# ASPECTS OF STRUCTURE AND BONDING IN INORGANIC PHOSPHORUS COMPOUNDS

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## ABSTRACT

The structures of the allotropic modifications of phosphorus are briefly mentioned. The varying and interconvertible ring sizes of cyclopolyphosphines are considered, as is the use of these compounds as ligands in coordination chemistry. Aspects of structure and stability of cyclic phosphinoborines are followed by a discussion of phosphorus cage compounds; particular reference will be made to bond length variations in the bridging framework. Analogous variations are then considered for acyclic phosphorus–nitrogen compounds. Cyclophosphazenes form the major part of the lecture. Ring shapes, conformations of substituents, bond lengths and angles, basicities and other properties are discussed in some detail. Differences in ground state and perturbed state properties are considered. A comparison of structural changes accompanying protonation is made of two phosphazenes, where x-ray crystallographic data are available for the free bases and their conjugate acids. Finally, the current stage of theoretical concepts of bonding in these compounds is briefly surveyed.

## INTRODUCTION

The interplay of synthesis, structure determination (such as x-ray crystallography, electron diffraction, and the various spectroscopies), and quantum chemistry, has been particularly fruitful in recent years. The cross-fertilization of these various facets of chemistry gave rise not only to whole classes of new compounds but, in addition, often gave a much more thorough insight into the structures and properties of compounds synthesized many years earlier. Not only did structure determinations and quantum chemical calculations increase in number, but their sophistication increased and more and more detailed information became available.

## ALLOTROPIC MODIFICATIONS OF PHOSPHORUS

Nowhere has this been more true than in phosphorus chemistry. The structures of most of the allotropic modifications of the element phosphorus have been established over the years, although the wide variety of colours displayed by them still presents a fascinating problem. Thus, white phosphorus[1] is crystalline and consists of discrete tetra-atomic molecules;

red phosphorus[2] is amorphous; the suggestion that its structure may be based on randomly crosslinked phosphorus tetrahedra is being questioned. Black phosphorus[3] is again crystalline and resembles a sort of corrugated graphite. Hittorf's violet phosphorus[4] (obtained on annealing phosphorus glasses) is the most recent modification to yield the secret of its structure, which consists overall of pentagonal cross sections, based on arrays of $P_8$ and $P_9$ units. The pentagonal tubes are crosslinked into perpendicular sheets through the $P_9$ units. This versatility of colour is also found in certain catenated compounds of phosphorus. For example, the ruby-coloured, needle-like, potassium polyphosphide[5], $KP_{15}$, shows some structural similarity to Hittorf's phosphorus in having a tubular array of phosphorus atoms.

## CYCLIC POLYPHOSPHINES

In contrast to the considerable stability of the high molecular weight phosphorus allotropes (in particular the black and violet varieties) is the instability and interchangeability of acyclic and cyclic polyphosphines. The first of these, a phenyl derivative, $(PhP)_n$, was synthesized by Michaelis[6] as early as 1877 from phenylphosphine and phenyldichlorophosphine. Its discoverer considered it to be a structural analogue of azobenzene and gave it the name of phosphorobenzene. Similar assumptions, equally erroneous, were made about arsenic and antimony derivatives. Not until many years later was the situation reinvestigated and it was shown that these compounds were not azobenzene analogues, i.e. were not of the type R—P=P—R (or its arsenic analogue) but that all of these, which to date have been investigated, are based on catenated singly-bonded structures, usually of a cyclic type, although polymeric compounds are not unknown. A typical example is Paul Ehrlich's compound, Salvarsan, which even to this day is still written from time to time incorrectly as an arsenobenzene structure instead of the polymer species which it really is.

Cyclopolyphosphines, $(RP)_n$, ($n$ = 3, 4, 5 and 6) have been characterized, although not necessarily all with the same group R attached to each of them. In some cases, in particular when $n = 3$, it may be a charged species. It would be inappropriate to give a detailed discussion of all the various cyclic polyphosphines here and their behaviour in solution and in the solid state. Suffice it to pick on one or two examples. The phenyl derivative $(PhP)_n$ has been isolated as four different compounds with different melting points[7]: (A) m.pt 150°, which is a pentamer in the solid state; (B) m.pt 190°, which is a hexamer in the solid state (and can occur as four different crystalline modifications); (C) m.pt 255°; (D) with an extended melting point range higher than the other three. Although compounds (A) and (B) are pentameric and hexameric respectively in the solid state, they appear to be tetrameric in solution, thus giving an illustration of the lability of the phosphorus–phosphorus bonds in this type of compound and the dangers of making too readily structural assumptions about them. The *para*-chlorophenyl analogue $(p\text{-}ClC_6H_4P)_n$ apparently gives rise to a pentamer when prepared in ether, a hexamer when in benzene and a tetramer in the absence of solvent[8].

This lability of the phosphorus–phosphorus bond caused a considerable degree of confusion when complexes of the cyclopolyphosphines, particularly

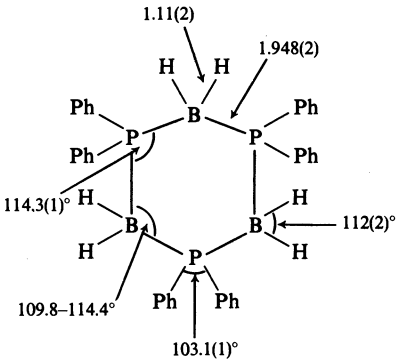
with transition metals, were prepared, complexes to some extent analogous to those of mononuclear phosphines. Two examples should suffice[9]: the pentamer, $(PhP)_5$, reacts with nickel tetracarbonyl in the absence of solvent, to yield $(PhP)_5Ni(CO)_3$, whilst in the presence of ether, it gives rise to $(PhP)_4Ni(CO)_3$. In both compounds, the cyclopolyphosphine acts as a monodentate ligand. Tetraethylcyclotetraphosphine, $(EtP)_4$, too can behave as a ligand, sometimes with retention, sometimes with change in the degree of oligomerization[10]. Thus, ring expansion occurs to give $(EtP)_5Mo(CO)_4$, the cyclopolyphosphine acting as a 1,3-*cis*-chelate[11]. As a final example of the chameleon-like character of these cyclopolyphosphines, it is worthwhile quoting the reaction of the pentameric methylcyclopolyphosphine, $(MeP)_5$, with different cupric halides giving cuprous complexes. With cupric bromide[10], the pentameric ligand structure is retained, $(MeP)_5CuBr$, whilst with cupric chloride ring contraction occurs $(MeP_4)CuCl$. A considerable body of evidence has arisen which suggests that the lability* of the cyclopolyphosphines and their ability for ring contraction and ring expansion is due to a reactive intermediate, a phosphinidene[9], which bears some resemblance to carbenes.

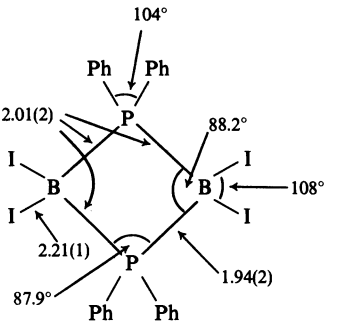
## PHOSPHINOBORINES

The ability to form rings of different sizes is not confined to compounds where all the ring atoms are phosphorus. Numerous examples exist when this element alternates with others, such as sulphur, boron, oxygen, nitrogen, etc., and I will consider just a few of these.

Burg and Wagner[12] were the first to discover those based on phosphorus–boron skeletons and they also noted then their remarkable stability. These phosphinoborines (other nomenclatures are also used) are of the general formula $(R_2PBX_2)_n$, ($n$ = 2, 3 or 4). The main methods for synthesizing these cyclic phosphinoborines consist of first forming an adduct of the phosphine and borane or boron halides and then to cyclize these by elimination of hydrogen or hydrogen halide respectively. Diphenylphosphine-boron triiodide and tribromide adducts yield dimeric four-membered phosphinoborines[13], $(Ph_2PBX_2)_2$ (X = I or Br), of which the iodo-derivative has had its crystal structure determined[14]. Notable features which emerged from this were that the four-membered phosphorus–boron ring is non-planar and that one of the P—B bonds is noticeably shorter (1.94 Å), than the other three (2.01 Å). This compound is hydrolytically stable and fails to react with most reagents unless conditions are so drastic that complete breakdown of the molecule occurs. This is in complete contrast with the behaviour of mononuclear boron halides, whose ready reaction with nucleophilic reagents is well known. The phosphine–borane adducts, $R_2PH \cdot BH_3$ (R = Ph[15] or Me[12]), give rise on heating to cyclic products, $(R_2PBH_2)_n$. When R = Ph, only the six-membered ring was observed, whilst when R = Me, both six- and eight-membered rings were obtained, although the latter slowly contracted to the former at temperatures of just under 200°C.

* Since completion of this manuscript, evidence has been accumulating, that some of the apparent lability is due to the effect of impurities.



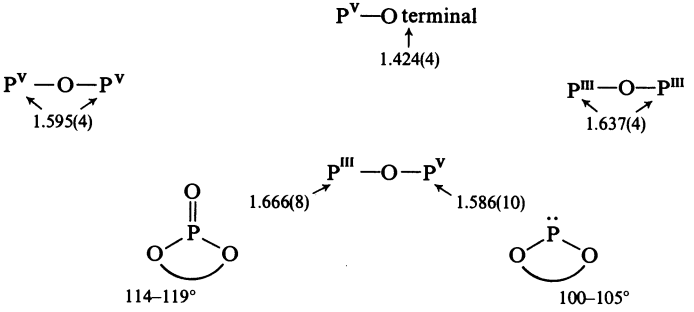

Unlike other boron–hydrogen bonds, which react readily with air, water, acids and bases, the boron–hydrogen bonds in these compounds are exceptionally stable and require temperatures of 300° before they react. The only exception to this is the fairly ready halogenation of these boron–hydrogen bonds[15, 16] by elemental halogen, inter-halogen compounds, or *N*-halogenosuccinimides. The resultant halogenophosphinoborines of the six-membered ring compounds are again exceptionally inert to every sort of attack unless their molecular framework is broken down under drastic conditions. The trimeric phenyl derivative, $(Ph_2PBH_2)_3$, occurs in two crystalline modifications of m.pt 161 and 179° respectively[17]. A complete crystal structure[18] of the former has been carried out. The molecule has a chair conformation, all P—B bonds are equal (1.95 Å) (similar to the short bond reported in the dimer, cf. above), the positions of the hydrogen atom of the B—H bonds were accurately located and the authors conclude that there is no evidence for B → P $\pi$-bonding put forward by others to explain the stability of these B—H bonds. The crystal structures[19] of the trimeric and tetrameric methyl analogues, $(Me_2PBH_2)_{3\text{ or }4}$, have also been solved, though with lesser accuracy.

The stability of the B—H as well as of the boron–halogen bonds, is thus still not satisfactorily explained and one wonders if there may not be a case for investigating whether *trans*-annular interreactions of a type which have been observed in phosphazenes and aluminium–nitrogen ring compounds (see later) play a part.

## PHOSPHORUS CAGE COMPOUNDS

I now wish to consider briefly a number of phosphorus cage compounds, all of which are based on a $P_4$ unit, the phosphorus–phosphorus bonds being wholly or partly broken and oxygen, sulphur or nitrogen bridging atoms inserted. In addition, some or all of the tervalent phosphorus atoms have been oxidized to the quinquevalent state. The ability of the bridging atoms, sulphur, oxygen and nitrogen, to back-donate their lone-pairs of electrons into suitable vacant orbitals increase in that order. Hence, we would expect to find the smallest effects with sulphur and the largest with nitrogen.

Of the binary phosphorus–oxygen compounds, until recently only the small molecules, $P_4O_6$ and $P_4O_{10}$, were known. Recently, this list has been extended to $P_4O_7$, $P_4O_8$ and $P_4O_9$, in which one or more of the phosphorus atoms have been oxidized to a quinquevalent stage. The molecular structures of most of these series have been recently investigated with great accuracy. As previously known, the terminal $P^V$—O bonds are by far the shortest, 1.424(4) Å. Significant differences are, however, found in the bridging P—O bonds, depending on the valency state of the phosphorus atoms[20]. These are summarized below:



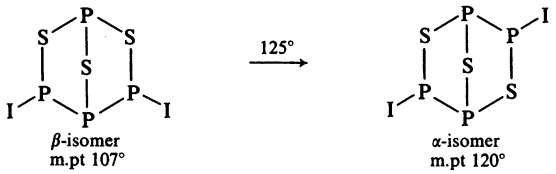

$P_4O_6$, $P_4O_7$, $P_4O_8$, $P_4O_9$, $P_4O_{10}$

It is obvious that a phosphoryl phosphorus is much more effective than a tervalent phosphorus in syphoning off the lone-pairs of electrons of the bridging oxygen atoms. This is also reflected in the endocyclic $O\hat{P}O$ bond angles; these range for the phosphoryl oxides 114–119°, and for the phosphines 100–105°. We shall see similar examples in the phosphorus–nitrogen system.

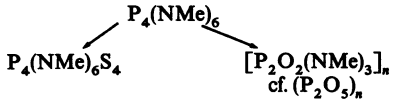
The binary phosphorus sulphur system has been thoroughly investigated by x-ray crystallography, as well as $^{31}P$ n.m.r. spectroscopy and the structures of the compounds $P_4S_3$, $P_4S_5$, $P_4S_7$ and $P_4S_{10}$, are well established and will not be discussed here. Suffice it to say that, with the exception of the last mentioned one, they bear no analogy to the binary phosphorus–oxygen system inasmuch as the first three mentioned retain phosphorus–phosphorus bonds in their structures. For some reason, the compound $P_4S_6$ is unknown and hence the tetraoxide, $P_4S_6O_4$, cannot be prepared by an analogous route as $P_4O_{10}$ from $P_4O_6$. In contrast, the $P_4O_6$ cage adds four terminal sulphur atoms[21] to give $P_4O_6S_4$. $P_4S_6O_4$ has recently, however, been synthesized by an alternative route by treating phosphorus oxychloride with hexamethyldisilthiane[22], $(Me_3Si)_2S$. Finally, before leaving this type of system, we might mention ternary phosphorus–sulphur–iodine compounds. If $P_4S_3$ is treated with iodine[23] and the reaction temperature is kept fairly low, we get the β-isomer, of m.pt 107°, which at temperatures of about 125° isomerizes to the α-isomer of m.pt 120°. Both structures are known and are displayed below.

Finally, amongst this type of cage compounds, we come to that based on phosphorus and nitrogen, $P_4(NMe)_6$.

No detailed structural studies appear to be available. Oxidation[24] gives




a polymeric species $[P_2O_2(NMe)_3]_n$ (cf. polymeric $P_2O_5$ modifications); with sulphur[25] on the other hand, the familiar cage structure is maintained to yield $P_4(NMe)_6S_4$.

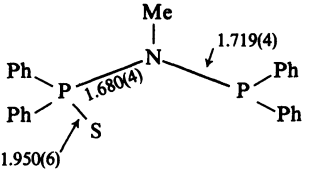


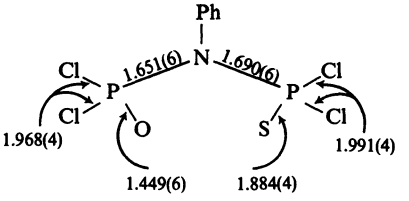

## ACYCLIC PHOSPHORUS–NITROGEN COMPOUNDS

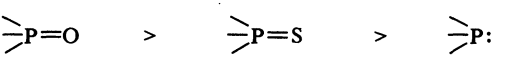
I will now consider other phosphorus–nitrogen compounds and make no apology for these being the major part of my talk. Not only is it the subject with which I am most familiar, but even a cursory glance at the literature shows that this is the field of phosphorus chemistry which is the one most actively investigated. It is here too that we shall see the greatest effect on variation in bond lengths and bond angles caused by different substituents and different oxidation states of phosphorus.

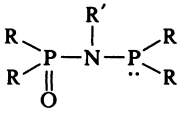
Let me commence with some acyclic phosphorus–nitrogen compounds, where a central nitrogen atom is linked to two phosphorus moieties which are slightly different in chemical character. In one case, we compare a phosphine oxide with a phosphine sulphide; in the other, a quinquevalent phosphorus with a tervalent phosphorus. At first glance, we can see significant variations in the phosphorus–nitrogen bond lengths. Thus, we see that a quinquevalent phosphorus is more effective in competing for nitrogen lone-pair electron-density than a tervalent phosphorus and that a phosphine oxide grouping is more effective than a phosphine sulphide grouping[26]. [Unfortunately, we have as yet no data on the most telling example, $R_2P—NR'—P(O)R_2$.] We can thus arrange an order of electron-withdrawing power: $\equiv P: < \equiv P{=}S < \equiv P{=}O$. This has been justified by *ab initio* quantum chemical calculations by Labarre and Serafini[27]. They reason that oxygen is more electronegative than sulphur and withdraws more electron-density via the σ-bond, but also that it has a lesser power to effect back π-bonding than the sulphur atom in this situation. In addition, we note that the phenylated derivative has a considerably longer P—S bond than the chlorinated one[26], in keeping with the more electronegative substituents on the latter.

Finally, I would like to consider the phosphorus–chlorine bond lengths in the above compound. As expected, the P—Cl bonds attached to the phosphine sulphide grouping are significantly longer than those attached to the phosphoryl grouping, in keeping with observations on other pairs of related



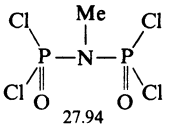

compounds $R_2P(O)Cl$ and $R_2P(S)Cl$. We have shown elsewhere that in cyclophosphazenes, when one plots the length of the P—Cl bond against the $^{35}Cl$ n.q.r. frequency (provided the other substituent on the phosphorus atom in question is either chlorine or nitrogen) a fairly good straight-line relationship between bond length and frequency (and hence presumably ionic character) is obtained[28]. For four-coordinated phosphorus compounds where P=O is replaced by P=S, this relationship does not pertain and the longer (S)P—Cl bond-lengths are associated with higher $^{35}Cl$ n.q.r. frequencies than the corresponding shorter (O)P—Cl bonds. The reason for this is as yet not understood.

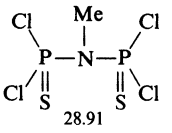
$^{35}Cl$ n.q.r. frequency measurements on a set of three related compounds has brought to light interesting observations. Here again, one nitrogen atom is flanked by two phosphorus atoms, both quinquevalent.

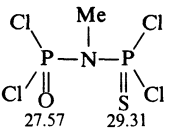
The compounds are the symmetrical dioxide, the symmetrical disulphide and the mixed oxide-sulphide. In all three compounds each phosphorus has also two chlorine atoms bonded to it.

In the symmetric dioxide, the mean $^{35}Cl$ n.q.r. frequency is lower than the mean frequency of the corresponding symmetric disulphide. However, if one compares these with the frequencies in the asymmetric compound, one notices that the $^{35}Cl$ frequency of the oxide grouping has moved to lower field and that of the sulphide to higher field[29]. Here we have another example that the phosphoryl grouping is gaining electron-density at the expense of the thiophosphoryl group from the lone-pair electrons of the nitrogen atom, as shown by the considerable increase in frequency difference.

Mean $^{35}Cl$ n.q.r. frequencies (MHz)




## CYCLOPHOSPHAZENES[30–32]

This section is devoted to cyclophosphazenes, which form a homologous series of formula $(NPX_2)_n$, ($n$ = 3, 4 . . . 8 . . .) where X in the same molecule may represent different substituents. A number of these, particularly homogeneously substituted ones, have been investigated by x-ray crystallography and/or electron diffraction. Trimeric derivatives, $(NPX_2)_3$, (X = F, Cl, Br, Me, Ph, $NMe_2$, OPh, NCS, etc.), and the next higher homologue, $(NPX_2)_4$, [X = F, Cl (K and T forms), Br, Me, OMe, $NMe_2$, etc.][33], have received almost equal attention from the crystallographers. The higher homologues ($n \geqslant 5$) have received less attention and the largest monocyclic species so far investigated is the octamer, $(NPX_2)_8$, (X = OMe)[34].

X-Ray data

| | |
|---|---|
| $(NPX_2)_3$ | (X = F, Cl, Br, Me, Ph, $NMe_2$, OPh, NCS, etc.) |
| $(NPX_2)_4$ | [X = F, Cl (K and T forms), Br, Me, OMe, Ph, $NMe_2$, NCS, etc.] |
| $(NPX_2)_5$ | [X = F (2 forms), Cl, Br] |
| $(NPX_2)_6$ | (X = $NMe_2$, OMe) |
| $(NPX_2)_7$ | |
| $(NPX_2)_8$ | (X = OMe) |

For a variety of reasons, in a given homologous series, $(NPX_2)_n$ ($n$ = 3, 4, 5, etc.), not always the same degree of accuracy has been obtained by x-ray crystallographic investigations. Thus, whilst it is possible to compare and sometimes draw some conclusions about variations in structural features such as bond angles and ring conformation, this is not always the case for other parameters.

Thus, at present for a given substituent X, few conclusions can be drawn about variations in phosphorus–nitrogen ring bond lengths within a given homologous series, say trimer, tetramer, etc. Considerable variations in bond angles at ring nitrogen atoms have been observed, whilst those at phosphorus are much less marked. The situation is rather different if a ring carries two or more different substituents (see later).

Very remarkable is the great variety of molecular shapes the eight-membered ring system, $(NPX_2)_4$, can assume, even when all the substituents in the molecule are the same. Thus, the fluoride $(NPF_2)_4$, is planar[35]. The chloride $(NPCl_2)_4$, occurs in two different shapes, the K[36] and the T[37] form, depending at which temperature it is crystallized. Many of the other derivatives occur in a variety of shapes, described as crown, chair, saddle, boat, etc.

| $(NPCl_2)_4$ | $2[(NPMe_2)_4H]^+CoCl_4^{2-}$ |
|---|---|
| K and T forms | 2 different ring conformations in unit cell |

By analogy with carbon chemistry, one would expect unsaturated, ten-membered cyclic molecules to have some structural peculiarities. One is not disappointed. The pentameric chloride[38], $(NPCl_2)_5$, is almost planar with two re-entrant angles at nitrogen, whilst the bromide[39], $(NPBr_2)_5$, is considerably more puckered, with only one re-entrant angle at nitrogen, but with the opposite phosphorus considerably below the mean plane of the molecule. We shall see later that a similar situation arises in the diprotonated species of the pentameric methyl derivative[40], $[(NPMe_2)_5H_2]^{2+}$. Consideration of the intramolecular geometry of the pentameric chloride and bromide suggested to the investigators[37] that there was no obvious reason, such as molecular crowding, why two such related molecules should assume such different conformations.

| $(NPCl_2)_5$ | $(NPBr_2)_5$ $[(NPMe_2)_5H_2]^{2+}$ |
|---|---|
| almost planar | more puckered |
| 2 re-entrant angles at N | 1 re-entrant angle at N, opposite P below mean plane of ring |

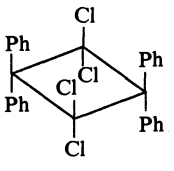
Whilst the trimer molecules are all more or less planar, presumably because of the rigidity of the six-membered ring system (although small deviations of one or more atoms are frequent), the higher membered ring systems show that the cyclophosphazenes must be very flexible molecules to arrange themselves in such a variety of different conformations. Not only have we noted already that $(NPCl_2)_4$ can be obtained in two crystalline forms, each having a different ring conformation, but in a protonated species $[(NPMe_2)_4H^+]_2CoCl_4^{2-}$, two different ring conformations occur in the same unit cell[41]. With this variety of conformations exhibited in the solid state, it is interesting to speculate whether the same or different conformations predominate in solution, but relatively little is known about this at the present time.

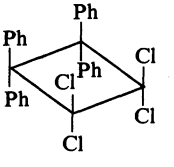
Whilst, as mentioned above, little significant variation has so far been detected in phosphorus–nitrogen ring bond lengths in homogeneously substituted homologous series, $(NPX_2)_n$ (where X is the same substituent for a given series), significant differences, albeit usually small, can be observed with homogeneously substituted derivatives for a given homologue, $(NPX_2)_n$, when the substituents X have different electronegativities. Thus, Ahmed and co-workers have shown that phosphorus–nitrogen bond lengths, $N\hat{P}N$ bond angles, $P\hat{N}P$ bond angles, as well as $X\hat{P}X$ exocyclic bond angles, can be fairly satisfactorily correlated with Pauling electronegativity values[42]. The same pertains (with some modifications, e.g. sometimes mean values have to be taken) to six-membered ring systems which are non-homogeneously substituted, e.g. $N_3P_3X_{6-n}Y_n$. We shall see later that this gives rise to

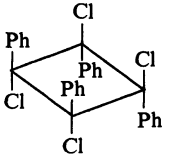
significant variations in individual bond lengths and bond angles, but here I wish to draw attention to the fact that these compounds too fit the above correlation with Pauling electronegativities.

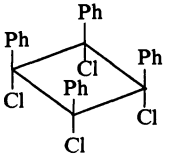
However, in the more flexible eight-membered ring system, a similar plot of either homogeneously substituted, $N_4P_4X_8$, or non-homogeneously substituted molecules, $N_4P_4X_{8-n}Y_n$, is not satisfactory. Wagner[43], as well as Bullen[44] and co-workers have shown that a more satisfactory relationship (although the exact shape of the line is as yet not clear) is obtained if one plots P—N bond length (and some other parameters, except $P\hat{N}P$ bond angles) against group orbital electronegativities. The shapes of the ring systems are, however, not entirely dominated by the nature, e.g. the electronegativity of the exocyclic substituents. Thus, Bullen and his co-workers have determined the structures of three of the five known $N_4P_4Ph_4Cl_4$ isomers, one geminal[45] 2,2,6,6-, and two non-geminal 2,4,6,8-derivatives (one centrosymmetric[47], the other with all chlorine atoms *cis* to each other[44]). Whilst in the first mentioned one, variations in phosphorus–nitrogen ring bond length occur, due to the different electron requirements of $PPh_2$ groups and $PCl_2$ groups (see below), the same cannot be said of the other two, where each phosphorus atom (PClPh) carries the same substituents, albeit that these have different stereochemical relationships. Thus, in addition to polar effects, steric effects due to intramolecular repulsion (and in the solid state possibly also intermolecular effects), can play a major part in determining the shape of the molecule. Indeed, one might speculate (see below) whether some bond-length variations might not also be caused by intra- and/or inter-molecular repulsions and strains set up in the molecule.

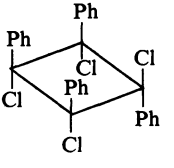
$N_4P_4Ph_4Cl_4$



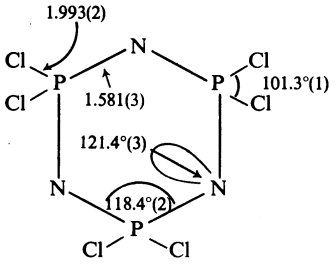



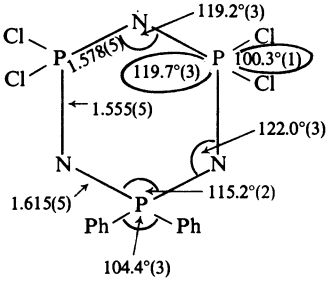




Some decades ago the Mills–Nixon effect was proposed, which suggested that by suitable substitution of the benzene nucleus, partial fixation into single and double bonds could occur. We now know that this effect, if it exists at all, is only a very minor one. The situation is very different in the cyclophosphazenes. Ahmed and co-workers were the first to demonstrate that in non-homogeneously substituted cyclophosphazenes, significant variations in bond length and bond angles can occur. Thus, in the geminal series, $N_3P_3Ph_{6-n}Cl_n$, ($n$ = 2, 4 or 6) considerable differences in phosphorus–

nitrogen bond lengths in different PNP segments are observed[48,49]. An excellent example is the first compound in this series, the geminal $N_3P_3Ph_2Cl_4$, which possesses a mirror plane[48]. Three different types of phosphorus–nitrogen bond lengths are observed. The one in the $Cl_2P—N—PCl_2$ segment is identical to that in the recently[50] refined structure of the parent compound, $N_3P_3Cl_6$.




Of the other two, one is shorter, $Cl_2P—NPPh_2$, the other longer, $Ph_2P—NPCl_2$. The mean P—N bond length in such segments remains, however, approximately the same as that in the homogeneously substituted parent molecule, $N_3P_3Cl_6$. It appears that the total electron-density in these P—N—P segments remains approximately the same, but that it is unequally shared. As with the acyclic compounds discussed earlier that phosphorus atom which carries the more electronegative substituents and hence possesses the greater fractional positive charge, competes more successfully for electron-density in the bonding segments and hence has a shorter phosphorus–nitrogen bond; the less successful competitor has the longer bond.




The phosphorus atom of the latter has less electron-density in adjacent ring segments, hence a somewhat smaller endo $N\hat{P}N$ and a somewhat larger exo $X\hat{P}X$ bond angle, than in the parent compound[50], $N_3P_3Cl_6$. Similar changes, smaller in magnitude and in the opposite sense, occur at that phosphorus atom which gains electron-density.

Similar observations pertain to other non-homogeneous trimeric and tetrameric derivatives. In the latter series, we have one example, geminal $N_4P_4F_6Me_2$, where changes in P—N bond length are observed not directly affected by such substituent differences[51].

Some of these structural variations can be justified on quantum chemical grounds (although these are by no means universally accepted), others are wholly unexplained. We shall see later on that if the other substituent on the same phosphorus as the chlorine is, e.g. a phenyl or dimethylamino group, then considerable variation in P—Cl bond lengths occurs. But why are these statistically significant in phosphorus–chlorine bond length in geminal[48] $N_3P_3Ph_2Cl_4$, although all chlorine atoms belong to $PCl_2$ groups? Had the variations at least been of such a nature that the two longer P—Cl bonds belong either to the slightly axial or the slightly equatorial type, it would have been somewhat easier to explain. As it is, the two long P—Cl bonds occur on opposite sides of the ring and hence one belongs to each category. Another, more pronounced difference in phosphorus–chlorine bond length in a geminal $PCl_2$ group will be discussed later.

What is the cause of this particular variation which is statistically significant? Is it due to steric causes? Is it a through-bond effect of a type which we at present do not understand? Is it a through-space effect? The rationale of this still represents a major challenge.

Another interesting set of compounds are the three isomers: *cis*- and *trans*-, and geminal $N_3P_3Cl_3(NMe_2)_3$, all of whose structures have now been solved by Ahmed and co-workers[52–54]. The structures proposed earlier by Keat and Shaw[55] on the basis of chemical and physical data have been confirmed and much detailed light has been thrown on the conformation, bond lengths, bond angles, etc. Thus, in these molecules as, indeed, in all others investigated to date, geminal $PCl_2$ groupings have shorter P–Cl bonds than non-geminal groupings of the type PClR, where R = Ph[44,56] or $NMe_2$[52–54,57–59]. Again, variations in parameters such as bond lengths, etc. exhibit a similar trend as in the series $N_3P_3Ph_{6-n}Cl_n$.

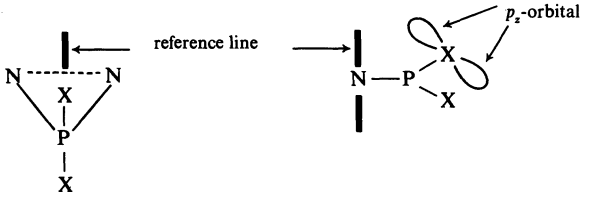
There are many other interesting features in these and related compounds. I will touch only on one or two of these. The exocyclic P—N bond lengths to the $NMe_2$ group appear to be somewhat longer in geminal groupings, $P(NMe_2)_2$, than in non-geminal $PCl \cdot NMe_2$, in keeping with the greater electron demand by the chlorine atom than from the dimethylamino group. In the *trans*-isomer $N_3P_3Cl_3(NMe_2)_3$, the unique P—Cl bond length is the longest one in the molecule[54], as predicted by the '*cis*-effect'[60]. Other observations defy or even contradict present explanations, deduced mainly from solution data. This could be because the bulk of the most accurate data is obtained from measurements in the solid state. Significant structural changes could occur on passing from the crystalline state to a solution. We have already noted earlier the great flexibility of these molecules.

I will now consider the conformation of the substituents. If these are halogen atoms, this question does not arise. On the other hand, other substituents such as the phenyl or dimethylamino groups can, in principle, take up a variety of different conformations with respect to the adjacent ring segment and, indeed, such differences have been observed by x-ray crystallography.

I will consider the conformation of three substituents: the first two, the $NMe_2$ and Ph groups because they have been studied in a large number of structures; the third, the $NPPh_3$ group because of its special interest in connection with basicity studies (see later). All three have a common fea-

ture. The atom, carbon or nitrogen, linking the group to the phosphorus atom of the ring is $sp^2$-hybridized or nearly so (e.g. $NMe_2$ groups attached to phosphazenes are planar or deviate only slightly from this).

As I wish to consider in addition to cyclophosphazatrienes also higher homologues and as they occur in many types of ring conformations, I will use as reference the plane of the triangle formed by the NPN ring segment, to which the substituents, whose conformation we are discussing, are attached. The triangle XPX (where X is the first atom of each substituent) bisects, or nearly does so, the above mentioned NPN angle. An imaginary line, which I shall call the reference line, perpendicular to the plane of the NPN triangle and bisecting the line of the two nitrogen atoms, allows us to discuss the conformation of the substituents.




The above mentioned three: Ph, $NMe_2$ and $NPPh_3$ have all a *p*-orbital perpendicular to the plane, containing the $sp^2$-hybridized bonds of the atom directly linked to phosphorus. In the many examples studied of $PCl \cdot NMe_2$ and PClPh groups in rings of different sizes, as well as the few examples of $PBrPh$[61] and $PCl \cdot NPPh_3$ groups[46], the axis of the above mentioned *p*-orbital of the substituent intersects (or nearly does so) the reference line. It does appear that in the absence of other effects this is the preferred conformation of this type of substituent.

The conformational situation is very different when we have groupings such as $PPh_2$, $P(NMe_2)_2$, or $PPh \cdot NPPh_3$. Let us examine initially the geminal structures $N_3P_3Ph_2X_4$ (X = F, Cl or Ph). When X = F[62], the conformation of each Ph group is the same as in the PClPh moiety. This is the only example of this type so far known. When X = Cl[48] or Ph[42], the *p*-orbitals of the two Ph substituents rotate in opposite directions with respect to the reference line. The angle of rotation varies but straddles frequently 45°, so that often an edge to face conformation of the two substituents is approximated to. The same pertains to a geminal pair of $NMe_2$ groups in the numerous examples of $P(NMe_2)_2$ units studied[52, 59, 63–65] and this seems to hold regardless of ring size. Thus, so far geminal $N_3P_3Ph_2F_4$ has a unique conformation[62]. It is interesting to speculate on the conformations in the geminal compounds, $N_3P_3F_4(NMe_2)_2$, $N_3P_3F_4Ph \cdot NMe_2$ and $N_3P_3Cl_4Ph \cdot NMe_2$).

We have, however, structural data available on the geminal compound, $N_3P_3Cl_4Ph \cdot NPPh_3$, and here another novel conformation is found[66]. In the $NPPh_3$ group the exocyclic P—N—P segment is at right angles to the ring N—P—N segment and approximately coplanar with the ring of the Ph substituent. Here the *p*-orbitals of both substituents, Ph and $NPPh_3$,

have turned through approximately 90° with respect to the reference line. Here again, as the geminal compounds $N_3P_3Cl_4(NPPh_3)_2$[67] and $N_3P_3Cl_4$-$(NMe_2)(NPPh_3)$[68] are known, further structural work would be rewarding.

I now leave the subject of the conformation of the substituents and will consider two structures containing acyclic phosphazenyl groups. Both are based on the triphenyl phosphazenyl group, $NPPh_3$, in the first case, bonded to the *p*-tolyl sulphonamide grouping, *p*-tol-$SO_2N{=}PPh_3$[69], and in the second to a cyclotriphosphazatriene residue, geminal $N_3P_3Cl_4Ph \cdot NPPh_3$ (already referred to in the conformational section). In both cases, it is obvious that the acyclic phosphazenyl phosphorus–nitrogen bond is short, of the order of 1.58 Å and hence, possesses considerable multiple bond character. Whilst in the first case the nitrogen is bonded to sulphur, in the second case it is bonded to a phosphazenyl phosphorus atom. In both cases, possibly by coincidence, all bonds S—N—P and P—N—P are approximately of equal length, ~1.58 Å. In both molecules the bond angle at the acyclic nitrogen atom is large, indicating extensive delocalization of the lone-pair of electrons. We note thus a structural similarity between cyclic and acyclic phosphazene units. The phosphazenylcyclotriphosphazatriene shows a number of other interesting features. The conformational aspects have already been discussed. The ring phosphorus–nitrogen bonds immediately adjacent to the phosphorus atom carrying the triphenylphosphazenyl and the phenyl substituents, are substantially longer, about 1.625 Å, i.e. about the same as the equivalent bonds in the geminal $N_3P_3Ph_2Cl_4$ molecule. The adjacent nitrogen–phosphorus bonds, $Cl_2P—NPPh \cdot NPPh_3$, are short (of the order of 1.55 Å) (cf. comparable bonds in $N_3P_3Ph_2Cl_4$); the remaining segment, $Cl_2P—N—PCl_2$ strongly resembles that in the parent hexachloride[50], $N_3P_3Cl_6$, and in the geminal diphenyl derivative[48] referred to above. Thus, in the ground state the triphenylphosphazenyl group releases about as much electron-density as the phenyl group and this is borne out by other measurements, such as $^{35}Cl$ n.q.r. spectroscopic studies reported elsewhere. We referred earlier to an unexpected non-equivalence of P—Cl bonds in two geminal pairs of $PCl_2$ groups in the $N_3P_3Ph_2Cl_4$ molecule. In the structure considered now, $N_3P_3Cl_4Ph \cdot NPPh_3$, the two long phosphorus–chlorine bonds are both placed on the same side of the ring (the side of the phenyl group) and the difference between the long and the short phosphorus–chlorine bonds is much more pronounced[66], about twice that in the geminal diphenyl derivative.

I now come to consideration of the basicity of phosphorus–nitrogen compounds. In general, a nitrogen atom attached to phosphorus is weakly basic, resembling more an acid amide than an alkylamine. This is borne out by the fact that usually three coordinate nitrogen atoms attached to phosphorus are usually trigonal planar, indicating complete or almost complete delocalization of the lone-pair of electrons from the nitrogen towards the phosphorus atom and, in some cases, transmitted from there to other parts of the molecule.

Some years ago we reported[70] the then rather surprising observation that on treating the hexachloride, $N_3P_3Cl_6$, with the relatively strongly basic aliphatic primary amines, the fully aminolysed derivatives, $N_3P_3(NHAlk)_6$, competed usually successfully (with the excess of the amine present) for the

hydrogen chloride eliminated giving rise to compounds of formulae $N_3P_3(NHAlk)_6 \cdot HCl$, which had frequently been confused in the literature with the penta-aminomonochloro-derivatives, $N_3P_3Cl(NHAlk)_5$. A systematic physicochemical study of the basicities[71–77] of these cyclophosphazenes and related compounds, extending over many years and involving a large number of compounds, revealed the following interesting features, the salient points of which I wish to enumerate.

The first is that for homogeneously substituted cyclophosphazenes, e.g. $N_3P_3X_6$ (or $N_4P_4X_8$, when available), one can construct a basicity series[75, 76, 78], an abbreviated version being given here: $Ph_3PN \gg NHAlk > Alk > Ph \sim NHPh > OAlk > SAlk > SPh > OPh > OCH_2CF_3 > Cl$.

A number of compounds, including the parent hexachloride, are too weakly basic for direct measurement by our technique. We were, however, able to calculate their basicities from other data involving compounds with two or more different types of substituents.

The second feature of interest was that if one used non-homogeneously substituted derivatives, in particular certain chloroamino-derivatives, surprisingly large differences in basicity were observed for compounds which had hitherto been believed to have similar structures. Thus, for example, certain tetra-alkylaminodichloro-derivatives, $N_3P_3Cl_2(NRR')_4$, fall clearly into two classes[74]. The difference between these two classes is of the order of 4 to 5 $pK'_a$ units and this magnitude suggested that structural differences must be the cause of this. Up to that time, it had been assumed by workers in this field that amino groups entered the cyclophosphazenes in a non-geminal manner. We were able to show that the stronger bases had geminal, the weaker bases non-geminal, structures.

For one such compound, $N_3P_3Cl_2(NHPr^i)_4$, a detailed x-ray structure of its hydrochloride was carried out by Mani and Wagner[79], who showed that the proton was attached to the ring and indeed, at that site which we had predicted earlier, the nitrogen atom flanked by two $P(NHPr^i)_2$ groups. In the course of further studies, it became clear that both first and second protonations in cyclotriphosphazatrienes and cyclotetraphosphazatetraenes, regardless of the substituents (except $NPPh_3$, see later), took place at ring nitrogen atoms[72, 77] in all compounds which by then had been studied.

The third salient feature which has come out of these studies is that at least for the cyclotriphosphazatriene ring, the effect of the substituents (with respect to the parent compound, $N_3P_3Cl_6$, is additive and that one can assign $\alpha$ and $\gamma$ values[75–77] (with respect to any given ring nitrogen atom) to every substituent and hence one can calculate the basicity of this particular ring nitrogen atom (taking into account statistical effects) and these calculated $pK'_{a,1}$ values agree remarkably well with those observed by experiment. This enabled, in a number of cases, structures to be assigned which were otherwise difficult to prove[76, 77]. Furthermore, using data from substituent constants it is possible to calculate the basicity of the parent hexachloride, $N_3P_3Cl_6$, to be approximately $-20.4$ on our $pK'_a$ scale[80]. As the most basic compounds measured by us have a $pK'_a$ value of the order of $+9$, cyclophosphazenes (at least those based on a trimer ring), cover a $pK'_a$ range of approximately thirty units. A selection of $\alpha$ and $\gamma$ substituent constants is appended in *Table 1*.

*Table 1.* Selected substituent constants (in $pK_a$ units)

| R | $\alpha_R$ | $\gamma_R$ | R | $\alpha_R$ | $\gamma_R$ |
|---|---|---|---|---|---|
| $NH_2$ | 6.0 | 2.7 | Ph | 4.2 | 2.3 |
| NHMe | 5.8 | 3.1 | OMe | 3.6 | 1.8 |
| NHEt | 5.8 | 3.6 | SEt | 3.6 | 1.8 |
| $NMe_2$ | 5.6 | 2.8 | OPh | 3.1 | 1.3 |
| $NEt_2$ | 5.5 | 3.1 | | | |

Another important feature which arose from these investigations was the concept of a 'saturation effect'[77]. Certain substituents, in particular primary alkylamino groups, show a lower experimentally observed $pK'_{a,1}$ value for their hexa-alkylamino-derivatives, $N_3P_3(NHAlk)_6$, than would have been predicted from substituent constants derived from less basic compounds, such as the tri-, $N_3P_3Cl_3(NHAlk)_3$, and tetra-amino-derivatives, $N_3P_3Cl_2(NHAlk)_4$. We tentatively rationalize this behaviour by suggesting that once phosphorus atoms have accumulated a certain amount of electronic charge their *d*-orbitals expand, the effective $\pi$-orbital overlap decreases and hence this balance of opposing effects causes a levelling out of $pK'_a$ values; hence, we named this the 'saturation effect', which apparently does not permit an accumulation of electronic charge to give rise to $pK'_{a,1}$ values greater than +8 to +9. If we apply a correction factor, the apparent anomaly in $\Delta pK'_a$ ($= pK'_{a,1} - pK'_{a,2}$) values between primary alkylamino (9–10 $pK'_a$ units) and secondary alkylamino (11–12 $pK'_a$ units) disappears (see *Table 2*).

*Table 2.* The 'saturation effect' in hexakisaminocyclotriphosphazatrienes, $N_3P_3R_6$

| Compound | $pK'_{a,1}$ Obsd | $pK'_{a,1}$ Corrd | $pK'_{a,2}$ | $\Delta pK'_a$* Obsd | $\Delta pK'_a$* Corrd |
|---|---|---|---|---|---|
| $N_3P_3(NHMe)_6$ | 8.8 | 9.6 | −2.0 | 10.8 | 11.6 |
| $N_3P_3(NHEt)_6$ | 7.8 | 10.5 | −1.3 | 9.1 | 11.8 |
| $N_3P_3(NHPr^n)_6$ | 7.9 | 10.7 | −1.3 | 9.2 | 12.0 |
| $N_3P_3(NHPr^i)_6$ | 8.4 | 10.1 | −1.2 | 9.6 | 11.3 |
| $N_3P_3(NHBu^n)_6$ | 7.9 | 10.5 | −1.8 | 9.7 | 12.3 |
| $N_3P_3(NHBu^t)_6$ | 8.0 | 9.9 | −1.7 | 9.7 | 11.6 |
| $N_3P_3(NHC_6H_{11})_6$ | 7.9 | 10.3 | −1.4 | 9.3 | 11.7 |
| $N_3P_3(NMe_2)_6$ | 7.5 | 7.7 | −3.1 | 10.6 | 10.8 |
| $N_3P_3(NEt_2)_6$ | 8.2 | 8.9 | −4.0 | 12.2 | 12.9 |
| $N_3P_3(pip)_6$ | 8.4 | 8.2 | −3.2 | 11.6 | 11.5 |

* $\Delta pK'_a = pK'_{a,1} - pK'_{a,2}$.

Up to now, we have considered cyclophosphazenes where first and second protonations take place exclusively at the ring nitrogen atoms. In the course of the last few years a variety of cyclophosphazenes with phosphazenyl substituents, $NPR_3$, have been prepared by different synthetic routes. A detailed examination of the basicities of these derivatives indicates that they fall into two classes which, for brevity, we will call type I and type II. The $pK'_a$ data within each class is fairly self-consistent, but not consistent with

that in the other class. To explain this difference in behaviour we postulated that compounds of type II protonate on the exocyclic phosphazenyl nitrogen atom, whilst on those of type I, the normal endocyclic protonation occurs. By making various assumptions which I will not go into here, we were able to calculate the basicities within each type and showed them to be self-consistent[78]. We also suggested that the reason why some exhibit type I and others type II behaviour, was probably connected with the conformation of the phosphazenyl group relative to the NPN ring segment, to whose phosphorus atom it is attached. This is borne out by recent crystallographic investigations. I have already referred to one compound, $N_3P_3Cl_4Ph \cdot NPPh_3$, which according to our basicity determinations, protonates exocyclically, i.e. type II, and I have discussed the conformation of the triphenylphosphazenyl group in an earlier part of this lecture.

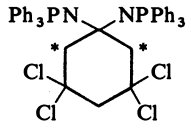
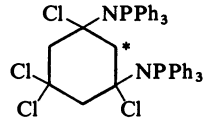
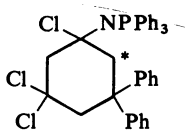
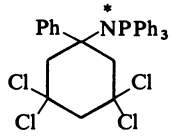
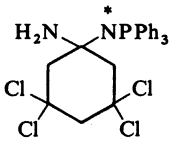
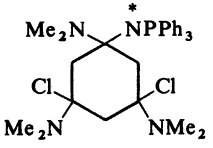
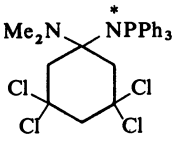
Preliminary unpublished x-ray crystallographic work by Bullen and Dann on a compound, $N_4P_4Cl_6(NPPh_3)_2$, which we postulated from basicity data to belong to type I (and hence endocyclic protonation[68, 78]) suggests that the *p*-orbital of the nitrogen atom of triphenylphosphazenyl intersects the reference line. In the two compounds thus far investigated, each one representing one type, the *p*-orbital referred to on passing from one to the other, has been rotated through an angle of approximately 90°.

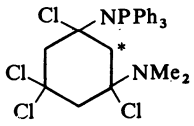
Whilst the data refer to the solid state and to the free bases, they are in keeping with our postulate that triphenylphosphazenyl groupings will take up different conformations, depending on the nature of the other substituents on the same phosphorus atom and that this conformation will determine whether exocyclic or endocyclic protonation will occur.

A selection of $pK'_a$ values experimentally observed and compared with calculated endo- and exo-cyclic values is appended (*Table 3*)[78]. The difference is particularly striking in pairs of isomeric compounds, e.g. the geminal and non-geminal derivatives, $N_3P_3Cl_4(NMe_2)(NPPh_3)$. If ring protonation had occurred in both cases (apart from a statistical effect), their $pK'_a$ values ought to have been the same. The general trend is clear, although slight deviations from calculated values are observed: this is not unexpected. With a grouping such as the phosphazenyl substituent, the possibilities of variation in the exocyclic $P\hat{N}P$ angle varying must be considered and hence differences in electron supply to the exocyclic nitrogen, or to the ring nitrogens, might be anticipated. Similarly, the different conformations of the *p*-orbitals need not be exactly 90° with respect to each other. Additionally, if one turns this grouping through 90°, it could in theory be turned clockwise or anti-clockwise. If the cyclophosphazene ring has a plane of symmetry perpendicular to it and bisecting it from the point of attachment of the phosphazenyl substituent which is being consistent, the above is immaterial. However, if this is not so, the direction of rotation will matter and, as yet, we do not know how and why. It seems likely that basicity measurements, supported by x-ray crystallographic investigations of suitably chosen key compounds, will enable us to develop a conformational analysis of phosphazenylcyclophosphazenes.

A number of other interesting physicochemical generalizations can already be made at the present time. If one considers the frequencies obtained by $^{35}Cl$ n.q.r. spectroscopy of chlorines on the same phosphorus as either phenyl,

*Table 3.* Observed and calculated $pK'_{a,1}$ values for some triphenylmonophosphazenylcyclotriphosphazatrienes

| Structure † | $pK'_{a,1}$ Obsd | Calc. (endo) | Calc. (exo) |
|---|---|---|---|
|  | +0.4 | +0.5 | +1.7 |
|  | +0.2 | +0.2 (standard) | −4.7 |
|  | −1.8 | −1.7 | −4.3 |
|  | −4.7 | −5.6 | −4.7 (standard) |
|  | −2.9 | −3.8 | −2.9 |
|  | +2.6 | +4.2 | +2.3 |
|  | −2.0 | −4.2 | −3.0 |




−4.8 −4.7 −3.6

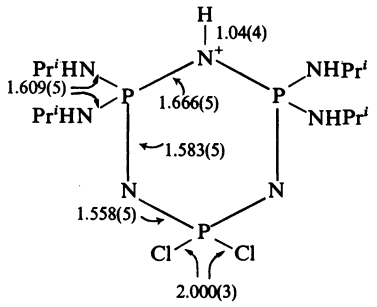
* Denotes position(s) of protonation.

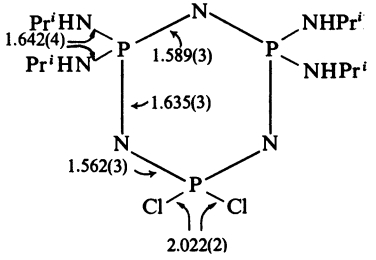
†  denotes cyclotriphosphazatriene ring.

dimethylamino or triphenylphosphazenyl substituents, we note that they all have values in the region of 23.0–24.5 MHz (at 293°K) and thus, in the ground state, these P—Cl bonds appear to have approximately the same degree of ionic character[28]. Thus, in the unperturbed state, the electron release from these three different groupings appears to be of the same order. The same conclusions can be drawn from phosphorus–chlorine bond lengths obtained by x-ray crystallographic investigations (e.g. refs. 44, 57).

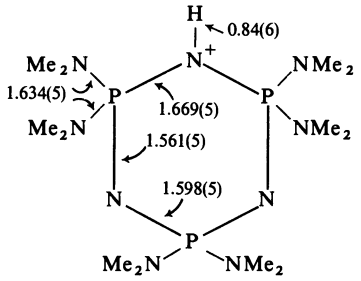
The situation is drastically altered when we consider the perturbed state of the molecule, for instance, when the free base is protonated. Here, for ring protonation, the triphenylphosphazenyl group is a vastly stronger electron-supplying substitutent than the dimethylamino group which, in turn, is stronger than the phenyl group. Obviously, at the demand of the reagent (here the proton), these groups are capable of supplying electron-density of quite different magnitudes, the triphenylphosphazenyl grouping being particularly effective in supplying almost twice as much electron-density as any other of the most strongly electron-supplying groups so far investigated.

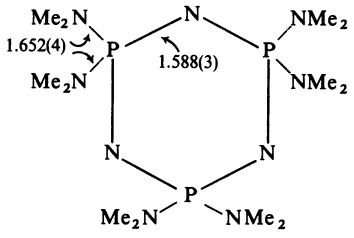
Thus, difference in bond length, bond angles and possible conformations can be expected between the free bases and their conjugate acids and indeed, in two sets of examples where x-ray crystallographic data are available, this has been observed. These are the geminal $N_3P_3Cl_2(NHPr^i)_4$[81], $N_3P_3(NMe_2)_6$[65], and their respective monoprotonated species, $[N_3P_3Cl_2(NHPr^i)_4H]^+Cl^-$[79], and $[N_3P_3(NMe_2)_6H^+]_2Mo_6O_{19}^{2-}$[82].




If we compare the first of these, geminal $N_3P_3Cl_2(NHPr^i)_4$, and its hydrochloride, a number of interesting features emerge. In the former there




is a fairly striking similarity to related bond angles and bond lengths in the geminal $N_3P_3Ph_4Cl_2$[49]. Even in the free base we note an unusually large ring $\hat{PNP}$ bond angle of 124° at that nitrogen atom which is flanked by the two $P(NHPr^i)_2$ units. This ring bond angle is increased on protonation to 132°, giving a completely trigonal planar ring nitrogen atom, x-ray crystallography confirming the position of protonation predicted earlier by Feakins, Shaw and co-workers from their basicity studies. Whilst in the free base the phosphorus–nitrogen ring bond lengths in the segment $(Pr^iNH)_2P—N—P(NHPr^i)_2$ are unexceptional ~1.59 Å, they are considerably longer in the conjugate acid (of the order of 1.67 Å) in keeping with the character of these bonds being rather more like phosphazanes than like phosphazenes. Phosphorus–nitrogen bond lengths of this order of magnitude, i.e. 1.67 Å, have been observed in neutral four-membered $[PhP(S)NR]_2$, (R = Me[83], Et[84], Ph[85]), and six-membered cyclophosphazanes, $N_3Me_3P_3O_3(OMe)_3$[86]. as well as in ionic six- and eight-membered cyclophosphazanes, $N_3H_3P_3O_6Na_3 \cdot 4H_2O$[87] and $N_4H_4P_4O_8H_4 \cdot 2H_2O$[88].

The difference in the bond lengths between phosphazanes and phosphazenes is probably due to the former having only one set of $\pi$-bonding orbitals available, whilst the latter have two, perpendicular to each other. On protonation, a phosphazene assumes a phosphazane-like character and hence the bond lengths increase to those of the latter. The positive charge of the ring nitrogen atom makes the adjacent phosphorus somewhat more positive in the conjugate acid than in the free base. Nevertheless, this increase in positive character does not compensate for the even larger positive character of the phosphorus atom of the $PCl_2$ group and the bond-length variations in the fragment, $(Pr^iNH)_2P—N—PCl_2$, show the former phosphorus–nitrogen ring bond to be longer and the latter to be shorter.

A similar difference in the ring P—N bond length in the same segment of the free base, $N_3P_3Cl_2(NHPr^i)_4$, is more pronounced, as would be expected, in view of the absence of the positive charge due to the proton. Worthy of comment also are the bond angles at the aminolysed phosphorus atoms, $P(NHPr^i)_2$. Whilst the ring $\hat{NPN}$ bond angles are drastically decreased (~7°) on passing from the free base to its conjugate acid, the exocyclic $\hat{NPN}$ bond angles decrease only by ~1–2° for the same pair of compounds.

Another important feature is the comparison of the exocyclic phosphorus–nitrogen bond lengths between the free base and its conjugate acid. Whilst in the free base they are fairly long, 1.64 Å, they are considerably shortened,

~1.61 Å, in the conjugate acid, probably due to the increased back-bonding induced by the positive charge on the ring nitrogen atom.

A final and important point in the structure of $N_3P_3Cl_2(NHPr^i)_4 \cdot HCl$ pertains to hydrogen-bonding[79]. The chloride ion exhibits close distances to five NH groups belonging to three different cyclotriphosphazatriene molecules. The shortest, 3.19 Å, is that to the ring nitrogen atom. The other, rather longer, ones, 3.31–3.36 Å, are to four exocyclic nitrogen atoms of isopropylamino groups in two geminal pairs, $P(NHPr^i)_2$, situated in two other molecules. The coordination around the chloride ion is approximately square-pyramidal and gives rise to a macromolecular hydrogen-bonded structure. This may have some bearing on the following observation. It has frequently been observed that hydrochlorides of aminophosphazenes are formed in the presence of (and hence in competition with) an excess of free primary, but not secondary amines. It may be that a greater degree of conformational freedom allows primary amino groups to take up conformations so as to permit the formation of an intermolecular hydrogen-bonded network and it may be this which plays a part in the formation of aminophosphazene hydrochlorides in the presence of free aliphatic amine. Additionally, secondary amino-derivatives, apart from the greater constraints on their conformational freedom lack of course the N—H bonds on the substituents necessary for the above type of interaction.

We now come to a comparison between the second free base[65], $N_3P_3(NMe_2)_6$, and its conjugate acid[82], $[N_3P_3(NMe_2)_6H^+]_2Mo_6O_{19}^{2-}$. Here too, as predicted from basicity data, the proton is located at a ring nitrogen atom. However, in keeping with the greater basicity of this free base[74] and possibly also perhaps with the lesser hydrogen-bonding demands from the hexamolybdate anion, the nitrogen–hydrogen bond distance is approximately 0.2 Å shorter than in the compound recorded by Mani and Wagner[79]. Many other structural features are similar in these two protonated compounds and hence will be mentioned only briefly.

The ring segment, which is protonated, has phosphorus–nitrogen ring bond lengths in keeping with a phosphazane-like character. However, the other two phosphorus–nitrogen ring bonds in the adjacent P—N—P segments, although they differ in length, do so in the reverse order to that observed for $N_3P_3Cl_2(NHPr^i)_4 \cdot HCl$. This indicates that the effect of the ring proton induces on the adjacent phosphorus atoms, $P(NMe_2)_2$, a greater positive charge and hence a greater electron demand for the electrons of this ring segment than the $P(NMe_2)_2$ group opposite to the protonation site. Hence, the phosphorus–nitrogen bond adjacent to the protonated site is somewhat shorter than the one leading to the $P(NMe_2)_2$ phosphorus atom opposite to the protonated site.

One other important feature emerges from a comparison between the exocyclic phosphorus–nitrogen bond length in the conjugate acid in this derivative, as well as the one discussed earlier. In the structure by Mani and Wagner containing primary alkylamino-groups, the exocyclic phosphorus–nitrogen bond distances adjacent to the protonated ring nitrogen are of the order of 1.61 Å. In this compound, containing secondary dialkylamino groups, i.e. the dimethylamino group, the exocyclic P–N bond length is of the order of 1.62–64 Å, i.e. considerably longer. This is in keeping with our

observations on substituent constants (obtained from basicity measurements) where, in general, secondary amino groups are weaker electron-releasing agents than primary amino groups, e.g. $NHEt > NMe_2$[77]. As this finding is the reverse of that expected from inductive effects, we postulate steric hindrance as the probable cause. We note that the amount of multiple bond character of the exocyclic phosphorus–nitrogen bond (if we use bond length as the criterion) is less in the dimethylamino- than in the isopropylamino-system. Furthermore, the shortening of these exocyclic P—N bonds on passing from free base to conjugate acid is less for the $NMe_2$ system ($\sim$0.02 Å) than for the $NHPr^i$ ($\sim$0.03 Å) system. Similar types of ring bond length variations were observed in the diprotonated cation $[N_5P_5Me_{10}H_2]^{2+}$, although here the positions of the protons were not directly located but deduced from P—N bond length data[40].

Finally, let me deal briefly, because I feel least competent in this area, with some aspects of the quantum chemistry of inorganic phosphorus compounds. Even in such simple systems like phosphorus trifluoride and phosphorus oxyfluoride *ab initio* calculations have given rise to discordant results between two different groups of workers as different basis sets were used[89, 90]. If this is so, it is perhaps not surprising that in the phosphazenes a very much more complex system — which does not lend itself in the present state of the art to *ab initio* calculations — some of the earlier theoretical investigations gave rise to considerable controversies. I will deal with these only cursorily as most of you will be familiar with them. The first theoretical treatment proposed $\pi$-electron delocalization extending over the whole ring, with $\pi$-electron clouds above and below the plane of this ring[91]. This was followed by another theoretical model which suggested $\pi$-electron delocalization over P—N—P three-centre islands[92], which only weakly interacted with each other. Later on, a secondary $\pi'$-system in the plane of the ring was postulated[93]. In recent years, more detailed calculations[94] tend to support the three-centre island model proposed earlier by Dewar, Lucken and Whitehead, and indicate that at least for the six-membered ring system, conjugation beyond the three-centre islands is only of minor importance. Similar deductions can be reached by a consideration of variations in bond lengths in non-homogeneously substituted cyclotriphosphazatrienes (but contrast $N_4P_4F_6Me_2$)[51] as referred to in an earlier part of my lecture. The much larger values for $\alpha$ than for $\gamma$ substituent constants derived from basicity work[75–77], point in the same direction, though here we deal with a perturbed molecule, as borne out by x-ray crystallographic data.

Calculations on the larger rings are scarcer, mainly because of the greater complexity of these systems. Faraday effect measurements suggest that there is little difference in delocalization between six- and eight-membered ring phosphazenes as the magnetic-optic rotation is proportional to the number of PNP units[95]. There is, to date, only one exception to this— the chlorophosphazenes, $(NPCl_2)_n$[94, 95]. It is unexplained and yet it is precisely this system which has been most intensively investigated, both theoretically as well as experimentally. Recently both Perkins, and Labarre, and their respective co-workers[96], have postulated *trans*-annular phosphorus–phosphorus bonding to account for the stability of the six-membered ring system. In addition, Labarre and Faucher have postulated for eight-

membered ring phosphazenes, *trans*-annular bonding for phosphorus atoms separated by two bonds and *trans*-annular antibonding for the same atoms four bonds apart[97]; the cause of the latter may be the change of sign of the wavefunction of the phosphorus *d*-orbitals involved.

Finally, let me refer briefly to a quantum chemical investigation of the three isomeric derivatives, geminal, *cis* and *trans*, $N_3P_3Cl_3(NMe_2)_3$[98]. I will only mention that the calculations performed were based on the x-ray crystallographic data by Ahmed and co-workers, on the *cis*[53] and geminal[52] isomers and on an assumed structure of the *trans*-isomer. The latter[54] has since been solved. These quantum chemical calculations are correlated with data from $^{35}Cl$ n.q.r. spectroscopy, $pK_a'$ values, etc. The *cis* effect[60] is also discussed. I will not pre-empt this paper by going into this in any further detail. All I would like to mention is that in the *trans* structure, which came to hand only recently, that phosphorus–chlorine bond, which on the basis of the *cis* effect has been predicted to be the longest, is indeed found to be so.

I hope that this lecture has given an idea of the current state of structure and bonding in some inorganic phosphorus compounds. Needless to say, they have been coloured by my preferences, prejudices and experience.

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