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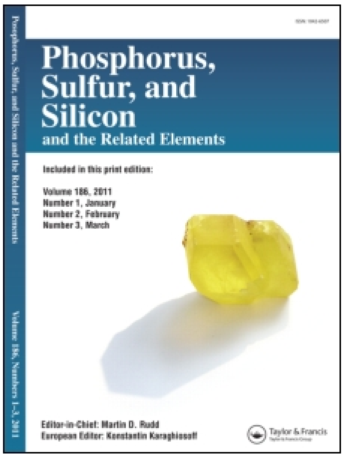

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# Phosphazenyl Derivatives, $R_3P=NX$

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# REVIEW

# Phosphazenyl Derivatives, $R_3P{=}NX$

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(Plenary lecture presented at The Memorial Conference of Organophosphorus Chemistry in honour of the 100th Anniversary of Academician A. E. Arbusov's birth, Kiev, USSR, December 12–16, 1977)

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The synthesis, reactions, physical properties, and structures of phosphazenyl derivatives, $R_3P{=}NX$ are discussed. Of the three types of bond formation involved in the synthesis of phosphazenyl compounds (a) R—P, (b) P=N, and (c) N—X, the greatest accent is placed on (b) and (c). R can be Cl, Ph, Me, $NMe_2$, OAlk etc.; X can be Ar, $SO_2$-*p*-tol, $N_3C_3Cl_2$, $N_3P_3Cl_5$, $N_4P_4F_7$, etc. Basicities, bond lengths and angles, conformations, and spectroscopic properties are analysed.

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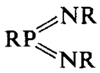
## INTRODUCTION

Phosphazenes of three types are now known.[1,2] I have classified these according to the co-ordination number of phosphorus and called them types **A**, **B**, **C**.[3]

$RP{=}NR$

**(A)**



$RP({=}NR)_2$

**(B)**

$R_3P{=}NR$

**(C)**

We owe phosphazenes of type **A** and **B** to the work of Niecke and Scherer.[4–7] I have compared the structures of the three types in my lecture in Madrid.[3] In my present lecture, I will confine myself to phosphazenes of type **C**.

## SYNTHESIS[1,2]

When one synthesizes phosphazenyl derivatives, $R_3P{=}NX$, in a given reaction sequence, one or more of the bonds (a) R—P, (b) P=N, or (c) N—X are formed. If R = Cl, the usual range of reactions with amines, alcohols, Grignard reagents, etc. have been studied. These retain, in general, the phosphazenyl structure.

$$\begin{tikzcd}
\text{P—R} & \text{P—Cl} \arrow[l, "RMgX"'] \arrow[r, "R_2NH"] \arrow[d, "ROH"] & \text{P—NR}_2 \\
 & \text{P—OR} &
\end{tikzcd}$$

Hydrolysis on the other hand leads by a prototropic shift to phosphazane derivatives, e.g. $R_2(O)P\text{–}NHX$.[8] Alkoxyphosphazenes $R_2(RO)\text{-}P{=}NX$, undergo a rearrangement to oxophosphazanes,[9a,b] $R_2(O)P\text{—}NRX$, a phenomenon observed in cyclophosphazene chemistry, e.g. $N_4P_4(OMe)_8 \rightarrow N_4Me_4P_4O_4(OMe)_4$[10–12] where both species have been investigated by X-ray crystallography.[3,13–15]

$$X\text{–}N{=}PR_2\text{–}Cl \xrightarrow{H_2O} X\text{–}N{=}PR_2(OH) \rightleftharpoons X\text{–}NH\text{–}PR_2(O)$$

$$X\text{–}N{=}PR_2(OR') \xrightarrow{\Delta} X\text{–}NR'\text{–}PR_2(O)$$

$$R' = Alk$$

A wide variety of methods are available to form the P=N bond. The first monophosphazene was reported by Staudinger,[16] who used the azide route.

$$XN_3 + R_3P \longrightarrow XN{=}PR_3$$

This reaction has been widely applied by others.[1,2,17]

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Kirsanov[1,18] has pioneered another, very versatile, route using aromatic amines, or organic or inorganic acid amides containing an $NH_2$ group and allowing these to react with phosphorus pentachloride.

$$X{-}NH_2 + PCl_5 \longrightarrow XN{=}PCl_3$$

A vast literature has accumulated on this subject.[1,2] Horner[19a] introduced a modification involving the use of substituted phosphoranes, e.g. $Ph_3PCl_2$.[19a,b]

$$XNH_2 + Ph_3PCl_2 \longrightarrow XN{=}PPh_3.$$

Other methods for synthesizing the P=N bond involve:

i) *N*-halogenoamides, e.g. $RCONCl_2$[20a,b]

$$RCONCl_2 + Ph_3P \xrightarrow{Cu} RCON{=}PPh_3$$

ii) Chloramine-T, $p\text{-}MeC_6H_4SO_2NaCl$,[21] and related compounds, e.g.

$$p\text{-}MeC_6H_4SO_2NaCl + PR_3 \longrightarrow p\text{-}MeC_6H_4SO_2N{=}PR_3$$

iii) a route due to Appel[22] involving the use of $CCl_4$, tertiary phosphines and amides, e.g.

$$R_2(S)PNH_2 + Ph_3P + CCl_4 \longrightarrow R_2(S)P{=}NPPh_3$$

iv) the use of aminophosphites introduced by Pudovik,[23] e.g.

$$(EtO)_2PNHAc + CH_2{=}CYR \longrightarrow (EtO)_2(CHYRCH_2)P{=}NAc$$

v) the reaction of certain nitriles with $PCl_5$, due to Fluck,[24] e.g.

$$PhCH_2CN + PCl_5 \longrightarrow PhCCl_2CCl_2N{=}PCl_3$$

vi) the tautomeric shift in certain aminophosphines, first observed by Schmidpeter,[25] e.g.

$$R_2PCl + H_2NX + NEt_3 \longrightarrow R_2P{-}NHX \rightleftharpoons R_2HP{=}NX$$

vii) the reactions of organometallic reagents, PhMgBr or $Ph_2Mg$, with $N_3P_3Cl_6$ or $N_4P_4Cl_8$,[26,27] give rise *inter alia* to acyclic, $Ph_3P{=}N{-}PPh_2{=}NH$, HX, and cyclic phosphazenyl derivatives, $N_3P_3Cl_5(NPPh_3)$ and $N_3P_3Cl_5[NPPh(NPPh_3)_2]$, the structure of the latter being deduced by $^{31}P$ nmr spectroscopy.[28]

The above list is by no means comprehensive.

The formation of the N–X bond is generally achieved by allowing the monophosphazene, $R_3P{=}NH$,[29] to react with an acid halide,[29–31]

$$Ph_3P{=}NH + RCOCl \longrightarrow Ph_3P{=}NCOR$$

or to use silylated derivatives, e.g. $R_3P{=}NSiMe_3$[32–35a,b]

$$R_3P{=}NSiMe_3 + YX \longrightarrow R_3P{=}NX + Me_3SiY \quad (Y = F, Cl)$$

The various advantages or disadvantages of the above methods have been discussed in some detail elsewhere, e.g. (Ref. 35b). Perhaps one example might be of note here. In cyanuric chloride, $N_3C_3Cl_3$, one, $N_3C_3Cl_2(NPPh_3)$ or two Cl atoms, $N_3C_3Cl(NPPh_3)_2$, could be readily replaced by triphenylmonophosphazene, $Ph_3P{=}NH$; attempts to replace the third Cl atom were unsuccessful.[35b] On the other hand a Kirsanov type reaction eventually yielded the tris-derivative, $N_3C_3(NPPh_3)_3$.[36]

$$[N_3C_3(NH_2)_3 + Ph_3PCl_2 \longrightarrow N_3C_3(NPPh_3)_3].$$

The reactivity of a given silylated monophosphazene, $Me_3SiN{=}PA_3$ towards a given substrate, e.g. $N_3P_3F_6$ or $N_3P_3Cl_6$,[37] follows the basicity series established for cyclotriphosphazatrienes, $N_3P_3A_6$,[38a,b] where the basicity decreases A = $NMe_2$ > Me > Ph > OEt > SEt >OPh > $OCH_2CF_3$ > Cl, and the reactivity of the above reagent, $Me_3SiN{=}PA_3$ decreases likewise.[37]

$$\text{Reactivity: } Me_3SiN{=}PA_3 + \underset{(\text{or } N_3P_3Cl_6)}{N_3P_3F_6} \longrightarrow \underset{[\text{or } N_3P_3Cl_5(NPA_3)]}{N_3P_3F_5(NPA_3)}$$

$$\text{Basicity: } N_3P_3A_6 + H^+ \rightleftharpoons N_3P_3A_6H^+$$

$$A = NMe_2 > Me > Ph > OEt > SEt > OPh > OCH_2CF_3 > Cl$$

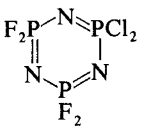
With silylating reagents in general, $Me_3SiB$ (B = $NMe_2$, OMe, SMe, $NPA_3$, etc.), reactivity is greater with fluorides, FX, than with chlorides, ClX.[37] Roesky and Grosse-Böwing[39a,b] observed a decreased susceptibility to reaction with the silylamine, $Me_3SiNMe_2$, $-N{=}PF_2Cl > -N{=}PF_3 > -N{=}PCl_3 > -N{=}PF_2NMe_2 > -N{=}PCl_2NMe_2$. Dahmann, Rose and Shaw[37] showed that towards a given silylmonophosphazene, $N_3P_3F_6$ was more reactive than $N_3P_3Cl_6$.

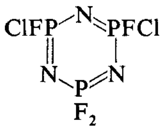
Mixed chlorofluoro-derivatives of phosphorus appear to be an exception to the generalization that P–F bonds react preferentially to P–Cl bonds with silylating agents. Thus, reaction of chlorine rather than of fluorine with $Me_3SiNMe_2$ is reported for $-N{=}PF_2Cl$.[39a,b] Similarly Binder and Fischer[40] report the following reaction

$$(RO)PFCl + (Me_3Si)_2NMe \longrightarrow (RO)PF(NMeSiMe_3) + Me_3SiCl \text{ and}$$

$$(RO)PF(NMeSiMe_3) + (RO)PFCl \longrightarrow [(RO)PF]_2NMe + Me_3SiCl.$$

It would seem worthwhile investigating the reactions of geminal and nongeminal chlorofluorocyclophosphazenes, e.g. $N_3P_3F_4Cl_2$,





with monophosphazenes, $R_3P{=}NH$, and silylated derivatives, $R_3P{=}NSiMe_3$, and to establish which are the most reactive sites in these isomers for the two types of reagents.

In the synthesis of (polyphosphazenyl)cyclophosphazenes, steric, as well as polar effects are of importance. Thus the highest degree of substitution of $N_3P_3F_6$ with $Ph_3P{=}NSiMe_3$, is a bis-compound, $N_3P_3F_4(NPPh_3)_2$, whilst with $Me_3P{=}NSiMe_3$ a tris-derivative (soluble in water), $N_3P_3F_3(NPMe_3)_3$ can be obtained.[35a]

The maximum degree of phosphazenylation of the tetramer, $N_4P_4X_8$($X$ = F or Cl) has not yet been explored. The bis(triphenylphosphazenyl) derivatives, $N_4P_4Cl_6(NPPh_3)_2$[31] and $N_4P_4F_6(NPPh_3)_2$[35a] have been prepared. In the reaction of $N_4P_4F_8$ with ammonia, a bis-derivative, $N_4P_4F_6(NH_2)_2$, was obtained and a 2,6-structure ascribed to it. This compound can be converted with thionyl chloride to $N_4P_4F_6(NSO)_2$, which under the influence of pyridine loses sulphur dioxide to give a bicyclic structure, $N_4P_4F_6N_2S$ (cf. Ref. 3). This has been shown by X-ray crystallography to have a 2,4-fusion. Hence it is likely, that the substituents in its monocyclic precursors, have a similar disposition.

$$N_4P_4F_8 \xrightarrow{NH_3} N_4P_4F_6(NH_2)_2 \xrightarrow{SOCl_2}$$

$$N_4P_4F_6(NSO)_2 \xrightarrow{C_5H_5N} N_4P_4F_6N_2S$$

(Bicyclic; 2,4-fusion)

$$N_4P_4Cl_8 + Ph_3P{=}NH \longrightarrow N_4P_4Cl_6(NPPh_3)_2$$

*trans*-2,6

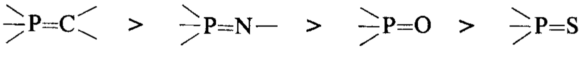
$$N_4P_4F_8 + Ph_3P{=}NSiMe_3 \longrightarrow N_4P_4F_6(NPPh_3)_2$$

(2,4 ?)

The silylation method of synthesis is by no means confined to phosphorus–halogen bonds. Hexafluorobenzene, $C_6F_6$, reacts with $Me_3SiN{=}PR_3$ ($R$ = $NMe_2$, Me, or Ph) to give the respective monophosphazenylated derivatives, $C_6F_5(N{=}PR_3)$ ($R$ = $NMe_2$, Me, or Ph).[42] $p$-$FC_6H_4NO_2$ also reacts in a similar fashion with $Me_3SiN{=}PMe_3$ to give $p$-$Me_3P{=}NC_6H_4NO_2$.[42] Similar reactions with hexachlorobenzene, $C_6Cl_6$, have, to date, been unsuccessful.[42]

## BASICITY

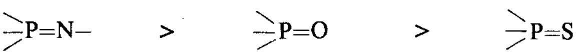
It is a happy coincidence that much of the work in this field, especially, quantitative basicity measurements has been carried out, here in the USSR, and in my own group at Birkbeck College. Again, because of lack of time, I must select some aspects from the wealth of data available, and will often refer to summarizing review articles. Kabatschnik[43] wrote a most valuable review article on acyclic monophosphazenes. If one considers compounds containing "formal" double bonds of phosphorus to another element the basicity decreases in the order



$$\gtrdot P{=}C\lessdot \;>\; \gtrdot P{=}N- \;>\; \gtrdot P{=}O \;>\; \gtrdot P{=}S$$

Obviously, for meaningful comparisons, we must compare like with like, i.e. the substituents on the phosphorus atom should be the same in all four types of compound and the same pertains to substituents (where applicable) to its multiple bonded partner.

Both groups, the one of Kabatschnik, Giljarow and co-workers,[43] as well as my own (cf. Ref. 38a,b), used perchloric acid for these measurements. However, the Soviet group[43] used, nitromethane as solvent, whilst we used nitrobenzene.[38a,b] Quantitative data on the phosphorus–carbon system is scarce; most data is available on the phosphorus–nitrogen class of compounds. We too can confirm the order



$$\gtrdot P{=}N- \;>\; \gtrdot P{=}O \;>\; \gtrdot P{=}S$$

The last mentioned one is often too weakly basic to be studied by our technique. Like our Soviet colleagues, we too have observed basicities for phosphazenyl compounds of the order of magnitude of tertiary bases and guanidines.

Most of the work on acyclic monophosphazenes was done here in the USSR, and hence you will be familiar with it.[43] Changes of substituents on phosphorus can alter the basicity by six orders of magnitude; the effect at nitrogen is, as expected, even larger and it can be up to (and possibly exceeding) nine orders of magnitude. Detailed investigations of substituent effects and their correlation with Hammett constants were carried out in the USSR.

My own group has concentrated mainly on compounds where the phosphazenyl group is at-

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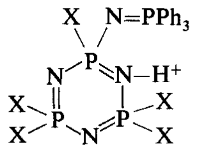
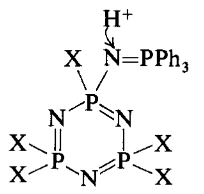
tached to a heterocyclic ring system, usually a cyclophosphazene, occasionally a 1,3,5-triazine. We observed two types of behaviour with triphenylphosphazenylcyclotriphosphazatrienes.[44] Within each type the results were self-consistent, but they were not consistent with each other. We postulated that in one type protonation occurred on ring nitrogen atoms, as had been observed for all other substituents hitherto investigated. For the other type, we suggested protonation on the exocyclic phosphazenyl nitrogen atom. Subsequent crystallographic work on selected compounds showed that the first type of behaviour in basicity studies (endocyclic protonation) coincided with Type I conformation (see structural section), the second type (exocyclic protonation) with Type II conformation (see structural section). Thus, $pK'_{a,1}$ measurements can be used for suitable compounds as a tool for a novel type of conformational analysis.



Type I

e.g., $PCl \cdot NPPh_3$



Type II

$PPh \cdot NPPh_3$
$P(NMe_2)(NPPh_3)$

We also discovered that the triphenylphosphazenyl group was by far the most powerful electron-releasing group (in basicity studies) of all the substituents so far investigated.[38a,b] A selection of $\sigma_R$-substituent constants is given below

$N_3P_3Cl_{6-n}R_n$

| R | $\sigma_R$ |
|---|---|
| $NPPh_3$ (Type I) | 10.3 |
| $NH_2$ | 6.0 |
| $NMe_2$ | 5.6 |
| Ph | 4.2 |
| OMe | 3.6 |
| OPh | 3.1 |

Thus, two $NPPh_3$ substituents (Type I conformation) e.g. ng-$N_3P_3Cl_4(NPPh_3)_2$, give a $pK'_{a,1}$ value of 0.2,[44] whilst all other disubstituted hexachlorocyclotriphosphazatriene derivatives, $N_3P_3Cl_4R_2$,[45] have $pK'_{a,1}$ values below the level of detection by our experimental technique ($< -6.0$). Three phosphazenyl groups, e.g. $N_3P_3F_3(NPPh_3)(NPMe_3)_2$,[46] give very high basicities, e.g. $\sim +7.0$, whilst the hitherto most basic trisubstituted chloro-derivatives, $N_3P_3Cl_3R_3$, gave values e.g. for ng-$N_3P_3Cl_3(NMe_2)_3$ of $-5.5$,[45] and for g-$N_3P_3Cl_3(NMe_2)_3$ of $-4.4$.[45] It is important to stress that we are discussing "perturbed" state properties, i.e. the potential electron-supply available at the demand of a proton. Whilst we do know that the $NPh_3$ group, as well as the $NMe_2$ group, supplies electrons (relative to a Cl atom) in the "unperturbed" state[38b] to an adjacent P—Cl bond [longer P—Cl bond length (X-ray crystallography), lower frequency ($^{35}Cl$ nqr spectroscopy)], we do not have sufficient information, as yet, to distinguish their relative magnitudes.

| Compound | $pK'_{a,1}$ |
|---|---|
| ng-$N_3P_3Cl_4(NPPh_3)_2$ | +0.2 |
| ng-$N_3P_3Cl_4R_2$ (R = $NMe_2$, pip, etc.) | $< -6.0$ |
| ng-$N_3P_3F_3(NPPh_3)(NPMe_3)_2$ | $\sim +7.0$ |
| ng-$N_3P_3Cl_3(NMe_2)_3$ | $-5.5$ |
| g-$N_3P_3Cl_3(NMe_2)_3$ | $-4.4$ |

Basicity studies on cyclotetraphosphazatetraene derivatives, $N_4P_4Cl_6(NPPh_3)_2$ $pK'_{a,1} = -4.6$),[44] and $N_4P_4F_6(NPPh_3)_2$ ($pK'_{a,1} = -1.3$)[46] shed some light on their structures. We do know from X-ray crystallographic studies[47a] (recently refined)[47b] that the former, $N_4P_4Cl_6(NPPh_3)_2$, has a *trans*-2,6-structure. The much higher basicity of the latter, $N_4P_4F_6(NPPh_3)_2$, suggests (but does not prove) a 2,4-structure [e.g. synthesis section on $N_4P_4F_6(NH_2)_2$, $N_4P_4F_6(NSO)_2$ and bicyclic, $N_4P_4F_6N_2S$ (proven 2,4-fusion) derived from latter].

Similar remarks to phosphazenylcyclophosphazenes pertain to 1,3,5-triazine derivatives.[46]

| Compound | $pK'_{a,1}$ |
|---|---|
| $N_3C_3Cl(NMe_2)_2$ | $-2.0$ |
| $N_3C_3(NMe_2)_3$ | +3.2 |
| $N_3C_3Cl(NPPh_3)_2$ | +8.0 |
| $N_3C_3Cl(NMe_2)(NPPh_3)$ | +3.3 |

In all 1,3,5-triazine compounds hitherto studied by X-ray crystallography, the $NMe_2$ and $NPPh_3$ groups adopt Type I conformations.[38b,49,50] As in the cyclophosphazenes the electron-releasing capacity of the $NPPh_3$ group (at the demand of a proton) is much greater than that of the $NMe_2$ group.

## STRUCTURE AND CONFORMATION

Fortunately, a considerable number of accurate crystal structure determinations of phosphazenyl derivatives have been carried out. Again I will try and highlight certain aspects, which I consider of special interest.

The nature of the substituents on nitrogen and phosphorus can, and does, affect profoundly the phosphorus–nitrogen bond lengths. Thus, although

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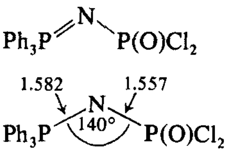
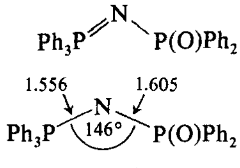
we write the two compounds, $Ph_3P{=}N{-}P(O)X_2$ (X = Cl or Ph)[51] with similar conventional valence bond formulations,

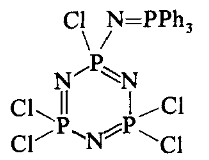
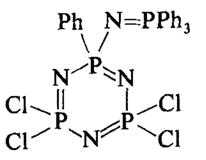
the relative lengths of the two P–N bonds in the two compounds are inverted, demonstrating the greater electron withdrawing power $Cl_2 > Ph_2$, and O > Ph.

The cation $[(Ph_3P)_2N]^+$ has been widely used as a counter ion for complex organometallic and inorganic compounds, and has been extensively investigated. It is usually observed in a bent form, but more recently linear structures have been discovered.[38b,52] One case has been reported where both bent and linear forms occur in the same unit cell;[52] hence the energy of deformation is not very large. Conformational isomerism is also fairly frequent in cyclophosphazenes. In the above cation $[(Ph_3P)_2N]^+$, the bent form ($P\hat{N}P$ = 135–142°) has somewhat longer P–N bonds (1.570–1.586 Å) than the linear one ($P\hat{N}P$ = 180°) (1.539 Å).[38b] This is in line with expectations, as in the linear form the resonance form (**B**) will make a greater contribution than in

$$\underset{\textbf{(A)}}{Ph_3P{=}N{-}\overset{+}{P}Ph_3} \qquad \underset{\textbf{(B)}}{Ph_3P{=}\overset{+}{N}{=}PPh_3} \qquad \underset{\textbf{(C)}}{Ph_3\overset{+}{P}{-}N{=}PPh_3}$$

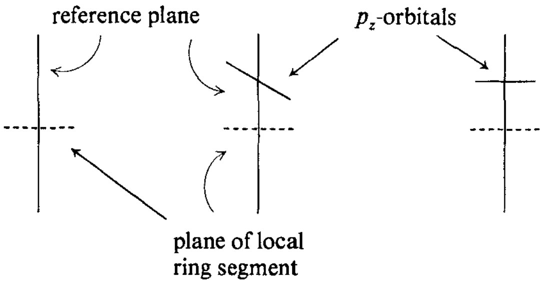
the bent forms.

Of particular interest, to me personally, are the phosphazenylcyclophosphazenes. Basicity measurements, to which I have already referred, indicated two types of behaviour; we postulated that these might be due to conformational effects.[44] This was indeed confirmed by X-ray crystallography. Thus in the two compounds[53,54]

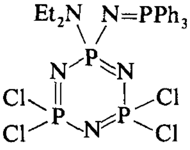
the conformation of the triphenylphosphazenyl group, $NPPh_3$, with respect to the $N_3P_3$ ring is quite different. In $N_3P_3Cl_5(NPPh_3)$[53] the N–P segment of the $NPPh_3$ group projects more or less parallel to the local NPN segment of the ring. The dihedral angle $Cl{-}P_{endo}{-}N_{exo}{-}P_{exo} = -83°$, i.e. the bonds $Cl{-}P_{endo}$ and $N_{exo}{-}P_{exo}$ are almost perpendicular. In contrast, in $N_3P_3Cl_4Ph(NPPh_3)$,[54] the N–P bond of the $NPPh_3$ group is perpendicular to the local NPN ring segment, and $C_{arom.}{-}P_{endo}{-}N_{exo}{-}P_{exo}$ are almost coplanar.

I have generalized the conformations of substituent groups, such as $NPPh_3$, $NMe_2$ (planar or almost so, due to electron delocalization) and Ph, where the atom (N or C) linked to the P atom of the ring is $sp^2$-hybridized, or nearly so, and have called the conformation exhibited by the $NPPh_3$ group in $N_3P_3Cl_5(NPPh_3)$ Type I, in $N_3P_3Cl_4Ph(NPPh_3)$ Type II, and the intermediate position Type III.[3,38a,b]

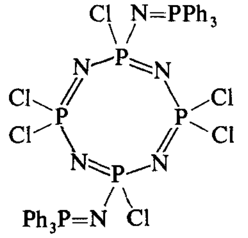
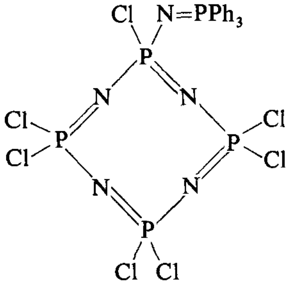


Type I Type III Type II

In *trans*-2,6-$N_4P_4Cl_6(NPPh_3)_2$, the structure[47a] of which has been recently[47b] refined, the two $NPPh_3$ groups have Type I conformation, whilst in $N_4P_4Cl_7(NPPh_3)$[48] the $NPPh_3$ group tends to Type III (the first of this type reported for an $NPPh_3$ group), possibly for steric reasons. In $N_3P_3Cl_4(NEt_2)(NPPh_3)$,[55] the $NPPh_3$ group also tends to a Type III conformation



*trans*-2,6-$N_4P_4Cl_6(NPPh_3)_2$

The above are examples where the phosphazenyl group is attached to phosphorus. X-ray crystallographic data are also available on compounds where such groups are linked to other elements such as

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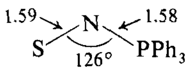
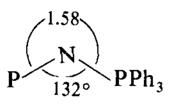
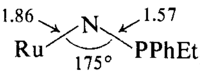
carbon, sulphur, or ruthenium.[38b] The 1,3,5-triazine ring, $N_3C_3$, has similarities to the cyclotriphosphazatriene ring, $N_3P_3$. Bullen[49] and Cameron,[50] and their respective co-workers, have investigated two interesting structures.



$p$-$MeC_6H_4SO_2NPPh_3$

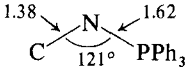


$N_3P_3Cl_4Ph \cdot NPPh_3$

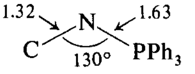


$(Et_2PhP)_2RuCl_3 \cdot NPPhEt_2$

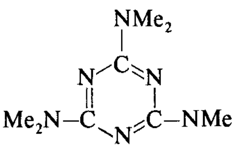
$C_6(NO_2)_3(NPPh_3)_3$

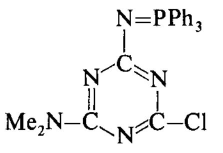


$N_3C_3Cl(NMe_2)(NPPh_3)$



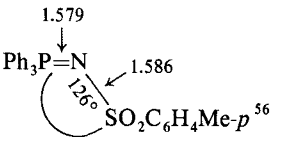
$C_6NO(N_2O)_2(NPPh_3)$

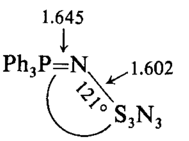




In both compounds, $N_3C_3(NMe_2)_3$,[49] and $N_3C_3Cl(NMe_2)(NPPh_3)$,[50] the $NMe_2$ and the $NPPh_3$ groups adopt Type I conformations. An interesting feature of the latter structure is that of the two possible conformations, the $NPPh_3$ group has adopted the one, where it is turned away from the $NMe_2$ group and towards the Cl atom. The solution of other structures, where such syn- and anti-configurations are possible, will be awaited with interest.

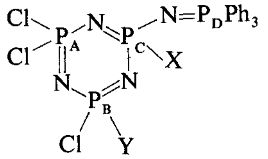
Brief reference ought to be made to structures where the $NPPh_3$ group is bonded to sulphur. I have shown elsewhere,[3] that P—N and S—N bonds closely resemble each other in bond-length and multiple bond character.





Whilst in most $Ph_3P{-}N{-}P$ structures both P—N bonds are of approximately equal length, indicating a fairly even 3-centre delocalization, in $Ph_3P{=}NS_3N_3$,[57] it appears that the multiple bond character is more localized in the exocyclic S—N segment, rather than in the P—N bond. We have observed elsewhere that in general, in heterocyclic ring systems containing $Cl_2P{-}N{-}S(O)Cl$ segments, the N—S bonds are shorter and the P—N bonds longer, than in the homogeneous segments $Cl_2P{-}N{-}PCl_2$ and $Cl(O)S{-}N{-}S(O)Cl$. It is noteworthy that in the above structure[57] five atoms of the $N_3S_3$ ring are coplanar, whilst the sixth (the one joined to the $NPPh_3$ group) is below this plane.

The above crystallographic studies pertain to the solid state. Obviously, we need information about conformations in solution. A recent, nmr study[59] indicates that for $R_3PN$ groups attached to cyclophosphazenes, four-bond phosphorus–phosphorus spin–spin coupling can give information (provided the groups R are the same in the compounds compared) about conformation in solution. Large positive coupling constants $^4J_{PP}$ (3.5 to 5.5 Hz) indicate Type I conformation; small positive, zero, or small negative values of $^4J_{PP}$ (0.1 to −0.4 Hz) suggest Type II conformation. Obviously a great deal more work needs to be done in this field to correlate solid state and solution conformations as well as other properties



| X | Y | $^4J(PP)$ Hz. |
|---|---|---|
| Cl | Cl | $P_A \ldots P_D$ +3.4 |
| Ph | Cl | $P_A \ldots P_D$ −0.4 |
| Cl | $NMe_2$ | $P_A \ldots P_D$ +5.5<br>$P_B \ldots P_D$ +3.3 |
| $NMe_2$ | Cl | $P_A \ldots P_D$ <0.1 |
| OEt | Cl | $P_A \ldots P_D$ +0.9 |

2-*trans*-6-$N_4P_4Cl_6(NP_DPh_3)_2$ $P \ldots P_D$ + 4.6

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