The Reactions of Halogenocyclophosphazenes with Nitrogenous Bases*

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Halogenocyclophosphazenes, Substitution Patterns, Nitrogenous Bases,
Quantum Chemistry, Conformational Analysis

The reactions of hexachlorocyclotriphosphazatriene, \( \text{N}_3\text{P}_3\text{Cl}_6 \), and to a lesser extent octachlorocyclotetraphosphazatetraene, \( \text{N}_4\text{P}_4\text{Cl}_8 \), and other halogenocyclophosphazenes with primary, secondary, and tertiary amines, are described. The effect on the substitution pattern of variables such as the structure of the amine, nature of the reaction solvent, etc., are discussed in some detail. Attention is drawn to the importance of steric effects. Isomerisation reactions are referred to.

The physical properties of aminocyclophosphazenes and aminohalogenocyclophosphazenes are discussed in some detail. These include basicity studies, \(^1\text{H} \) and \(^3\text{P} \) NMR and \(^3\text{Cl} \) NQR studies, Faraday effect measurements, etc. Attempts are made to correlate the above properties with X-ray crystallographic studies and quantum chemical calculations. The distinction between ground state and perturbed state properties is emphasised.

Synthesis, structure, and properties of phosphazeneylecyclophosphazenes and related compounds are described and a novel conformational behaviour is discussed and rationalised.

Aminolysis reactions of hexachlorocyclotriphosphazatriene, \( \text{N}_3\text{P}_3\text{Cl}_6 \), are amongst the earliest recorded reactions of this particular ring system and date back to the last century; only the complete replacement of the chlorine atoms by amino residues was investigated. The same ring system has since been the subject of numerous detailed investigations with a variety of nitrogenous bases. I will attempt to summarise and, if possible, rationalise the great quantity of data available on this system in this lecture. Other systems, such as octachlorocyclotetraphosphazatetraene, \( \text{N}_4\text{P}_4\text{Cl}_8 \), hexafluorocyclotriphosphazatriene, \( \text{N}_3\text{P}_3\text{F}_6 \), etc., have been investigated to a lesser extent and, where appropriate, I will refer to these.

The first systematic attempts of studying the aminolysis of hexachlorocyclotriphosphazatriene were carried out in the 1940's by Bode and co-workers. They obtained only derivatives where two, four, or six chlorine atoms had been replaced by amino residues, and they concluded (i) that replacement was always pairwise and geminal, and (ii) that with alkylamines di- and hexa-substitution and with arylamines, tetra- and hexa-substitution was the rule. Whilst some of the structures postulated were later shown to be correct, the bulk of the assumptions made were overtaken by later events and shown either to be incorrect or oversimplified.

The subject obtained new impetus in the 1950's and in the later years of this decade, reports occurred almost simultaneously from laboratories from different parts of the world, which indicated that contrary to the earlier assumption of Bode, aminolysis proceeded by a nongeminal pattern. Again, these generalisations were premature and whilst some of the structures proposed were later...
proven to be correct, the overall assumption of non-
geminality for aminolysis has since been shown to
be a great oversimplification and that a very much
more complex replacement pattern prevailed
frequently deviating from the generalised patterns
displayed below. [Throughout this paper, the
substituents already present prior to reaction,
(usually chlorine atoms) have for clarity's sake,
frequently been omitted.]

\[\begin{array}{c}
\text{II} \\
\| \\
\text{V} \\
\text{K} \\
\text{R} \\
\text{R'} \\
\end{array}\]

The first indications that a nongeminal replace-
ment pattern of chlorines by amino-residues was by
no means universal, arose from the results of
basicity studies. We had observed earlier that
hydrochlorides of hexaalkylaminocyclotriphospha-
zatrienes, \(N_3P_3(NH_{Alk})_6 \cdot HCl\), were isolated in the
presence of an excess of the
aliphatic amine, indicating that these hexa-amino-derivatives were
bases of comparable strength to those of aliphatic
amines.\(^3\)

\[\begin{array}{c}
P_3N_3(R) \cdot HCl \\
\| \\
\| \\
\text{Cl} \\
\text{Nme}_2 \\
\end{array}\]

The basicities of these tetra-amino derivatives,
\(N_3P_3Cl_2(NR')_4\), fell obviously into two classes
– one a good deal more basic than the other – and
this became particularly apparent on comparing the
difference in basicity of hexa-amino and tetra-
amino derivatives having the same amino residues,
\(NR'\). It became clear that this pronounced differ-
ence in basicity could arise only from structural
differences amongst the
tetra-amino derivatives,
and first intuitively, then by logical argument, later
by a variety of physico-chemical techniques, and
finally, by X-ray crystallography, the stronger
bases were assigned geminal, the weaker bases
nongeminal structures.

<table>
<thead>
<tr>
<th>Hydrochlorides of some Aminophosphazenenes</th>
<th>m.p. [°C]</th>
<th>Free base m.p. [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(P_3N_3(NH_{Et})_6 \cdot HCl)</td>
<td>197</td>
<td>(P_3N_3(NH_{Et})_6)</td>
</tr>
<tr>
<td>(P_3N_3(NH_{Pr''})_6 \cdot HCl)</td>
<td>184</td>
<td>(P_3N_3(NH_{Pr''})_6)</td>
</tr>
<tr>
<td>(P_3N_3(NH_{Pr'})_6 \cdot HCl)</td>
<td>203</td>
<td>(P_3N_3(NH_{Pr'})_6)</td>
</tr>
<tr>
<td>(P_3N_3(NH_{Bu''})_6 \cdot HCl)</td>
<td>132</td>
<td>(P_3N_3(NH_{Bu''})_6)</td>
</tr>
<tr>
<td>(P_3N_3(NH_{Bu})_6 \cdot HCl)</td>
<td>211</td>
<td>(P_3N_3(NH_{Bu})_6)</td>
</tr>
</tbody>
</table>

That in itself was surprising, as up to that time,
nitrogen attached to phosphorus was considered to
be weakly basic – i.e., having a basicity more akin
to that of acid amides rather than that of aliphatic
amines. Whilst all hexa-alkylaminocyclotriphospha-
zatrienes, \(N_3P_3(NR')_6\), had, regardless of the structure of the aliphatic amines, about the same
\(pK_{a1}\) values in nitrobenzene, considerable differ-
ences were observed in the tetra-alkylaminidichlorocyclotriphospha-
zatrienes, \(N_3P_3Cl_2(NR')_4\).\(^4\)

<table>
<thead>
<tr>
<th>(pK_{a1}) of (N_3P_3R_6)</th>
<th>(pK_{a1}) of (N_3P_3ClR_4)</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMe(_2) 7.5</td>
<td>-1.4</td>
<td>8.9</td>
</tr>
<tr>
<td>NC(<em>6)H(</em>{10}) 8.4</td>
<td>-0.9</td>
<td>9.3</td>
</tr>
<tr>
<td>NH(_2)But 8.0</td>
<td>3.5</td>
<td>4.5</td>
</tr>
<tr>
<td>NH(_2)Pri 8.4</td>
<td>3.4</td>
<td>5.0</td>
</tr>
</tbody>
</table>

This caused a complete and careful reinvestigation
of the aminolysis products of hexachlorocyclotri-
phospha-zatriene with a variety of amines.\(^5\) The
detection, isolation, and purification of various
degrees of replacement, as well as of different
isomers, were facilitated by the advent and adap-
tation of chromographic techniques – column,
thin-layer and gas-liquid. Even so, in the earlier
days, the occasional derivative, present only in
small yield, was overlooked, and was later detected
by more sensitive techniques. The replacement
patterns of ammonia and many of those amines,
NHRR', primary and secondary, which were investigated in considerable detail will be shown later. No distinction will be made between primary reaction products and those obtained by isomerisation processes, which will be discussed later. These isomerisations, seem to be somewhat solvent dependent, and at this stage it is uncertain whether some of the isomers are solely secondary, or in part primary, reaction products.

It will be seen that almost every amine looked at in some detail displays its own characteristic reaction pattern and that this differs from that of other amines investigated. (The two which seem to be most closely related - dimethylamine and piperidine - show however considerable differences in the behaviour of their aminochlorocyclotriphosphazatriene-derivatives in Friedel-Crafts reactions with benzene)\(^6,7\). Some of the variations in aminolysis patterns may be due to experimental conditions, as only very recently an awareness has arisen of the importance of reaction variables such as temperature, solvent, and stoichiometry, which in some circumstances may determine the presence or absence of a particular isomer, or at least its relative proportions.

Before commenting on the different replacement patterns, let me briefly refer to the subject of cis-trans-isomerisation as, on the one hand, it adds an extra degree of complexity to an already complex situation and on the other, it presents a useful method for obtaining some isomers in better yields than those obtained in the original reaction mixtures. Additionally it gives, in some cases, evidence of a chemical nature regarding geminal versus nongeminal structure. Cis-trans-isomerisation reactions have been carried out on those compounds which undergo this type of reaction (and it must be emphasised that apparently not all nongeminal compounds do undergo this reaction) by a variety of techniques which include: (i) amine hydrochlorides\(^8\) (and possible other soluble chlorides), probably via a nucleophilic mechanism, (ii) aluminium chloride\(^9\), probably via an electrophilic mechanism, (iii) hydrogen halides\(^10\), (iv) purely thermal methods\(^11\), although whether impurities contribute is by no means certain and (v) bases\(^12\), probably by a proton abstraction mechanism.

The reason why in some circumstances one can obtain better yields of some isomers by isomerisation techniques rather than by direct aminolysis, is presumably that in the latter case kinetic control is often the dominating factor, whilst obviously in an equilibration method thermodynamic control will be of paramount importance.

Having referred to the cis-trans-isomerisation of certain nongeminal aminochlorocyclophosphazenes and their possible effect on the cis-trans-isomer ratio of certain derivatives, let me now return to the problem of degrees of replacement and different types of isomers obtained in different amine-hexachlorocyclophosphazatriene systems.

Let me first of all, deal with secondary amines (see diagram below). Amongst those investigated in considerable detail is, first and foremost, dimethylamine\(^13,14\); others include diethylamine\(^15,16\), piperidine\(^17\), pyrrolidine\(^16,18-21\), aziridine\(^22-26\) and, more recently, and as yet not completely, N-methyl aniline\(^27\). Allowing for possible experimental difficulties, in detecting or isolating certain compounds, one can make the following statements. Monoamino-pentachloride-derivatives, \(N_3P_3Cl_5\cdot NRR'\), are readily obtainable in all the above-mentioned amino-systems. Leaving aside for the moment aziridine - a rather unusual amine in any case – and N-methyl aniline, which has not yet been completely investigated, the others follow related patterns. All tend to give nongeminal bis-aminotetrachloro-derivatives, \(N_3P_3Cl_4(NRR')_2\), the yield of the trans-isomer normally being bigger than that of the cis. With the smallest secondary amines, such as dimethylamine, small proportions of a geminal bis-derivative, \(N_3P_3Cl_4(NMe_2)_2\), have been isolated, and with pyrrolidine, another amine also not making large steric demands, there are indications that traces of a similar derivative may be present. Whilst the proportion of trans- to cis-isomer varies considerably with reaction conditions, in particular
The reactions of halogenocyclophosphazenes

R. A. SHAW • THE REACTIONS OF HALOGENOCYCLOPHOSPHAZENES

with the nature of the solvent and hence possible incursion of isomerisation reactions – the proportion of the geminal derivative, although somewhat affected by the nature of the reaction conditions, is not so to any dramatic extent.

The situation changes drastically when we look at the trisaminotrichloro-derivatives, \( \text{N}_3\text{P}_3\text{Cl}_3(\text{NRR})_3 \). By carefully choosing our reaction conditions – in particular the nature of the solvent and, to some extent, also the exact stoichiometry of the amine used, we can achieve in a solvent such as acetone almost, exclusive nongeminal substitution, again the trans-isomer usually predominating over the cis-, and again the ratio varies with the type of amine and the reaction conditions. If, however, we choose an aromatic solvent such as benzene, toluene, or xylene, in which the reaction proceeds a good deal slower, we notice the incursion of the geminal derivative, although somewhat affected by the nature of the reaction conditions, is

We observed some time ago that a variety of phosphorus compounds exhibit in their proton NMR spectra solvent shifts, if their chemical shifts in carbon tetrachloride and an aromatic solvent, such as benzene are compared. Methoxy, dimethylamino, and other groupings appear at higher field in the aromatic solvent and this effect is more pronounced the larger the number of electron-withdrawing groups, such as chlorine atoms, attached to the same phosphorus atom.

**Solvent shifts in the \( ^1\text{H} \) spectra of some mononuclear phosphorus compounds.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \tau (\text{CCl}_4) )</th>
<th>( \tau (\text{C}_6\text{H}_6) )</th>
<th>( \Delta \tau \text{ ppm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{POCl}_2\text{NMMe}_2 )</td>
<td>7.14</td>
<td>7.77</td>
<td>+0.63</td>
</tr>
<tr>
<td>( \text{POCl}\text{NMMe}_2)</td>
<td>7.29</td>
<td>7.67</td>
<td>+0.38</td>
</tr>
<tr>
<td>( \text{PO}(\text{NMMe}_2)_3 )</td>
<td>7.42</td>
<td>7.56</td>
<td>+0.14</td>
</tr>
<tr>
<td>( \text{PO}(\text{OMe})_3 )</td>
<td>6.23</td>
<td>6.62</td>
<td>+0.39</td>
</tr>
</tbody>
</table>

**Solvent shifts in the \( ^1\text{H} \) NMR spectra of some chlorodimethylaminocyclophosphazatreniens.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \tau (\text{CCl}_4) )</th>
<th>( \tau (\text{C}_6\text{H}_6) )</th>
<th>( \Delta \tau \text{ ppm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Na}_3\text{P}_3\text{Cl}_6 )</td>
<td>7.25</td>
<td>7.82</td>
<td>+0.57</td>
</tr>
<tr>
<td>( \text{trans-N}_3\text{P}_3\text{Cl}_4(\text{NMMe}_2)_2 )</td>
<td>7.27</td>
<td>7.66</td>
<td>+0.39</td>
</tr>
<tr>
<td>( \text{cis-N}_3\text{P}_3\text{Cl}_4(\text{NMMe}_2)_2 )</td>
<td>7.29</td>
<td>7.71</td>
<td>+0.42</td>
</tr>
<tr>
<td>( \text{trans-N}_3\text{P}_3\text{Cl}_4(\text{NMMe}_2)_3 )</td>
<td>7.28</td>
<td>7.49</td>
<td>+0.21</td>
</tr>
<tr>
<td>( \text{cis-N}_3\text{P}_3\text{Cl}_4(\text{NMMe}_2)_3 )</td>
<td>7.34</td>
<td>7.61</td>
<td>+0.27</td>
</tr>
<tr>
<td>( \text{gem-N}_3\text{P}_3\text{Cl}_4(\text{NMMe}_2)_3 )</td>
<td>7.32</td>
<td>7.59</td>
<td>+0.27</td>
</tr>
<tr>
<td>( \text{trans-N}_3\text{P}_3\text{Cl}_4(\text{NMMe}_2)_3 )</td>
<td>7.36</td>
<td>7.51</td>
<td>+0.11</td>
</tr>
<tr>
<td>( \text{cis-N}_3\text{P}_3\text{Cl}_4(\text{NMMe}_2)_4 )</td>
<td>7.35</td>
<td>7.48</td>
<td>+0.13</td>
</tr>
<tr>
<td>( \text{trans-N}_3\text{P}_3\text{Cl}_4(\text{NMMe}_2)_4 )</td>
<td>7.36</td>
<td>7.34</td>
<td>-0.02</td>
</tr>
<tr>
<td>( \text{Na}_3\text{P}_3(\text{NMMe})_6 )</td>
<td>7.44</td>
<td>7.33</td>
<td>-0.11</td>
</tr>
</tbody>
</table>

It appears that the average solvation of such molecules, or of particular sites in complex molecules such as cyclophosphazenes, is of such a nature that the shielding cone of the aromatic solvent causes a shift of the proton signals to higher \( \tau \)-values. These observations pertain to mononuclear phosphorus compounds, as well as to cyclophosphazenes, and only a few exceptions to the above rule are known. All of these are fully dimethylaminolysed compounds of cyclophosphazenes, trimer, tetramer, pentamer, etc., [\( \text{NP}(\text{NMMe}_2)_n \), (\( n \) = 3, 4, 5, 6 or 7). In all of these a slight negative solvent shift is observed and this may perhaps be due to the fact that the electron-density is now so large on the cyclophosphazene molecule that the benzene molecules prefer on average an edge-on orientation towards the cyclophosphazene and thus, in effect, cause a deshielding of the dimethylamino protons.

**Dimethylamino-cyclophosphazenes.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \tau (\text{CCl}_4) )</th>
<th>( \tau (\text{C}_6\text{H}_6) )</th>
<th>( \Delta \tau \text{ ppm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Na}_3\text{P}_3(\text{NMMe}_2)_4 )</td>
<td>7.44</td>
<td>7.33</td>
<td>-0.11</td>
</tr>
<tr>
<td>( \text{Na}_3\text{P}_3(\text{NMMe}_2)_8 )</td>
<td>7.43</td>
<td>7.28</td>
<td>-0.15</td>
</tr>
<tr>
<td>( \text{Na}_3\text{P}_3(\text{NMMe}_2)_10 )</td>
<td>7.42</td>
<td>7.26</td>
<td>-0.16</td>
</tr>
<tr>
<td>( \text{Na}_3\text{P}_3(\text{NMMe}_2)_12 )</td>
<td>7.41</td>
<td>7.25</td>
<td>-0.16</td>
</tr>
</tbody>
</table>
The above suggests that solvation by aromatic molecules is probably largest for the $≡\text{PCl}_3$ grouping, less for $≡\text{PClR}$, and least for $≡\text{PR}_2$ ($R =$ amino group) and it may well be that this has some bearing on the solvent effects observed in the formation of the tris-derivatives.

$$X≡\text{PCl}_3 > X≡\text{PClR} > X≡\text{PClR}_2 > X≡\text{PR}_2$$

We have noticed again very recently\textsuperscript{16,28}, (as well as some years ago\textsuperscript{29}) that the geminal isomer in a particular system such as the tris-amino-derivative of the hexachloride, $\text{N}_3\text{P}_3\text{Cl}_6(N\text{RR'})_3$, or the bis-amino-derivative of the gem-diphenyltetrachloride, $\text{N}_3\text{P}_3\text{Ph}_2\text{Cl}_2(N\text{RR'})_2$, occurs in greater proportion if the conditions are such that an aromatic solvent is used and hence slow reactivity pertains and, at the same time, if the stoichiometry of the amine is in excess of that required for the given degree of substitution. Thus we must consider, in addition to the above hypothesis of solvation by aromatic molecules, the possibility that the excess of amine present may also in some way be pertinent to the increase of the geminal, isomer at the expense of the nongeminal ones, perhaps through nitrogen lone-pair electrons being donated to some sites of the molecule, or to base catalysed proton abstraction.

When we consider tetra-aminodichloro-derivatives, $\text{N}_3\text{P}_3\text{Cl}_6(N\text{RR'})_4$, the situation is different again. Only nongeminal isomers are observed in these systems ($\text{NHEt}_2$, $\text{NHC}_5\text{H}_10$, $\text{NCl}_2\text{H}_8$) and geminal isomers have to date not been detected, regardless of the choice of solvent, which however does effect to some extent the cis-trans ratio. Not in all systems have cis- and trans-isomers been isolated, definitely characterised, and unambiguous structure assigned. In the dimethylamino system the cis-isomer is present in much larger proportion than the trans, and in this case an unambiguous structural assignment by $^1\text{H}$NMR spectroscopy is feasible. In the case of the diethylamino-system, the trans-isomer is present in far greater proportion than the cis, both having been isolated, and again an unambiguous assignment by the above spectroscopic method is possible. With the piperidino-system only one isomer has been isolated to date, and that has been assigned (not by spectroscopic methods, as the proton NMR spectrum is too complex, but by the synthesis of derivatives, an admittedly somewhat less reliable technique) the cis-structure. With pyrrolidine the present evidence is confusing as dipole moment data, melting point, and gas chromatographic retention times, appear to be in contradiction with one another, and at present it is uncertain to which of the two isomers isolated cis- and trans-structures should be assigned. We invoked earlier the "cis-effect"\textsuperscript{17} to explain the overwhelming preponderance of the cis-derivative in the dimethylamino-system (and also in the piperidino-system, provided the assignment is correct). It is possible that in the diethylamino-system the preference for the trans-isomer is due to steric causes, the 'cis-effect' being outweighed by the steric demands of the bulkier diethylamino group. As I have discussed elsewhere\textsuperscript{31}, however, the 'cis-effect,' whilst unambiguously present in those compounds where only nongeminal amino-chloro moieties, $≡\text{PClR}$, are present, is not based on quite the same safe premises when geminal bis-amino groups $≡\text{PR}_2$, are present, or perhaps we are dealing with the superimposition of two competing effects.

Let me now refer to the other two secondary amines mentioned earlier, namely, aziridine and N-methyl aniline. Aziridine has small steric demands and has weak nucleophilic and basic properties, its general behaviour is rather unlike that of most other amines. It is perhaps thus not surprising, that it differs in its replacement pattern from the other secondary amines above. Clapp and co-workers\textsuperscript{22} have shown and we have confirmed and extended in our own laboratory\textsuperscript{26}, that the replacement pattern throughout is predominantly geminal in nature, this differing considerably from the other secondary amines so far mentioned. With N-methylaniline, which we are currently investigating in collaboration with our colleagues in Bangalore\textsuperscript{27}, we have other interesting phenomena to report. Preliminary results suggest that in the early stages of replacement, \textit{i.e.}, with the bisamino-derivatives, a nongeminal pattern is important. At the trisamino stage both a nongeminal (probably \textit{cis}) and the geminal isomer are formed, but the ratio of these two appears to be, unlike that of the other secondary amines previously discussed, very little affected by the reaction medium, \textit{viz.} acetonitrile or an aromatic solvent. Tetra-substitution with this amine requires fairly drastic reaction conditions, and side-reactions are observed, \textit{e.g.} dealkylation of N-methylaniline,
and the aniline thus formed competes for the substrates in the reaction mixture.

It would be premature to speculate as to the causes of the above, but it might be worth noting that N-methyl aniline is a slowly reacting amine and that it contains an aromatic grouping as one of its substituents. It could thus act both as a nucleophile and a complexing agent (π- and/or lone-pair-electron donation).

Penta-aminomonochloro-derivatives of an authentic nature are few and far between. Many of those reported could not be substantiated and indeed were often confused with the above mentioned hexa-alkylaminocyclotriphosphazatriene monohydrochlorides, \( \text{Na}_2\text{P}_3(\text{NHMe})_6 \cdot \text{HCl} \). Amongst the authentic ones are the penta-aziridino-monochloro-derivative, \( \text{Na}_2\text{P}_3\text{Cl}(\text{NC}_2\text{H}_4)_5 \), and monochloropentakisdimethylamino-derivative, \( \text{Na}_2\text{P}_3\text{Cl}(\text{NMe}_2)_5 \), present only in small yield; it is very unstable and difficult to isolate. More recently, we have discovered a new penta-aminomonochloro-derivative – this time stable. We achieved this by having a bulky amino-group, dibenzylamino, bonded to the phosphorus atom carrying the last remaining chlorine atom and probably steric shielding is the cause of the increased stability of this derivative, \( \text{Na}_2\text{P}_3\text{Cl}[\text{N}([\text{CH}_2\text{Ph})_2](\text{NMe}_2)_4 \).

That dibenzylamine is a bulky nucleophile and gives rise to a sterically very demanding substituent is borne out by the fact that under the most forcing conditions investigated by us, we were unable to introduce more than two of these substituents, \( \text{Na}_2\text{P}_3\text{Cl}_2[\text{N}([\text{CH}_2\text{Ph})_2]_3 \), into the hexachloride, an observation hardly attributable to polar effects. A further two less sterically demanding amino residues could be introduced successively on the same phosphorus atom, \( \text{Na}_2\text{P}_3\text{Cl}_2(\text{NMe}_2)_2[\text{N}([\text{CH}_2\text{Ph})_2]_2 \), whilst the smallest nucleophilic reagent investigated, the methoxide ion, replaced with comparative ease all four remaining chlorine atoms, \( \text{Na}_3\text{P}_3(\text{OMe})_4[\text{N}([\text{CH}_2\text{Ph})_2]_2 \), of the original bisdibenzylamino-compound.

A further pointer to the steric demands of dibenzylamine as a reagent and/or substituent is the observation that in a number of mononuclear phosphorus compounds, \( \text{PhP}(\text{S})\text{Cl}_2 \) (\( \text{X} = \text{O}, \text{S} \)), we were unable to attach more than one dibenzylamino-group to a given phosphorus atom. In this study we noted competitive solvolysis by water and/or ethanol. We have observed a competitive hydrolysis when the hexachloride, \( \text{Na}_2\text{P}_3\text{Cl}_6 \), is allowed to react with diethyamine, another bulky nucleophile. The product, \( \text{Na}_3\text{HP}_3(\text{O})\text{Cl}_2(\text{NET}_2)_3 \), is derived from the geminal tris-derivative, \( \text{Na}_3\text{P}_3\text{Cl}_3(\text{NET}_2)_3 \), and molecular weight studies in benzene indicate a stable dimeric unit, \( [\text{Na}_3\text{HP}_3(\text{O})\text{Cl}_2(\text{NET}_2)_3]_2 \), in solution.

An X-ray crystallographic investigation, albeit not yet very precise, reveals the same aggregate present in the solid state, held together by means of two hydrogen-bonds, thus forming a tricyclic unit. The structure shown below represents the first mixed cyclophosphazene-cyclophosphazane com-
pound investigated by this technique. The PCl₂-N-P(NEt₂)₂ segment has bond-lengths typical of a phosphazene and the P(NEt₂)₂-NH-P(O)NEt₂ segment those of a phosphazane. The remaining segment, PCl₂-N-P(O)NEt₂, is more difficult to classify, the short ring P-N bond-lengths indicate the powerful electron-withdrawing properties of both the \[ \equiv \text{PCl}_2 \] and the \[ \equiv \text{P}(\text{O}) \text{moieties} \].

Let us now consider the system hexachlorocyclo-triphosphazatriene-ammonia and primary amines. Least is known about the first, ammonia, partly at least because of experimental difficulties. Methylamine has been investigated, although not quite as extensively as its homologues. The two non-geminal bis- and a small amount of the geminal bis-derivatives have been observed. As the series, ethylamine, isopropylamine, and tert-butylamine, give geminal tetrakis derivatives, the alkylaminochloro-compounds, are thermally considerably less stable than the corresponding dialkylaminochloro-derivatives. This instability is the greater, the smaller the alkyl group, i.e., largest with the ethyl and least with the tert-butyl-derivatives. Considerable amounts of gummy resins and other products, as yet not characterised, are obtained, particularly in the higher stages of aminolysis and this behaviour is again most pronounced with the smallest of the amines, namely ethylamine. The above factors add extra experimental difficulties to these systems. One is less able to use gas-liquid chromatography for the separation and isolation of some of these compounds. Many of them tend to decompose on standing prior to physico-chemical determinations. In addition, the tendency to resin formation has to date either prevented or hindered the isolation, at least in reasonable quantities, of some of the higher aminolysed derivatives. The exceptions are the fully aminolysed derivatives, \( \text{N}_3\text{P}_3\text{Cl}_3(\text{NH}_2)_6 \), which can usually be obtained in fair to excellent yields when considerable excess of the amines are used.

Bearing in mind the above provisos and, in particular, the large amount of resin formation, we can make the following generalisations. Monoamino-pentachlorides, \( \text{N}_2\text{P}_2\text{Cl}_5\text{R} \), can be isolated in all the above systems, although the parent compound, \( \text{N}_3\text{P}_3\text{Cl}_5\text{NH}_2 \), has only been obtained by deammonolysis of the bis-derivatives, \( \text{N}_3\text{P}_3\text{Cl}_5(\text{NH}_2)_2 \). The bisamino-compounds, \( \text{N}_2\text{P}_2\text{Cl}_4\text{R}_2 \), exhibit a trend.

Ammonia gives a geminal compound, \( \text{N}_3\text{P}_3\text{Cl}_4(\text{NH}_2)_2 \) (earlier, erroneously ascribed a nongeminal structure). With the smallest primary amine, methylamine, predominantly nongeminal derivatives, \( \text{N}_3\text{P}_3\text{Cl}_4(\text{NHMe})_2 \), are obtained; the same pertains for ethylamine, \( \text{N}_3\text{P}_3\text{Cl}_4(\text{NHMe})_2 \). The situation is at present rather confused for isopropylamine but we can say with reasonable certainty that with the tert-butylamine, the geminal bis-derivative, \( \text{N}_3\text{P}_3\text{Cl}_4(\text{NHBut})_2 \), is either the sole, or at least the predominant, product.

Trisamino-derivatives, \( \text{N}_3\text{P}_3\text{Cl}_4\text{R}_3 \), have either not been isolated at all or only in very small amounts. For instance, in the ethylamino series, we have isolated traces of a nongeminal compound, \( \text{N}_3\text{P}_3\text{Cl}_4(\text{NHEt})_3 \), but are uncertain whether it has a \( \text{cis-} \) or \( \text{trans-} \)-structure. However, all three amines: ethylamine, isopropylamine, and tert-butylamine, give geminal tetrakis derivatives, \( \text{N}_3\text{P}_3\text{Cl}_4\text{R}_4 \), although when the reaction is carried out in stabilised chloroform, the incursion of an ethoxy-derivative, \( \text{N}_3\text{P}_3\text{Cl}_4(\text{OEt})\text{R}_3 \) (2, 2 : 4 : 6, 6), is observed — another example of competitive solvolysis. Here, however, this is greatest for the smallest amine, ethylamine, less for isopropylamine, and either very small or not present at all for tert-butylamine. It appears that this ethoxy-compound, \( \text{N}_3\text{P}_3\text{Cl}_4(\text{OEt})\text{R}_3 \), as well as
the geminal tetraamino-derivative, $\text{N}_3\text{P}_3\text{Cl}_2\text{R}_4$, must pass through a common (as yet not isolated) precursor, the geminal tris-amino-derivative, $\text{N}_3\text{P}_3\text{Cl}_3\text{R}_3$. This, possibly by a proton abstraction and chloride ion elimination process, might give rise to a reactive intermediate, for which the various nucleophiles present, amine and alcohol, compete to give rise to the two products mentioned above.

\[
\begin{array}{c}
\text{R} = \text{Et} \quad (\text{NHET}) \\
\text{IP} \quad (\text{NHPR'}) \\
\text{TB} \quad (\text{NHBU'})
\end{array}
\]

Whilst with ethylamine there is a change from the predominantly geminal replacement at the tetra-amino stage, with tert-butylamine, a geminal pattern prevails throughout. Isopropylamine is undoubtedly intermediate in behaviour.

Before attempting to rationalise the above behaviour, let me briefly refer to two other systems, namely, aniline and benzylamine. With the anilino-system geminal replacement of chlorine prevails throughout with minor nongeminal incursions at the bis-stage. Note-worthy is the isolation of the geminal tris-amino-derivative, $\text{N}_3\text{P}_3\text{Cl}_3(\text{NHPh})_3$, the only primary amino-derivative of this type to date. Benzylamine exhibits a behaviour somewhat intermediate between that of ethylamine and tert-butylamine. A nongeminal bis-derivative, $\text{N}_3\text{P}_3\text{Cl}_4(\text{NHCH}_2\text{Ph})_2$, is predominant, although a geminal isomer can be obtained as a minor product when toluene is used as a reaction medium. Here again we have an example of a solvent effect. No tris-derivative has been observed, and the only tetra-compound, $\text{N}_3\text{P}_3\text{Cl}_2(\text{NHCH}_2\text{Ph})_4$ is geminal.

\[
\begin{align*}
\text{N}_3\text{P}_3\text{Cl}_6 + \text{NH}_2\text{CH}_2\text{Ph} & \quad \xrightarrow{\text{Et}_2\text{O}, \text{reflux}} \quad \text{N}_3\text{P}_3\text{Cl}_2(\text{NHCH}_2\text{Ph})_4 \\
\text{nongem.} - \text{N}_3\text{P}_3\text{Cl}_4(\text{NHCH}_2\text{Ph})_2 & \quad (45\%) \\
\text{N}_3\text{P}_3\text{Cl}_6 + \text{NH}_2\text{CH}_2\text{Ph} & \quad \xrightarrow{\text{toluene}, \text{reflux}} \quad \text{N}_3\text{P}_3\text{Cl}_3(\text{NHCH}_2\text{Ph})_2 \\
\text{nongem.} - \text{N}_3\text{P}_3\text{Cl}_4(\text{NHCH}_2\text{Ph})_2 & \quad (32\%) \\
\text{gem.} - \text{N}_3\text{P}_3\text{Cl}_4(\text{NHCH}_2\text{Ph})_2 & \quad (13\%)
\end{align*}
\]

How can we rationalise all of the above? If we consider di-substitution, $\text{N}_3\text{P}_3\text{Cl}_2\text{R}_2$, the predominant patterns are shown in the following table.

<table>
<thead>
<tr>
<th>$\text{N}_3\text{P}_3\text{Cl}_2\text{R}$</th>
<th>$\text{N}_3\text{P}_3\text{Cl}_2\text{R}_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{NH}_3$</td>
<td>$\text{geminal}$</td>
</tr>
<tr>
<td>$\text{NH}_2\text{Me}$</td>
<td>$+$</td>
</tr>
<tr>
<td>$\text{NH}_2\text{Et}$</td>
<td>$+$</td>
</tr>
<tr>
<td>$\text{NH}_2\text{Pr}_3$</td>
<td>$+$</td>
</tr>
<tr>
<td>$\text{NH}_2\text{Bu}_4$</td>
<td>$+$</td>
</tr>
<tr>
<td>$\text{NH}_2\text{CH}_2\text{Ph}$</td>
<td>$+$</td>
</tr>
<tr>
<td>$\text{NH}_2\text{Ph}$</td>
<td>$+$</td>
</tr>
</tbody>
</table>

Thus, on ascending the series from ammonia to tert-butylamine, it commences with geminal substitution, passes over to nongeminal substitution, and returns with tert-butylamine, again to geminal substitution. Obviously neither steric effects nor nucleophilicities on their own, can be the deciding factors. The same is borne out by aniline, a somewhat bulkier, but weaker nucleophile than ammonia.

The less clear-cut behaviour of benzylamine, sterically not very demanding, and in nucleophilicity intermediate between aliphatic amines and aniline, has already been mentioned.

We have attempted a rationalisation based on chelated hydrogen-bonding. As long as the affinity between a given substrate and a given nucleophile is very high, it does not need the extra aid provided by such chelating hydrogen-bonds, and hence the nucleophile will attack the most electrophilic phosphorus, usually a $\equiv\text{PCl}_2$ group. However, a lot of evidence based on other data summarised in the paper, in which we put the above proposal forward, suggest that a ring nitrogen (most basic site) and a nongeminal chlorine atom (most ionic character in P-Cl bond), to be the most likely sites for chelating hydrogen-bonds (as shown below), provided the affinity has dropped sufficiently to need that extra help. This hypothesis also rationalises the change from nongeminal to geminal reaction patterns for ethylamine, as the electrophilic activities of the phosphorus atoms in the ethylaminochlorophosphazenes decrease with increasing amination and hence, a similar need for “aid” arises for the higher aminolytic replacement stages.
It may be mentioned in passing that even the fully aminolysed hexa-amides, $N_3P_3(NH_2)_6$, and octamides, $N_4P_4(NH_2)_8$, decompose thermally, both giving amorphous macromolecules called phosphams, $(NPNH)_n$. We were able to show that phosphams derived from the hexa-amide and octa-amide respectively, differ however considerably in density, in line with known density differences in homologous cyclophosphazenes, $N_3P_3X_6$ and $N_4P_4X_8$, based on six- and eight-membered rings respectively. This suggested that the resultant macromolecules retain respectively their six- and eight-membered rings as structural units.

In an attempt to throw further light on the very complex problem of different replacement patterns we prepared a number of “mixed” aminophosphazenes, introducing different amino groups, $X$ and $Y$, in different orders. The diagram below, shows that if one ethylamino- and one tert-butylamino-groups are used to replace two chlorine atoms in the hexachloride, $N_3P_3Cl_6$, to give “mixed” diamino-derivatives, $N_3P_3Cl_4XY$, isomers result, which arise from the different order in which these two groups $X$ and $Y$ are introduced into the ring. It is clear that in this case at least, the entering nucleophile, rather than the substituent present, determines the structure of the resultant product. We have numerous examples with other amines and not only confined to di-substitution, which bear out that in most, but not all, circumstances the entering nitrogenous nucleophiles, rather than the substituents already present determine the position of attack.

The same pertains to the geminal diphenyltetra-chloro-derivative, $N_3P_3Ph_2Cl_4$, and an outline of some of its reactions with different amines is shown overleaf. It can be seen that here too it is the nature of the nucleophile rather than that of the substituents already present which determines the nature of the product.
Rather different is the situation when a triphenylphosphazenyl-substituent, NPPh₃, is present in the hexachloride, N₃P₃Cl₆. This is clearly demonstrated in the diagram below. We note that disubstitution with dimethylamine, NHMe₂, or with triphenylnmonophosphazene, HNPPh₃, gives nongeminal derivatives. If “mixed” derivatives are made and dimethylamine is introduced first, followed by triphenylnonophosphazene, the above rule is obeyed. When the above two substituents are introduced in the reverse order the same, anticipated, nongeminal product is not obtained. Instead a geminal product is isolated. This at present unexplained observation also applies to piperidine.

It is worth mentioning that in other systems which contain the triphenylphosphazenyl-substituent, we have observed other, as yet unexplained, phenomena.

Relatively little is known about the reaction of the hexachloride with tertiary amines. More forcing reaction conditions are required as instead of a nitrogen-hydrogen bond, a nitrogen-carbon (and in some cases a carbon-hydrogen) bond needs to be cleaved. Burg and co-workers reported that trimethyamine reacts with hexachlorocyclophosphazatriene to give tetramethylammonium chloride and mixtures of chlorodimethylamino-derivatives, N₂P₃Cl₆-n(NMe₂)ₙ.

Following earlier observations of ours that NN-dialkylanilines react as ambident nucleophiles with cyanuric chloride, N₃C₃Cl₃, giving rise to both “nitrogen-” and “carbon-substitution,” with the former prevailing, we investigated the reactions of NN-dimethylaniline with phosphoryl chloride, P(0)Cl₃, thiophosphoryl chloride, P(S)Cl₃, and chlo-
rocylophosphazenes. With the mononuclear phosphorus species, "carbon-substitution" very much preponderated, with the hexachloride, \( \text{N}_3\text{P}_3\text{Cl}_6 \), mainly "nitrogen," with a small proportion of "carbon-substitution" was observed\(^{49}\).

Let me now refer, very briefly, to some other less intensively investigated systems. The hexafluoride, \( \text{N}_3\text{P}_3\text{F}_6 \), reacts with ammonia\(^{50}\), primary\(^{51}\) and secondary\(^{51}\),\(^{52}\) amines, to give monoaminopentafluoro-derivatives, \( \text{N}_3\text{P}_3\text{F}_5\text{R} \). With amines some examples of di-, \( \text{N}_3\text{P}_3\text{F}_4\text{R}_2 \)\(^{53}\), and tri-aminolysis products, \( \text{N}_3\text{P}_3\text{F}_3\text{R}_3 \)\(^{53}\), all to date nongeminal, have been reported. Higher aminolysed aminofluoro-derivatives have been prepared; usually however indirect methods involving e.g., fluorination of chloro-precursors, or deamination of higher aminoderivatives by means of antimony trifluoride, were employed. These are however outside the scope of my present talk. Some aminobromofluoro-, aminochlorofluoro-, as well as aminofluoro-derivatives were obtained by aminolysis of bromofluoro-, or chlorofluoro-precursors, or by indirect methods\(^5\).

Hexabromocyclotriphosphazatriene, \( \text{N}_3\text{P}_3\text{Br}_6 \), has received even less attention. Its reaction with dimethylamine has been investigated\(^5\) and there are indications that mono-, cis- and trans-bis-, and cis- and trans-tris-dimethylamino-derivatives, \( \text{N}_3\text{P}_3\text{Br}_{6-n}(\text{NMe}_2)_n \) \((n = 1, 2, 3)\) occur. Many of these have not been isolated pure, only spectroscopic evidence being presented for their existence. The presence of the tetrakis-dimethylaminodibromoc-derivative, \( \text{N}_3\text{P}_3\text{Br}_4(\text{NMe}_2)_4 \), is indicated from thin-layer chromatographic data but pertains to deaminolysis studies\(^{10}\). We don’t know whether these aminobromo-derivatives are inherently less stable than the corresponding aminochloro-derivatives, or whether, to date, experimental difficulties are the cause of this apparent lack of understanding of this system. It may be mentioned in passing that deamination of hexakisdimethylaminocyclotriphosphazatriene, \( \text{N}_3\text{P}_3(\text{NMe}_2)_6 \), with hydrogen chloride or hydrogen bromide passes through the tetraamino-, \( \text{N}_3\text{P}_3\text{X}_4(\text{NMe}_2)_4 \), to the cis- and trans-trisamino-derivatives, \( \text{N}_3\text{P}_3\text{X}_3(\text{NMe}_2)_3 \) \((\text{X} = \text{Cl} \text{ or Br})\)^{10}. In neither deamination process was there any evidence of a geminal product being present at the tris-stage.

Before leaving the synthetic aspects of the trimer system, let me reiterate the importance of steric effects. We have noted that both with dibenzyl-amine\(^{32}\), as well as with triphenylmonophosphazene\(^{44}\), direct replacement stops at di-substitution, \( \text{N}_3\text{P}_3\text{Cl}_2\text{R}_2 \), of the hexachloride. We attribute this to steric hindrance to further reaction with the same type of nucleophile. This has been outlined earlier in this paper and in greater detail elsewhere\(^{32}\); it has been shown that further replacement of chlorine atoms by smaller, sometimes less nucleophilic species, can be achieved\(^{32}\).
Investigations to date have shown that this system is indeed very complex. Thus for the bis-dimethylaminohexachloride, $N_4P_4Cl_4(NMe_2)_4$, five isomers are possible and all have been reported by LEHR. This system has also been investigated by SOWERBY and co-workers, as well as ourselves, and we all can confirm its great complexity, the presence of isomerism, and the occurrence of both geminal and nongeminal compounds. The rationale for this is on even less secure ground than in the trimer system. A further complication is that structural assignments are not always as certain as those in the trimer system because of the greater complexity of the tetramer molecules and, in particular, their ability to pucker. However, a number of structures have been solved by X-ray crystallography and these are displayed below.

Crystal structure determinations of $N_4P_4Cl_8-n(NMe_2)_n$.

We have also made observations regarding the presence and degree of virtual coupling in the $^1$H NMR spectra of chlorodimethylamino- and phenyldimethylamino-derivatives and their relationship to structure and some examples of this are given below.

Together with our colleagues in Bangalore, we have recently begun a systematic study of the octachloride $N_4P_4Cl_8$, with other amines, such as ethylamine, tert-butylamine, and N-methylaniline. I will not go into this in any detail as the investigations are as yet incomplete. Suffice it to say that the problems are complex; difficulties are encountered in separation, purification and in structure determination. Resin formation occurs again, as in the trimer system, with primary amines, which further complicates this already difficult system. In a number of cases several isomers have been isolated. Solvent effects, as yet incompletely understood, also appear to be of importance.

Let me briefly highlight some findings of these studies involving two secondary and two primary amines: dimethylamine, N-methyl aniline, ethylamine, and tert-butylamine. With the first two, geminal 2,6,6,6-tetakis-derivatives, $N_4P_4Cl_4(R = NMe_2, NMePh)$, have been observed. All four nongeminal 2,4,6,8-tetra-amino-stereoisomers have been reported, although not necessarily with the same amine system. Of the four possible isomers of this type displayed in a diagram above, the one with
substituent groups alternating above and below the framework of the ring appears to be the least prevalent, if present at all, whilst the one with all four groups, \textit{cis}, seems to be reasonably common. The most common one, and usually the one obtained in highest yield, is the one which is centro-symmetric. These observations tally with those observed for the nongeminal 2,4,6,8-tetraphenyl-tetrachloro-derivatives, \( \text{N}_4\text{P}_4\text{PI}_{14}\text{Cl}_4 \) (albeit synthesised by a different route)\(^6\), were three isomers of this type were found, their structures initially determined by NMR spectroscopy and two confirmed since by X-ray crystallography.

Finally, let me only mention, because it is somewhat outside the scope of my topic, that systems related to cyclophosphazenes, but containing in their ring skeleton apart from phosphorus and nitrogen, also either carbon or sulphur atoms, and which have been investigated by Schmidpeter and co-workers\(^5\), and by Van der Grampel and co-workers\(^6\), respectively, show aminolysis patterns with different amines, which strongly resemble those of the chlorocyclophosphazenes. Chloro-precursors representative of each type are shown below.

\[
\text{R I}^+ \quad \text{N Cl}^\text{I} \quad \text{^Cl} \\
\text{Cu}^+ \quad \text{Cl}^\text{N} \quad \text{^Cl} \\
\text{C Kn} \quad \text{Cl}^\text{N} \quad \text{^Cl}
\]

Having discussed up to now mainly the synthetic and mechanistic aspects of my subject, I now turn to some physico-chemical measurements on amino-cyclophosphazenes, aminohalogenocyclophosphazenes and related compounds. In this part, I will also refer in greater detail to the findings of X-ray crystallography. I have referred earlier to the considerable basicity of hexa-alkylaminocyclophosphatrienes. For the last ten years or more we have investigated in considerable depth the basicities of a whole variety of cyclophosphazenes. Here I wish to stress only a few salient points. One of these, as can be seen from the table below, is that in homogeneously substituted cyclophosphazenes based on six-, \( \text{N}_3\text{P}_3\text{R}_6 \), and eight-membered rings, \( \text{N}_4\text{P}_4\text{R}_8 \), alkylamino- (and amino-)derivatives are the most basic so far observed\(^6\).\(^8\).

I have mentioned earlier that with suitable compounds, such as the tetra-aminodichloro-derivatives, \( \text{N}_4\text{P}_4\text{Cl}_2\text{R}_4 \), basicity measurements can be used to distinguish between geminal and nongeminal isomers\(^4\). In addition, we have been able to deduce substituent constants for the cyclotriposphazatriene system\(^7\)-\(^2\), where \( \alpha_R \) and \( \gamma_R \) refer to the effect of substituents on the phosphorus atoms, \( \alpha \) and \( \gamma \) to a given ring nitrogen atom (cf. diagram below).

### Basicity of cyclophosphazenes in nitrobenzene towards perchloric acid.

<table>
<thead>
<tr>
<th>( \text{N}_3\text{P}_3\text{R}_6 )</th>
<th>( \text{pK}'\text{a}_1 )</th>
<th>( \text{pK}''\text{a}_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{N}_3\text{P}_3\text{NMMe}_2 )</td>
<td>7.6</td>
<td>8.3</td>
</tr>
<tr>
<td>( \text{N}_3\text{P}_3\text{Ph} )</td>
<td>6.4</td>
<td>7.6</td>
</tr>
<tr>
<td>( \text{N}_3\text{P}_3\text{Cl} )</td>
<td>1.5</td>
<td>2.2</td>
</tr>
<tr>
<td>( \text{N}_3\text{P}_3\text{OEt} )</td>
<td>-0.2</td>
<td>0.6</td>
</tr>
<tr>
<td>( \text{N}_3\text{P}_3\text{OMe} )</td>
<td>-1.85</td>
<td>-0.95</td>
</tr>
<tr>
<td>( \text{N}_3\text{P}_3\text{OPh} )</td>
<td>-5.8</td>
<td>-6.0</td>
</tr>
<tr>
<td>( \text{N}_3\text{P}_3\text{Cl} )</td>
<td>( \langle -6 \ast )</td>
<td>( \text{N}_4\text{P}_4\text{Cl}_8 )</td>
</tr>
</tbody>
</table>

\* Calc. = 20.4.

### Substituent effects and positions of protonation of aminochlorocyclotriphosphazatrienes

### Tris:

**Geminal**

![Geminal Tris Diagram]

**Non-geminal**

![Non-geminal Tris Diagram]

### Tetrakis:

![Tetrakis Diagram]

Expected position of protonations, pattern (i) \( \alpha > \gamma \)

### Tetra-

![Tetra Diagram]

\* Indicates position of protonation.
We have been able to compare the calculated and observed pK'\text{a,1} values and in the vast majority of cases a satisfactory agreement has been obtained. Furthermore, we deduced that both first and second protonations take place (for all the cyclophosphazene ring systems investigated so far) at the ring nitrogen atoms (the sole exceptions being some phosphazenylycyclophosphazenes, which will be discussed later) and this has been confirmed by X-ray crystallography for two mono-protonated species\textsuperscript{73,74}. Whilst, to date, all known protonations of phosphazenes, including phosphazenylycyclophosphazenes, take place at phosphazenyl nitrogen atoms, be they endocyclic or exocyclic, these sites of attack by electrophilic species are not unique when other, more bulky, reagents are involved. Examples of this are the methylaizations with trimethyloxonium tetrafluoroborate, Me\textsubscript{3}O+BF\textsubscript{4}\textsuperscript{-}\textsuperscript{75}, where the dimethylamino-trimer-derivatives, N\textsubscript{3}P\textsubscript{3}Cl\textsubscript{6-n}(NMe\textsubscript{2})\textsubscript{n}, alkylate on the exocyclic nitrogen atoms of the dimethylamino-groups. However, in some mixed dimethylamino-isopropylamino-derivatives, N\textsubscript{3}P\textsubscript{3}(NMe\textsubscript{2})\textsubscript{6-n}(NHPri\textsubscript{n})\textsubscript{n}, alkylations of the ring phosphazenyl nitrogen atoms take place; again we note the complexity and versatility of the cyclophosphazene system and the subtle balance of steric and polar effects. Whilst this methylation reaction has not been extended to many types of compounds, the lesser steric demands of primary than of secondary alkylamino groups undoubtedly plays a part.

We come to the same conclusion from basicity studies and indeed found it necessary to postulate a “saturation effect” for primary alkylamino (and amino-), but not for secondary dialkylamino-derivatives\textsuperscript{72}. It appears that in some compounds the substituents are inherently capable of supplying more electron-density than the phosphazene ring can tolerate and hence, to date, the highest basicities observed do not exceed pK'\text{a} values of +9, although, were it not for the “saturation effect,” higher values should be obtainable.

I referred above to phosphazenylycyclophosphazenes not always conforming to the general pattern of ring protonation. Indeed, we discovered two types of behaviour\textsuperscript{45}. In both, protonation takes place at phosphazenyl nitrogen atoms. In one type however it is at an endo-, in the other at an exo-position. Whether protonation takes place at an endocyclic or exocyclic site seems to depend on the
structure of the triphenylphosphazenylcyclophosphazene and by examining the data summarized in the tables below, we can tentatively deduce some of the structural features which seem to be responsible for this.

It appears, if the other group on the same ring phosphorus atom as the triphenylphosphazenyl group, NPPh₃, in question, is either a chlorine atom or another triphenylphosphazenyl group, endo-protonation occurs. If the other group is however amino, NH₂, dimethylamino, NMe₂, or phenyl, Ph, exo-protonation takes place. The reason for this divergence in behaviour is probably – at least in part – steric in origin. The chlorine atom is axially symmetric and mono-co-ordinated; the nitrogen atom of the triphenylphosphazenyI is two-co-ordinated. The atoms, nitrogen or carbon, linking the other group of substituents, amino, dimethylamino and phenyl to the ring, are all three-co-ordinate, and hence sterically more demanding. Supporting evidence for the above line of argument comes from a selection of substituent constants, αᵣ, displayed below.

αᵣ-values

R = Ph₃PN > NHAlk > Alk > Ph ~ NHPh > OAlk > SAIk > SPh > OPh > OCH₂CF₃ > Cl

<table>
<thead>
<tr>
<th>Structure</th>
<th>pKᵣ,₁ (Observed)</th>
<th>pKᵣ,₁ (Calc. (endo))</th>
<th>pKᵣ,₁ (Calc. (exo))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph*NPPh₃</td>
<td>-4.7</td>
<td>-5.6</td>
<td>-4.7 (standard)</td>
</tr>
<tr>
<td>Cl*Cl</td>
<td>-2.9</td>
<td>-3.8</td>
<td>-2.9</td>
</tr>
<tr>
<td>Me₂N*NPPh₃</td>
<td>+2.6</td>
<td>+4.2</td>
<td>+2.3</td>
</tr>
<tr>
<td>Cl*Cl</td>
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<td>-3.0</td>
</tr>
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<td>-4.7</td>
<td>-3.6</td>
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<td>-5.9</td>
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<tr>
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<td>1.6</td>
<td>0.3</td>
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Selected Substituent constants (in pKᵣ units).

<table>
<thead>
<tr>
<th>R</th>
<th>αᵣ</th>
<th>γᵣ</th>
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<tr>
<td>NH₂</td>
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<tr>
<td>NHMe</td>
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<td>1.8</td>
</tr>
<tr>
<td>OPh</td>
<td>3.1</td>
<td>1.3</td>
</tr>
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</table>
αR-values

-\text{NH}_2 (6.0) > -\text{NHMe} (5.8) > -\text{NMe}_2 (5.6)
-\text{NHEt} (5.8) > -\text{NM}_{3} (5.6)
-\text{OPr}^1 (4.2) > -\text{OEt} (3.9) > -\text{OMe} (3.6)
-\text{N} = \text{PPh}_3 \leftrightarrow \text{N} = \text{PPh}_3 (10.3)

For alkylamino groups (three-co-ordinate nitrogen, one lone-pair of electrons), αR values trend in the opposite sense to that expected from inductive effects. On the other hand, for alkoxy groups (two-co-ordinate oxygen, two lone-pairs of electrons), αR values are in line with expected inductive effects. The exceptional high αR value (10.3)\(^{45}\) of the triphenylphosphazenyl group is highlighted by one of its resonance forms (two-co-ordinate nitrogen, two lone-pairs of electrons).

We postulated\(^{45}\) that this difference in behaviour (endo- or exo-protonation) was probably caused by a conformational change of the triphenylphosphazenyl group and fortunately for us, two crystallographic studies — one of each type of behaviour — have been carried out and proved our point. In those compounds where we postulate endocyclic protonation the triphenylphosphazenyl-group takes up a position such that the p\text{z}-orbital of the nitrogen atom is in the same plane as the reference line (for a discussion and definition of this reference line, see my Prague lecture\(^{66}\), i.e., the triphenylphosphazenyl group or at least its NP segment, projects more or less parallel to the local ring segment NPN of the phosphazene ring. I shall call this type I conformation.

On the other hand, in those compounds where exocyclic protonation is postulated, the NP segment of the triphenylphosphazenyl-group projects vertically downwards, i.e., perpendicular to the local NPN ring segment and the p\text{z}-orbital is now parallel to the reference line. This is type II conformation. We have made use of the above to suggest that basicity measurements of phosphazenylic phosphazenes can be used as a tool for the conformational analysis of this particular substituent.

You may have noted one or two examples in the table, where there was some discrepancy between the calculated and observed pK\text{a,1} values. Amongst possible causes contributing to this could be (a) variation in bond angle at the exocyclic nitrogen atom. [See the variety of bond angles in phosphazenylic-derivatives, R\text{3}P—N—X, ranging from 121° (sp\text{2}-hybridised) to 175° (sp\text{3}-hybridised)].

(b) rotations of the phosphazenyl groups such that the p\text{z}-orbital is not exactly in Type I or II conformation; (c) in asymmetric molecules, rotations can take place clockwise or anti-clockwise, etc.

It is perhaps appropriate to discuss in somewhat greater detail than I did in my lecture in Prague\(^{66}\), the conformation of suitable substituents in relation to the local cyclophosphazene segment, NPN. In particular, I will discuss the conformation of the dimethylamino, the phenyl, and the triphenylphosphazenyl group, all of which have either a nitrogen or carbon atom (all sp\text{2}-hybridised or approximating to this), attached to the ring phosphorus atom and hence the former, the linking atoms, have p\text{z}-orbitals available for interaction with suitable orbitals on the phosphorus atom.

\begin{align*}
\text{NMe}_2 & \quad \text{Ph} \\
\text{NPPh}_3 & \quad \text{sp}^2\text{hybridised}
\end{align*}

Three main types of conformational behaviour have, to date, been observed from X-ray crystallographic studies — I shall call them types I, II and III, and these are summarised in the diagrams below, together with structural examples.
In conformation I (already defined) the $p_z$-orbital of one or both substituents on the phosphorus atom is parallel with the reference line. This is usually observed only in compounds where one of the substituents belongs to the class of the three mentioned above (NMe$_2$, Ph, NPPPh$_3$) and the other is an axially symmetrical substituent such as the chlorine or bromine atom. An interesting example of this type is provided by a tetramer derivative, N$_3$P$_3$Cl$_4$(NPPh$_3$)$_2$, where the two NPPPh$_3$ groups have a 2,6-trans-disposition with their exocyclic NP segments approximately parallel to the local NPN ring segments, and the two substituents project in an opposite sense.

There is however one proven exception to the above. In the geminal diphenyltetrafluoride, N$_3$P$_3$Cl$_4$Ph(NPPh$_3$)$_2$, (both substituents, Ph and NPPh$_3$ are in type II conformation), although it would be tempting to predict other structures in which type II behaviour might occur.

Type III conformations are intermediate between those of types I and II. The reference line and the $p_z$-orbital of the substituent form an angle intermediate between those of types I and II, usually straddling the halfway mark. This usually pertains to structural situations where two substituents with $p_z$-orbitals are situated on the same phosphorus atoms. It has been observed in numerous geminal bismethylamino- =P(NMe$_2$)$_2$ and diphenyl-groupings, =PPh$_2$ (cf. ref. 66). Unless however a phosphazenyl group is attached to the cyclophosphazene ring, conformations I and III give rise to endocyclic protonation. Type II has only been observed with a suitable combination of a phosphazenyl with another fairly sterically demanding substituent and, as mentioned above, gives rise to exocyclic protonation.

If one took the above arguments on conformational behaviour a step further, type I behaviour should be the dominant one for the types of substituent discussed, if no other substituent was present. This is, of course, a hypothetical case for cyclophosphazenes but can be tested in the 1,3,5-triazines, N$_3$C$_3$R$_3$, whose similarity to the phosphazenes has been mentioned in this paper and elsewhere. In hexamethylmelamine, N$_3$C$_3$(NMe$_2$)$_3$, observed, namely in N$_3$P$_3$Cl$_4$Ph(NPPh$_3$)$_2$, (both substituents, Ph and NPPPh$_3$ are in type II conformation), although it would be tempting to predict other structures in which type II behaviour might occur.
Bond lengths (Å) and bond angles. E.s.d.s: for the lengths P-Cl 0.003, P-N 0.005—0.007, P-C 0.006 Å; for the angles Cl-P-Cl 0.1, N-P-N 0.3, P-N-P 0.4°.

An important test case was the structure of a triphenylphosphazenyl-substituted 1,3,5-triazine, \( \text{N}_3\text{C}_3\text{Cl}(\text{NMe}_2)(\text{NPPh}_3) \). This has just been solved by Cameron and Mannan\(^8\). It has many interesting features – I wish to stress only two of these: (i) the NP segment of the triphenylphosphazenyl group is deviating only slightly from co-planarity with the ring, \( i.e., \) the predicted type I conformation is observed; (ii) the same group, NPPh₃, is projecting into space in such a manner as to point towards the chlorine atom and away from the dimethylamino-group. I have alluded to this type of problem earlier in my lecture, when discussing cyclophosphazenes; in that system we have at present no information pertaining to this aspect.

The \( \text{sp}^2 \)-hybridised character of the dimethylamino-substituent when attached to cyclophosphazenes or 1,3,5-triazine, demonstrates that even in the ground state these ring systems possess strong “electron-sink” character. Their high basicities, discussed earlier, have already indicated this property in the perturbed state.

It will be of considerable interest to correlate other properties with the different types of conformation of the substituents, as well as that of the...
ring itself (in those cases where it is significantly puckered). Such conformational studies might well throw light on aspects such as the shielding effects experienced by certain proton containing substituents, if other substituents containing aromatic groups are on the same or adjacent phosphorus atoms (cf. eg., ref. 83). Similarly, the directing effect which some substituents seem to exert on incoming groups, causing them to enter, more or less specifically, specific sites in the cyclophosphazene ring system, may well also be affected by conformational aspects.

I would now like to discuss some other physicochemical data – in the first instance, the Faraday effect. Measurements on cyclophosphazenes homogeneously substituted, and of different ring sizes \((\text{NPR}_2)_n\) (except \(R = \text{Cl}, \ n = 3\)), indicate a proportionality in relation to a number of monomer units\(^84\), thus supporting the island model originally proposed by DEWAR and co-workers\(^85\). More refined quantum chemical calculations by two independent groups of workers have more recently supported this concept\(^86\)–\(^87\). Another aspect of our joint studies on the Faraday effect deals with the effect of different solvents on the magneto-optical rotations of homogeneously substituted cyclotriphosphazatrienes, \(\text{N}_3\text{P}_3\text{R}_6\) (\(R = \text{C}1, \text{OMe}, \text{SEt}, \text{NMe}_2, \text{Ph}, \text{OPh}, \text{etc.}\)). In all these compounds the magnetic-optical rotation is concentration independent but in a number of the compounds, particularly for \(\text{N}_3\text{P}_3(\text{NMe}_2)_6\), the magneto-optic rotation is strongly dependant on the solvent, whilst in others, such as \(\text{N}_3\text{P}_3\text{Cl}_6\), it appears to be independent of this parameter\(^88\). These observations are in strong contrast to organic aromatic systems where the magneto-optic rotation is both solvent and concentration dependant.

A further study using the same technique pertains to aminochlorocyclotriphosphazatriene-derivatives, \(\text{N}_3\text{P}_3\text{Cl}_6\text{R}_n\) (\(R = \text{amino group}\)). Some results of this work have already been reported\(^89\) and I will only briefly summarise the findings. We observed that on plotting magneto-optical rotation against the degree of substitution \((n)\), those compounds which contain only "pure" geminal structural units, \(\text{i.e.}, \equiv \text{PR}_2\) and/or \(\equiv \text{PCl}_2\), give points which fall on or near the straight line joining the rotation of the hexachloride, \(\text{N}_3\text{P}_3\text{Cl}_6\), and that of the hexamide, \(\text{N}_3\text{P}_3\text{R}_6\), whilst those compounds containing nongeminal units, \(\equiv \text{PClR}\), deviate in a positive sense to a lesser or greater extent from this line.

Hence it was of considerable interest to discover a similar relationship for the \(\text{^31P}\) NMR spectra of related compounds\(^90\). We shall report on this in detail elsewhere: here I will touch only upon a few salient points. Together with Dr. KEAT in Glasgow, we are carrying out a systematic study of the \(\text{^31P}\) NMR spectra of a variety of cyclophosphazenes.
On examining the chemical shifts of \( \equiv \text{PCl}_2 \), \( \equiv \text{PClR} \), and \( \equiv \text{PR}_2 \) groups in a series of compounds \( \text{N}_3\text{P}_3\text{Cl}_{6-n}\text{R}_n \), we find some relationships – admittedly, at present, on somewhat limited data. For instance, with increasing degree of aminolysis the chemical shift of the \( \equiv \text{PCl}_2 \) group moves asymptotically to high field-strength. We have at present too little data to make any meaningful statement on the shifts of the \( \equiv \text{PR}_2 \) group. Those of the \( \equiv \text{PClR} \) group, however, particularly when \( \text{R} = \text{NMe}_2 \), give an almost straight-line relationship (with increasing overall degree of aminolysis) with a very pronounced slope and it appears that the \( ^{31}\text{P} \) signal arising from this structural unit is the one most dependant on the degree of aminolysis and in the case of isomers also on structure. You will recall that precisely those compounds which contained \( \equiv \text{PClR} \) units, were the ones to deviate most strongly from the straight-line relationship in the Faraday effect measurements. On plotting the weighted mean of the \( ^{31}\text{P} \) resonances of a given compound against the degree of aminolysis, \( (n) \), we find a relationship which closely parallels that observed in the Faraday effect\textsuperscript{89}. Those compounds which deviate from the straight-line relationship are the ones which do so in both types of measurement and furthermore the relative magnitude of deviation appears to be the same for different degrees of aminolysis and for different isomers for both of these two physico-chemical techniques. The parallelism of these two techniques is most close for the dimethylamino-series, \( \text{N}_3\text{P}_3\text{Cl}_{6-n}\text{R}_n \ (\text{R} = \text{NMe}_2) \), where we also have the largest number of examples available. It is less close for the isopropylamino- \( (\text{R} = \text{NHPr}^\prime) \) and \( \text{tert} \)-butylamino-derivatives \( (\text{R} = \text{NHBu}^\prime) \). Firstly, we have fewer compounds available; secondly, one must draw an important distinction between the two techniques. The Faraday effect measures a molecular property and has a bond-additivity relationship. Hence minor deviations arising from effects pertaining to the cyclophosphazene ring may well be swamped by contributions from carbon-carbon and carbon-hydrogen bonds derived from larger substituents, \( e.g. \), \( (\text{R} = \text{NHPr}^\prime \) or \( \text{NHBu}^\prime) \). On the other hand, \( ^{31}\text{P} \) NMR chemical shifts probe the environment right in the cyclophosphazene moiety. The fact that some slopes are positive whilst others are negative is not relevant to the present discussion. However the steepness of the slope is, and we must compare the degree of deviation of a given point from the straight-line, in relation to the slope of this line. If we do so, bearing in mind the above remarks pertaining to these two physico-chemical techniques, the behaviour of the isopropylamino- and \( \text{tert} \)-butylamino-derivatives resemble each other in the two sets of measurements, although not as closely as that of the dimethylamino-series (diagrams overleaf).

Let me briefly mention the proton NMR spectra of aminocyclophosphazenes. In contrast to mononuclear phosphorus compounds\textsuperscript{91}, we often find additional features of complexity in the spectra of
Typical spectrum

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta_{P-H}$ c./sec</th>
<th>$\tau$</th>
</tr>
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<tbody>
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<td>POCl$_2$·NMe$_2$</td>
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<tr>
<td>POCl(NMe$_2$)$_2$</td>
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<td>PO(NMe$_2$)$_3$</td>
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</tr>
<tr>
<td>PS(NMe$_2$)$_3$</td>
<td>11.3</td>
<td>7.38</td>
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</tbody>
</table>

cyclophosphazenes$^{92,93}$. These appear either as extra fairly sharp lines, e.g., in some ethoxyphosphazenes$^{93}$, or as broad humps, e.g., in some dimethylaminophosphazenes$^{92}$, in addition to the lines anticipated from the usual parameters. They arise from a phenomenon frequently termed as "long range virtual coupling," and although this causes sometimes some complication (e.g., in integration of signals), one can also make use of it in structural assignments. Thus, the presence (and degree) or absence, of virtual coupling, can give structural information about a molecule when other NMR parameters (e.g., chemical shift and/or coupling constant) do not do so. An example of this is the three isomers, $N_3P_3(NMe_2)_{2}(NHPr')_4$, where the geminal isomer (absence of hump in the NMe$_2$ signal) can be distinguished from the two non-geminal isomers (presence of hump)$^{38}$. I have already given other examples of this earlier in this paper when discussing dimethylamino-derivatives of the tetramer, $N_4P_4Cl_{8-n}(NMe_2)_n$.$^{62}$.

Let me now consider another magnetic resonance technique – this time pertaining to the solid state, $^{35}$Cl nuclear magnetic resonance (NQR) spectroscopy. We have shown elsewhere that for some chlorocyclophosphazanes a straight-line relationship exists between phosphorus-chlorine bond length and $^{35}$Cl NQR frequency$^{94}$. Hence, we can use this relationship to predict either frequency from bond-length or bond-length from frequency. We have shown in another study$^{95}$ that we can distinguish very readily from their frequency ranges between geminal $\equiv$PCl$_2$ groups and nongeminal PCiR (R = Ph or NMe$_2$) structural units. It is usually,
The dimethylamino $^1$H NMR spectra of isomeric bis(dimethylaminotetraakis(isopropylamino)cyclotriphosphazatrienes, $N_3P_3(NMe_2)_2(NHPr_i)_4$.

however, not feasible to distinguish with any degree of certainty between cis- and trans-isomers, although when data is available on both isomers, usually the trans shows a wider spread of signal range than the corresponding cis-isomer.

I will now discuss very briefly just one aspect of infrared spectroscopy pertaining to the cyclotriphosphazatriene system. CHAPMAN and co-workers\(^9^6\) have pointed out that in chlorofluorocyclotriphosphazatrienes, the absence or presence (and relative magnitude), of a splitting of the ring P-N vibration, can give structural information and can in suitable compounds permit a distinction between geminal and nongeminal isomers. This rule pertains strictly only to the axially symmetric groups, such as the halogen atoms, but we found in a preliminary study\(^9^7\) that many other groups, including phenyl and a variety of amino groups, frequently, although not always, conformed to this pattern. I do not wish to discuss this here, except to point out that this technique drew our attention to an apparent anomaly (and this will need further verification) for

<table>
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<tr>
<th></th>
<th>P = N [cm$^{-1}$]</th>
<th>Splitting [cm$^{-1}$]</th>
<th>$^{35}$Cl NQR frequency at 293° [MHz]</th>
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<tr>
<td></td>
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<td>$\equiv PCl_2$</td>
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<td>gem.-$N_3P_3Cl_4(NMe_2)_2$</td>
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<td>trans-$N_3P_3Cl_4(NMe_2)_2$</td>
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<tr>
<td>trans-$N_3P_3Cl_4(NC_5H_{10})_2$</td>
<td>1190, 1225</td>
<td>35</td>
<td></td>
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</tbody>
</table>
one particular compound. In two pairs of cis-trans-isomers, \( \text{N}_3\text{P}_3\text{Cl}_3\text{R}_2 \) (\( \text{R} = \text{NMe}_2 \) or \( \text{NC}_3\text{H}_5 \)), three out of four have splittings of a similar magnitude for the ring P–N vibration, whilst the fourth, trans-\( \text{N}_3\text{P}_3\text{Cl}_4(\text{NC}_3\text{H}_5)\), has an anomalously large splitting. This observation pertains both to the solid state and in solution. Hence it is of some interest that on comparing the \( ^{35}\text{Cl} \) NQR spectra of these four compounds, that it is the very same one which differs considerably from the other three. For some reason, to date unknown, this compound exhibits an anomaly, observed by two different techniques and this seems to pertain in solution as well as in the solid state. Whether this is due to a conformational aspect of the substituents and/or due to the ring itself remains at present speculative. It seems to me that this might well be a topic worthy of the attention of an X-ray crystallographer.

A number of X-ray crystallographic studies on amino- and amino-halogenocyclophosphazenes have been carried out. I have referred already to some pertaining to the tetramer system. Three homologues, \( \text{N}_3\text{P}_3(\text{NMe}_2)_6 \) \(^{98}\), \( \text{N}_4\text{P}_4(\text{NMe}_2)_8 \) \(^{99}\), and \( \text{N}_4\text{P}_6(\text{NMe}_2)_{12} \) \(^{99}\), have been studied by this technique. The first of these is planar, or nearly so; the latter two are highly puckered. The ring bond-lengths within each of the homologues are all equal within experimental error and appear to be the same for the three compounds (there appears to be a slight tendency for the ring phosphorus-nitrogen bonds to be marginally shorter in the hexamer, although whether this difference is meaningful is as yet uncertain). In all three compounds, the geminal dimethyl-amino-groups, \( =\text{P}(\text{NMe}_2)_2 \), adopt type III conformations.

Accurate crystallographic data is also available on two pairs of base and conjugate acid: \( \text{Na}_3\text{P}_3(\text{NMe}_2)_6 \) \(^{98}\) and \( \{[\text{Na}_3\text{P}_3(\text{NMe}_2)_6\text{H}^+\}3\text{MoO}_4\text{O}_{19}^{-} \) \(^{74}\), and \( \text{Na}_3\text{P}_3\text{Cl}_3(\text{NHPr}^+) \) \(^{100}\), and \( \text{Na}_3\text{P}_3\text{Cl}_3(\text{NHPr}^+)\text{H}^+\text{Cl}^- \) \(^{73}\).

I discussed these two pairs in some detail in Prague \(^{66}\) and today wish to draw attention only to two or three salient features. Protonation takes place at the ring, as (and where) deduced from basicity data. The segments containing the protonated ring nitrogen atom have a bond-length more in keeping with a phosphazane rather than a phosphazene character. This has some bearing on some quantum-chemical calculations, I will refer to below. The exocyclic phosphorus-nitrogen bond lengths of substituents (\( \text{NMe}_2 \) or \( \text{NHPr}^+ \)) on the phosphorus atoms adjacent to the protonation site, are shorter in the conjugate acid than in the free base. This shortening is approximately 0.02 Å for the secondary amino-derivative and 0.03 Å for the primary amino-derivative. I have not sufficient expertise in crystallography to judge whether this difference is statistically meaningful. Intuitively, I believe however, that this is the case. We have seen from \( pK_a \) studies that primary amino-groups are better electron-supplying groups than secondary (of related structure), which is reflected in their higher \( q_R \)-values. I believe that it would be of particular interest to compare the detailed structures of free base and conjugate acid for both types (I, endo-, II, exo-protonation) of isomeric phosphazenylicyclophosphazenes.

Finally, in this section I would like to refer to the structures of the three isomers, \( \text{N}_3\text{P}_3\text{Cl}_3(\text{NMe}_2)_3 \), carried out by AHMED and his co-workers at Ottawa \(^{101-103}\).
The structures deduced earlier by Keat and Shaw on the basis of $^1$H NMR data were confirmed and many additional interesting features were brought to light. Thus, for instance in the geminal derivative we note an inequality in the lengths of the ring phosphorus-nitrogen bonds of a type observed already earlier in the series, $N_nP_3Cl_{6-n}Ph_n$ ($n = 2^{78}$ and $4^{104}$), which can be rationalised in a similar manner, the ring bond (in a given P-N-P segment), adjacent to the phosphorus atom carrying the more powerful electron-withdrawing groups, is shorter, whilst the other one is correspondingly larger. The mean length of the two bonds is, however, the same, within experimental error, as that of a symmetrically substituted segment. The phosphorus-chlorine bonds on the same phosphorus atom as a dimethyl-amino-group, are significantly longer than those of a $=PCl_2$ group, indicating a greater degree of ionic character in the former than in the latter. The same deduction has already been made from $^{35}$Cl NQR measurements. As Friedel-Crafts phenylation demands departure of a chlorine atom as an ion, we would expect, and we do observe, preferential phenylation of the nongeminal site, $=PCl \cdot NMe_2$. I consider this to be a particularly nice example of the interplay and cross-fertilisation of different techniques here: X-ray crystallography, $^{35}$Cl NQR spectroscopy, mechanistic speculation and synthetic application.

Let us now consider an aspect of scientific studies which I consider to be of considerable importance: the difference between properties observed by measurements pertaining to the ground state and those obtained from either chemically or physically perturbed states. X-ray crystallography, NQR and NMR spectroscopies provide the ground state data; basicity measurements give information on the state of the molecule perturbed by the positive charge of a proton. The former types of measurements tell us, within the limits of the accuracy of our present experimental data, that in the ground state phenyl-, dimethylamino-, and triphenylphosphazenyl-groups, supply about the same amount of electron-density to their nearby phosphazene environment. This can be deduced from the bond-length of adjacent phosphorus-chlorine and (ring) phosphorus-nitrogen bonds, and $^{35}$Cl NQR frequencies. The situation is drastically altered when we consider the perturbed state due to protonation of such molecules. Now we find the triphenylphosphazenyl group to be a vastly stronger electron-donor than the dimethylaminol-, which in turn is stronger than the phenyl group.

**Ground state**

1. Crystallography
   - effect on adjacent $\{P-Cl, P-N (\text{ring})\}$ bonds
2. $^{35}$Cl NQR frequencies in $=PClR$
   - $R = NPPh_3 \sim NMe_2 \sim Ph$

**Perturbed state**

Basicity studies: substituent constants
- $\alpha_{NPPh_3} = 10.3 \gg \alpha_{NMe_2} = 5.6 \gg \alpha_{Ph} = 4.2$

I have already drawn attention, here and elsewhere in some detail, to changes in such parameters as bond-angles and bond-lengths in pairs of free base and conjugate acid, where accurate crystallographic data is available.

X-ray crystallographic studies show that already in the ground state the lone-pair of electrons of the dimethylamino-group is already largely delocalised towards the phosphazene ring, as borne out by the approximately trigonal planar structure of the nitrogen atom and hence not much further electron-density can be siphoned off to the ring on protonation. On the other hand, in the triphenyl-phosphazenyl-group, where the bond angle suggests sp$_2$-hybridisation, there is still potentially another electron-pair available for back-conjugation, given in an extreme case a sp-hybridised nitrogen. This potential ability for additional electron-supply might account for the very high basicities of triphenylphosphazenylecyclophosphazenes. A recent X-ray crystallographic study with a diethylphenylphosphazenyl-substituent of a ruthenium complex showed a Ru–N–P bond-angle of 175°, an apparent sp-hybridisation.
Very briefly, let us consider some aspects of bonding theory pertaining to cyclophosphazenes: they will probably be discussed in greater detail by others during this Symposium. We are all familiar with the two earliest theories, one due to Craig and Paddock\(^\text{106}\), involving a molecular orbital covering the whole of the cyclic molecule, and the other due to Dewar, Lücke and Whitehead\(^\text{85}\), postulating three-centre PNP islands, only weakly, if at all, interacting with each other. More recent calculations involving more refined quantum-chemical techniques have tended to support the latter views\(^\text{86,87}\).

In addition, trans-annular phosphorus-phosphorus bonding has been postulated for trimer derivatives, \(N_3P_3Cl_3(NMe_2)_3\), \(\text{trans-isomer}\), and a similar trans-annular phosphorus-phosphorus bonding has been suggested for phosphorus atoms separated by two ring bonds in tetramer derivatives, \(N_3P_3R_8\), with a trans-annular anti-bonding effect for phosphorus atoms separated by four ring bonds\(^\text{107}\). It is possible that the balance of trans-annular bonding and anti-bonding effects may bear a relationship to the shapes of the tetramer ring systems.

\[\begin{align*}
\text{Trans-annular bonding and anti-bonding} \\
\text{gem-isomer} \\
\text{cis-isomer} \\
\text{trans-isomer} \\
\text{gem-}N_3P_3Cl_3(NMe_2)_3 \\
\text{cis-}N_3P_3Cl_3(NMe_2)_3
\end{align*}\]

Finally, let me give you another example of the cross-fertilisation due to interdisciplinary research. Using the data from the crystallographic investigations by Ahmed and co-workers\(^\text{101,102}\) on the three isomers, \(N_3P_3Cl_3(NMe_2)_3\), quantum-chemical calculations were performed, based on the (at the time) known parameters of the geminal\(^\text{101}\) and cis-isomers\(^\text{102}\) (that of the trans-isomer\(^\text{103}\) had to be assumed from that of the cis-, as the data was then

\[\begin{align*}
\text{Calc.} & & \text{Obs.} \\
N_6 & 5.318 & 8.493 & -3.6 & -4.4 \\
N_2 & 5.164 & 8.380 & -6.4 \\
N_4 & 5.212 & 8.363 & -9.2 \\
\end{align*}\]
not yet available). We attempted to correlate these calculations with chemical and physical properties, especially basicities\(^1\). Using charge densities Qs of the ring nitrogen atoms only, the agreement was less satisfactory than if these were summed with the Wiberg indices \(W_{P,N}\) of the adjacent phosphorus-nitrogen bonds. Apart from chemical intuition, this seems justified by the X-ray crystallographic data on the pairs of free bases and conjugate acids referred to earlier. Calculations, in agreement with experiment, showed the geminal isomer to be a stronger base than the nongeminal cis. Within the geminal isomer calculations showed the order of basicity of the three chemically different ring nitrogen atoms to be the same as that predicted from our basicity work.

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R. A. Shaw • The Reactions of Halogenocyclophosphazenes

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