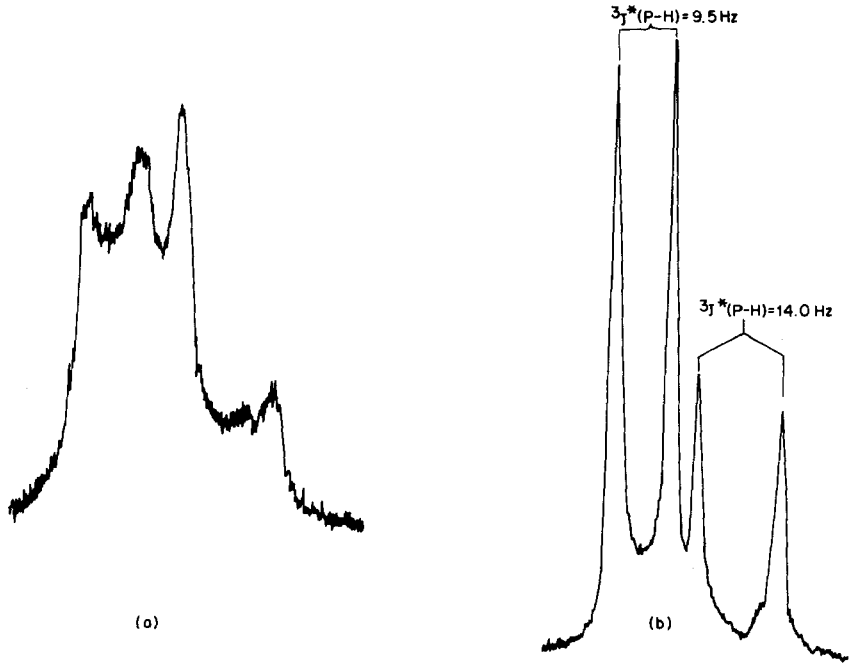


FIG. 9. The ^{1}H NMR spectrum of 2-*trans*-6-$N_4P_4Cl_2(NMePh)_6$ at (*a*) 100 MHz and (*b*) 220 MHz in $CDCl_3$ (methyl signals only).

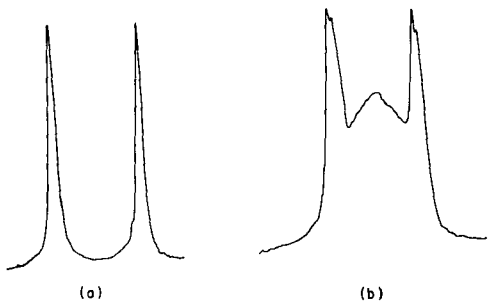


FIG. 10. The ^{1}H NMR spectrum (100 MHz) of (*a*) 2,2,6,6-$N_4P_4Ph_4(NMe_2)_4$ and (*b*) 2,2,4,4-$N_4P_4Ph_4(NMe_2)_4$ in $CDCl_3$ (methyl signals only). [Reproduced from Biddlestone *et al.* (*65*) by permission of Gordon and Breach Science Publishers Ltd., London.]

the absence of the virtual coupling effect in the former derivative (Fig. 10) (*65*).

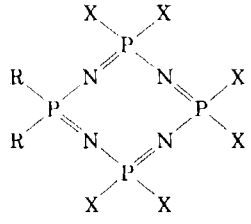
The ^{1}H NMR study of dimethylamino and/or methoxy derivatives of partially substituted cyclophosphazenes has been utilized to obtain

structural information on the halogeno precursors (*140*, *142*, *148*, *153*, *334*, *355*, *371*). This indirect approach must be used with caution in view of the tendency of aminohalogenocyclophosphazenes to undergo cis–trans isomerization in the presence of amine hydrochlorides (see Section III,A,3) and of methoxy compounds to rearrange to oxocyclophosphazanes on heating (see Section III,C).

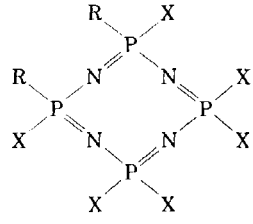
Proton resonance data for the hydrogen halide adducts of aminocyclophosphazenes provide evidence for ring protonation (*220*, *313*, *355*, *373*). Flow of electron density from the exocyclic nitrogen atoms results in the deshielding of the exocyclic N--*H* or N—*R* protons in the adducts compared to the corresponding free bases. In most cases, the detection of the signal arising from the acidic proton(s) attached to the ring nitrogen is difficult (*313*, *355*, *371*). A study of the proton NMR spectrum of the hydrochloride adduct, $N_4P_4(NHBu^t)_8 \cdot HCl$, at different temperatures shows that the exchange of the proton among the four, equivalent, ring nitrogen atoms is slow on the NMR time scale (*373*). The proton NMR spectrum of the dihydrochloride adduct, 2-*trans*-6-$N_4P_4(NHEt)_2(NMe_2)_6 \cdot 2HCl$ (*372*), can be interpreted on the basis of protonation occurring at two far off ring nitrogen atoms [cf. crystal structure of 2-*trans*-6-$N_4P_4Et_2Me_6 \cdot 2HCl$ (*99*)].

2. ^{31}P NMR

Many unsymmetrically substituted cyclophosphazene derivatives constitute a complex multispin system and the ^{31}P spectra of these compounds can rarely be analyzed on a first-order basis. However, in many cases ^{31}P NMR data have served to confirm the structural assignments made on the basis of ^1H NMR spectra. In several instances ^{31}P NMR spectroscopy can provide independent structural evidence where proton NMR spectra are inadequate for this purpose [e.g., the assignment of geminal structures to $N_3P_3Cl_2(NHBu^t)_4$ (*140*), $N_3P_3Cl_4(NHPh)_2$ (*153*), $N_3P_3Cl_4(NCS)_2$ (*155*), and $N_3P_3Br_4(NH_2)_2$ (*156*)]. In principle, ^{31}P NMR spectroscopy can distinguish the isomeric structures (**34**–**36**). The spectra of these cyclotetraphosphazene isomers



(34)



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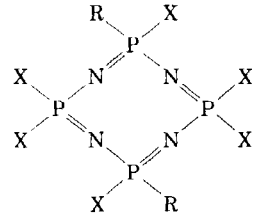
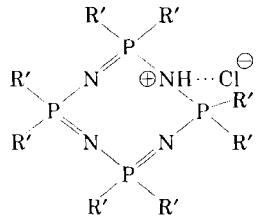


(36)



(R′ = NHBu′)

(37)

would be of the types, AB_2C, $AA'BB'$, and A_2B_2, respectively, and these can be recognized readily.* It is not possible to differentiate cis and trans isomers in this way because the spin system will remain unchanged, assuming that possible differences in ring conformations are small and do not affect the ^{31}P spectra. The two bis-*t*-butylamino isomers, $N_4P_4Cl_6(NHBu^t)_2$, m.p. = 171° and 128°, give rise to symmetrical A_2B_2 and $AA'BB'$ ^{31}P spectra, respectively: a 2,6- and a 2,4-disposition of *t*-butylamino groups is established (Fig. 11) (*373*). Other examples of A_2B_2 [2-*trans*-6-$N_4P_4(NHEt)_2R_6$ (R = Cl, NMe_2)

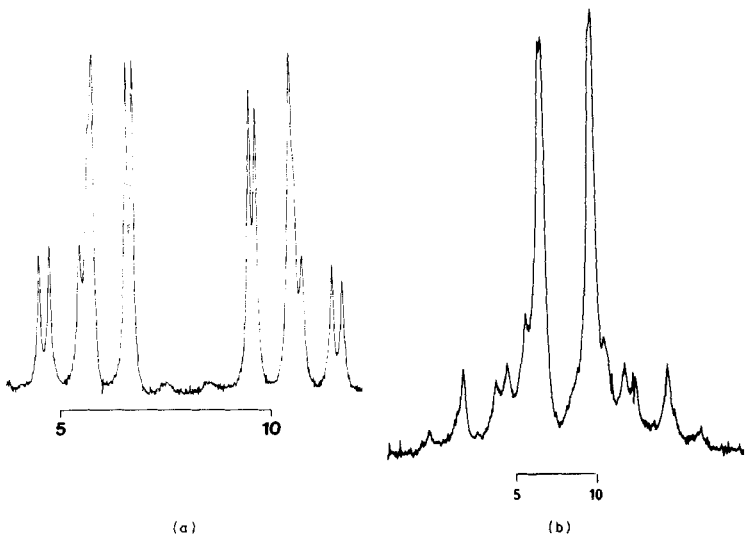


FIG. 11. The ^{31}P NMR spectra (36.7 MHz, CH_2Cl_2) of (*a*) 2,6-$N_4P_4(NHBu^t)_2Cl_6$ and (*b*) 2,4-$N_4P_4(NHBu^t)_2Cl_6$.

* It may not be easy to distinguish $AA'BB'$ and A_2B_2 spin systems when J/δ becomes relatively small.

TABLE II

^{31}P NMR DATA FOR SELECTED CYCLOPHOSPHAZENES[a]

Compound[b]	Structure	δ_{PX_2}	δ_{PClR}	δ_{PR_2}	^2J(P–P) (Hz)	Ref.
$N_3P_3F_6$	—	13.9	—	—	—	*33*
$N_3P_3Cl_6$	—	19.3	—	—	—	*252*
$N_3P_3Br_6$	—	−49.5	—	—	—	*234*
$N_3P_3(NMe_2)_2Cl_4$	2-*trans*-4	21.5	25.2	—	44.4	*252*
$N_3P_3(NMe_2)_3Cl_3$	2,2,4	21.7	27.3	21.7	44.8	*252*
$N_3P_3(NMe_2)_6$	—	—	—	24.6	41.2	*252*
$N_3P_3(NEt_2)_6$	—	—	—	22.5	—	*252*
$N_3P_3(NH_2)_6$	—	—	—	15.3	—	*294*
$N_3P_3(NMe_2)_2(NHEt)_4$	2-*trans*-4	—	22.8[c]	18.9[d]	42.1	*252*
$N_3P_3(NMe_2)_2(NHEt)_4 \cdot HCl$	2-*trans*-4	—	17.3[c]	12.3[d]	30.0	*252*
$N_3P_3(NHEt)_6$	—	—	—	18.0	—	*252*
$N_3P_3(NHPr^i)_6$	—	—	—	12.6	—	*252*
$N_3P_3(NHPh)_2Cl_4$	2,2	20.4	—	2.3	48.0	*277*
$N_3P_3(NHBu^t)_2Cl_4$	2,2	17.5	—	0.7	44.7	*252*
$N_3P_3Cl_2(NHBu^t)_4$	2,2	19.7	—	3.9	52.6	*252*
$N_3P_3Ph_2Cl_4$	2,2	17.1	—	19.5	12.1	*252*
$N_3P_3Cl_2Ph_4$	2,2	14.8	—	17.1	9.3	*252*
$N_3P_3(SEt)_2Cl_4$	2,2	17.7	—	51.7	4.8	*76*
$N_3P_3(SEt)_6$	—	—	—	45.7	—	*76*
$N_3P_3Cl_5(OMe)$	—	22.5	16.7	—	63.3	*223*
$N_3P_3(OMe)_6$	—	—	—	20.7	—	*12*
$N_3P_3(OEt)_6$	—	—	—	14.3	—	*12*
$N_4P_4F_8$	—	−17.0	—		—	*294*
$N_4P_4Cl_8$	—	6.7		—	—	*252*
$N_4P_4Br_8$	—	−71.8	—	—	—	*234*
$N_4P_4Cl_2(NMe_2)_6$	2-*trans*-6	—	4.4	9.9	47.1	*252*
$N_4P_4(NMe_2)_8$	—	—	—	9.6	—	*252*
$N_4P_4(NHEt)_2Cl_6$	2-*trans*-6	−3.4	−4.9	—	46.0	*265*
$N_4P_4(NHEt)_8$	—	—	—	4.3	—	*265*
$N_4P_4(NHBu^t)_2Cl_6$	2-*trans*-6	−5.8	−10.6	—	38.1	*373*
$N_4P_4(NHBu^t)_8$	—	—	—	−3.1	—	*373*
$N_4P_4(NHBu^t)_8 \cdot HCl$	—	—	—	−5.0[e]	—	*373*

[a] The chemical shifts are with reference to 85% H_3PO_4 (external); upfield shifts are negative.

[b] Disposition of one set of substituent groups defined where necessary.

[c] $=P(NMe_2)(NHEt)$.

[d] $=P(NHEt)_2$.

[e] Center of AA'BB' multiplet (not fully analyzed).

(*265*), 2-*trans*-6-$N_4P_4Cl_2(NMe_2)_6$ (*252*), and 2,2,6,6-$N_4P_4Cl_4(NMePh)_4$ (*355*)] and AA'BB' spectra [2,4-$N_4P_4R_2Cl_6$ (R = NMePh) (*250, 355*) and $NHCH_2Ph$ (*353*)] are known. The ^{31}P NMR spectrum of the hydrochloride (**37**) constitutes a symmetrical AA'BB' pattern, and a variable

temperature study confirms the conclusion drawn from ^{1}H NMR data that the exchange of the acidic proton at a ring nitrogen atom(s) is slow (*373*).

The ^{31}P chemical shifts and phosphorus–phosphorus coupling constants, ^{2}J(P—N—P), for a large number of cyclophosphazene derivatives have been determined (*35*, *123*, *184*, *186*, *223*, *224*, *252*, *294*, *381*, *395*, *399*). The data for some selected compounds are shown in Table II. It has been suggested that changes in electronegativity, π-bonding, and bond angles influence ^{31}P chemical shifts (*223*, *284*). In addition, the chemical shift of a particular phosphorus atom may be affected by substituents elsewhere on the ring. It is also possible that a bromo substituent may shield the phosphorus by a neighbor anisotropy effect (*21*). Empirical relationships have been proposed (*186*, *395*) to correlate ^{2}J(P—N—P) with electronegativity of the substituents, but it has been noted that other factors (stereochemistry of the substituents, substituents on other phosphorus atoms) may also contribute (*35*, *123*, *252*). A comprehensive theoretical treatment of ^{31}P chemical shifts and phosphorus–phosphorus coupling constants in cyclophosphazenes has not yet emerged. Recently, four-bond phosphorus–phosphorus coupling constants have been measured for a number of phosphazenylcyclotriphosphazenes and their magnitude (+7.5 to −0.4 Hz) appears to be related to the conformation of the phosphazenyl group relative to the phosphazene ring (*70*).

3. ^{19}F NMR

The fluorine chemical shifts* observed for fluorocyclophosphazenes span a wide range from −18.0 for $\equiv$PFBr in *trans*-$N_3P_3F_3Br_3$ to −71.9 for the $\equiv PF_2$ unit in $N_3P_3F_6$ (*21*, *123*). Because of strong P—F coupling [^{1}J(P—F) $\approx$ 840–1056 Hz], complex spectra are often encountered and a first-order analysis is difficult. The observed chemical shifts appear to be more useful than simple environment count or coupling constant values in determining the disposition of the substituents (*22*). Recently, the ^{19}F NMR spectra of a number of fluorocyclophosphazenes were recorded and analyzed by iterative computational methods. The NMR parameters (in particular the coupling constants) show marked structural dependencies. The magnitude of ^{4}J(F—F) is sensitive to the cis or trans orientation of the relevant P—F bonds (ca. −1.0 and ca. +12.0 Hz, respectively) (*123*).

* The shifts are expressed in parts per million relative to $CFCl_3$; upfield shifts are negative.

The ^{19}F NMR spectra of fluorodimethylamino derivatives of cyclotri- and cyclotetraphosphazenes confirm the structures assigned to isomeric products on the basis of ^{1}H NMR data, although a detailed analysis of the ^{19}F spectra of many derivatives could not be made (*209*, *210*, *213*, *307*, *308*). Some typical spectra are shown in Fig. 12. The structures of many chlorofluoro- (*108*, *163*, *223*, *224*), bromofluoro- (*120*), and phenylfluorocyclophosphazenes (*32*, *33*, *116*) have been established mainly on the basis of ^{19}F NMR data. Also ^{19}F NMR data for a series of fluoroalkylamino- (*113*, *114*, *196*, *197*, *327*), fluoroalkyl- (*354*), and fluoroalkoxycyclophosphazenes (*441*) have been reported.

The ^{19}F NMR spectroscopic data for trifluoroethoxy derivatives, $N_3P_3R_{6-n}(OCH_2CF_3)_n$ (R = alkylamino, dialkylamino, alkoxy) can be used as an indirect method of establishing the structures of the chlorocyclophosphazene precursors, $N_3P_3R_{6-n}Cl_n$ (*63*, *139*), but this technique has received very little attention.

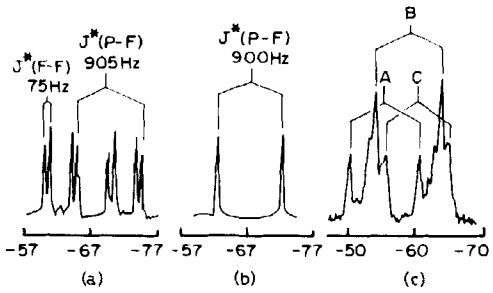


FIG. 12. The ^{19}F NMR spectra of (*a*) 2,2:4-*cis*-6:4,6-$N_3P_3F_2Cl_2(NMe_2)_2$, (*b*) 2,2:4-*trans*-6:4,6-$N_3P_3F_2Cl_2(NMe_2)_2$, and (*c*) 2-*cis*-4-*cis*-6-*trans*-8-$N_4P_4F_4(NMe_2)_4$ [$^{1}J^{*}$(P-F): A = 870 Hz, B = 880 Hz, and C = 840 Hz]. [Reproduced from Green and Sowerby (*209*) and Millington and Sowerby (*307*) by permission of The Chemical Society, London.]

B. Vibrational Spectroscopy

Infrared spectroscopic studies of cyclophosphazene derivatives have been primarily used for "fingerprint" identification and differentiation of homologs (*137*). Attempts to determine the disposition of substituents solely on the basis of infrared spectroscopic data have been largely unsuccessful. The most noteworthy feature in the infrared spectra of cyclophosphazenes is a strong broad band in the region 1150–1450 cm^{-1} attributable to a degenerate ring-stretching vibration, ν(P=N) (*109*). The values of ν(P=N) for a large number of cyclophosphazene derivatives have been compiled (*21*, *125*, *203*, *273*, *336*), and

selected data are shown in Table III. The magnitude of ν(P=N) increases with increasing electronegativity of the substituents. This effect presumably operates by contraction of phosphorus 3d orbitals permitting more effective π'-donation (Section VI) of lone pair of electrons from the ring nitrogen atom to phosphorus: the consequent strengthening of skeletal π-bonding is reflected in the increase in ν(P=N). In the ammono and amino derivatives, the electron flow from the exocyclic nitrogen atom reduces the delocalization of the lone-pair electrons on the ring nitrogen atom and weakens the skeletal π-bonding, thereby depressing the ring P=N frequency. The extent of lowering of the ring P=N frequency is less for aminocyclotriphosphazene derivatives than for the corresponding cyclotetraphosphazene derivatives [relative to the magnitude of ν(P=N) in $N_3P_3Cl_6$ and $N_4P_4Cl_8$, respectively] (*235, 260, 355, 371*).

TABLE III

VALUES OF ν(P=N)(cm^{-1}) FOR SOME SELECTED CYCLOTRI- AND CYCLOTETRAPHOSPHAZENES[a]

R	$N_3P_3R_6$	$N_4P_4R_8$
F	1300	1436
Cl	1218	1315
Br	1175	1275
Ph	1190	1213
OMe	1275	1337
NH_2	1170	1240
NHMe	1175	1215
NHEt	1180[b]	1250[c]
NHPr^n	1183	1266
NHBu^n	1197	1260
NH-*n*-C_5H_{11}	1190	1265
NMe_2	1195	1265

[a] From Paddock (*336*).
[b] From Shaw *et al.* (*409*).
[c] From Sau (*371*).

It may be noted that ν(P=N) for the dimethylamino derivatives, $[NP(NMe_2)_2]_{3,4}$, occur at higher frequencies than for the corresponding ethylamino derivatives. This observation is contrary to that anticipated purely on the basis of inductive effect and can be explained on the basis of greater steric hindrance to multiple bonding of the exocyclic nitrogen atom to the ring for secondary than for primary amino groups (*336*). The inability of the bulky substituents to assume

the planar configuration required to supply electrons from exocyclic nitrogen to phosphorus is also clearly revealed by the magnitude of ν(P=N) in a series of primary alkylaminocyclotri- and cyclotetraphosphazene derivatives (Table III) (*235*, *260*, *355*, *371*). A similar steric effect has been invoked to account for the greater base strengthening effect of a primary amino group compared to that of a secondary amino group in aminocyclotriphosphazenes (*180*). Infrared frequencies reflect ground-state properties, whereas basicity measurements pertain to perturbed state of molecules. However, it seems likely that a similar effect operates in both ground and perturbed states.

The precise assignment of ν(P=N) in amino derivatives of cyclophosphazenes is often difficult because (*a*) ν(P=N) invariably has a bandwidth of ca. 100 cm^{-1} and appears to become narrower with increasing degree of replacement of chlorine atoms, (*b*) multiple peaks can occur within the broad peak, and (*c*) some of the fundamental vibrations of the amino substituent occurring in the 1200–1400 cm^{-1} region may overlap considerably with ν(P=N). In some cases, no broad band attributable to ν(P=N) may be discerned at all. A careful study of the spectra of a series of aminohalogenocyclophosphazene derivatives as well as a close scrutiny of the spectra of analogous derivatives of cyclotri- and cyclotetraphosphazenes is necessary before an unambiguous assignment can be made. The infrared spectra of some *t*-butylamino derivatives in the region 1100–1500 cm^{-1} (Fig. 13) clearly illustrate this problem.

The feasibility of using infrared data for distinguishing positional isomers has been suggested (*108*, *253*, *420*) because the ring P=N stretching band is more resolved in geminal than in nongeminal isomers. Unfortunately, there are many geminal derivatives that show no splitting of ν(P=N) (*409*) and, hence, this differentiation must be considered as unreliable. The dimethylamino derivatives of $N_3P_3Cl_6$ (*420*) and $N_4P_4Cl_8$ (*305*), which contain $\equiv P(NMe_2)_2$ groups, exhibit two strong and widely separated bands in the 700-cm^{-1} region and these are assigned to the symmetric and asymmetric $\equiv P\begin{matrix}\diagup N \\ \diagdown N\end{matrix}$ exocyclic stretching modes. For compounds containing only $\equiv PCl(NMe_2)$ groups, a single strong band at an intermediate position is observed. This approach also appears to be of limited applicability (*220*, *371*).

Infrared spectra can be used to distinguish cyclophosphazene hydrogen halide adducts from their free bases. In general, ν(P=N) undergoes an upward shift of ca. 40–60 cm^{-1} in the hydrogen halide adduct compared to that in the free base (Table IV). This observation

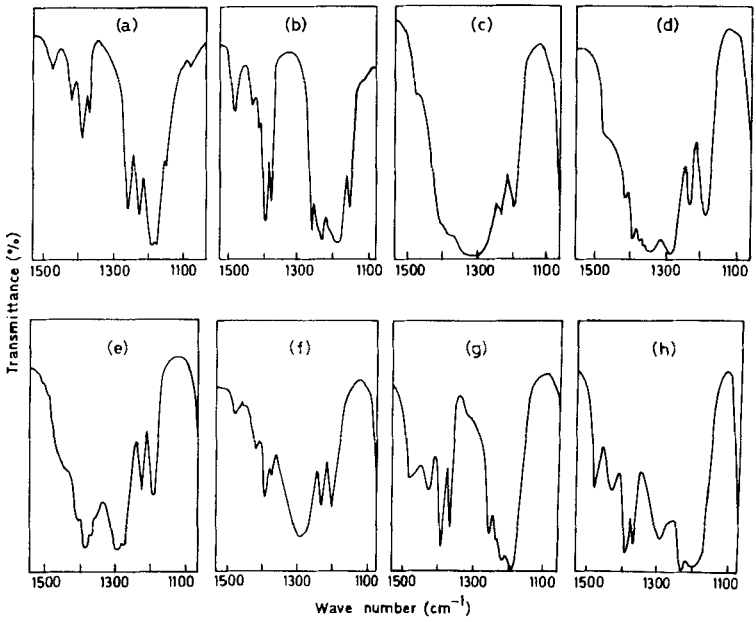


FIG. 13. Infrared spectra of (*a*) *gem*-$N_3P_3Cl_4(NHBu^t)_2$, (*b*) *gem*-$N_3P_3Cl_2(NHBu^t)_4$, (*c*) $N_4P_4Cl_7(NHBu^t)$, (*d*) 2,4-$N_4P_4(NHBu^t)_2Cl_6$, (*e*) 2,6-$N_4P_4(NHBu^t)_2Cl_6$, (*f*) 2,4,6-$N_4P_4(NHBu^t)_3Cl_5$, (*g*) $N_4P_4(NHBu^t)_8$, and (*h*) $N_4P_4(NHBu^t)_8$·HCl in the region 1100–1500 cm^{-1} (KBr pellet).

TABLE IV

VALUES OF ν (P=N) FOR SOME SELECTED CYCLOPHOSPHAZENE HYDROCHLORIDE ADDUCTS AND THEIR FREE BASES

Adduct	ν (P=N) (cm^{-1})	Free base	ν (P=N) (cm^{-1})	Ref.
$N_3P_3(NMe_2)_6$·HCl	1253	$N_3P_3(NMe_2)_6$	1195	*220*
$N_3P_3(NMe_2)_3(NHPh)_3$·HCl	1180, 1220	$N_3P_3(NMe_2)_3(NHPh)_3$	1165	*220*
$N_3P_3(NHEt)_6$·HBr	1230	$N_3P_3(NHEt)_6$	1180	*355*
$N_3P_3(NHPr^n)_6$·HCl	1235	$N_3P_3(NHPr^n)_6$	1183	*313*
$N_3P_3(NHBu^n)_6$·HCl	1252	$N_3P_3(NHBu^n)_6$	1197	*313*
$N_3P_3Me_6$·HCl	1170, 1230	$N_3P_3Me_6$	1180	*331, 396*
$N_4P_4(NHEt)_2(NMe_2)_6$·2HCl (2-*trans*-6)	1300	$N_4P_4(NHEt)_2(NMe_2)_6$ (2-*trans*-6)	1270	*372*
$N_4P_4(NHBu^t)_8$·HCl	1300	$N_4P_4(NHBu^t)_8$	1235	*371*
$N_4P_4(NHBu^t)_2(NMe_2)_6$·HCl (2,6)	1320	$N_4P_4(NHBu^t)_2(NMe_2)_6$ (2,6)	1280	*371*
$N_4P_4Me_8$·2HCl	1282, 1322	$N_4P_4Me_8$	1220	*331, 396*

TABLE V

X-RAY STRUCTURAL DATA FOR SOME CYCLOPHOSPHAZENES[a]

Compound[b]	X	Y	Ring shape	Average ring P—N bond length Å	Average P—N—P bond angle (°)	Average ring N—P—N bond angle (°)	X—P—Y bond angle (°)	Ref.
$N_3P_3F_6$	F	F	Planar	1.57	120.3	119.4	99.1	*161*
$N_3P_3Cl_6$	Cl	Cl	Very nearly planar	1.58	121.4	118.4	101.4	*83*
$N_3P_3Br_6$	Br	Br	Slightly chair	1.58	122.7	117.0	102.5	*195*
$N_3P_3Ph_6$	Ph	Ph	Slightly chair	1.597	122.1	117.8	103.8	*3*
$N_3P_3(NMe_2)_6$	NMe_2	NMe_2	Distorted boat	1.588	123.0	116.7	101.5	*360*
$N_3P_3F_3Cl_3$ (2-*cis*-4-*cis*-6)	Cl	F	Slightly boat	1.567	120.9	118.8	99.7	*122*
$N_3P_3Ph_2F_4$ (2,2)	F	Ph	Slightly boat	1.57[c]	120.5	118.0[d]	X—P—X = 96.9 Y—P—Y = 107.9	*31*
$N_3P_3Ph_2Cl_4$ (2,2)	Cl	Ph	Slightly chair	1.58[c]	121.1	118.2	X—P—X = 100.3 Y—P—Y = 104.4	*290*
$N_3P_3(NMe_2)_3Cl_3$ (2-*trans*-4-*trans*-6)	Cl	NMe_2	Slightly boat sofa	1.573	120.6	119.0	104.9	*6*
$N_4P_4F_8$	F	F	Planar	1.51	147.2	122.7	99.9	*302*
$N_4P_4Cl_8$(K)	Cl	Cl	Boat	1.57	131.3	121.2	102.8	*222*
$N_4P_4Cl_8$(T)	Cl	Cl	Chair	1.56	135.6	120.5	103.1	*443*
$N_4P_4Br_8$(K)	Br	Br	Nearly boat	1.575	131.0	120.1	103.9	*459*
$N_4P_4(NMe_2)_8$	NMe_2	NMe_2	Puckered	1.58	133.0	120.0	104.0	*82*
$N_4P_4(OMe)_8$	OMe	OMe	Saddle	1.57	132.0	121.0	105.5	*38*
$N_4P_4Ph_8$	Ph	Ph	Hybrid boat–saddle	1.59	127.8	119.8	105.1	*50*

$N_4P_4Me_8$	Me	Me	Puckered	1.60	131.6	119.8	104.0	*160*
$N_4P_4Me_2F_6$ (2,2)	F	Me	Saddle	1.52[c]	145.0	122.5	X—P—X = 93.6 Y—P—Y = 105.7	*298*
$N_4P_4(NMe_2)_4F_4$ (2-*trans*-4-*cis*-6-*trans*-8)	F	NMe_2	Saddle	1.557	134.6	122.3	105.3	*51*
$N_4P_4Ph_4Cl_4$ (2-*cis*-4-*cis*-6-*cis*-8)	Cl	Ph	Irregular crown	1.57	137.5[c]	121.0	102.8	*85*
$N_4P_4Ph_4Cl_4$ (2,2,6,6)	Cl	Ph	Saddle	1.57[c]	132.1	120.6	X—P—X = 100.8 Y—P—Y = 107.5	*90*
$N_4P_4(NMe_2)_2Cl_6$ (2-*trans*-6)	Cl	NMe_2	Chair	1.57[c]	134.2[c]	120.6	X—P—X = 101.7 Y—P—Y = 107.9	*87*
$N_4P_4(NMe_2)_4Cl_4$ (2-*cis*-4-*trans*-6-*trans*-8)	Cl	NMe_2	Hybrid crown-saddle	1.556	136.8[c]	121.1	105.1	*86*
$N_4P_4Cl_3(NMe_2)_5$ (2-*cis*-4-*cis*-6)	Cl	NMe_2	Hybrid crown-saddle	1.57[c]	135.8[c]	122.0[c]	X—P—Y = 104.2 Y—P—Y = 103.6	*46*
$N_4P_4Cl_2(NMe_2)_6$ (2-*trans*-6)	Cl	NMe_2	Chair	1.57[c]	135.4	120.7	X—P—Y = 103.8 Y—P—Y = 103.6	*89*
$N_4P_4Et_2Me_6 \cdot 2HCl$ (2-*trans*-6)	Me	Et	Chair	1.665 1.572	133.2	112.2	X—P—Y = 109.1 Y—P—Y = 106.1	*99*
$N_5P_5Cl_{10}$	Cl	Cl	Very nearly planar	1.52	148.6[c]	118.4	102.0	*377*
$N_5P_5Br_{10}$	Br	Br	Puckered	1.571	135.9[c]	117.5[c]	103.3	*218*
$N_6P_6(NMe_2)_{12}$	NMe_2	NMe_2	Double-tub[d]	1.563	147.5	120.0	102.9	*444*
$N_8P_8(OMe)_{16}$	OMe	OMe	*e*	1.561	136.7[c]	116.7[d]	101.3	*338*

[a] Crystal structures of the following cyclophosphazenes (which are not mentioned in the table or in Sections IV,A; V,C and D) have also been reported: $N_3P_3(NCS)_6$ (*173*), $N_3P_3(OPh)_6$ (*297*), $N_3P_3FCl_5$ (*333*), *cis*-$N_3P_3F_3Br_3$ (*122*), $N_3P_3F_5NH_2$ (*347*), *gem*-$N_3P_3Cl_3(NMe_2)_3$ (*4*), *cis*-$N_3P_3Cl_3(NMe_2)_3$ (*5*), 2,2,6,6-$N_4P_4F_4Me_4$ (*299*), 2-*cis*-4-*trans*-6-*trans*-8-$N_4P_4F_4(NMe_2)_4$ (*306*), 2-*cis*-4-*trans*-6-*trans*-8-$N_4P_4Cl_4Ph_4$ (*93*), 2-*cis*-4-*trans*-6-*trans*-8-$N_4P_4(NHMe)_4Ph_4$ (*84*), 2-*trans*-6-$N_4P_4(NMePh)_2Cl_6$ (*59*), and $N_5P_5F_{10}$ (*219*).

[b] Disposition of one set of substituent groups defined where necessary.

[c] Significant deviations from the stated mean value.

[d] Figure 15a.

[e] Figure 15b.

is consistent with protonation occurring at a ring nitrogen atom (*313*). In addition, a fairly strong band in the region 915–935 cm^{-1} and a medium to weak band at 2300–2650 cm^{-1} appear in the spectra of hydrogen chloride adducts. These have been assigned to the $P—\overset{\oplus}{N}(H)—P$ linkage with no ring resonance (*413*) and the N—H stretching frequency of the group $=\overset{\oplus}{N}H—$, respectively (*220, 313, 371*).

Several attempts have been made to determine the symmetry (and hence the conformation of the phosphazene ring) of halogenocyclophosphazenes in the solid, liquid, and solution states using infrared and Raman spectroscopy (*2, 136, 249, 255, 255a, 422*). With some exceptions, there is reasonable agreement between the structures determined by diffraction methods and those predicted by vibrational spectroscopy. The calculation of force constants in $N_3P_3Cl_6$ and assignment of vibration frequencies have been discussed (*118*).

C. X-Ray Diffraction Studies

The structures of a large number of cyclophosphazene derivatives have been determined by X-ray diffraction, and the data obtained have helped to clarify the nature of the bonding in this class of compounds. Corbridge (*125*) has recently reviewed this work.

X-Ray crystallographic data for some cyclophosphazene derivatives are shown in Table V. The P—N skeletal bond lengths in cyclophosphazenes lie in the range 1.51–1.60 Å and are shorter than the accepted value (1.77 Å) for a P—N single bond (*21, 125*). This bond contraction provides good evidence for some kind of π-interaction between the skeletal phosphorus and nitrogen atoms. The presence of π-bonding between phosphorus and exocyclic groups, such as $—NMe_2$ or —OR, has also been inferred from X-ray crystallographic data. In homogeneously substituted cyclophosphazenes, the ring P—N bond lengths are equal and decrease with increasing electronegativity of the substituents. This attenuation 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 PNP angle. In a heterogeneously substituted compound, the ring P—N bonds are unequal. Thus, in 2,2,4,4,6,6:8,8-$N_4P_4F_6Me_2$ (*298*), there are four different P—N bond lengths with mean values 1.584, 1.470, 1.532, and 1.487 Å. Similar variations have been observed for *gem*-$N_3P_3Cl_4Ph_2$ (*290*), *gem*-$N_3P_3Cl_2Ph_4$ (*291*), *gem*-$N_3P_3F_4Ph_2$ (*31*), and 2-*cis*-4 *cis*-6:2,4,6,8,8,-$N_4P_4Cl_3(NMe_2)_5$ (*46*). These variations have been rationalized in terms of different degrees of ring π-bonding resulting from greater d-orbital contraction at the phosphorus atom bearing the most

electronegative substituents. An observation that defies explanation is the presence of two different P—Cl bond lengths in *gem*-$N_3P_3Cl_4Ph_2$ (*290*) and *gem*-$N_3P_3Cl_2Ph_4$ (*291*). In cyclophosphazenes that contain nongeminal $\equiv PCl(NMe_2)$ groups, cooperative electron withdrawal by chlorine and electron donation by the amino nitrogen result in longer P—Cl and shorter P—N exocyclic bonds than are encountered in geminal $\equiv PCl_2$ and $\equiv P(NMe_2)_2$ groups (*4*, *5*, *86*, *87*, *89*).

Cyclophosphazene rings can be planar or puckered. Generally, the six-membered cyclophosphazenes are more or less planar, although in some cases small deviations from planarity have been observed. The octachloride, $N_4P_4Cl_8$, exists in two crystallographic modifications—the metastable K form having a boat conformation (*222*) and the T form having a centrosymmetric chair shape (*443*). The crystal structure analyses of a number of cyclotetraphosphazene derivatives show that the eight-membered P—N ring can adopt any of several possible conformations (planar, chair, boat, crown, saddle, or hybrid conformation). The saddle conformation of the ring in 2-*trans*-4-*cis*-6-*trans*-8:2,4,6,8-$N_4P_4F_4(NMe_2)_4$ is illustrated in Fig. 14 (*51*). Evidently, the energy differences among the various conformations are small and the attainment of a particular conformation depends on a delicate balance of a number of intra- and intermolecular factors (maximization of skeletal π-bonding, orientation of the substituents and their polar and steric nature, crystal-packing effects, and hydrogen-bonding interactions) (*85*, *86*, *90*, *161a*, *306*, *336*).

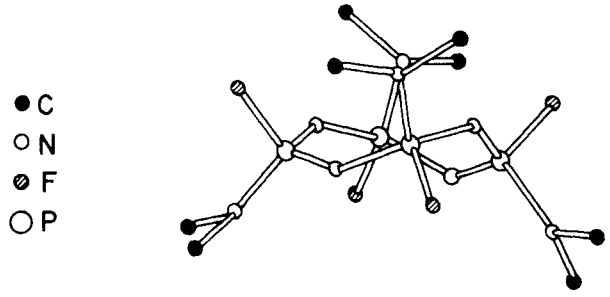


FIG. 14. Molecular configuration of 2-*trans*-4-*cis*-6-*trans*-8-$N_4P_4F_4(NMe_2)_4$. [Reproduced from Begley *et al.* (*51*) by permission of The Chemical Society, London.]

Higher oligomeric rings are generally puckered with the exception of $N_5P_5Cl_{10}$ (*377*). The ring conformations in $N_6P_6X_{12}$ (*161a*, *444*) and $N_8P_8X_{16}$ (*338*, *99a*) (X = OMe and NMe_2) are shown in Fig. 15. The sixteen-membered ring (Fig. 15b) consists of two planar and parallel segments joined by a step at two opposite nitrogen atoms. A striking

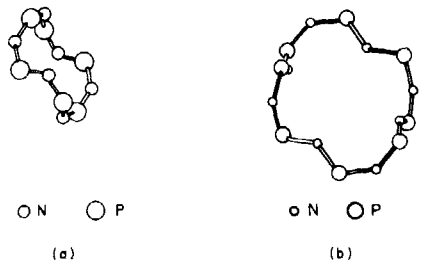


FIG. 15. Conformations of the P—N rings in (*a*) $N_6P_6X_{12}$ and (*b*) $N_8P_8X_{16}$ (X = OMe, NMe_2). [Adapted from Dougill and Paddock (*161a*) and Paddock *et al.* (*338*) by permission of The Chemical Society, London.]

feature of the structure of $N_8P_8(NMe_2)_{16}$ is that it exhibits both the largest angle (170.2°) at nitrogen in a cyclophosphazene and the largest mean value (156.5°) (*99a*).

The crystal structure of the bicyclic phosphazene $N_4P_4(NMe_2)_5$ (NHEt)(NEt) (**12**) shows that the original P—N heterocycle retains its phosphazene character but that P—N bonds at the bridgehead are longer and close to the accepted P—N single bond length (*100*). The bridgehead nitrogen atom has a pyramidal configuration and possesses considerable sp^3 character. An X-ray crystallographic study (*217a*) of nitrilohexaphosphonitrilic chloride, $N_7P_6Cl_9$ [discovered by Stokes (*429*) in 1897], confirms the tricyclic condensed-ring structure (**28**) suggested earlier for this compound (*263a*). The central P—N bonds (mean value 1.723 Å) are longer than for any other cyclophosphazene derivative and reflect a compromise between the requirements for optimum σ- and π-bonding (*330*). A centrosymmetric structure has been established for the two-ring assembly phosphazenes, **25** (*460*) and **32** (*385*).

It has been pointed out that most cyclophosphazene derivatives undergo protonation at a ring nitrogen atom (Section IV,A,2). X-Ray crystallographic studies of bases and their corresponding protonated species confirm that the skeletal nitrogen atom is the site of protonation and also reveal interesting bond length variations (*23*, *99*, *287*, *292*, *360*, *408*). Figure 16 shows the observed bond lengths for two bases and their conjugate acids. The P—N lengths involving the protonated nitrogen atom are longer than in the free base and are phosphazane-like (*38a*). The exocyclic P—N bonds of $NHPr^i$ and NMe_2 substituents on the phosphorus atoms adjacent to the protonation site are shorter in the conjugate acid than in the free base. The greater shortening observed for the $-NHPr^i$ group (0.034 Å) than for the $-NMe_2$ group

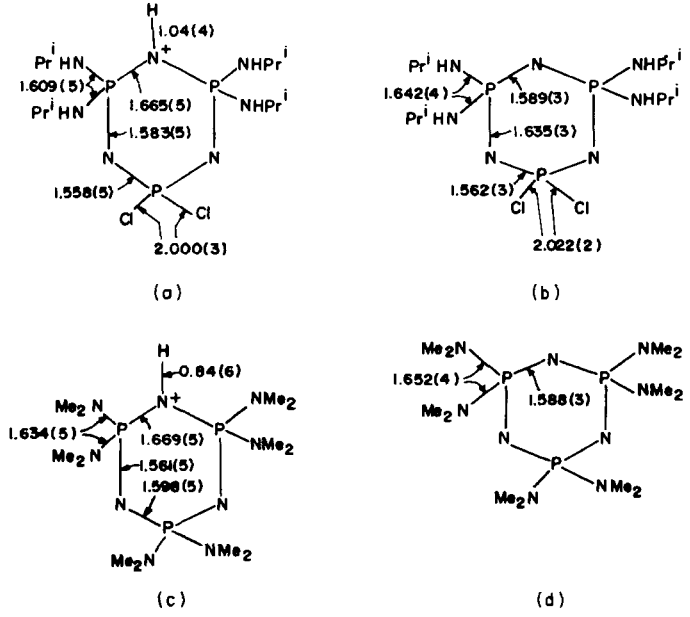


FIG. 16. Bond lengths (Å) in (*a*) $N_3P_3(NHPr^i)_4Cl_2 \cdot HCl$, (*b*) $N_3P_3(NHPr^i)_4Cl_2$, (*c*) $[HN_3{}^{\oplus}P_3(NMe_2)_6]_2Mo_6O_{19}{}^{2-}$, and (*d*) $N_3P_3(NMe_2)_6$. [Data from Shaw (*408*).]

(0.020 Å) is in keeping with the greater base strengthening effect of primary amino groups over that of secondary amino groups (see Sections V,B and D).

D. Basicity Measurements

The potentiometric titration of cyclophosphazene derivatives with perchloric acid in nitrobenzene (*174*) gives a relative measure of their base strength (pK_a'). Different organic substituents have a marked effect on the basicity of cyclophosphazenes (*175–179*) (Table VI). It has been suggested that protonation occurs at a ring nitrogen atom, and the X-ray crystal structures of protonated cyclophosphazenes substantiate this idea (Section V,C). A useful application of basicity measurements is the assignment of structures to isomeric compounds. Such assignments utilize the observation that compounds with geminal structures usually have a higher basicity than nongeminally substituted derivatives. Cis and trans isomers cannot be distinguished by this method because they have identical basicities (*177*).

TABLE VI

BASICITIES OF SOME CYCLOPHOSPHAZENE DERIVATIVES[a]

Compound	pK_a'	Compound	pK_a'
$N_3P_3(NHMe)_6$	8.8	$N_3P_3Ph_2Cl_2(NHMe)_2$ (2,2:4,6:4,6)	−2.8
$N_3P_3(NHEt)_6$	7.8	$N_3P_3Ph_2Cl_2(NHMe)_2$ (2,2:4,4:6,6)	−0.4
$N_3P_3(NHPr^n)_6$	7.9	$N_3P_3Cl_2(NHEt)_4$ (*gem*)	3.2
$N_3P_3(NHBu^t)_6$	7.9	$N_3P_3Cl_2(NHBu^t)_4$ (*gem*)	3.5
$N_3P_3(NMe_2)_6$	7.6	$N_3P_3Cl_5(NPPh_3)$	< −6.0
$N_3P_3(NEt_2)_6$	8.2	$N_3P_3Cl_4Ph(NPPh_3)$[b] (2,2,4,4:6:6)	−4.7
$N_3P_3(OEt)_6$	−0.2	$N_3P_3Cl_4(NH_2)(NPPh_3)$[b] (2,2,4,4:6:6)	−2.9
$N_3P_3Et_6$	6.4	$N_3P_3Cl_4(NPPh_3)_2$ (*gem*)	0.4
$N_3P_3Ph_6$	1.5	$N_3P_3Cl_4(NPPh_3)_2$ (nongem)	0.2
$N_3P_3Cl_3(NMe_2)_3$ (*trans*)	−5.4		
$N_3P_3Cl_3(NMe_2)_3$ (*gem*)	−4.4		

[a] Data from Refs. (*177, 178, 408*).

[b] Exocyclic protonation postulated; in other cases data consistent with protonation at a ring nitrogen atom.

As a result of the extensive compilation of basicity data for cyclotriphosphazenes, it has been possible to evaluate substituent constants for different groups (*178–180*). These constants, can be used to calculate the pK_a' value of a cyclophosphazene derivative containing one or more substituents (*179, 180*). Hence, a comparison of calculated and observed pK_a' values can often provide information for the complete characterization of a derivative (*180*). Basicity data for cyclotetraphosphazenes and higher homologs are limited (*175, 321*), and substituent constants have not been evaluated.

Basicity measurements for cyclophosphazenes containing a triphenylphosphazenyl substituent (—N=PPh_3) (*323*) suggest that protonation can take place either at a ring nitrogen atom (Type I) or at the nitrogen atom of the phosphazenyl substituent (Type II) (Table VI). It is believed that in Type I compounds, the N—P bond of the triphenylphosphazenyl group is more or less parallel to the local N—P—N ring segment, whereas in Type II compounds it is approximately perpendicular (*408*). The X-ray crystal structures of $N_3P_3Cl_4Ph(NPPh_3)$ (**22**) (*67*) and $N_3P_3Cl_5(NPPh_3)$ (**23**) (*44*) show that these compounds have Type II and Type I conformations, respectively.

Also noteworthy is the observation that in the ground state, the electron-releasing power of the $—N{=}PPh_3$ group is of the order of that of $—NR_2'$ and $—NHR'$ groups, whereas at the demand of a proton, the $—N{=}PPh_3$ group behaves as a much stronger electron donor. This behavior may be due to a major contribution from the resonance form $—\overset{\ominus}{N}—\overset{\oplus}{P}Ph_3$.

E. Nuclear Quadrupole Resonance Spectroscopy

Chlorocyclophosphazenes and their derivatives can be studied in the solid state by NQR spectroscopy. The hexachloride, $N_3P_3Cl_6$, has a slight "chair" configuration and the molecule is bisected by a mirror plane (*83*). Although the P—Cl bond lengths are almost identical, there are 4 structurally distinct chlorine atoms and these give rise to a four-line ^{35}Cl NQR spectrum (*124*). The ^{35}Cl NQR spectra of the K and T forms of the octachloride, $N_4P_4Cl_8$, have been reported, and the multiplicity of the signals observed has been related to the symmetry of each molecule (*157*, *238*).

There is an approximately linear relationship between ^{35}Cl NQR frequencies and P—Cl bond lengths in closely related chlorocyclophosphazene derivatives [e.g., $N_3P_3Cl_{6-n}Ph_n$ (n = 0, 2, 4); $N_3P_3Cl_3(NMe_2)_3$ isomers). An increase in bond length is accompanied by a decrease in the NQR frequency, and this change presumably reflects an increase in the ionic character of the bond (*248*).

The use of ^{35}Cl NQR spectroscopy to identify chemically distinct nuclei in chlorocyclophosphazene derivatives is limited by problems of signal sensitivity and crystal packing effects in the sample. Consequently, unambiguous structural assignments cannot always be made solely on the basis of NQR data. The ^{35}Cl NQR frequencies characteristic of $\equiv PCl_2$, $\equiv PCl(NMe_2)$, and $\equiv PPhCl$ occur in the ranges 26–29, 22–25, and 23–25 MHz, respectively, and permit a distinction of geminal and nongeminal isomers (*138*).

F. Other Techniques

The potential of dipole moment measurements for structural assignments in cyclophosphazene chemistry has been noted. The cis and trans isomers of $N_3P_3Ph_3Br_3$ (*315*, *316*), $N_3P_3Cl_4(NMe_2)_2$, $N_3P_3Cl_3(NMe_2)_3$ (*263*), $N_3P_3Cl_4(NHMe)_2$ (*279*), and $N_3P_3F_4Ph_2$ (*32*) have been distinguished from dipole moment data. Dipole moments for several *cis*- and *trans*-dialkylaminocyclotriphosphazenes have also been reported (*261*). In view of the uncertainties in allowing for the atom polarization term

and the possible deviations of the ring from planarity, dipole moment data cannot always be interpreted unambiguously (*392*).

The mass spectra of halogenocyclophosphazenes (*79*, *80*, *131*, *132*, *390*) and isothiocyanatocyclophosphazenes (*445*) show the inherent stability of P—N cyclic systems. The mass spectra of some aryl-substituted fluorocyclotriphosphazenes reveal differences in the major fragmentation process between geminal and nongeminal isomers (*36*). The fragmentation patterns of amino and aminohalogeno derivatives have not been investigated. The use of mass spectrometry for determining the disposition of substituents in cyclophosphazene derivatives is likely to be limited because the phosphazene ring does not undergo fragmentation until most substituent groups have been lost (*105*). The ionization potentials of several cyclophosphazene derivatives have been determined by mass spectrometry (*78*, *132*) and photoelectron spectroscopy (*78*, *212*).

Data obtained from other physical measurements (ultraviolet and electron-spin resonance spectroscopy, thermochemical measurements, polarography, etc.) have been compiled (*249*) and discussed (*21*). By and large, comparisons based on these data are not very instructive.

VI. Bonding and Electronic Structure

The nature of the bonding in cyclophosphazene rings has provided a considerable challenge for theoreticians. The shortness and equality of P—N bond lengths in homogeneously substituted cyclophosphazenes (Section V,C) can be interpreted as a conjugative interaction involving phosphorus and nitrogen. A precise description of this π-bonding is still a controversial point.

Craig and Paddock (*134*) initially suggested that the σ-bonded P—N skeleton is supplemented by π-bonding involving nitrogen p_z and phosphorus d_{xz} orbitals. Delocalization of electrons occurs through extended molecular orbitals covering all the ring nuclei. If the phosphazene ring deviates markedly from planarity, the π-bonding system can be maintained by using different combinations of d orbitals of the correct symmetry. This type of π-bonding bears a superficial resemblance to that of benzene. However, an additional type of π-bonding can be envisaged for phosphorus–nitrogen heterocycles that is not possible for aromatic carbon compounds. Overlap of the sp^2 orbital of nitrogen containing the lone-pair electrons and phosphorus d_{xy} and $d_{x^2-y^2}$ orbitals would permit "in-plane" π-bonding (designated as π'-bonding) (*135*). The puckering and greater PNP angles observed for cyclotetraphosphazene derivatives make conditions more favorable for significant π'-overlap. The presence of substituent groups or atoms

of high electronegativity will contract the phosphorus d orbitals and, hence, facilitate donation of the nitrogen sp^2 lone-pair electrons to the π'-system. Conversely, it would be anticipated that electron-donating substituents participate in exocyclic π-bonding by means of the d_{z^2} orbital on phosphorus and, thus, allow the remaining d orbitals to expand. This backbonding would effectively localize the lone-pair electrons at ring nitrogen atoms and disrupt the π'-system. Hence, the balance of π- and π'-bonding associated with the phosphazene skeleton will be influenced by the nature of the exocyclic substituents. The orbital overlap schemes for π-bonding in cyclophosphazenes are shown in Fig. 17.

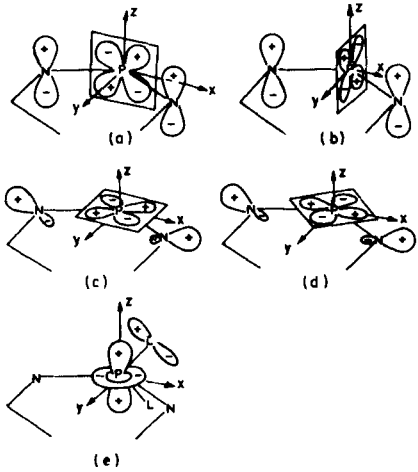


FIG. 17. Orbital overlap schemes for ring π-bonding of (*a*) d_{xz} and (*b*) d_{yz} orbitals with p_z orbitals; (*c*) π'-bonding of d_{xy} and (*d*) $d_{x^2-y^2}$ with an s-p_y hybrid, and (*e*) π-bonding of d_{z^2} with exocyclic substituent p orbital. [Reproduced from Corbridge (*125*) by permission of Elsevier Scientific Publ. Co., Amsterdam.]

The theory proposed by Dewar *et al.* (*154*) is also based on a σ-bonded P—N skeleton of sp^2-hybridized nitrogen and sp^3-hybridized phosphorus but postulates a pair of linear combinations of phosphorus d_{xz} and d_{yz} orbitals for overlap with an adjacent nitrogen p_z orbital. The result is a system of almost independent three-center π-bonds containing two phosphorus atoms and one nitrogen atom (Fig. 18). More detailed calculations appear to support this theoretical treatment (*167, 168, 171, 172, 318*) and indicate that conjugation beyond the three-center islands is of minor importance in cyclotriphosphazene derivatives (*167*). X-Ray crystallographic data for heterogeneously substituted cyclophosphazene derivatives (Section V,C) and evidence

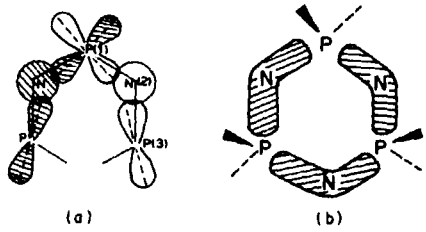


FIG. 18. (*a*) Orbital overlap scheme for three-center P—N—P bonds. (Shaded atomic orbitals are combined in molecular orbitals.) [Reproduced from Craig and Mitchell (*135a*) by permission of The Chemical Society, London.] (*b*) Three-center P—N—P islands in $N_3P_3R_6$.

from other physicochemical measurements (*81*, *170*, *310*) are compatible with this bonding picture. The recent work of Doggett (*158*) suggests that the delocalized model of Craig and Paddock and the three-center P—N—P approach of Dewar *et al.* are fundamentally very similar and differ only in the choice of parameters.

Recently, trans-annular phosphorus–phosphorus bonding has been postulated to account for the stability of the cyclotriphosphazene system (*40–42*, *169*). In eight-membered phosphazene rings, it is believed that trans-annular bonding occurs for phosphorus atoms separated by two bonds, and trans-annular antibonding for phosphorus atoms four bonds apart (*408*).

VII. Potential Applications

The potential use of cyclophosphazene derivatives as ultrahigh-capacity fertilizers (*446*), flame retardants (*199*), pesticides (*216*), and chemosterilant insecticides (*111*) has been demonstrated. Phosphazene high polymers and, in particular, linear polyorganophosphazenes offer considerable promise as materials suitable for aerospace applications, heat-resistant coatings for electrical components, low- and high-temperature elastomers, textile impregnating agents, fire-resistant foams (*21*, *24*), and body implantation plastics (*110*). By and large, phosphazenes are expensive. Prices will have to come down considerably if they are ever to gain widespread use.

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Appendix

The following represents a brief account of recent papers (June 1976–July 1977) which are relevant to the theme of this Review:

A novel synthesis of phospham from red phosphorus and ammonia has been discovered (*37*):

$$4n\mathrm{NH_3} + 2n\mathrm{P} \rightleftharpoons 2[\mathrm{PN_2H}]_n + 5n\mathrm{H_2} \quad (1)$$

Preliminary experiments confirm the prediction that ammono-cyclophosphazenes may be prepared at high pressures:

$$n\mathrm{NH_3} + [\mathrm{PN_2H}]_n \rightarrow [\mathrm{NP(NH_2)_2}]_n \quad (2)$$

The reaction of $N_3P_3(NH_2)_6$ with formaldehyde (*27*) and the hydrolysis of $N_4P_4(NH_2)_8$ (*23*) have been studied. Wanek has reviewed the use of ammonophosphazenes as fertilizers (*39*).

The alkaline hydrolysis of $[NP(OMe)_2]_{3,4}$ gives the monohydroxy derivatives, $N_3P_3(OMe)_5(OH)$ and $N_4P_4(OMe)_7OH$ which exist in the tautomeric oxo-form (*38*). The rearrangement of octamethoxycyclotetraphosphazene, $N_4P_4(OMe)_8$, in the presence of methyl iodide yields two isomeric phosphazanes; the more abundant isomer has the 2-*trans*-4-*cis*-6-*trans*-8 structure (*13*).

The reactions of $N_3P_3Cl_6$ with ethylenediamine and ethanolamine give spirocyclic derivatives (*25*) and *not ansa*-compounds. Aliphatic and alicyclic diols also yield spirocyclic derivatives (*26*, *31*). Inclusion clathrates formed by spirocyclic phosphazenes with aryldioxy substituents (*2*) have been studied by mass spectrometry, broadline ^{1}H NMR, and X-ray techniques (*4*). Some conclusions on molecular motion in these compounds have been deduced.

The replacement of chlorine atoms of $N_3P_3Cl_6$ by fluoroalkoxy groups proceeds nongeminally (*21*). Phosphorus–oxygen and carbon–oxygen bond cleavage have been observed in the reactions of $N_3P_3(OAr)_6$ with several nucleophiles (*3*).

Methylcyclophosphazenes, $(NPMe_2)_n$, n = 6–10, are conveniently prepared by the reaction of MeMgBr with the fluorides, $(NPF_2)_n$ [18]. The crystal structures of $N_5P_5Me_{10}$ (*16*), $N_6P_6Me_{12}$ (*29a*), $N_7P_7Me_{14}$ (*18*) and $N_8P_8Me_{16}$ (*29*) have been determined. Modified syntheses of $N_3P_3Me_6$ and $N_4P_4Me_8$ have been reported. When these compounds are heated at 200–350°C, an equilibrium is established but a high polymer is not formed (*5*):

$$3[\mathrm{NP(Me)_2}]_4 \rightleftharpoons 4[\mathrm{NP(Me)_2}]_3 \quad (3)$$

Phosphazenyl cyclophosphazenes have been synthesized by a silylation method (*15*, *17*).

Cyclophosphazene derivatives, $(NPR_2)_4$ (R = Me, NHMe) and the polymeric phosphazene, $[NP(NHMe)_2]_n$ react with K_2PtCl_4 in organic media to yield square-planar complexes, $(NPR_2)_4 \cdot PtCl_2$ and a product

of composition $[NP(NHMe)_2]_n \cdot (PtCl_2)_x$ ($x:n$ = 1:17), respectively (*6*). The salts, $[H_2N_4P_4R_8]^{2+}$ $[PtCl_4]^{2-}$ are formed in aqueous hydrochloric acid. The crystal structure of $[NP(NHMe)_2]_4 \cdot PtCl_2$ shows that the platinum atom is bonded to two antipodal ring nitrogen atoms (*10*). These water-soluble complexes show significant antitumor activity (*6*). The crystal structure of the nickel complex, $[N_3P_3Ph_4(Me)S]_2$ Ni, has been determined; the nickel atom is bonded to sulfur and two ring nitrogen atoms in a planar coordination (*1*). The platinum(II) and palladium(II) analogs have also been prepared (*34*). Infrared spectra and ^{35}Cl and $^{121,123}Sb$ NQR suggest that the adducts, $SbCl_5 \cdot (NPCl_2)_n$, n = 3,4 and $TaCl_5 \cdot N_3P_3Cl_6$, have the ionic formulas, $[N_nP_nCl_{2n-1}]$ $MCl_6]$ (*24*).

A more general route to spirobi(cyclotriphosphaza)pentaene derivatives [*e.g.*, compound (**4**) in Fig. 1] has now been developed. The octaphenyl derivative (**4**) can be deprotonated to give the hitherto unknown spirobi(cyclotriphosphazene) anion, $(P_5N_6Ph_8)^-$ (*32*). Methylation of these anions (*32*) and also of the cyclotriphosphazene derivatives, $N_3P_3Ph_4X_2$(X = Me, NH_2) (*33*) has been investigated.

Further reactions of *P*-hydridocyclotriphosphazenes (See Section IV,E) have been described. They undergo insertion reactions with aldehydes, ketones, isothiocyanates and electrophilic olefins. Addition of sulfur or oxidation with $KMnO_4$ gives thioxo-or oxo-cyclotriphosphazene derivatives which are methylated at the chalcogen to afford methylthio- and methoxy- cyclotriphosphazenes (*36*). Hydridocyclophosphazenes can also be oxidized to give symmetric and unsymmetric bis(cyclotriphosphazenyl) oxides (*35*).

^1H[8] and ^{13}C[9]NMR data for phenyl-substituted fluorocyclotriphosphazenes indicate that there is a strong conjugative electron release from the phenyl group into the phosphazene ring. Single crystal Raman polarization data are reported for $N_3P_3X_6$(X = Cl, Br) (*22*). Conformational analysis of halogenocyclophosphazenes has been carried out (*12*). Cyclophosphazenes add electrons to form phosphoranyl radical anions. The ESR evidence for these anions is inconsistent with the postulate of extensive π-bonding within the P–N ring. A partial ionic structure with extensive σ-delocalization to achieve charge neutralization is proposed (*28*).

Details of crystal structures of the two-ring assembly phosphazene (**32**) (*1*) and the bicyclic phosphazene (**12**) (*14*) have been published. X-Ray crystallography shows that the compound, $N_4P_4F_6$(NSN) has a 2,4-fusion of rings (*19*) rather than the 2,6-fusion suggested earlier. The crystal structures of $N_3P_3F_4(NH_2)_2$ (*30*), 2-*trans*-4-$N_4P_4(NMePh)_2$ Cl_6 (*10a*) and 2-*cis*-4-*cis*-6-*trans*-8-$N_4P_4Cl_4(NMe_2)_4$ (*11*) have also been reported. Glidewell has noted that the P . . . P nonbonded contacts in

many cyclophosphazenes remain constant (2.90 Å) and that this may have some bearing on the unusually large ring PNP angles in some of these compounds (*20*).

Recent developments in phosphazene high polymer chemistry have been summarized (*7*).

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