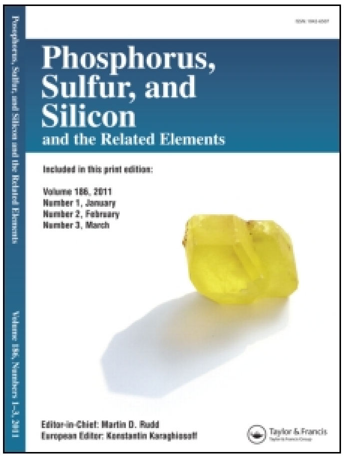


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

PHOSPHAZENES AND PHOSPHAZANES

Robert A. Shaw[a]
[a] Department of Chemistry, Birkbeck College (University of London), London, UK

To cite this Article Shaw, Robert A.(1978) 'PHOSPHAZENES AND PHOSPHAZANES', Phosphorus, Sulfur, and Silicon and the Related Elements, 4: 1, 101 — 121

To link to this Article: DOI: 10.1080/03086647808079969

URL: http://dx.doi.org/10.1080/03086647808079969

Phosphorus and Sulfur
1978, Vol. 4, pp. 101-121

Review

PHOSPHAZENES AND PHOSPHAZANES†

ROBERT A. SHAW

Department of Chemistry, Birkbeck College
(University of London), Malet Street, London WC1E 7HX, UK

(*Received July 17, 1977*)

Three types of phosphazene and four types of phosphazane structural units are classified on the basis of the coordination number of the phosphorus atoms involved. Phosphorus-nitrogen bond lengths are discussed in acyclic compounds and this information is used in analysing ring systems consisting wholly or partially of phosphorus-nitrogen skeletons.

Four-, five-, six-, seven-, eight-, ten-, and twelve-membered rings are surveyed, as are polycyclic systems. Methods of synthesis for cyclophosphazanes, and mixed cyclo-phosphazene-phosphazanes are briefly considered, as are some of their reactions. The minimum ring size where stable phosphazenes have been observed is referred to.

The effect of protonation, methylation, or coordination to a metal moiety on adjacent phosphorus-nitrogen bonds is discussed. The conformations of dimethylamino and phenyl substituents on phosphorus are considered, as is the conformations of the ring skeletons.

The flexibility of acyclic and cyclic phosphorus-nitrogen skeletons is noted, and factors governing phosphorus-nitrogen bond lengths are analysed. On the basis of this and by analogy with sulphur-nitrogen chemistry predictions are made about conditions favouring very long and very short phosphorus-nitrogen bonds.

The nomenclature of phosphorus-nitrogen compounds has been discussed in some detail in a review article about fifteen years ago.[1] Hence here I wish to emphasize only a few salient points pertaining to the subject of my lecture. Phosphazenes are compounds containing *formal* phosphorus-nitrogen double bonds (localized in certain monomers, delocalized over three-centre islands in others, as in oligomeric and polymeric derivatives), whilst phosphazanes contain *formal* phosphorus-nitrogen single bonds. I stress the term *formal* as the bonding situation is much more complex than implied by the simple formulae usually and conveniently used. Phosphazenes are usually based on four-coordinate, quinquevalent phosphorus (**1-4**). However, recently the elegant work by Niecke and Scherer and their coworkers has demonstrated the existence of phosphazenes based on three-coordinate quinquevalent phosphorus (**5**) and on two-coordinate tervalent phosphorus (**6**).[2-5]

Phosphazenes can be classified into three types depending on the coordination number of the phosphorus atom; all contain *formal* phosphorus-nitrogen multiple bonds. Type A contain two-coordinate tervalent phosphorus (**6**), Type B three-coordinate quinquevalent phosphorus (**5**), and Type C (by far the most frequently observed) four-coordinate quinquevalent phosphorus (**1-4**).

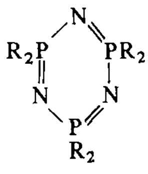
Phosphazenes

$R_3P{=}NR$

(1)

$[R_3P{=}N{-}PR_3]^+$

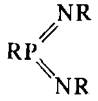
(2)



(3)

$\{N{=}PR_2\}_n$

(4)



(5)

$RP{=}NR$

(6)

Phosphazanes can be classified into four types, depending on the coordination number of the phosphorus atom; all contain *formal* phosphorus-nitroger single bonds. Type A contain three-coordinate tervalent phosphorus (**7-9**), type B four-coordinate quinquevalent phosphorus with either a *formal* double bond to an atom (other than the one described in the phosphazane linkage) such as oxygen, sulphur, nitrogen, or carbon (**10-12**), or a positive charge on phosphorus ("onium" type) (**13**). In type C phosphorus is quinquevalent and five-coordinate

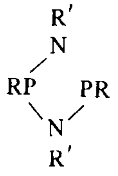
---

† Plenary Lecture presented at the 2nd meeting of the 1st International Symposium on Inorganic Heterocycles, Madrid, Spain, 22-26 June 1977.

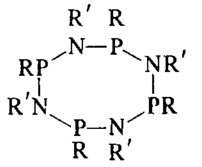
Phosphazanes Type A

$R_2P{-}NR'$

(7)

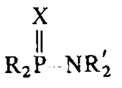


(8)



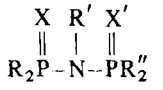
(9)

Phosphazanes Type B



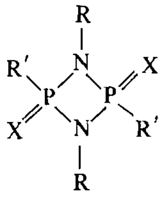
$R_2\overset{\overset{X}{\parallel}}{P}{-}NR'_2$

(10)



$R_2\overset{\overset{X}{\parallel}}{P}{-}\overset{\overset{R'}{|}}{N}{-}\overset{\overset{X'}{\parallel}}{P}R''_2$

(11)



(12)

$(R_3\overset{\oplus}{P}{-}NR'_2)X^{\ominus}$

(13)

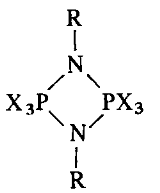
(14-15), and in type D quinquevalent and six-co-ordinate (16-17).

Examples of compounds containing almost all of the various combinations of two of the structural types A to D are known.

Phosphazanes Type C

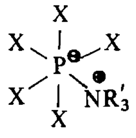
$R_4P{-}NR'_2$

(14)

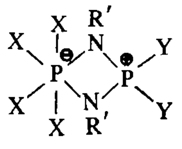


(15)

Phosphazanes Type D



(16)



(17)

In a lecture attempting to cover a fairly large field it is of course impossible to be comprehensive, and I shall not even attempt to be so. Instead I intend to highlight selected areas.

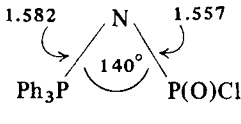
I shall commence by examining structural details of some monophosphazenes and monophosphazanes. Diffraction data are available on a number of these. Unlike with bonds exclusively between first row elements, such as carbon, a definition of single, double, triple, and aromatic bonds must be hedged with numerous reservations. Nevertheless an attempt of an approximate classification will be made.

In this section a very brief outline of bond lengths in monophosphazenes and monophosphazanes will be given. Perhaps one should commence with the short-lived gaseous species P≡N (18)[6] for which it is possible (though not necessarily correct) to write a triple bond.

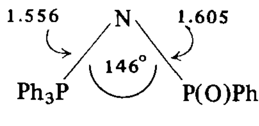
Monophosphazenes, where the multiple bond character is largely confined to a P–N bond are scarce, but a suitable example is available in $Ph_2FP{=}NMe$ (19).[7]

The example usually quoted as the standard for the P–N "single" bond $H_3\overset{\oplus}{N}{-}PO_2^{2\ominus}Na^{\oplus}$(20),[8] is attributed to Cruickshank.

P≡N	$Ph_2FP{=}NMe$	$H_3\overset{\oplus}{N}{-}PO_2^{2\ominus}Na^{\oplus}$
1.491	1.641	1.769
(18)[6]	(19)[7]	(20)[8]



(21)[9]

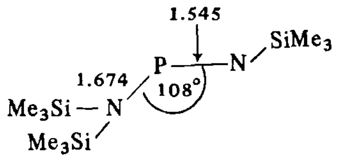


(22)[9]

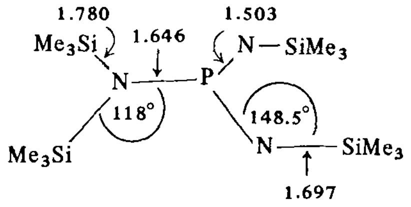
It should be emphasized that the nature of the substituents on phosphorus and nitrogen can and do affect profoundly the P–N bond length. This is particularly the case if phosphorus carries large numbers of fluorine atoms, and/or if nitrogen is attached to a group capable of accepting lone-pair donation.

The latter effect is elegantly demonstrated by two related compounds $Ph_3P{=}N{-}P(O)X_2$ [X = Cl (21) or Ph (22)],[9] where the relative lengths of the two P–N bonds are inverted.

The structures of the novel P(III) and P(V) monophosphazenes, viz. $(Me_3Si)_2NP{=}NSiMe_3$ (23)[10] and $(Me_3Si)_2NP({=}NSiMe_3)_2$ (24)[11] also deserve mentioning here. It is obvious that in these two examples, one deals with a wide range of bond lengths and bond angles. Some of the general trends will be discussed later. Some points are, however, worth stressing here.



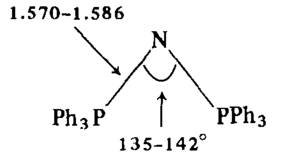
(23)[10]



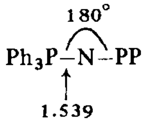
(24)[11]

The phosphazane and phosphazene linkages can be clearly distinguished, the greater length of the phosphazene (and to a lesser extent of the phosphazane) bond in the P(III), compared to that in the P(V), compound is a general feature of bonds involving phosphorus and atoms having lone-pairs of electrons, and has been already discussed in my lecture in Prague.[12] The above effects are transmitted to the Si–N bond whose lengths and angles vary in a predictable manner. The three-coordinate phosphorus atom of the P(V) compound (**24**) is trigonal planar.[11] The Si_2NPNSi skeleton in the P(III) compound is coplanar.[10]

The cation $[Ph_3P{=}N{-}PPh_3]^+$, rather widely used as a counter ion for complex inorganic and organometallic anions, has been extensively investigated (for summary see Ref. 13). It usually occurs in a bent form (**25**) (longer bonds), but a linear species (**26**) (shorter bonds) has been observed. Recently both types, bent and linear, have been observed in the same unit cell, indicating that here, as for cyclic species discussed later, changes of shape involving P–N skeletons, do not seem to require a great deal of energy.



(25)[13]



(26)[13]

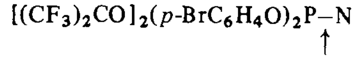
Data for monophosphazanes type A show that in general their P–N bonds are longer (**27–28**)[7] than those for monophosphazenes, but also demonstrate the bond shortening effect of fluorine substituents (**29**).[7] It is also noteworthy that the P–N bond length is considerably increased if the nitrogen atom is pyramidal as in $[(CH_2)_2N]_3P$ (**30**).[7] (As some of the data are based on electron-diffraction, others on X-ray crystallography, one cannot read too much into minor differences, particularly as the accuracy of individual determinations varies considerably.)

$(Me_2N)_2P{-}NMe_2$	$Cl_2P{-}NMe_2$	$F_2P{-}NMe_2$
1.700 (**27**)[7]	1.69 (**28**)[7]	1.628 (**29**)[7]
$[(CH_2)_2N]_2P{-}N(CH_2)_2$		$(Me_2N)_2(S)P{-}NMe_2$
1.750 (**30**)[7]		1.64 (**31**)[7]
$Cl_2(O)P{-}NMe_2$	$Ph_2(O)P{-}NMe_2$	$(H_2N)_2(O)P{-}NH_2$
1.67 (**32**)[7]	1.67 (**33**)[7]	1.65 (**34**)[5]

Infrared spectroscopy can in suitable circumstances throw light on relative P–N bond strength, and this has been reviewed by Mathis.[14]

Monophosphazanes of type B, being based on quinquevalent four-coordinate phosphorus, show in general somewhat shorter P–N bond length than related structures of type A. These differences are not, however, very great and can be obscured by substituent effects.

Most examples of phosphazanes of type C have their nitrogen atom incorporated into a ring structure and will be discussed elsewhere. Type C are based on a trigonal bipyramid; it is known that bonds to like atoms are shorter in the equatorial plane, than those in apical positions. An example of an acyclic equatorial P–N bond has recently been reported.[16] The nitrogen atom is almost trigonal planar and the NMe_2 group adopts a conformation such that



$$[(CF_3)_2CO]_2(p\text{-}BrC_6H_4O)_2P\underset{\uparrow}{-}NMe_2$$

(**35**)[16] 1.66

its p-orbital lies in the equatorial plane.

It can be seen from the above that phosphazene linkages are generally significantly shorter than phosphazane linkages. In the latter, there is evidence from bond-lengths, as well as from bond-angles, that the lone-pair of electrons on the nitrogen atom is partially or wholly delocalized towards the phosphorus atom. If this is prevented by donation of the lone-pair to an acceptor such as a proton, metal ion, etc. considerably longer phosphorus-nitrogen bonds (e.g. 1.77 Å in $H_3\overset{\bullet}{N}{-}PO_2^{2\ominus}\,Na^{\oplus 8}$) are observed. In the example quoted a positive charge resides on the nitrogen atom, but several other examples of very long phosphorus-nitrogen bonds (in four-, five- and six-coordinate phosphorus compounds) have been reported. In the first two, the nitrogen atom is formally neutral (in the third it may carry a positive charge) and presumably back-donation is inhibited by the unavailability of suitable acceptor orbitals. Thus, we can note broadly two types of phosphazane linkage: (*a*) one in which back-donation of the lone-pair of electrons on the nitrogen atom is possible and for this generally phosphorus-nitrogen bond-lengths of approximately 1.65–1.69 Å are observed and (*b*) those where back-donation is for various reasons not possible, and bond-lengths of the order of 1.75–1.78 Å are found.

We will now commence a comparison of cyclophosphazenes and cyclophosphazanes (and where appropriate phosphinoborines), classifying them according to ring size.

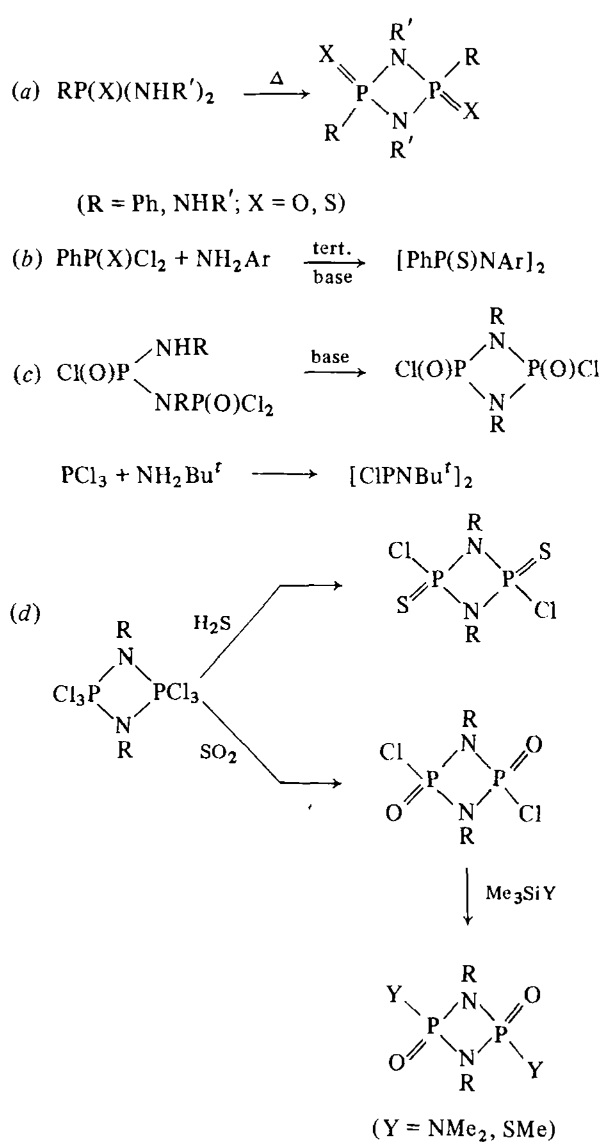
FOUR-MEMBERED RING SYSTEMS

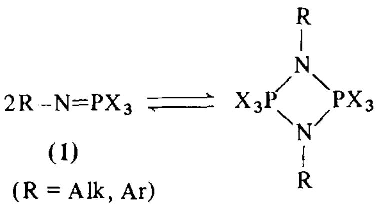
No phosphazenes of this type are known, either based on an alternating P–N cyclic framework or where only one P–N bond is present and the other two atoms belong to different elements, such as carbon. However, numerous examples of cyclodiphosphazanes have been synthesized and characterized, many of type B, somewhat fewer of types A and C.

Let us first consider the formation of cyclodiphosphazanes. Those of Type B (The diagrams of types A and B displayed do not imply stereochemical assignments. The latter, where known, and where appropriate to the discussion are specifically mentioned.) can be made by (*a*) thermal condensation methods of mononuclear phosphorus amides;[17–20] (*b*) by a similar process to (*a*) but where the condensation is carried out in solution, usually by the elimination of hydrogen halide in the presence of a suitable acceptor, such as a tertiary base, etc.;[20] (*c*) cyclization of isolated, observed, or postulated acyclic diphosphazanes, based on quinquevalent or tervalent phosphorus, and the reactions of the latter cyclic species;[21,22] and (*d*) the conversion of cyclodiphosphazanes of type C into type B.[23] It is not certain at this stage to what extent methods (*a*) to (*d*) share common intermediates and/or mechanistic features.

Cyclophosphazanes of Type C can be considered to be based on equilibria between monomeric phosphazenes and dimeric cyclodiphosphazanes, and these have been investigated for suitable systems.[24–28] Numerous examples of both types are known, and some of the factors governing, which species arise from a given set of experimental conditions have been elucidated. In practice cyclodiphosphazanes of

Synthetic Routes to Cyclodiphosphazanes, Types A and B





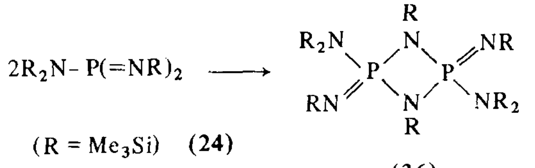
(1)

(R = Alk, Ar)

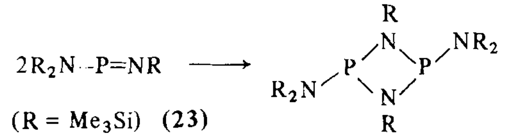
(15)

type C, as well as monophosphazenes are usually prepared by the reaction of halogenophosphoranes R_nPX_{5-n}(n = 0, 1, 2 or 3; R = Alk or Ar, X = Cl or Br), most frequently phosphorus pentachloride, with alkylamine, arylamine, or amides. If the product is a monophosphazene, the synthesis is usually described as the Kirsanov reaction.[29]

In a few cases dimerization of phosphazenes to cyclodiphosphazanes or the reverse process has been utilized synthetically. The examples of the dimerization processes[30,31] given are based on the novel phosphazenes recently discovered.

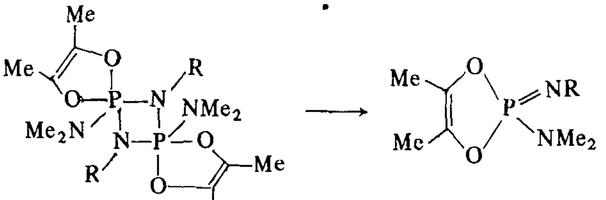


(36)



(37)

The reverse type of synthesis dimer → monomer has also been reported.[32]



(38) (39)

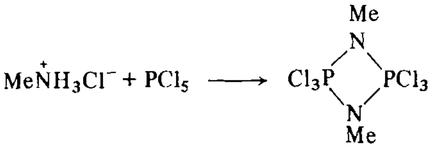
(R = Me_3Si)

By means of the thermal method,[17-20] (*a*) numerous cyclodiphosphazanes especially of the type $[PhP(S)NR]_2$ (40) and $[(RNH)P(S)NR]_2$ (41) have been synthesized and at least in one case *cis*- (42) and *trans*-isomers (43) $[PhP(S)NEt]_2$,[19] were isolated and characterized. In general, this method seems to lead to the preferential formation of the *trans*-isomer. In the thermolysis of phenylphosphonothioic diamides, $PhP(S)(NHR)_2$ (44), the normal cyclodiphosphazanes $[PhP(S)NR]_2$ (40) of type B are obtained. When R = H, or alkyl groups branching at the α-carbon atom, the dealkylated cyclotriphosphazane, $[PhP(S)NH]_3$ (45), is the only product so far isolated (see under six-membered ring compounds). Most of the normal products e.g. $[PhP(S)NEt]_2$ (42 and 43) dealkylate and ring expand at higher temperatures to give the trimer, $[PhP(S)NH]_3$ (45). When R is cyclohexylamino, an unusual product (46)[33] is obtained, whose crystal structure has been determined (see under five-membered ring compounds). By a suitable combination of thermal (*a*) and tertiary base (*b*) methods the formation of the more elusive *cis*-isomer can sometimes be enhanced.[20] At present, no detailed study of the *cis*-*trans*-isomerization has been carried out.

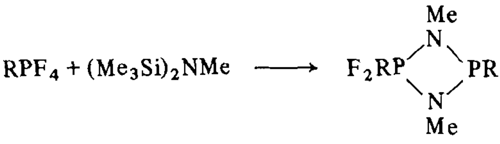
However the triamides, $P(S)(NHR)_3$ (47) seem to give by the thermal method (*a*), regardless of the nature of R, the cyclodiphosphazanes, $[(RNH)P(S)\text{-}NR]_2$ (41). For most of the isolated products, a *trans*-structure appears probable.[20]

Monophosphazanes and cyclodiphosphazanes type C, can also be prepared by silylation methods from fluorophosphoranes.[34]

Synthetic Routes to Phosphazanes, Type C, and Monophosphazenes



(48)



(49)

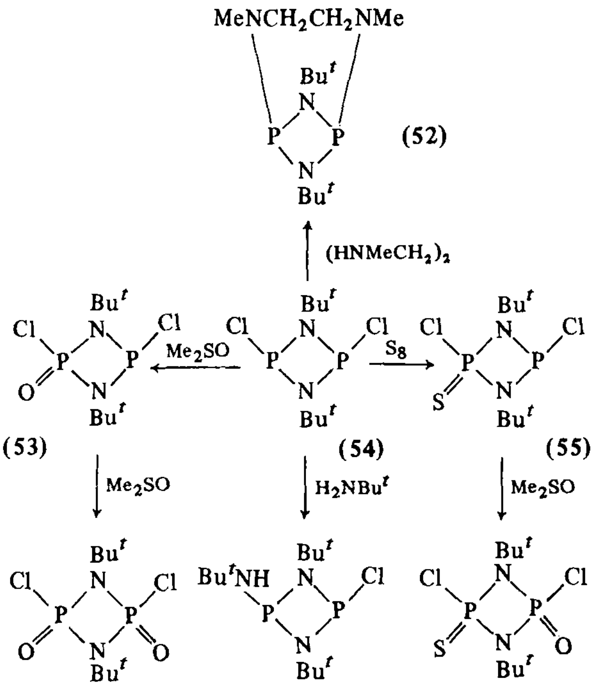
(R = Me, Ph)

$$PF_5 + Me_3SiNMe_2 \longrightarrow Me_2N\text{-}PF_4 \qquad (50)$$

$$p\text{-tol-}SO_2NH_2 + PCl_5 \longrightarrow p\text{-tol-}SO_2N{=}PCl_3 \qquad (51)$$

The main emphasis of the present lecture will be on quinquevalent phosphorus compounds. A detailed discussion of tervalent phosphazanes will be given by Rodney Keat elsewhere. Hence I will confine myself to a few salient points of the latter. These tervalent cyclic precursors can have one or both of their phosphorus atoms oxidized to give either mixed quinquevalent-tervalent, or wholly quinquevalent species, the latter in some cases with different multiply bonded atoms (O, S) on each phosphorus.[21]

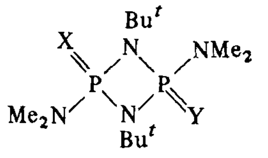
Novel bicycles (e.g. 52) starting with a *cis*-cyclodiphosphazane (54) of type A have been prepared by Keat.[35]



(52) (53) (54) (55) (56) (57) (58)

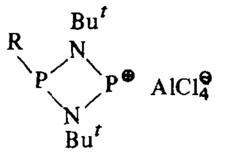
Dimethylamino-derivatives of cyclodiphosphazanes of type A, e.g. $(Me_2NPNBu^t)_2$ (59)[36] and of type B, e.g. $[Me_2N(X,Y)PNBu^t]_2$ (60)[35] show hindered rotation of the NMe$_2$ group.

Ionic species $[RP(NBu^t)_2P]^{\oplus}AlCl_4^{\ominus}$ [R = Me (61)[37]; R = NMe$_2$ (62)[35]] related to the above (54 and 57) have also been reported. Compound (62) has the highest barrier to rotation of the NMe$_2$ group, so far observed, in a compound of this type.[35]



(60)

(X, Y = lone-pair, O, S, Se)

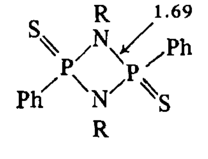


[R = Me, (61), NMe$_2$ (62)]

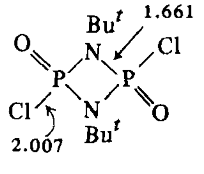
Cis–trans-isomerism[19,20,35,38,39] has been observed for all three cyclodiphosphazane systems: tervalent, quinquevalent-tervalent, and quinquevalent, though a complete rationale for this is presently lacking.

Cis–trans-equilibria have, however, been studied for compounds of type A.[35,38,39]

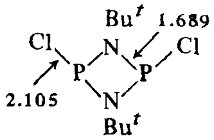
Several crystallographic investigations of cyclodiphosphazanes of type B and of type C have been reported. This includes a pair of *cis–trans*-isomers of the former, $[PhP(S)NEt]_2$ (42 and 43). These have been summarized elsewhere[40] and I will confine myself to discussing only some salient features.



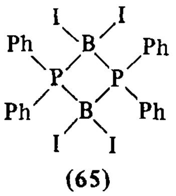
[R = Me, Et(*cis* and *trans*), Ph]
(63, 42, 43, 64)



trans (67)



cis (68)



(65)

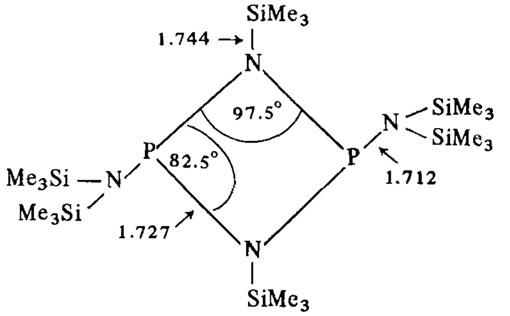
All the cyclodiphosphazanes of type B have similar and equal ring P–N bond-lengths (rounded off for simplicity's sake to 1.69 Å). All the three *trans*-structures [R = Me (63)[41], Et (43)[42] and Ph (64)[40]] have planar four-membered rings. The only *cis*-derivative [R = Et (42)[43]], of this series, whose structure has been investigated has again equal and similar P–N bond-lengths, but here the ring is puckered, probably, at least, in part, to relieve intramolecular crowding of the two phenyl substituents. Puckering of the four-membered (P–B)$_2$ ring in (65)[44] is more pronounced than that of the (P–N)$_2$ ring in the *cis*-compound (42),[43] although in the former the ring is symmetrically substituted. Intra- and/or inter-molecular crowding may be the cause of this. The dipole moment of $(Et_2PBBr_2)_2$ (66)[45] suggests that this somewhat less sterically crowded compound is also non-planar. Hence this phenomenon needs further investigation.

It is perhaps worth stressing that whilst in phosphazenes, phosphazanes type B, and phosphinoborines the phosphorus atom always carry two exocyclic substituents, the other ring atoms vary in their coordination number. Nitrogen in phosphazenes has no exocyclic substituents, in phosphazanes it has one; the boron atom is phosphinoborines has two. Phosphazanes of types A and C are different yet again. Similar to those of type B, nitrogen carries one substituent. However, at phosphorus the situation is different, type A compounds having one, type C compounds three exocyclic groups.

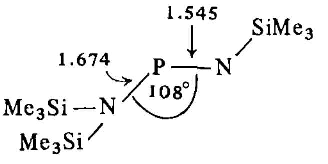
Predictably (because of the different electron-withdrawing powers of the substituents)[12] in $[ClP(O)NBu^t]_2$ (**67**),[46] the P–N bonds are somewhat shorter than those of compounds (**63, 42, 43, 64**). The *trans*-structure (**67**) has a planar ring and equal ring bonds.

Comparison of the tervalent compound $(ClPNBu^t)_2$ (**68**)[47] with the structurally closely related quinquevalent compound (**67**) is particularly revealing. Compound (**68**) has a *cis*-structure and the ring is slightly puckered. Its P–N bonds are equal, but significantly longer than those of compound (**67**); the same pertains to a lesser extent for the P–Cl bonds in both compounds. The probable explanation is again the same as put forward for acyclic species,[12] and briefly touched upon above.

A crystal structure of a type A dimer (**69**)[48] is of particular interest as it is derived by dimerization of a phosphazene precursor (**23**) whose structure has also been determined.[10] As might be anticipated the P–N bonds in the dimer are considerably longer than the two types of P–N bonds present in the monomer.

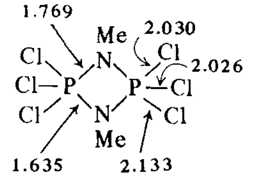


(**69**)

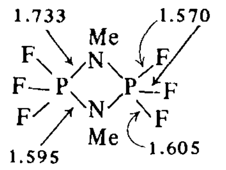


(**23**)

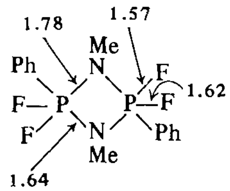
Within certain limits the geometry and bonding situation in compounds (**42, 43, 63-69**) have been similar. They differ considerably for compounds (**70-72**).[49] These are phosphazanes of type C. Each phosphorus is five-coordinate and of the phosphorane type with apical and equatorial bonds. The four-membered rings span as in monomeric phosphoranes apical-equatorial positions and as in the former class of compounds differ in bond-lengths for like groupings, the apical bonds being longer than the equatorial ones. This pertains to the ring P–N, as well as to the exocyclic P–Cl and P–F bonds. As in the phosphazenes large number of fluorines (much more than any other substituent) *affect significantly the P–N bond-lengths.* This is borne out by a comparison between structures (**70**) and (**71**). The replacement of one fluorine atom by a phenyl group in the *trans*-structure (**72**) makes its P–N bonds again comparable with those in (**70**).



(**70**)



(**71**)

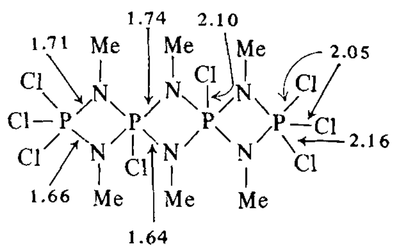


(**72**)

It is noteworthy, that particularly in compounds (**70**) and (**72**) the apical P–N bonds are as long or longer than that (1.77 Å) observed in the "single" bond in $H_3\overset{\bullet}{N}-PO_3^{2\bullet}Na^{\bullet}$.[8] In contrast to the latter, however, the nitrogen atom in (**70**) and (**72**), and indeed for (**71, 42, 43, 63, 64, 67, 68**) are all planar or very nearly so. Even allowing for the different hybridization states of phosphorus in the various P–N bonds, the bond lengths of the apical P–N bonds are closely similar to that of a "single" bond, although *the nitrogen is here formally neutral, as well as tri*gonal planar. The equatorial P–N bonds (the lone-pair of electrons of the nitrogen atom is again largely delocalized) are considerably shorter than the P–N bonds in compounds (**42, 43, 63, 64, 67, 68**). In the latter delocalization appears to take place equally into the two adjacent P–N bonds (in the former only into one). Electronegativity differences of the substituents may well also play a part, and have been discussed in some detail elsewhere.[12,50]

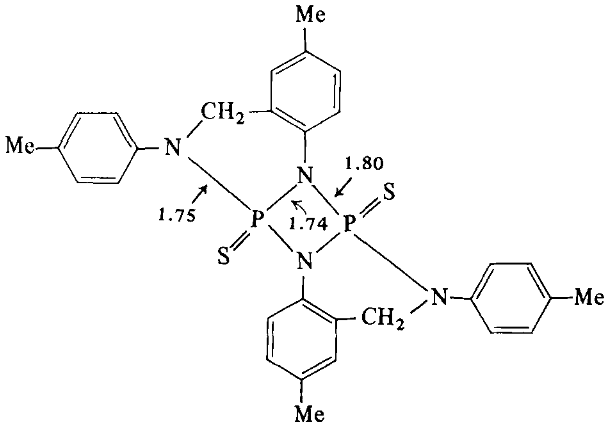
To demonstrate that the same principles pertain to a system containing three cyclodiphosphazane rings of type C, the structure of compound (**73**), $P_4Cl_8(NMe_2)_6$, is shown.[51]

Other complex cyclodiphosphazanes, where the $(P–N)_2$ units are part of pentacyclic structures

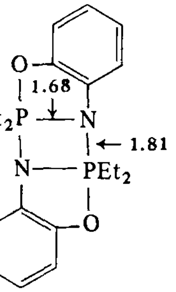


(73)

(74)[52,53] type B, and (75)[54] type C, have been reported. A crystal structure of (74)[53] reveals unequal P–N bond-lengths of 1.74 and 1.80 Å in the four-membered ring, the longer ones suggesting a "single" bond character. The nitrogen atom has predominantly sp^3-character. The P–N bond-lengths in the five-membered rings are also remarkably long 1.75 Å, and again the nitrogen atoms in question have considerably sp^3-character.



(74)



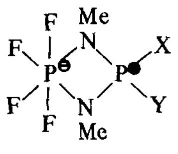
(75)

In compound (75) the $(P{-}N)_2$ ring spans apical-equatorial positions, the former having as usual the longer P–N bond-length. However, in this structure, unlike that of (74), the nitrogen atoms are trigonal planar (sp^2-hybridization).

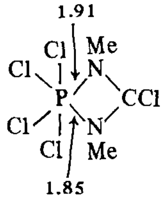
Structural information from diffraction studies can sometimes be extended by means of magnetic resonance techniques. The similarity of the ^{35}Cl nqr spectra of $(Cl_3PNR)_3$ [R = Me (70), Et or Ph][55] allows the deduction that the main structural features of the latter two are similar to that of the first (70), whose structure has been determined by X-ray crystallography.[49]

In passing it ought also to be mentioned that for cyclodiphosphazanes of type C (based on quinquevalent phosphorus); pseudorotation is possible, and indeed has been observed (mainly by ^{19}F nmr spectroscopy) in some fluoroderivatives.[56,57]

Cyclodiphosphazanes of type D, where one phosphorus atom is six-coordinate are very few. Only one crystal structure (76) is available.[58] The P–N bonds are so long (and the C–N bonds so short) as to suggest the participation of resonance structures involving a possible weak N → P donor bond. The P–Cl bonds have a mean length of 2.10 Å, and the coordination around the phosphorus atom is approximately octahedral. With a mean P–N bond-length of 1.88 Å compared to the "single" bond value of 1.77 Å, this structure has undoubtedly unique features. Other examples of type D (77, 78) have been characterized by nmr spectroscopy.[59]



(X = F, Y = Bu^t) (77)
[XY = $(NMeCH_2)_2$] (78)



(76)

Quantum chemical studies on cyclodiphosphazanes have been neglected compared to the volume of such work on cyclophosphazenes. The closeness of the approach of "non-bonded" atoms (both P···P and N···N) in cyclodiphosphazanes of type B and type C noted by Peterson and Wagner[40] suggests studies along these lines might be rewarding. Trans-annular (P···P) bonding has been demonstrated for cyclotriphosphazatrienes, the same interaction [as well as anti-bonding (P···P)] for cyclotetraphosphazatetraenes, and anti-bonding (N···N) for both of these classes of compounds.[60] Preliminary studies on cyclodiphosphazanes type A suggest the presence of some trans-annular (P···P) bonding.[61]

Finally before leaving the subject of four-membered ring system, I would like to consider the conformations of substituent groups on the phosphorus atoms. I have analysed elsewhere[12,50] the conformations of phenyl and dimethylamino groups bonded to the phosphorus atoms of six-membered and eight-membered cyclophosphazenes. In general, when the second substituent, e.g. chlorine or bromine, has axial symmetry, the phenyl or dimethylamino group adopts, what I call a Type I conformation, where the p_z-orbital of the trigonal planar carbon or nitrogen atom intersects with the reference line (defined earlier[12,50]).† I consider that it may be more useful to redefine the reference line as a reference plane. The latter is related to the reference line, by allowing it to bisect the NPN plane (or BPB or NCN planes depending on the ring system involved), as shown in diagram 1. Diagram 2 displays conformations Type I, II, and III.[50]

Diagram 1

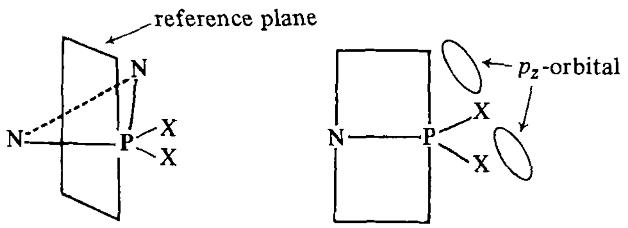
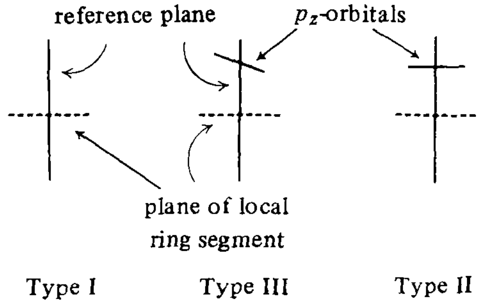
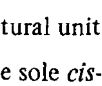
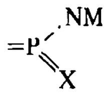


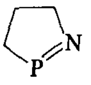
Diagram 2



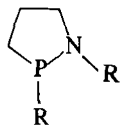
In cyclodiphosphazanes of type A, the phenyl groups in all *trans*-compounds (**43**, **63**, **64**)[40–42] containing the structural unit  $=P\begin{smallmatrix}Ph\\S\end{smallmatrix}$ adopt Type II conformations. In the sole *cis*-structure[43] of this class, the compound is close to Type III, probably because of steric effects. This is in contrast to cyclophosphazenes, where the grouping $\equiv PXPh$ (X = Cl or Br) adopts a Type I conformation.[12,50] A similar difference in behaviour as for the phenyl group, is also observed for the dimethylamino group. Diffraction data are available for dimethylaminocyclophosphazenes.[12,50] For dimethylaminocyclodiphosphazanes the evidence is based largely on the non-equivalence of the two methyl groups observed by ^1H nmr spectroscopy for the  $=P\begin{smallmatrix}NMe_2\\X\end{smallmatrix}$ moiety (X = lone-pair, O, S, or Se). The barriers to rotation vary considerably with the nature of X.[35,62] Bond-lengths and bond-angles in closely related cyclophosphazenes and cyclophosphazanes (discussed later under six- and eight-membered ring systems) indicate very different electron distributions in the two structural moieties $\equiv PXY$ (X = Cl, Br; Y = Ph, NMe_2) and $=P(X)Y$ (X = lone-pair, O, S, Se; Y = Ph, NMe_2). Hence different conformations of substituents are not entirely unexpected. In the phosphinoborine (**65**) the two geminal phenyl groups both adopt a Type I conformation, hitherto only observed in gem.-$N_3P_3Ph_2F_4$,[12,50] whilst in general PPh_2 groupings adopt a Type III conformation.[12,50]

Five-membered ring systems

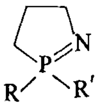
Alfred Schmidpeter[63] will report in detail on these systems at this Symposium. Hence my own observations on the five-membered rings will be very brief. They can broadly be classified into 5 groups (**79–83**) based on tervalent and quinquevalent phosphazenes and phosphazanes.



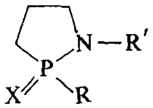
(79)



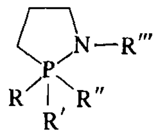
(80)



(81)



(82)



(83)

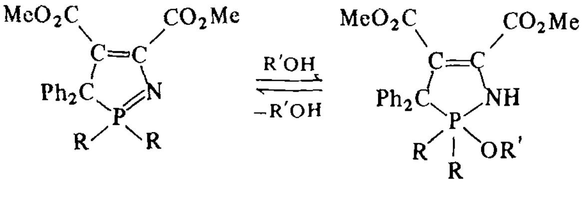
Apart from the phosphorus and nitrogen atom shown above, the remaining three atoms can be carbon and/or a variety of heteroatoms such as oxygen, sulphur, or nitrogen. Formal unsaturation can also occur amongst these atoms.

Monomer-dimer relationships involving 1,2-addition or -elimination processes are feasible. Indeed, in many cases where monomers of group (**81**) might be expected, complex cyclodiphosphazane dimers [e.g. (**75**)] were isolated.

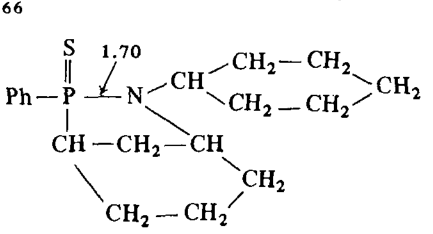
---

† A mistake has been noted in the Figure in the top left hand corner of p. 657,[50] where in the diagram, Type II and III ought to be interchanged.

Examples of structural groups (81) and (83) in equilibria have been observed by nmr spectroscopy. The equilibria are displaced further to the phosphazane structure (85) for R = Me than Ph.[64] Basicity studies show, in line with these observations, that the phosphazenyl nitrogen in (84) is more basic for R = Me than for Ph.[65]


(84) (R = Me, Ph) (85)

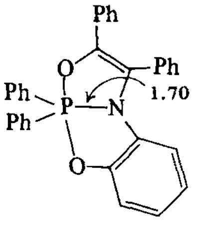
Finally, in this section it is appropriate to give some accurate structural data. I will quote four examples, all of phosphazanes: one of type B, three of type C. I mentioned earlier in the section on four-membered ring systems that thermolysis of $PhP(S)(NHC_6H_{11})_2$ gave an anomalous product (46).[33,66]

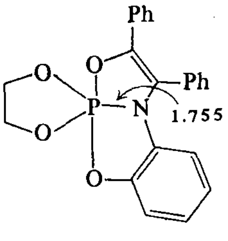

(46)

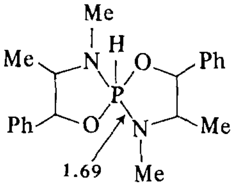
The other three examples are all based on spirophosphoranes (86-88). In compound (86) both nitrogen atoms are essentially planar and occupy equatorial positions.[67]

In the two closely related structures (87) and (88) the nitrogen occupies in (87) an equatorial, in (88) an apical position.[68]

Structures (46, 86, 87) all have essentially the same P–N bond-length, whilst the apical bond in (88) is substantially longer.


(87)


(88)


(86)

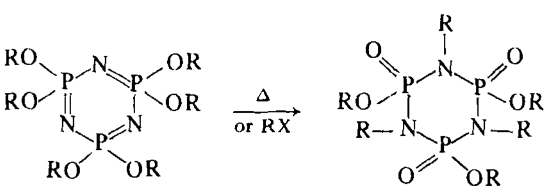
SIX-MEMBERED RING SYSTEMS

Whilst in the four-membered and five-membered ring systems most phosphazanes were neutral compounds, in the six-membered (and higher-membered) ring compounds, phosphazanes or mixed phosphazane-phosphazenes can be found as neutral, anionic, or "cationic" species. The synthetic routes to cyclotriphosphazanes (and larger ring phosphazanes) based entirely on phosphorus–nitrogen skeletons are rather different from those of cyclodiphosphazanes. The thermolysis method has so far given only one example of a cyclotriphosphazane, viz. $PhP(S)(NH_2)_2 \rightarrow [PhP(S)NH]_3$ (45)[20]. The same compound can also be obtained by dealkylation and ring expansion of certain cyclodiphosphazanes.[20] It would be interesting to discover whether the route from the above parent diamide, $PhP(S)(NH_2)_2$, gives originally a four-membered ring $[PhP(S)NH]_2$, which subsequently expands to the six-membered ring system (45). A number of putative synthetic routes to cyclotri- and cyclotetra-phosphazanes have subsequently been shown to be based on misconceptions: some products were cage compounds, others polymeric. Most were in any case restricted to P(III) compounds. (An authentic example will be given in the section dealing with eight-membered ring systems.) As most thermal and tertiary base methods lead to four-membered ring systems, other methods must be found to synthesize the six-membered ring system. Amongst these is the alkoxyphosphazene-oxophosphazane rearrangement, first discovered by Fitzsimmons and Shaw,[69-71] as well as the tautomerism involving hydroxyphosphazenes and oxophosphazanes.[1]

For most of the hydroxycyclophosphazenes investigated the equilibrium lies largely or wholly on the side of the oxocyclophosphazanes. If the latter are present as their metal salts, examples of anionic cyclotriphosphazanes are obtained.

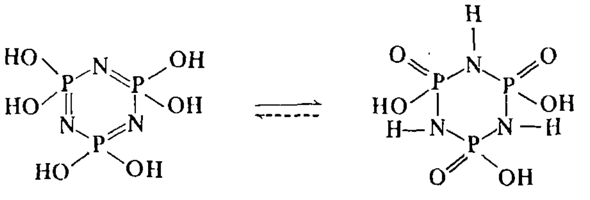
On the other hand, "cationic" derivatives of cyclotriphosphazanes, or related compounds with mixed phosphazane-phosphazene character, can

Neutral cyclotriphosphazanes



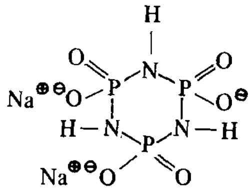
(89)[72] (90)[69-71]

(R = alkyl, but not fluorinated alkyl)

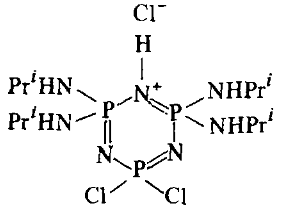


(91)[1] (92)[1]

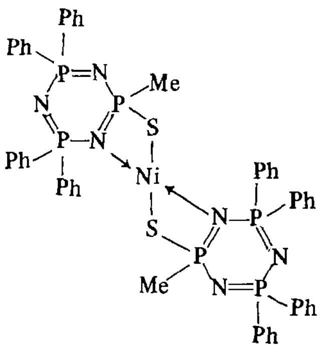
Anionic and "Cationic" cyclotriphosphazanes



(93)[1]



(94)[73,74]

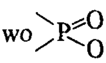


(95)[75,76]

be obtained by protonation or alkylation of cyclotriphosphazenes, or by coordination via the ring nitrogen atoms to e.g. metal derivatives. "Cationic" in this context need not mean actual ion formation, but could involve a coordinate bond. The "cationic" types, are usually represented by mixed cyclophosphazene-cyclophosphazane derivatives and for the six-membered (and higher membered) ring systems, diffraction methods have yielded valuable data.

This section (and those following on higher ring systems) would have become very long indeed if cyclophosphazenes would be discussed *per se.*[12,50] A great deal is known about cyclophosphazenes, but rather less about cyclophosphazanes based on six-membered and higher-membered rings. Hence only the comparative aspects will be stressed.

It is opportune to review the structural data available. Ansell and Bullen[77] determined the structure of a neutral six-membered ring cyclotriphosphazane, $N_3Me_3P_3O_3(OMe)_3$, (96) obtained by the above-mentioned alkoxyphosphazene-oxophosphazane rearrangement.[69-71] Unlike its cyclotriphosphazatriene precursor, $N_3P_3(OMe)_6$,[72] which, although its structure has not been determined, is almost certainly planar, the rearranged compound has a pronounced (twisted) boat conformation.[77] A detailed discussion of this type of compound will be deferred to the section dealing with eight-membered ring systems, where accurate X-ray data is available on a phosphazene, and two phosphazane isomers derived from it. Here I will confine myself to mentioning that the overall structure of $N_3Me_3P_3O_3(OMe)_3$ (96) has a *trans*-arrangement of the phosphoryl groups, which can be further defined as one occupying a flagpole, the other two axial positions. The nitrogen atoms are trigonal planar, the P–N bond distances considerably longer (1.66 Å) (five equal, one somewhat shorter) than in cyclophosphazenes. The P–O distances are, as expected, very different for the phosphoryl group (~1.45 Å) and the ester group (~1.56 Å).[77]

A brief comparison with the anionic structure of $Na_3[N_3H_3P_3O_6]$, $4H_2O$ (97),[78] seems appropriate. The phosphazane moiety here has a chair conformation, the P–N bonds are of equal length and of the order expected (1.68 Å), (slightly longer than in the ester, possibly connected with hydrogen-bonding). All the six P–O distances are equivalent (1.495 Å), intermediate to the two different types observed in the neutral ester molecule, indicating resonance between the two  canonical forms.

An X-ray structure determination of a mixed cyclophosphazene-cyclophosphazane, $[N_3HP_3Cl_2(NEt_2)_3O]_2$ (98)[79] obtained by a prototropic shift has also been carried out and the variations in the P–N bond-lengths are broadly as expected.

"Cationic" examples (as defined earlier) have also had their structures determined. Those of two protonated species gem.-$N_3P_3Cl_2(NHPr^i)_4$, HCl (94)[74] and $[N_3P_3(NMe_2)_6]_2$, $H_2Mo_6O_{19}$ (99)[80] together with their conjugate bases,[81,82] I have discussed in some detail in Prague[12] and Besancon.[50] Here I would like to demonstrate similar effects, if the nitrogen lone-pair of electrons is donated to a metal (e.g. Ni), rather than to a proton. The compound shown earlier (**95**),[76] has P–N bond distances of 1.64 Å adjacent to the N → Ni donor bond [somewhat shorter than the corresponding ones in protonated species (1.67 Å) e.g.[74,80]], the others fall in the normal phosphazene range (~1.59 Å).[76]

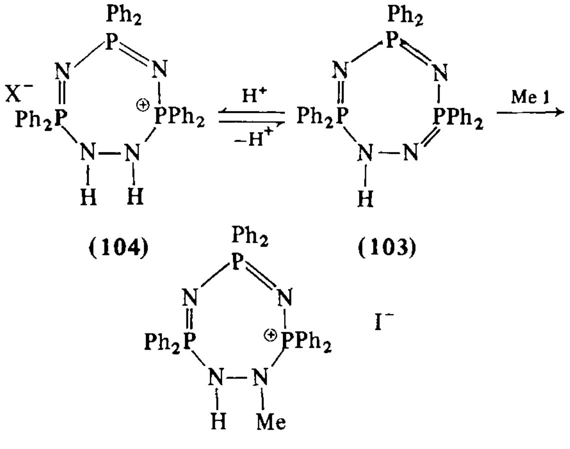
We can now very briefly compare the shape of six-membered ring systems based on cyclophosphazenes, cyclophosphazanes, and phosphinoborines. The first group of compounds, the cyclotriphosphazatrienes are planar, or very nearly so;[12] the cyclotriphosphazanes are highly puckered (both boat[77] and chair[78] conformations have been observed); the two phosphinoborines[84,84] investigated both have chair conformations.

An interesting extension for future work would be to determine the conformations of suitable groupings such as phenyl and dimethylamino, when attached to cyclotriphosphazanes, as well as the investigation of the presence or absence of trans-annular bonding and to compare these phenomena with those in cyclotriphosphazatrienes. For cyclotriphosphazanes and trimeric phosphinoborines, the conformations of the ring systems (boat, chair) might well add an additional complexity (axial, equatorial, flagpole positions of substituents) to the conformational preferences (Types I, II, or III) of the substituents relative to the ring segment to which they are attached.

I have mentioned earlier that protropic shifts can give rise to phosphazane structures. We postulated such a protropic shift for the compound $N_3P_3(OPh)_5OH$ (**100**).[85] Our conclusions were based mainly on infrared spectroscopic data.[85] Whilst we assume for this compound a mixed cyclophosphazene-cyclophosphazane structure, Schmulbach and Miller[86] prefer a cyclotriphosphazatriene structure for $N_3P_3Ph_5OH$ (**101**). The oxygen-bridged two-ring assembly $(N_3P_3Ph_5)_2O$ (**102**),[86] derived by pyridine treatment from the hydroxy compound (**101**), has been assigned a symmetric structure. Its ^{31}P nmr spectrum is very symmetric[35] which tends to corroborate this. Obviously, detailed structural investigations on these types of compounds could be rewarding.

SEVEN-MEMBERED RING SYSTEMS

Little is as yet known about this class. One mixed phosphazene-phosphazane system [in a neutral (**103**) and in cationic forms (**104**, **105**)] has been reported by Schmidpeter and Stoll.[87] No diffraction data are as yet available.

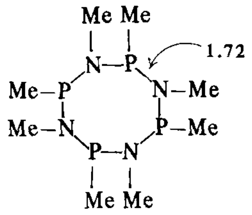


(**104**) (**103**) (**105**)

EIGHT-MEMBERED RING SYSTEMS

Much of what I have said about six-membered ring systems pertains here and need not be repeated. Two authentic samples of P(III) cyclotetraphosphazanes have been prepared by a silazane method, and the crystal structure of one (R = Me) (**106**)[88] determined.

$$RPCl_2 + (MeSi)_2NMe \rightarrow (RPNMe)_4 \ (R = Me, Et)$$



(**106**)

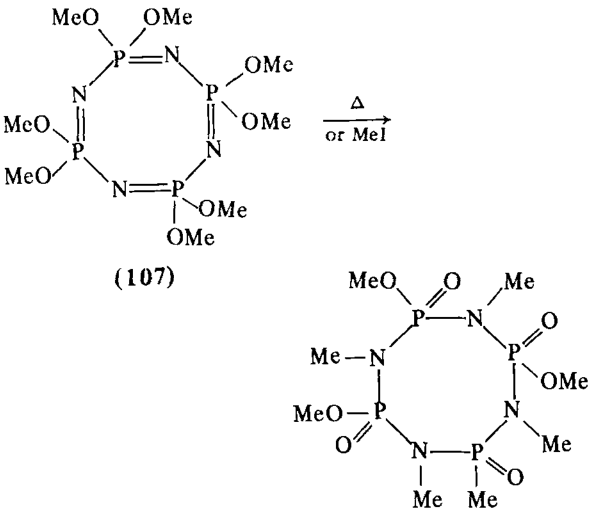
The molecule has a crown conformation, all the P–Me groups occupy equatorial positions, the nitrogen atoms are almost planar, and the P–N bond-lengths of 1.72 Å are [in line with other P(III) phosphazanes] rather longer than those in P(V) phosphazanes.

In general, alkyl group migration, tautomeric shift, or protonation, or metal co-ordination are the preferred routes to either wholly phosphazane or mixed phosphazene-phosphazane structures.

Whilst in the cyclodiphosphazanes, *cis*- and *trans*-isomers have been characterized, this has as yet not been the case for six-membered ring cyclophosphazanes. So far only one isomer of $N_3Me_3P_3O_3(OMe)_3$

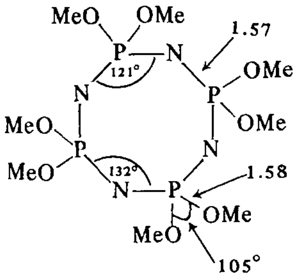
(**96**) has been observed, although Ansell and Bullen[77] have speculated about the possibility of another.

Perhaps one of the best set of examples for a comparative study of cyclophosphazenes and cyclophosphazanes has been provided by the crystallographic work of Bullen and coworkers. The synthesis of the eight-membered ring alkoxyphosphazene, $N_4P_4(OMe)_8$ (**107**),[72] its structure,[89] and its rearrangement to the oxophosphazane, $N_4Me_4P_4O_4(OMe)_4$, has been known for some time.[69–71] Recently two isomers (**108**, **109**) of the latter have been characterized and their structures determined.[90,91]

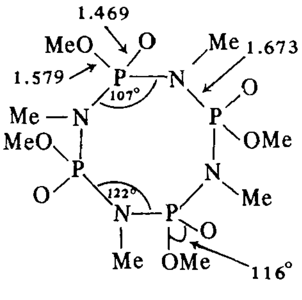


(**107**)

(**108**, **109**)



(**107**)



(**108**)

One phosphazane isomer (**108**),[90] mp 216–218°, has a 2-*trans*-4-*cis*-6-*trans*-8-structure; its ring has a slightly distorted boat conformation. All the phosphoryl groups occupy equatorial positions. The other isomer (**109**)[91], mp 212–214°, has a 2-*cis*-4-*trans*-6-*trans*-8-structure; its ring has a chair conformation.

At this point it is appropriate to mention the structure of the eight-membered ring acid, $N_4H_4P_4O_4(OH)_4$, $2H_2O$ (**110**),[92] and of two of its metal salts, $K_4(N_4H_4P_4O_8)$, $4H_2O$ (**111**)[93] and $Cs_4(N_4H_4P_4O_8)$, $6H_2O$ (**112**).[93] Their-rings have boat, chair, and saddle conformations respectively. Two distinct, but both short, P–O bond distances were found in the acid, leading to the suggestion that it might perhaps be best described as a hydroxonium salt, $(H_3O)_2[N_4H_4P_4O_6(OH)_2]$.[92]

As mentioned afore, eight-membered, and to a lesser extent six-membered rings are to-date the most prolific sources of structural data for phosphazenes and phosphazanes. Some structural details of eight related compounds (six eight-membered, and two six-membered) have been collected in Table I.

Before doing so, however, a few remarks relating to six- and eight-membered ring phosphazenes are pertinent. These will be confined to homogeneously substituted species, $(NPR_2)_n$ i.e., where each phosphorus atom in a given compound carries the same substituents PR_2. Cyclotriphosphazatrienes have planar structures or deviate only slightly from these. On the other hand cyclotetraphosphazatetraenes are generally puckered into a variety of shapes, the sole planar species being the octafluoride, $N_4P_4F_8$ (**113**).[12]

Ring P–N bonds (of both homologues) in a given compound are equal and are usually of the order of 1.57–1.59 Å, the octafluoride (**113**) being again the exception with a value of 1.51 Å.[12] We have seen earlier that a sufficient number of P–F bonds generally shorten P–N bonds relative to those where phosphorus carries other substituents.

Ring bond angles in the substantially planar cyclotriphosphazatrienes are subject to steric constraints. These are largely absent in its higher homologues and in cyclotri- and cyclotetra-phosphazanes, all of which [except $N_4P_4F_8$ (**113**)] are puckered. The situation bears some resemblance to benzene, cyclohexane, cyclooctane, etc. Endo N-P-N and P-N-P angles both straddle 120° in cyclotriphosphazatrienes. By contrast in cyclotetraphosphazatetraenes whilst the endo N-P-N angles have again a value close to 120°, the endo P-N-P angles are larger 130–135° [much larger, 147°, for $N_4P_4F_8$ (**113**)].

We can now consider the structural data of Table I in some detail. Whilst hydrogen atoms were either

TABLE I

Some structural data of six- and eight-membered cyclophosphazenes and cyclophosphazanes

	$N_4P_4(OMe)_8$ (107)	$N_4Me_4P_4O_4(OMe)_4$ 2-*trans*-4-*cis*-6-*trans*-8 (108)	$N_4Me_4P_4O_4(OMe)_4$ 2-*cis*-4-*trans*-6-*trans*-8 (109)	$N_3Me_3P_3O_3(OMe)_3$ (96)	$Na_3(N_3H_3P_3O_6)$, $4H_2O$ (97)	$N_4H_4P_4O_4(OH)_4$, $2H_2O$ (110)	$K_4(N_4H_4P_4O_8)$, $4H_2O$ (111)	$Cs_4(N_4H_4P_4O_8)$, $6H_2O$ (112)
Mean bond lengths (Å)								
P–N	1.57	1.673	1.670	1.663	1.683	1.661	1.673	1.676
P–O		1.469	1.467	1.45	1.495	1.517	1.500	1.498
P–OMe	1.58	1.579	1.572	1.56				
Mean bond angles (°)								
N–P–N	121.0	106.9	108.2	105.2	104.5	107.3	108.1	106.9
P–N–P	132.2	122.5	123.0	121.7	122.7	125.6	131.9	128.9
O–P–O	105.5	115.8	116.0	116.1	118.4	116.1	117.8	117.7
Ring conformation	saddle	slightly distorted boat	chair	twisted boat	chair	boat	chair	saddle

not, or not very accurately, located, nevertheless the observed P–N bond lengths (1.66–1.68 Å) show clearly that the "hydroxy" compounds are firmly of the tautomeric oxophosphazane type. The P–OMe bonds require no comment; the P–O phosphoryl distances are as anticipated much shorter than those of the ester linkage. A significant increase in the phosphoryl bond lengths occurs on passing from the ester ≡P(O)OMe to the acid or salt $\equiv PO_2^-$, because of resonance effects.

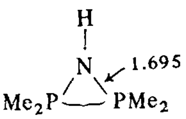
Bond angle effects in the three systems (cyclotriphosphazanes and cyclotetra-phosphazenes and -phosphazanes) where steric constraints are less dominant are in line with expectations based on the Gillespie-Nyholm rules.[94] A change from a phosphazene to a phosphazane structure transfers electron-density (multiply bond character) from ring bonds to exocyclic bonds. Predictably N-P-N bond angles decrease (from ~120° to 105–108°), and O-P-O bond angles increase (from ~105° to 116–118°). Variations in P-N-P bond angles are rationalized less easily; they decrease to a somewhat lesser extent (from ~132° to ~122–126°), and are almost unchanged for the two eight-membered ring metal salts (**111**, **112**)'(129–132°).

Ring shapes vary considerably both in cyclotri- and cyclotetra-phosphazanes indicating that the different ring conformations probably do not differ greatly in energy. The same pertains to (*a*) cyclophosphazenes [K and T forms of $N_4P_4Cl_8$ (**114**);[12] the three crystalline modifications of $N_5P_5F_{10}$ (**115**–**117**),[95] two of which (**115**, **116**) had their structures determined],[95] (*b*) to mixed cyclo-phosphazene-phosphazane structures, $[(NPMe_2)_4H]_2CoCl_4$ (**118**)[96] (two ring conformations in same unit cell), and (*c*) to the $[(Ph_3P)_2N^+]$ cation (linear and bent forms present in same unit cell).[13]

The one example of an eight-membered ring phosphinoborine, $(Me_2PBH_2)_4$, whose structure has been investigated has a saddle conformation.[83]

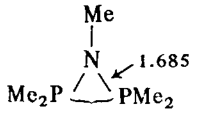
Eight-membered ring compound having mixed phosphazene-phosphazane character due to protonation, methylation, or complexation with a metal have been reported. Whilst interesting effects are observed in ring bonds not directly involved in the above mentioned interactions, I will confine my remarks to the latter. Three derivatives based on $N_4P_4Me_8$ (**119**)[97] (P–N 1.596 Å), will be discussed; only the segments involved are displayed.

The P–N ring bonds involved in the protonation (**120**, **122**) or methylation (**121**) process are all similarly affected (1.67–1.69 Å). The ones adjacent to the coordination site to the copper moiety (**123**) are substantially shorter (1.635 Å), indicating a lesser transfer of electron-density from the ring P-N-P segment.



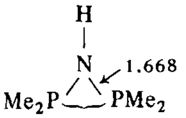
$[(NPMe_2)_4H]_2CoCl_4$

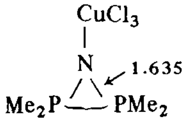
(120)[96]



$(N_4P_4Me_9)[Cr(CO)_5I]$

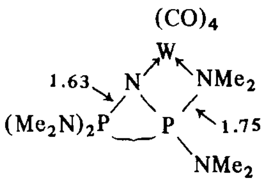
(121)[98]





(122)[99] $[(NPMe_2)_4H(CuCl_3)]$ **(123)**[99]

Similar conclusion can be drawn from $N_4P_4(NMe_2)_8$-$[W(CO)_4]$ (**124**)[100] both types of bonds adjacent to the donation sites to the metal, especially the endocyclic ones, being shorter than analogous ones involving protonated species.



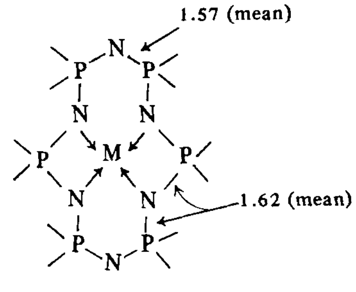
$N_4P_4(NMe_2)_8[W(CO)_4]$

(124)

HIGHER-MEMBERED AND POLYCYCLIC RING SYSTEMS

A diprotonated ten-membered ring compound, $[(NPMe_2)_5H_2](CuCl_4)(H_2O)$, (**125**)[101] gives rise to to the usual phosphazene-phosphazane character with a P–N bond length pattern similar to those in eight-membered ring systems.

Structural data are also available for two interesting metal complexes, $\{[NP(NMe_2)_2]_6CuCl\}$ $(CuCl_2)$ (**126**)[102] and $\{[NP(NMe_2)_2]_6CoCl\}_2(Co_2Cl_6)$, $2CHCl_3$ (**127**),[103] as well as for the twelve-membered ring phosphazene, $N_6P_6(NMe_2)_{12}$ (**128**),[104] from which they are derived. The last mentioned phosphazene has ring P–N bonds of 1.56 Å.[104] The two metal complexes have similar structures, outlined below, with the metal atom five-coordinate (to four nitrogens and one chlorine) and a geometry intermediate between that of a distorted square pyramid and of a distorted trigonal bipyramid.



(M = Cu or Co)

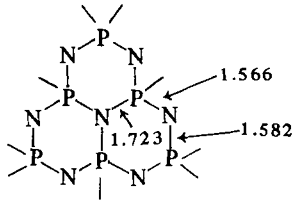
$\{[NP(NMe_2)_2]_6CuCl\}(CuCl_2)$ **(126)**

$\{[NP(NMe_2)]_6CoCl\}_2(Co_2Cl_6)$, $2CHCl_3$ **(127)**

The metal atoms are thus part of four-membered (already encountered in earlier described structures[76,100]) and six-membered ring systems. The P–N bonds adjacent to the nitrogen-metal bonds are ~1.62 Å (again shorter than those of protonated species), the others, although differences occur, fall in the usual phosphazene range 1.53-1.58 Å.[102,103]

These two last examples,[102,103] although derived from a twelve-membered ring precursor[104] give polycyclic structures based on four- and six-membered rings.

The same pertains to the tricycle, $N_7P_6Cl_9$ **(129)**,[105] generically related to $N_6P_6Cl_{12}$ **(130)**.

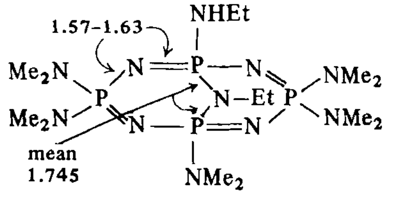


$N_7P_6Cl_9$

(129)

A crystal structure determination[106] shows that the perimeter P–N bonds are of two types, but both have phosphazene character. The central P–N bonds are rather exceptional. Although the central nitrogen atom is essentially trigonal planar its bonds to the three phosphorus atoms surrounding it are long (and weak as displayed by its chemistry[105]). Hence, when steric constraints are likely to be operative, caution must be exercised in too rigidly trying to correlate planarity, hybridization, and bond length.

Finally, very recently, bicyclic compounds have been prepared from cyclotetraphosphazatetraenes.[107,108] During aminolysis reactions of the octachloride, $N_4P_4Cl_8$, bicyclic amino-derivatives, e.g. $N_4P_4R_5(NHEt)(NEt)$ [R = NMe_2 **(131)** or NHEt **(132)**], were isolated, characterized, and the crystal structure of one (R = NMe_2) **(131)** determined.[107,109]



(131)

The bridging nitrogen atom has considerable sp^3-character, its P–N bonds are long (mean ~1.745 Å) and are close to that of a P–N "single" bond, although the lone-pair of electrons on the nitrogen atom is not donated to a proton, etc. Hence steric effects play again an important part. The perimeter P–N bonds have phosphazene character. The bicyclic structure consists in this case of two fused six-membered rings. The chemical shifts of its ^{31}P nuclei[108] are akin to those of related cyclotriphosphazatrienes, but not to those of cyclotetraphosphazatetraenes.[110]

Another tetramer derivative, $N_4P_4F_6(NSO)_2$ **(133)**, loses SO_2 under the influence of pyridine to give a product $N_4P_4F_6(NSN)$ **(134)**, for which a bicyclic structure with a 2,4-fusion has been demonstrated by x-ray crystallography.[111]

SUMMARY, CONCLUSIONS, AND FUTURE VISTAS

Three types (A, B, C) of acyclic monophosphazenes are now known, where the phosphorus atoms are two-, three-, or four- coordinate respectively. Phosphazanes have been classified into four Types (A, B, C, D), where the phosphorus atoms are three-, four-, five-, or six-coordinate respectively. Relationships (sometimes equilibria, sometimes apparently irreversible reactions) between these monophosphazenes and cyclodiphosphazanes have been demonstrated viz.: (i) **(1)** and **(15)** (Type C), (ii) **(5)** and **(12)** (Type B), and (iii) **(6)** and **(8)** (Type A).

Whilst the existence of acyclic monophosphazenes is amply documented, no report of cyclophosphazenes with a ring size of less than five has as yet been fully substantiated. Cyclophosphazenes of ring size six and greater abound. Those based on five-membered rings (e.g. **81**) have a tendency to dimerize to give polycyclic structures with a central cyclodiphosphazane ring (e.g. **75**). Some authentic examples of five-membered ring phosphazenes are, however, known.[63] Present knowledge suggests that five-membered ring systems appear to be the threshold, where stable phosphazenes can exist.

Numerous synthetic routes to acyclic phosphazene structural units[29,112–116] and six- (and higher-) membered cyclophosphazenes[1,117] are available. The same applies to acyclic phosphazanes and four-membered ring cyclodiphosphazanes. Authenticated syntheses of higher ring system phosphazanes based exclusively on phosphorus–nitrogen skeletons are at present scarce.

The ring skeleton of cyclodiphosphazanes is planar or nearly so. The same pertains to cyclotriphosphazatrienes. Cyclotriphosphazanes, cyclotetraphosphazanes, and cyclotetraphosphazatetraenes [except $N_4P_4F_8$ (**113**)] on the other hand are highly puckered.

Substituents on phosphorus, e.g. Ph or NMe_2, adopt in general conformations in cyclodiphosphazanes different to those in cyclophosphazenes.

Acyclic and cyclic P–N skeletons appear to be very flexible as demonstrated by conformational isomerism.

Flexibility of P–N skeletons

$N_4P_4Cl_8$	$N_5P_5F_{10}$	$[N_4P_4Me_8H]_2[CoCl_4]$	$[(Ph_3P)_2N]X$
boat (**114**)	boat (**115**)	tub (**118**)	bent (**25**)
chair (**114**)	puckered (**116**)	saddle (**118**)	linear (**26**)
	another (**117**)		

The bulk of the studies pertaining to this phenomenon (of which undoubtedly many more examples will be found) has been carried out on crystalline species. It seems likely that attention to the conformational behaviour in the liquid state (pure compounds or solutions) would be rewarding.

I will now summarize the parameters affecting the P–N bond lengths (and hence other properties depending on this). We can of course use the formal multiplicity of the bonds, as written in conventional structural formulae; by now, however, it must be apparent that this is not sufficient.

Let us consider the nitrogen atom first. Its coordination number obviously plays a part. In the shortest P–N bonds hitherto recorded PN (**18**) (gaseous) 1.49 Å, and gem.-$N_4P_4F_6Me_2$ (**135**) (solid) 1.47 Å,[118] the nitrogen is one-, and two-coordinate respectively. The nature of the phase, solid or gaseous, on which the structure determination has been carried will obviously play a part. What little data there are available suggests in general a shortening of P–N[119] and other bonds[120] in the solid phase. Some of this can be attributed to compressive crystal forces; changes of shape may also contribute. We badly need more and very accurate data in this field. When nitrogen is four-coordinate due to protonation (**20**), alkylation, or coordination to a metal (**124**), the longest types of P–N bonds are observed (1.77 Å). The same pertains if the nitrogen atom although neutral and three-coordinate retains its pyramidal distribution of valencies (**30, 74, 131**), i.e. the lone-pair of electrons acts as a phantom ligand. In general, for a given coordination number, protonation and methylation, give rise to longer P–N bonds, than interaction with a metal moiety: (i) four-coordinate (**20** *vs.* **124**) (barely significant), (ii) three-coordinate (**120–122** *vs.* **123, 124, 126, 127**). Other parameters are also the nature of the substituents on the nitrogen atom, in particular, if they compete for lone-pair electron delocalization.

P–N bond-lengths

$H_3\overset{+}{N}PO_3^{2-}Na^+$	Ph_2PFNMe	PN	
(**20**)	(**19**)	(**18**)	
1.77	1.64	1.49	
$[(CH_2)_2N]_3P$	$(Me_2N)_3P$	Cl_2PNMe_2	F_2PNMe_2
(**30**)	(**27**)	(**28**)	(**29**)
1.75	1.70	1.69	1.63
$Cl_2P(O)NMe_2$	$(H_2N)_3P(O)$		
(**32**)	(**34**)		
1.67	1.65		
$[PhP(S)NR]_2$	$[ClP(O)NBu^t]_2$	$[ClPNBu^t]_2$	
(**42, 43, 63, 64**)	(**67**)	(**68**)	
1.69	1.66	1.69	
$[MePNMe]_4$	$[Cl_3PNMe]_2$	$[F_3PNMe]_2$	
(**106**)	(**70**)	(**71**)	
1.72	1.77 apic.	1.73 apic.	
	1.64 equ.	1.60 equ.	

$Cl_4P(NMeCClNMe)$	**(76)**	1.88
$N_3P_3Cl_6$	**(136)**	1.58
$N_3P_3F_6$	**(137)**	1.56
$N_4P_4Cl_8$	**(114)**	1.57
$N_4P_4F_8$	**(113)**	1.51
$N_4P_4F_6Me_2$	**(135)**	1.47
$N_4P_4(OMe)_8$	**(107)**	1.57
$N_4Me_4P_4O_4(OMe)_4$	**(108, 109)**	1.67
$N_3Me_3P_3O_3(OMe)_3$	**(96)**	1.66
$[N_4P_4Me_8H]^+$	**(120, 122)**	1.67-1.69
$[N_4P_4Me_8M]^+$	**(123)**	1.63
$N_7P_6Cl_9$	**(129)**	1.57-1.58 (perimeter) 1.72 (bridging)
$N_4P_4(NMe_2)_5(NHEt)(NEt)$	**(131)**	1.57-1.63 (perimeter) 1.75 (bridging)

The same parameters (changes of P–N bond lengths with the coordination number of the phosphorus atom are, however, more complex than for nitrogen) must be considered for the phosphorus atom; there are, however, two further ones: (i) the two valency states [P(III) and P(V)], and (ii) the two different types of bonds (apical and equatorial) when the phosphorus atom has a trigonal bipyramidal distribution of valencies.

Fluorine compared to other substituents, frequently shortens P–N bonds very considerably: (i) (**29** *vs.* **28**), (ii) (**71** *vs.* **70**), (**137** *vs.* **136**); (iv) (**113** *vs.* **114**). Apical bonds are considerably longer than equatorial ones (**70-73**, **125**, **86-88**). Indeed, the former, although the nitrogen atom is often trigonal planar, are of similar lengths to those in four-coordinate phosphorus compounds linked to tetrahedral (or pyramidal) nitrogen. Equatorial P–N bonds in trigonal bipyramidal structures are of similar length to those in phosphazanes Type B, where the phosphorus atom is approximately tetrahedral.

Comparisons of three-coordinate P(III) and four-coordinate P(V) compounds show the latter to have shorter P–N bonds: (i) (**28** *vs.* **32**), (ii) (**68** *vs.* **67**), (iii) (**106** *vs.* **108**, **109**). The same applies to two-coordinate P(III) and three-coordinate P(V) compounds (**23** *vs.* **24**), the latter (**24**) having one of the shortest (1.50 Å) P–N bonds recorded.

The longest P–N bond (1.88 Å), hitherto reported (**76**), can probably be regarded as having considerable N → P donor character. In this structure the phosphorus atom is six-coordinate and approximately octahedral.

What of the future? We can probably generalize from the last example, and suggest that in a series of related compounds P–N bond lengths will decrease: $X_5\overset{\ominus}{P}\text{–}\overset{\oplus}{N}R_3 > X_4P\text{–}NR_{2(\text{apical})} > X_4P\text{–}NR_{2(\text{equatorial})} > X^{\ominus}X_3\overset{\oplus}{P}\text{–}NR_2$. Indeed structural work on coordination compounds, which might well have to be carried out at low temperatures, of nitrogen donors with different types of phosphorus compounds [PX_5, $P(Y)X_3$, PX_3], seems likely to be a fertile field.

In addition to the above, long P–N bonds can be expected from a suitable combination of the following: (i) pyramidal nitrogen, (ii) P(III) compound, (iii) apical bond in P(V) compound, (iii) electron-releasing substituents on phosphorus; and (iv) electron-withdrawing substituents on nitrogen.

As mentioned earlier, shorter P–N bonds can generally be expected on passing from P(III) compounds, $X_2P\text{–}NR_2$, to the related P(V) compounds $X_2(Y)P\text{–}NR_2$; this effect would be especially pronounced for Y = O, and perhaps NR.

Where should we look for the shortest P–N bonds? I suggest we can get some pointers from the above, and from a comparison with sulphur-nitrogen chemistry. Cyclic species of the latter were surveyed by Oskar Glemser in Besancon.[121] In this class of compounds too, the higher valency states of sulphur, together with fluorine substituents give rise to the shortest S–N bond distances. A positive charge, (obtained by the nominal ionization of a group X^-) gives rise to similar effects, e.g. $[N(SCl)_2]^{\oplus}(BCl_4)^{\ominus}$ (**138**) (N–S 1.535 Å). We have noted this already for the cation $[(Ph_3P)_2N]^+$ (**26**) (short P–N bonds, 1.539 Å). Hence in positively charged species (obtained not, however, by protonation, etc. of the nitrogen atom), but by nominal ionisation of a group X^-, one might expect to find short P–N bonds.

The analogy can be pressed further. We have shown the close similarity between P–N–P and P–N–S ring systems.[122] Johan van de Grampel[123] will report on the latter in some detail at this Symposium. The S–N "single" bond distance is essentially the same as the P–N "single" bond distance.[122] Hence we can compare the gaseous species S≡N (**139**) (1.494 Å)[124] with P≡N (**18**) (1.491 Å) (the triple bond shown, is done so with due reservations). [A positive charge

$(NS)^{\bullet}$] (**140**) (1.25 Å)[125] decreases this much further.]

S–N and P–N bond-lengths

$S\equiv N$	$FS\equiv N$	$F_3S\equiv N$
(**139**)	(**141**)	(**142**)
1.494	1.446	1.416

$P\equiv N$	$(F_2P\equiv N)$
(**18**)	(**144**)
1.491	~1.43 (estimated)

An extension of earlier described effects leads one to expect the progressive S–N bond shortening in the three gaseous species, SN (**139**),[124] FSN (**141**) (1.446 Å),[126] and F_3SN (**142**) (1.416 Å).[127] The chloride ClSN (**143**) (1.450 Å),[121] has only a marginally longer S–N bond than the related fluoride (**141**). Other interesting S–N bonds have recently been discussed.[128]

Hence one would expect a P–N bond length shorter than any hitherto observed, for the species X_2PN (X = F, Cl, or other very electronegative groups). Such species might be obtained by halogenation of gaseous PN (**18**), or more likely by the cracking of oligomeric or polymeric $(NPX_2)_n$ (**145**). By extrapolation of the above data I would expect the gaseous F_2PN species (**144**) difluorophosphazyne, to have a P–N bond length of ~1.43 Å.

ACKNOWLEDGEMENT

I am most grateful to my colleagues who allowed me to quote their unpublished results.

REFERENCES

1. R. A. Shaw, B. W. Fitzsimmons and B. C. Smith, *Chem. Rev.* **62**, 247 (1962).
2. E. Niecke and W. Flick, *Angew. Chem. Intern. Ed.* **12**, 585 (1973).
3. E. Niecke and W. Flick, *Angew. Chem. Intern. Ed.* **13**, 134 (1974).
4. O. J. Scherer and N. Kuhn, *Chem. Ber.* **107**, 2123 (1974).
5. E. Niecke and O. J. Scherer, *Nachr. Chem. Techn.* **23**, 395 (1975).
6. D. E. C. Corbridge, *The Structural Chemistry of Phosphorus* (Elsevier Sci. Publ. Co., 1974), p. 272.
7. D. E. C. Corbridge, *The Structural Chemistry of Phosphorus* (Elsevier Sci. Publ. Co., 1974), p. 289.
8. D. W. J. Cruikshank, *Acta Cryst.* **17**, 671 (1964).
9. I. D. Cameron, Ph.D. thesis, University of Glasgow, 1976.
10. S. Pohl and E. Niecke, personal communication.
11. S. Pohl, E. Niecke, and B. Krebs, *Angew. Chem. Intern. Ed.* **14**, 261 (1975).
12. R. A. Shaw, *Pure and Applied Chemistry* **44**, 317 (1975).
13. R. D. Wilson and R. Bau, *J. Amer. Chem. Soc.* **96**, 7601 (1974).
14. F. Mathis, *Phosphorus and Sulphur* **1**, 109 (1976).
15. G. J. Bullen, F. S. Stephens and R. J. Wade, *J. Chem. Soc.(A)* 1804 (1969).
16. J. H. Barlow, S. A. Bone, D. R. Russell, S. Trippett and P. J. Whittle, *J. C. S. Chem. Comm.* 1031 (1976); D. R. Russell, personal communication.
17. H. Bock and W. Wiegräbe, *Chem. Ber.* **99**, 377 (1966).
18. S. Trippett, *J. Chem. Soc.* 4731, (1962).
19. C. D. Flint, E. H. M. Ibrahim, R. A. Shaw, B. C. Smith and C. P. Thakur, *J. Chem. Soc. (A)* 3513 (1971).
20. P. J. Argent, J. D. Healy, R. A. Shaw and M. Woods, unpublished results.
21. R. Jefferson, J. F. Nixon, T. M. Painter, R. Keat and L. Stobbs, *J. C. S. Dalton* 1414 (1973).
22. G. Bulloch and R. Keat, *J. C. S. Dalton* 2010 (1974).
23. M. Green, R. N. Haszeldine and G. S. A. Hopkins, *J. Chem. Soc. (A)* 1766 (1966).
24. I. N. Zhmurova and A. V. Kirsanov, *J. Gen. Chem. USSR* **30**, 3018 (1960).
25. I. N. Zhmurova, A. A. Kisilenko and A. V. Kirsanov, *J. Gen. Chem. USSR* **32**, 2544 (1962).
26. I. N. Zhmurova and B. S. Drach, *J. Gen. Chem. USSR* **34**, 3091 (1964).
27. V. Gutmann, K. Utvary and M. Bermann, *Monatsh. Chem.* **97**, 1745 (1966).
28. A. Schmidpeter, H. Rossknecht and K. Schumann, *Z. Naturforsch.* **25b**, 1182 (1970).
29. R. Keat, M. C. Miller and R. A. Shaw, *J. Chem. Soc. (A)* 1404 (1967) (and references cited therein).
30. R. Appel and M. Halstenburg, *J. Organomet. Chem.* **121**, C47 (1976).
31. E. Niecke, W. Flick and S. Pohl, *Angew. Chem. Intern. Ed.* **15**, 309 (1976).
32. W. Zeiss, *Angew. Chem. Intern. Ed.* **15**, 555 (1976).
33. E. H. M. Ibrahim and R. A. Shaw, *Chem. Comm.* 244 (1968).
34. R. Schmutzler, *Chem. Comm.* 19 (1965).
35. R. Keat, personal communication.
36. R. Keat and D. G. Thompson, *J. C. S. Dalton* (1977), in the press.
37. O. J. Scherer and G. Schnabel, *Chem. Ber.* **109**, 2996 (1976).
38. G. Bulloch, R. Keat and D. G. Thompson, *J. C. S. Dalton* 99 (1977).
39. W. Zeiss and J. Weis, *Z. Naturforsch.* **32b**, 485 (1977).
40. M. B. Peterson and A. J. Wagner, *J. C. S. Dalton* 106 (1973).
41. T. S. Cameron, C. K. Prout and K. D. Howlett, *Acta Cryst.* **B31**, 2333 (1975).
42. G. J. Bullen, J. S. Rutherford and P. A. Tucker, *Acta Cryst.* **B29**, 1439 (1973).
43. G. J. Bullen and P. A. Tucker, *Acta Cryst.* **B29**, 2878 (1973).
44. G. J. Bullen and P. R. Mallinson, *J. C. S. Dalton*, 1143 (1972).
45. H. Nöth and W. Schrägle, *Chem. Ber.* **98**, 352 (1965).
46. R. Keat, L. Manojlović-Muir and K. W. Muir, *Angew. Chem.* **85**, 343 (1973).

47. K. W. Muir and J. F. Nixon, *Chem. Comm.* 1405 (1971).
48. E. Niecke, W. Flick and S. Pohl, *Angew. Chem. Intern. Ed.* **15**, 305, (1976).
49. D. E. C. Corbridge, *The Structural Chemistry of Phosphorus* (Elsevier Sci. Publ. Co., 1974), p. 351.
50. R. A. Shaw, *Z. Naturforsch.* **31b**, 641 (1976).
51. D. E. C. Corbridge, *The Structural Chemistry of Phosphorus* (Elsevier Sci. Publ. Co., 1974), p. 352.
52. T. Demir and R. A. Shaw, unpublished results.
53. T. S. Cameron, K. D. Howlett and C. K. Prout, *Acta Cryst.* **B33**, 119 (1977).
54. M. I. Kabachnik, V. A. Gilyarov, N. A. Tikhonina, A. E Kalinin, V. G. Andrianov, Yu. T. Struchkov and G. I. Timofeeva, *Phosphorus* **5**, 65 (1974).
55. R. Keat, A. L. Porte, D. A. Tong and R. A. Shaw, *J. C. S. Dalton* 1648 (1972).
56. R. K. Harris, J. R. Woplin, R. E. Dunmur, M. Murray, and R. Schmutzler, *Ber. Bunsengesellschaft Phys. Chem.* **76**, 44 (1972).
57. O. Schlak, R. Schmutzler, R. K. Harris and M. Murray, *J. C. S. Chem. Comm.* 23 (1973).
58. M. L. Ziegler and J. Weiss, *Angew. Chem. Intern. Ed.* **8**, 455 (1969).
59. O. Schlack, R. Schmutzler, H. M. Schiebel, M. I. M. Wazeer and R. K. Harris, *J. C. S. Dalton* 2153 (1974).
60. J.-P. Faucher, J.-F. Labarre and R. A. Shaw, *Z. Naturforsch.* **31b**, 677 (1976).
61. J.-P. Faucher and J.-F. Labarre, personal communication.
62. G. Bulloch, R. Keat and D. G. Thompson, *J. C. S. Dalton* 1044 (1977).
63. A. Schmidpeter, T. v. Criegern, J. Gross, J. Luber, J. H. Weinmaier, H. Tautz and W. Zeiss, this Symposium.
64. A. Schmidpeter and T. v. Criegern, personal communication.
65. S. N. Nabi and R. A. Shaw, unpublished results.
66. J. D. Healy, E. H. M. Ibrahim, R. A. Shaw, T. S. Cameron, K. D. Howlett and C. K. Prout, *Phosphorus* **1**, 157 (1971).
67. M. G. Newton, J. E. Collier and R. Wolf, *J. Amer. Chem. Soc.* **96**, 6888 (1974).
68. A. Schmidpeter, D. Schomburg, W. S. Sheldrick and J. H. Weinmaier, *Angew. Chem.* **88**, 851 (1976).
69. B. W. Fitzsimmons and R. A. Shaw, *Proc. Chem. Soc.* 258 (1961).
70. B. W. Fitzsimmons, C. Hewlett and R. A. Shaw, *J. Chem. Soc.* 4459 (1964).
71. B. W. Fitzsimmons, C. Hewlett and R. A. Shaw, *J. Chem. Soc.* 7432 (1965).
72. B. W. Fitzsimmons and R. A. Shaw, *J. Chem. Soc.* 1735 (1964).
73. S. K. Das, R. Keat, R. A. Shaw and B. C. Smith, *J. Chem. Soc. (A)* 1677 (1966).
74. N. V. Mani and A. J. Wagner, *Acta Cryst.* **B27**, 51 (1971).
75. A. Schmidpeter, K. Blanck and F. R. Ahmed, *Angew. Chem. Intern. Ed.* **15**, 488 (1976).
76. F. R. Ahmed, *Acta Cryst.* **B32**, 3078 (1976).
77. G. B. Ansell and G. J. Bullen, *J. Chem. Soc. (A)* 3026 (1968).
78. R. Olthof, T. Migchelsen and A. Vos, *Acta Cryst.* **19**, 596 (1965).
79. G. J. Bullen, P. E. Dann, M. L. Evans, M. B. Hursthouse, R. A. Shaw, K. Wait, M. Woods and H. S. Yu, *Z. Naturforsch.* **31b**, 995 (1976).
80. H. R. Allcock, E. Bissell and E. T. Shawl, *Inorg. Chem.* **12**, 2963 (1973).
81. W. Polder and A. J. Wagner, *Cryst. Struct. Comm.* **5**, 253 (1976).
82. S. J. Rettig and J. Trotter, *Canad. J. Chem.* **51**, 1296 (1973).
83. D. E. C. Corbridge, *The Structural Chemistry of Phosphorus* (Elsevier Sci. Publ. Co., 1974), p. 391.
84. G. J. Bullen and P. R. Mallinson, *J. C. S. Dalton* 1295 (1973).
85. B. W. Fitzsimmons, C. Hewlett, K. Hills and R. A. Shaw, *J. Chem. Soc. (A)* 679 (1967).
86. C. D. Schmulbach and V. R. Miller, *Inorg. Chem.* **5**, 1621 (1966).
87. A. Schmidpeter and K. Stoll, *Phosphorus* **1**, 101 (1971).
88. W. Zeiss, W. Schwarz and H. Hess, *Angew. Chem.* Int. Ed. Eng. **16**, 407 (1977).
89. G. B. Ansell and G. J. Bullen, *J. Chem. Soc. (A)* 2498 (1977).
90. G. J. Bullen, N. L. Paddock and D. J. Patmore, *Acta Cryst.* **B33**, 1367 (1977)
91. G. J. Bullen, personal communication.
92. T. Migchelsen, R. Olthof and A. Vos, *Acta Cryst.* **19**, 603 (1965).
93. B. Berking and D. Mootz, *Acta Cryst.* **B27**, 740 (1971).
94. R. J. Gillespie and R. S. Nyholm, *Quart. Rev. Chem Soc.* **11**, 339 (1957).
95. J. G. Hartsuiker and A. J. Wagner, 2nd (IUPAC) Symposium on Inorganic Phosphorus Compounds, Prague, 1974; J. G. Pauzenga-Hartsuiker, Ph.D. Thesis, University of Groningen, 1975.
96. J. Trotter and S. H. Whitlow, *J. Chem. Soc. (A)* 460 (1970).
97. M. W. Dougill, *J. Chem. Soc.* 5471 (1961).
98. H. P. Calhoun and J. Trotter, *J. C. S. Dalton* 377 (1974)
99. J. Trotter and S. H. Whitlow, *J. C. S. Dalton* 455 (1970).
100. H. P. Calhoun, N. L. Paddock and J. Trotter, *J. C. S. Dalton* 2708 (1973).
101. H. P. Calhoun and J. Trotter, *J. C. S. Dalton* 382 (1974).
102. W. C. Marsh and J. Trotter, *J. Chem. Soc. (A)* 1482 (1971).
103. W. Harrison and J. Trotter, *J. C. S. Dalton* 61 (1973).
104. A. J. Wagner and A. Vos, *Acta Cryst.* **B24**, 1423 (1968).
105. R. T. Oakley and N. L. Paddock, *Can. J. Chem.* **51**, 520 (1973).
106. W. Harrison and J. Trotter, *J. C. S. Dalton* 623 (1972).
107. T. S. Cameron, Kh. Mannan, S. S. Krishnamurthy, A. C. Sau, A. R. Vasudeva Murthy, R. A. Shaw and M. Woods, *J. C. S. Chem. Comm.* 975 (1975).
108. S. S. Krishnamurthy, A. C. Sau, A. R. Vasudeva Murthy, R. A. Shaw, M. Woods and R. Keat, *J. Chem. Research* (1977) (*S*) 70; (*M*) 0860–0884.
109. T. S. Cameron and Kh. Mannan, *Acta Cryst.* **B33**, 443 (1977).
110. R. Keat, R. A. Shaw and M. Woods, *J. C. S. Dalton* 1582 (1976).
111. A. Gieren, B. Dederer, H. W. Roesky and E. Janssen, *Angew. Chem. Intern. Ed.* **15**, 783 (1976).
112. M. Biddlestone and R. A. Shaw, *J. C. S. Dalton* 2740 (1973).
113. M. Biddlestone and R. A. Shaw, *J. C. S. Dalton* 2527 (1975).
114. J. A. K. du Plessis, H. Rose and R. A. Shaw, *Z. Naturforsch.* **31b**, 997 (1976).

115. D. Dahmann, H. Rose and R. A. Shaw, *Z. Naturforsch.* **32b**, 236 (1977).
116. A. Schmidpeter and H. Eiletz, *Phosphorus* **6**, 113 (1976).
117. S. S. Krishnamurthy, R. A. Shaw and M. Woods, *Current Science* **45**, 433 (1976).
118. W. C. Marsh and J. Trotter, *J. Chem. Soc. (A)* 573 (1971).
119. D. E. C. Corbridge, *The Structural Chemistry of Phosphorus* (Elsevier Sci. Publ. Co., 1974), p. 337.
120. D. E. C. Corbridge, *The Structural Chemistry of Phosphorus* (Elsevier Sci. Publ. Co., 1974), p. 276.
121. O. Glemser, *Z. Naturforsch.* **31b**, 610 (1976).
122. J.-P. Faucher, J. C. van de Grampel, J.-F. Labarre, S. N. Nabi, B. de Ruiter and R. A. Shaw, *J. Chem. Research* (1977), (*S*) 112; (*M*) 1257-1294.
123. J. C. van de Grampel, this Symposium.
124. T. Amano, S. Saito, E. Hirota and Y. Morino, *J. Mol. Spectroscopy* **32**, 97 (1969).
125. *Tables of Interatomic Distances and Configurations in Molecules and Ions* (The Chemical Society), Spec. Public. No. 11, 1958.
126. W. H. Kirchhoff and E. B. Wilson, Jr., *J. Amer. Chem. Soc.* **85**, 1726 (1963).
127. W. H. Kirchhoff and E. B. Wilson, Jr., *J. Amer. Chem. Soc.* **84**, 334 (1962).
128. P. Cassoux, R. L. Kuczkowski and R. A. Cresswell, *Inorg. Chem.*, in the press.