Phosphorus–Nitrogen Compounds. Part 50.[1] Further Studies on the Formation of Bicyclic Cyclotetraphosphazatetraene Derivatives

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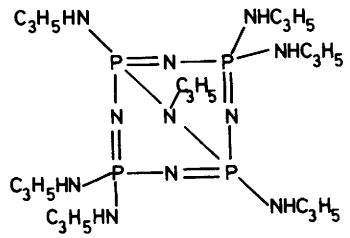
The reactions of hexachloro-2,6-bis(ethylamino)cyclotetraphosphazatetraene, $N_4P_4Cl_6(NHEt)_2$, with pyrrolidine, piperidine, morpholine, diethylamine, or cyclopropylamine give bicyclic $N_4P_4(NRR')_5(NHEt)(NEt)$, as well as monocyclic derivatives $N_4P_4(NRR')_6(NHEt)_2$ (NRR′ = pyrrolidino, piperidino, morpholino, diethylamino, or cyclopropylamino). The reactions of $N_4P_4Cl_8$ with cyclopropylamine give the bicyclic, $N_4P_4(NHC_3H_5)_6(NC_3H_5)$, and monocyclic, $N_4P_4(NHC_3H_5)_8$, products, the former being the first structure of its kind with an α-branched alkyl group at the bridgehead to be isolated. Salient features of the ^1H and ^{31}P n.m.r. spectra of these bicyclic phosphazenes are discussed and related to their structures. Likely reaction mechanisms are considered.

Since the first report of a bicyclic compound based on cyclotetraphosphazatetraene in 1975,[2] several studies devoted to the formation of this class of compounds have appeared.[3–10] These involved the reactions of 2,6-*trans*-bis(primary alkylamino)hexachloro-derivatives $N_4P_4Cl_6(NHR)_2$ with a secondary amine, *viz.* dimethylamine,[3,5] or the reactions of the octachloride $N_4P_4Cl_8$ (**1**) with primary acyclic amines[3,4,8] NH_2R [where undoubtedly $N_4P_4Cl_6(NHR)_2$ is a reaction intermediate], to yield $N_4P_4(NMe_2)_5(NHR)(NR)$ and $N_4P_4(NHR)_6(NR)$, respectively. These bicyclic derivatives were invariably accompanied by larger or smaller amounts of monocyclic products, $N_4P_4(NMe_2)_6(NHR)_2$ and $N_4P_4(NHR)_8$, respectively, sometimes to the apparent exclusion of bicyclic derivatives. Variable amounts of resins were also formed. The reaction variables so far investigated included (*a*) the acyclic alkyl group R,[3–5] and it was reported that α-branching prevented bicyclic compound formation,[5] and (*b*) solvent effects,[5] the order of effectiveness in promoting bridgehead formation being $CHCl_3 > CH_2Cl_2 \gg MeCN \gg Et_2O, CCl_4$. With the last two solvents no bicyclic derivatives were reported.

We now report: (*a*) the first bicyclic derivatives with a cyclic aliphatic amine, *viz.* cyclopropylamine, where branching occurs at the α-carbon, $N_4P_4(NHC_3H_5)_6(NC_3H_5)$ (**2**); (*b*) the first bicyclic derivative where $N_4P_4Cl_6(NHR)_2$ is allowed to react with another primary amine NH_2R', *viz.* $N_4P_4(NHC_3H_5)_5(NHEt)(NEt)$ (**7**); (*c*) the effect of varying the nature of the secondary amine, NHR_2, in its reaction with $N_4P_4Cl_6(NHEt)_2$ (**3**); (*d*) further solvent-effect studies; and (*e*) the effect of a tertiary base, triethylamine. We also discuss the likely reaction mechanisms leading to bicyclic phosphazene formation.

Results and Discussion

Reactions.—The reactions of the octachloride (**1**) in diethyl ether and chloroform with an excess of cyclopropylamine were studied. In the former solvent only the fully aminolysed product, $N_4P_4(NHC_3H_5)_8$ (**4**), was observed. In chloroform, however, this was accompanied by a significant yield (38%) of the bicyclic derivative, $N_4P_4(NHC_3H_5)_6(NC_3H_5)$ (**2**). Earlier studies failed to observe bicyclic phosphazenes if the primary acyclic amine NH_2R was branched at the α-carbon atom [a small amount of $N_4P_4(NHPr^i)_6(NPr^i)$ was recently reported in solution, but not isolated[8]]. It may well be that the relatively small steric demands of the cyclopropyl group allow the bridging reaction to occur. Whether the unusual chemical properties of the cyclopropyl group (behaviour analogous to an unsaturated group, low basicity, low back donation to phosphorus[11]) also contribute is at present not clear. We have noted elsewhere[12] that whilst phenylphosphonothioic diamides, $PhP(S)(NHR)_2$, thermolyse to cyclodiphosphazanes, $[PhP(S)(NR)]_2$, when R is an alkyl group without α-branching, R = cyclopropyl represents the only example of an α-branched alkyl group which behaves in a like manner. All other α-branched alkyl groups investigated give different products involving dealkylation.[13]



(**2**)

The reactions of $N_4P_4Cl_6(NHEt)_2$ (**3**) with an excess of cyclopropylamine, pyrrolidine, piperidine, morpholine, and diethylamine were investigated in different solvents. Detection of the two types of compounds (bicyclic and monocyclic) in the presence of each other is relatively simple using ^{31}P n.m.r. spectroscopy[5] (fully aminolysed bicycles absorb at δ 16—23, the related monocycles at δ 2—11 p.p.m.). This is illustrated in the Figure. A fair yield of bicyclic compound (**2**) was obtained with cyclopropylamine in chloroform. From the reactions in ether or acetonitrile, between $N_4P_4Cl_8$ (**1**) and primary, NH_2R, and secondary amines, NHR_2, only the monocycles $N_4P_4(NHR)_8$ or $N_4P_4(NR_2)_8$ respectively were isolated. With $N_4P_4Cl_6(NHEt)_2$ (**3**) and secondary amines, NHR_2, in ether we observed small quantities (5—10%) of bicyclic derivatives (NR_2 = pyrrolidino or morpholino), these being the first reports of bicyclic derivatives in this solvent. In acetonitrile, monocycle formation is overwhelmingly preferred (95—100%), except with diethylamine where yields are < 10%, the remainder being bicyclic. This may well be connected with the greater ease of replacing all chlorine atoms by bulky amino groups in the bicycle than in the related six- and eight-membered monocycles. Thus $N_4P_4(NEt_2)_5(NHEt)(NEt)$ is prepared under milder conditions than either $N_3P_3(NEt_2)_6$ or $N_4P_4(NEt_2)_8$. The compound $N_4P_4[N(CH_2Ph)_2]_6(NCH_2Ph)$[7] has been isolated, but the maximum replacement by the dibenzylamino group in the monocycles has been confined to $N_3P_3Cl_4[N(CH_2Ph)_2]_2$[14] and $N_4P_4Cl_4[N(CH_2Ph)_2]_4$.[7] To test this steric hypothesis we

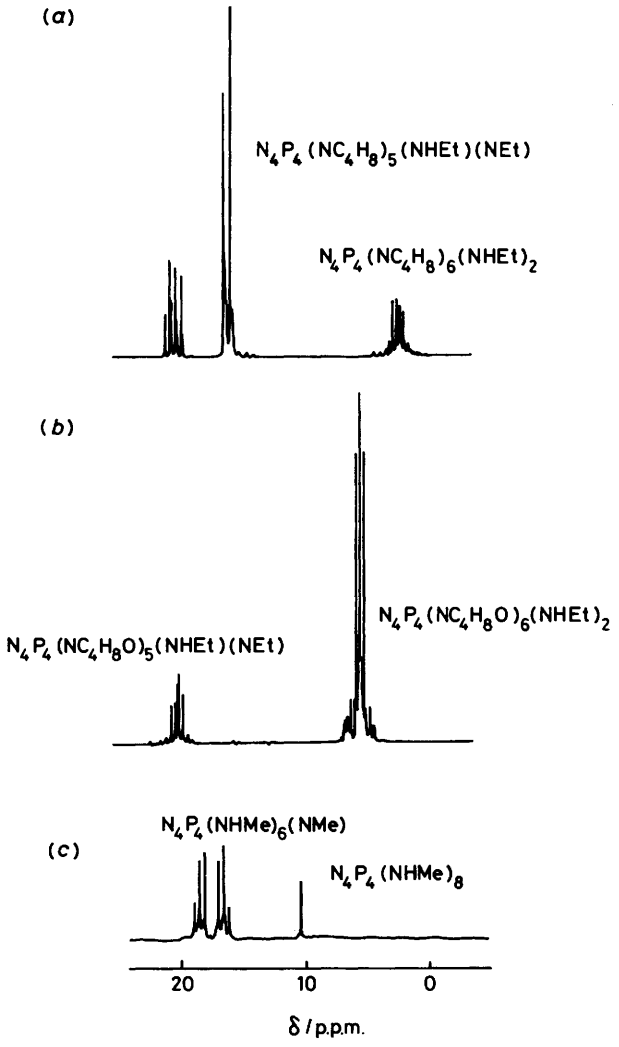


Figure. $^{31}P-\{^1H\}$ N.m.r. spectra of the reaction mixtures (*a*) compound (**3**), pyrrolidine, NEt_3 in $CHCl_3$, (*b*) (**3**), morpholine, NEt_3 in $CHCl_3$, and (*c*) (**1**), NH_2Me in $CHCl_3$

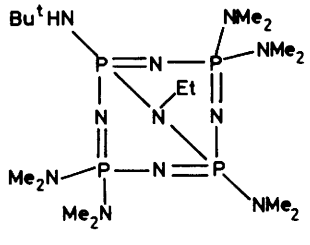
allowed (**3**) to react with dibenzylamine in acetonitrile as well as in $CHCl_3$–NEt_3 (see below) and in both cases the ratio of bicycles to monocycles was 70—85:30—15. Mass spectrometry indicated fully, $N_4P_4[N(CH_2Ph)_2]_5(NHEt)(NEt)$, and partially aminolysed bicycles, $N_4P_4Cl[N(CH_2Ph)_2]_4(NHEt)(NEt)$, but only partially aminolysed monocycles, $N_4P_4Cl_{6-n}[N(CH_2Ph)_2]_n(NHEt)_2$ [n = 2, 3, or 4 (trace)], in keeping with the findings above.

When $N_4P_4Cl_6(NHEt)_2$ (**3**) in chloroform in the presence of triethylamine (8—10 mol equiv.) is treated dropwise with an excess of secondary amine, bicyclic to monocyclic formation is in the ratio of 70—90 to 30—10%. An exception to this is the reaction with morpholine where the ratio is inverted, 15:85. A plausible rationalisation of this is that morpholine has an ether function, and we have noted above that in diethyl ether monocyclic formation is greatly preferred.

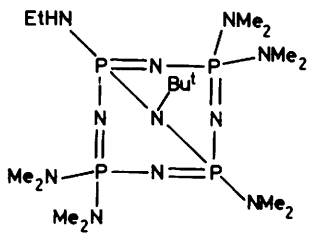
The octachloride $N_4P_4Cl_8$ (**1**) with an excess of primary amine (*viz.* NH_2R, R = Me or Et), but under otherwise similar conditions, gives also bicycles and monocycles in the ratio of 70—80 to 30—20%.

As in the case of the bicyclic compound derived from the reaction of $N_4P_4Cl_6(NHEt)(NHBu^t)$ with dimethylamine, so in that of $N_4P_4Cl_6(NHEt)_2$ (**3**) with cyclopropylamine two possible structures can be visualised, with different NR (R = Et or cyclopropyl) bridging units. It was shown in the former that an NEt group was the bridging unit, *i.e.* that the compound was $N_4P_4(NMe_2)_5(NHBu^t)(NEt)$ (**5**) and not its isomer, $N_4P_4(NMe_2)_5(NHEt)(NBu^t)$ (**6**).[5] In the present study we must consider the isomers $N_4P_4(NHC_3H_5)_5(NHEt)(NEt)$ (**7**) and $N_4P_4(NHC_3H_5)_4(NHEt)_2(NC_3H_5)$ (**8**). The latter, (**8**), would have a symmetric ^{31}P n.m.r. spectrum of the type A_2B_2, the former, (**7**), an asymmetric one of the A_2BC type. An asymmetric spectrum (not analysed) of the A_2BC type was observed [as for $N_4P_4(NR_2)_5(NHEt)(NEt)$ (NR_2 = NMe_2,[3] NEt_2, NC_4H_8, or NC_4H_8O) and for $N_4P_4(NMe_2)_5(NHR)(NR)$ (R = Me, Et, Pr^n, Bu^n, or CH_2Ph)[5]], whilst for the symmetric bicyclic compounds $N_4P_4(NHR)_6(NR)$ (R = Me,[4] Et,[3] Pr^n,[8] or Bu^n[8]), symmetric spectra of the A_2B_2 type are the norm. This clearly indicates that the compound is the asymmetric isomer, (**7**), with an NEt bridging group.

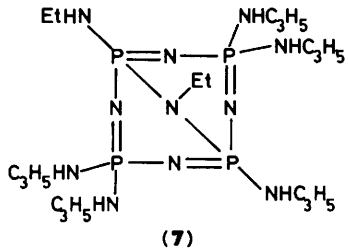
Reaction Mechanisms.—In an earlier paper[5] probable reaction mechanisms were discussed. The present work,



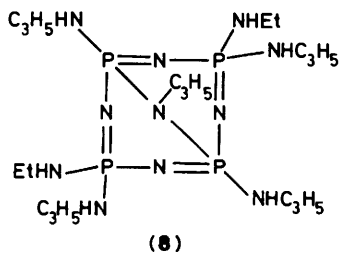
(**5**)



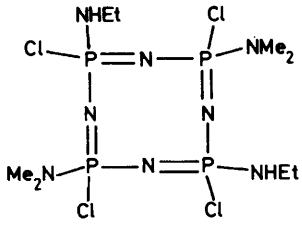
(**6**)



(**7**)



(**8**)



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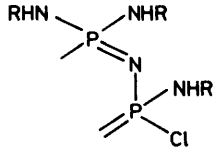

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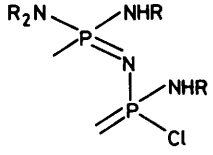


(17)

together with other recent findings,[10] allows us to make more specific interpretations. In addition to $S_N2(P)$ and $S_N1(P)$ mechanisms, we must consider, when $PCl(NH_2)$, PCl(NHR), or similar groups are present, a proton abstraction–chloride elimination ($-HCl$) mode. Evidence has been presented for all three types of mechanism.[15–28]

We note the following experimental observations. Proton abstraction–chloride-ion elimination proceeds more readily in the presence of tertiary base.

Many examples of mono(primary amino) derivatives, $N_3P_3Cl_5(NHR)$ (**9**), have been isolated,[29] as have been non-geminal bis derivatives, $N_3P_3Cl_4(NHR)_2$ (**10**),[29] whilst geminal tris(primary amino) derivatives, $N_3P_3Cl_3(NHR)_3$ (**11**), are rarely formed.[29] (A trace amount of the anilino derivative, $N_3P_3Cl_3(NHPh)_3$, has been reported.[30]) Apparently, compounds (**11**) react too fast by this mechanism and only the geminal tetrakis derivatives, $N_3P_3Cl_2(NHR)_4$ (**12**), are observed.[29] By contrast, numerous examples of geminal tris (secondary amino) derivatives, $N_3P_3Cl_3(NR_2)_3$ (**13**),[29] are known, but except for aziridino derivatives, no geminal tetrakis compounds, $N_3P_3Cl_2(NR_2)_4$ (**14**).[29]

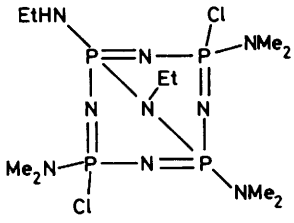
Amino groups on neighbouring phosphorus atoms obviously favour the proton abstraction–chloride elimination mechanism from PCl(NHR) groups. Similar observations have been made in the less well investigated tetramer system. Thus, in the systems $N_4P_4Cl_8/NH_2R \longrightarrow N_4P_4Cl_{8-n}(NHR)_n$, derivatives up to only $n = 4$ (R = Et)[31] or $n = 3$ (R = Bu^t)[32] [all derivatives containing only PCl(NHR) and/or PCl_2 groups] have been isolated. Further aminolysis yields only $N_4P_4(NHR)_8$ and/or resins. By contrast, chloroamino derivatives [$N_4P_4Cl_{8-n}(NR_2)_n$] up to and including $n = 6$ have been characterised with the secondary amine dimethylamine.[33–39]

In a given structural setting, proton abstraction–chloride-ion elimination proceeds much more readily than the normal $S_N1(P)$ mechanism, as in the former the generation of an integral negative charge on the adjacent nitrogen atom facilitates ionisation of the chlorine atom. Thus the moiety PCl(NHR) reacts faster than $PCl(NR_2)$.

It has been shown earlier[5] that $N_4P_4Cl_6(NHR)_2$-2,6 do not form bicyclic derivatives with tertiary base, in keeping with the above observation that neighbouring phosphorus atoms require amino substituents for hydrogen chloride elimination to become facile. As geminal $P(NHR)_2$ groups have not been observed in earlier studies in partially aminolysed tetramer derivatives, $N_4P_4Cl_{8-n}(NHR)_n$,[31,32] further aminolysis must be proceeding by an $S_N2(P)$ mechanism at P(4) and P(8), to give a non-geminal 2,4,6,8-tetra-amino derivative. An example of such, $N_4P_4Cl_4(NHEt)_2(NMe_2)_2$ (**15**), has recently been isolated and characterised.[10] This too will not form a bicyclic derivative with tertiary base.[10] It requires the replacement of one further chlorine atom before a *trans*-annular reaction can occur.[10]

As non-geminal ethylamino derivatives $N_3P_3Cl_4(NHEt)_2$,[40] $N_4P_4Cl_6(NHEt)_2$ (**3**),[31] and $N_4P_4Cl_4(NHEt)_4$[31] can all be isolated, it apparently requires moieties such as (**16**) or (**17**) to trigger a proton abstraction–chloride elimination mechanism. This seems to be feasible in the tetramer system discussed above with the replacement of the fifth chlorine atom by an aliphatic amino residue. At this stage, a proton abstraction–chloride-ion elimination mechanism is likely to operate and, depending on the concentration of the attacking amine, the nature and disposition of the primary amino groups [at least two in a 2,6 relationship; $N_4P_4Cl_7(NHEt)$ does not give a bicyclic derivative with dimethylamine[5]], and/or the nature of the solvent, either *trans*-annular attack to give a bicyclic derivative or a 2,2,4,6,8-monocyclic derivative will result.

Our mechanistic proposal differs from the one recently put forward by Narayanaswamy *et al.*[10] who suggested structure (**18**) for an oil of composition $N_4P_4Cl_2(NMe_2)_3(NHEt)(NEt)$. No evidence for this structure was presented.[10] Compound (**18**)



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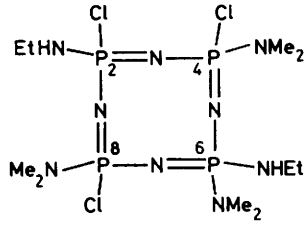
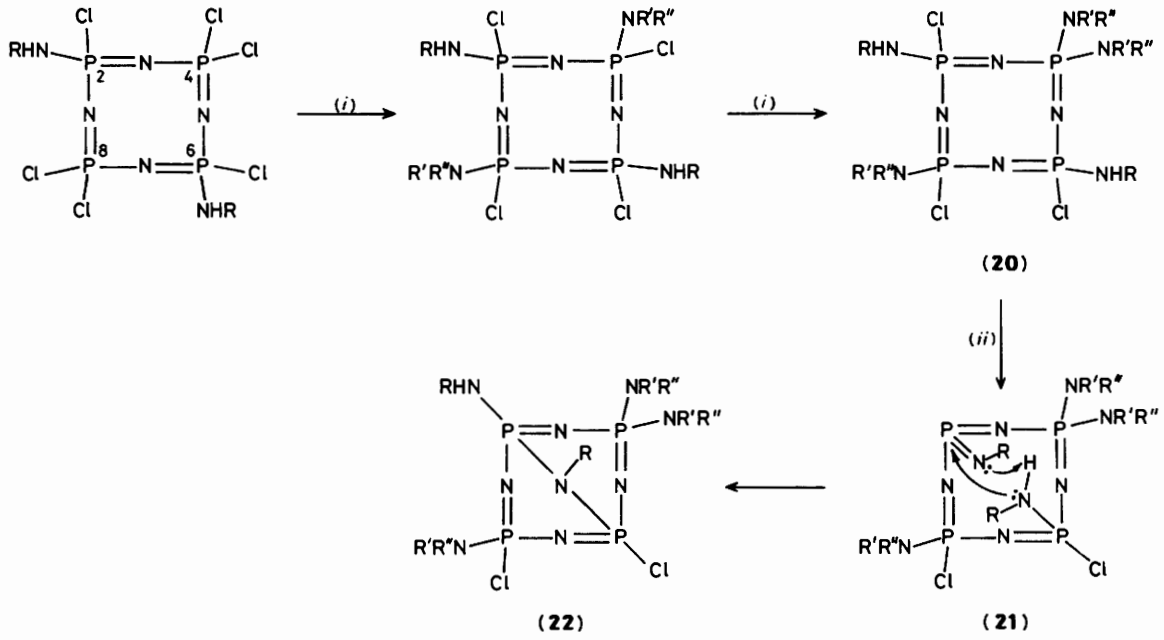


(19)

implies a precursor (**19**). We prefer isomeric structures, (**20**) for (**19**) and (**22**) for (**18**), as shown in Scheme 1 (R = Et, R′ = R″ = Me; in general R, R′, and R″ are alkyl). Our reasons for this preference are as follows: it has been shown[10] that the monocyclic precursor, (**15**), does not undergo a *trans*-annular reaction. The introduction of an additional amino group in (**19**) at P(6) is unlikely to alter drastically the electronic environment at the far-phosphorus atom, P(2), so as to allow either an $S_N1(P)$ or a proton abstraction–chloride elimination ($-H^+/-Cl^-$) mechanism. Additionally, neither of the substituent nitrogen atoms (NHEt, NMe_2) at P(6) is likely to be a strong nucleophile. We have seen, however, that moieties like (**16**) or (**17**) trigger a $-H^+/-Cl^-$ mechanistic process, and hence the pathway (**20**) ⟶ (**21**) ⟶ (**22**). The bicycle (**22**) can now react further either by $S_N2(P)$ or $S_N1(P)$ mechanisms, with probably the latter prevailing in the final stages of chlorine replacement. Compound (**19**), if it does occur, would either lead to monocycles, if further nucleophilic attack occurs at P(4) or P(8), or bicycles if it did at P(2).

The above pertains if NR′R″ is a secondary amino residue. If NR′R″ is a primary amino group, then further possibilities for the hydrogen chloride elimination mechanisms are feasible; bridge formation may result at 4,8 instead of 2,6. The very facile nature of the hydrogen chloride elimination mechanisms at advanced stages of aminolysis of tetramer derivatives would give rise only to fully aminolysed bicyclic, monocyclic, or resinous products in keeping with experimental observations.[3,4,30,31] This contrasts with the findings when $N_4P_4Cl_6(NHR)_2$ is allowed to react with secondary amines.[10]

We thus see the need for two primary alkylamino (or NH_2) groups in the 2,6 (and/or 4,8) positions for bridge formation. The geometric relationship (*cis* or *trans*) is immaterial as proton abstraction–chloride-ion elimination will give rise to a reactive species with a three-co-ordinate planar phosphorus atom,

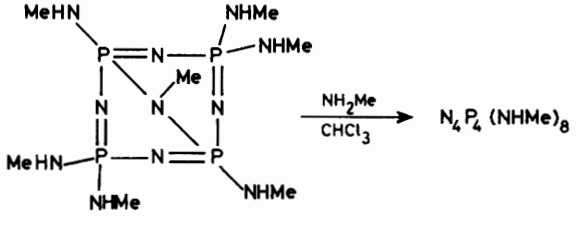


Scheme 1. (*i*) NHR′R″, $S_N2(P)$; (*ii*) $-H^+/-Cl^-$

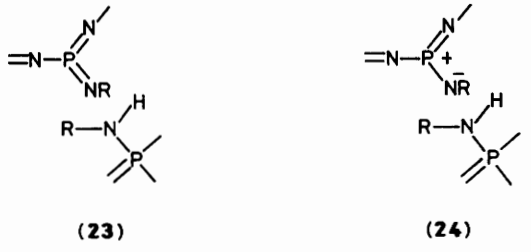
capable of attacking either side of the opposite phosphorus atom carrying an NHR group.

Reactivity.—We observed that whilst the monocyclic derivatives described in this paper appear to be almost indefinitely stable (both as solids and in solution), the bicycles exhibited instability to varying degrees in solution. This instability was more pronounced in polar solvents (*e.g.* $CHCl_3$, MeCN) than in non-polar ones (*e.g.* light petroleum). These bicyclic structures have five nitrogen sites with considerable electron density. These are the four phosphazene nitrogen atoms and the bridgehead nitrogen atom, which has a pronounced pyramidal character and long P–N lengths.[2,41–44] It seems probable to us that the junction phosphorus atoms, P(2) and P(6), are the most electrophilic sites in these molecules, as the bridgehead nitrogen shows little tendency for back donation of its lone pair of electrons to these phosphorus atoms. We think it possible that the decomposition observed in solution is of a self-quaternisation kind. As this would involve charge separation, the greater stability in non-polar solvents would be explicable.

As we suspected the junction phosphorus atoms to be more electrophilic than is usual in fully aminolysed cyclophosphazenes, we heated a mixture of predominantly $N_4P_4(NHMe)_6$-(NMe) with traces of $N_4P_4(NHMe)_8$ and an excess of NH_2Me in chloroform. Examination of the resultant solution by ^{31}P n.m.r. spectroscopy showed the complete disappearance of the bicycle and the only signal observed was due to the monocycle, which was isolated from the solution (Scheme 2). The postulated intermediate (**21**), containing a three-co-ordinate



Scheme 2.



(**23**) (**24**)

trigonal planar phosphorus(v) atom, helps to rationalise our findings on solvent effects. The moieties participating in bridge formation can be written in two resonance forms (**23**) and (**24**). Clearly, sterically not demanding donor molecules such as ether, morpholine, and acetonitrile can solvate the phosphorus atom in (**24**) and thus reduce its electrophilic reactivity towards the weaker nucleophile P–NHR, and hence *trans*-annular reaction, whilst stronger nucleophiles, *e.g.* amines, can still react at this centre.

Chloroform, on the other hand, will increase the electrophilic reactivity of the three-co-ordinate phosphorus atom by hydrogen bonding with –NR. Triethylamine can act in two ways. The first is as a proton abstractor, and hence this role will facilitate *trans*-annular reaction; the second one is as a lone-pair donor, which will deactivate the electrophilic phosphorus site in canonical form (**24**). Naturally it is a sterically more demanding molecule than ether, morpholine, or acetonitrile. To investigate these effects, we allowed $N_4P_4Cl_6(NHEt)_2$ (**3**) to react with pyrrolidine using triethylamine as the solvent. Yields of the monocycle were >95% indicating that, under those conditions, triethylamine acted as an inhibitor to *trans*-annular bonding.

We conclude that moderate amounts of proton-abstracting molecules, *e.g.* NEt_3, favour bicycle formation, whilst donor molecules inhibit this process and thus allow monocycle formation to proceed unhindered by the competitive process. Where the reagent is sterically very demanding, *e.g.* $NHEt_2$, $NH(CH_2Ph)_2$, this will affect nucleophilic attack on phosphorus more than proton abstraction and under those circumstances even in acetonitrile in the absence of triethylamine bicycle formation is favoured.

Table. Selected structural parameters and ^{1}H n.m.r. chemical shifts[a] of cyclophosphazanes and bridgeheads of bicyclic phosphazenes

Compound	P–N bond length/Å	Sum of bond angles around N atom/°	^{1}H Chemical shift of NCH_3
$N_4Me_4P_4O_4(OMe)_4$			
Isomer 1	1.670[b]	359.4	3.06[46]
Isomer 2	1.673[c]	358.7	3.00[46]
$N_3Me_3P_3O_3(OMe)_3$	1.663[d]	359.7	2.91(2)[46] 3.14(1)
$N_4P_4(NHMe)_6(NMe)$	1.716[42]	337.5	2.62[4]
$N_4P_4(NMe_2)_5(NHMe)(NMe)$	1.706—1.725[43]	337.5	2.49[5]
			NCH_2CH_3
$N_4P_4(NMe_2)_5(NHEt)(NEt)$	1.745[41] 1.717[44]	336.8 340.5	2.87[3,5]
$N_4P_4(NC_4H_8)_5(NHEt)(NEt)$			2.94
$N_4P_4(NC_4H_8O)_5(NHEt)(NEt)$			2.84
$N_3Et_3P_3O_3(OEt)_3$			3.56(2)[46] 3.46(1)

[a] In $CDCl_3$ solution, $SiMe_4$ as internal standard. [b] G. J. Bullen, S. J. Williams, N. L. Paddock, and D. J. Patmore, *Acta Crystallogr., Sect. B*, 1981, **37**, 607. [c] G. J. Bullen, N. L. Paddock, and D. J. Patmore, *Acta Crystallogr., Sect. B*, 1977, **33**, 1367. [d] G. B. Ansell and G. J. Bullen, *J. Chem. Soc. A*, 1968, 3026.

Structures.—In the Table the chemical shifts of the bridging NMe and NEt groups in three bicyclic structures studied by *X*-ray crystallography are compared with those for similar monocyclic structures containing the P^V–NR–P^V (R = Me or Et) moiety. For many of these crystallographic data are available and these are also compared.

The structural features are mirrored in the chemical shifts of the N–CH_3 and N–CH_2–CH_3 protons. Those of the bicyclic bridging units are substantially more shielded (N–CH_3, δ 2.49—2.62; N–CH_2–CH_3, 2.84—2.94) than those of the cyclophosphazanes (N–CH_3, δ 2.91—3.14; N–CH_2–CH_3, 3.46—3.56). *X*-Ray crystallographic and ^{1}H n.m.r. data thus both demonstrate an unusually small amount of back donation from nitrogen to phosphorus in the bridging units compared to that observed in related monocyclic P^V–NR–P^V structures.

Of the new bicyclic compounds reported here, we have been able to analyse the spectra of $N_4P_4(NHC_3H_5)_6(NC_3H_5)$ and $N_4P_4(NC_4H_8)_5(NHEt)(NEt)$. For the former, δ[P(4)/P(8)] 18.2, δ[P(2)/P(6)] 14.9 p.p.m., and ^2J(PP) 39.7 Hz. For the latter, δ[P(4)/P(8)] 14.7, δ[P(2)(PNC$_4$H$_8$)] 13.9, δ[P(6)-(PNHEt)] 18.9 p.p.m., ^2J[P(2)P(4)] 50.0, ^2J[P(4)P(6)] 38.0, and ^2J[P(2)P(6)] 35.0 Hz. The compound, $N_4P_4R_5(NHEt)$-(NEt) gave complex spectra centred at *ca.* 14 (R = NHC_3H_5), 20 (R = NC_5H_{10}), 19 (R = NC_4H_8O), and 19 p.p.m. (R = NEt_2) which were not analysed.

Where the (often very complex) spin system of the bicyclic compounds has been analysed and two-bond P–N–P spin–spin coupling constants obtained, those across the bridge are always substantially less than the remaining ones.[3—5,8,9] Thus P–NR–P coupling constants in these compounds are 50—75% of the related P–N–P ones. In oxocyclotriphosphazadienes[45] this ratio is 35—55%. In the rather less well documented rearranged methoxycyclophosphazenes[46] it is *ca.* 65%.

We have reported elsewhere[47,48] that ^3J(PNCC) values are dependent not only on the dihedral angles of the compounds in question, but also on other factors such as the P–N bond length and the state of hybridisation of the nitrogen atom. In these compounds, lengthening of the P–N bonds and changing the hybridisation of the nitrogen atoms from trigonal planar towards pyramidal cause a decrease in the three-bond coupling constants.

From the above data, we suggest that two-bond, *e.g.* ^2J(PNP), three-bond, *e.g.* ^3J(PNCC),[47,48] and four-bond spin–spin coupling constants, *e.g.* ^4J(PNPNP),[49,50] are all reduced by the above-mentioned factors.

Experimental

Chemicals and Spectroscopic Techniques.—Methylamine (97.8%), dimethylamine (99%), triethylamine (99.5%), t-butylamine (98%), acetonitrile (97%), and chloroform were obtained from B.D.H. Chemical Co., diethylamine (99.5%), pyrrolidine (99%), and piperidine (99%) from Fluka Ltd., ethylamine (anhydrous, 99%), morpholine (99%), and dibenzylamine (98%) from Aldrich Chem. Co. Chloroform was passed through a column of silica gel to remove ethanol prior to use.

Proton n.m.r. spectra were obtained in $CDCl_3$ solution from a JEOL FX-200 spectrometer ($SiMe_4$ as internal standard), ^{31}P n.m.r. spectra (in $CDCl_3$ solution, 85% H_3PO_4 as external standard) on JEOL FX-60 (24.15 MHz), Varian XL-200 (80.984 MHz), and Bruker WH-400 (162.0 MHz) spectrometers. Mass spectra of pure compounds were obtained from a VG 7070 mass spectrometer with a Finnigan INCOS data system, and of the high-molecular-weight reaction mixture from a VG-Analytical ZAB-IF double-focusing mass spectrometer [electron-impact mode, 70 eV (1.12×10^{-17} J); source temperature 240 °C]. Microanalyses were carried out by the microanalytical service of University College, London. The synthesis and characterization of 2-*trans*-6-$N_4P_4Cl_6(NHEt)_2$ (**3**) were reported elsewhere.[31]

Reactions of Hexachloro-2-trans-6-*bis(ethylamino)cyclotetraphosphazatetraene*, (**3**).—(*a*) *With an excess of pyrrolidine in chloroform.* Triethylamine (7.70 g, 76.1 mmol) was added to a stirred solution of compound (**3**) (3.20 g, 6.4 mmol) in chloroform (250 cm^3). The flask was placed in an ice-bath for 15 min. Then pyrrolidine (13.66 g, 19.2 mmol) in chloroform (75 cm^3) was added dropwise over half an hour. The mixture was boiled under reflux for 12 h, filtered, and the solvent removed. The ^{31}P n.m.r. spectrum of the mixture consisted of a symmetrical pattern (A_2B_2) at δ 1—4 and an asymmetric one (A_2BC or A_2MX) at δ 14—20. These signals arise from the monocyclic $N_4P_4(NC_4H_8)_6(NHEt)_2$ and bicyclic phosphazenes $N_4P_4(NC_4H_8)_5(NHEt)(NEt)$ in the ratio 25:75. The residue was dissolved in benzene, treated with a excess of triethylamine (12 cm^3), boiled under reflux (2 h), filtered, and the solvent removed. The residue was subjected to column chromatography [silica gel (100 g)] using tetrahydrofuran–CH_2Cl_2 (1:1) as eluant to remove salts and coloured products. The resulting solid was dissolved in boiling light petroleum (b.p. 40—60 °C) and from this was crystallised 2,6-*epimino*-9-*ethyl*-6-*ethylamino*-2,4,4,8,8-*pentakis(pyrrolidino)cyclotetraphos-*

phazatetraene, m.p. 190 °C, yield 2.29 g (58%) (Found: C, 46.7; H, 8.4; N, 24.9%; M^+ 617. $C_{24}H_{51}N_{11}P_4$ requires C, 46.7; H, 8.3; N, 24.9%; *M* 617). The solvent was then removed and the residue was dissolved in boiling acetonitrile and set aside for crystallisation of 2,6-*bis*(*ethylamino*)-2,4,4,6,8,8-*hexakis*(*pyrrolidino*)*cyclotetraphosphazatetraene*, m.p. 123.8 °C, yield 0.62 g (14%) (Found: C, 48.7; H, 8.8; N, 24.3%; M^+ 688. $C_{28}H_{60}N_{12}P_4$ requires C, 48.8; H, 8.8; N, 24.4%; *M* 688).

(*b*) *With an excess of pyrrolidine in acetonitrile.* Compound (**3**) (3.20 g, 6.4 mmol) was dissolved in acetonitrile (200 cm^3) and cooled in an ice-bath, then pyrrolidine (13.66 g, 19.2 mmol) dissolved in chloroform (75 cm^3) was added dropwise (0.5 h). The mixture was boiled under reflux (12 h), filtered, and the solvent removed. The residue was dissolved in benzene and an excess of triethylamine (12 cm^3) added. It was then boiled under reflux for 2 h, filtered, and subjected to column chromatography (silica gel, 75 g) using tetrahydrofuran–CH_2Cl_2 (1:1) as eluant. 2,6-*Bis*(*ethylamino*)-2,4,4,6,8,8-*hexakis*(*pyrrolidino*)*cyclotetraphosphazatetraene* was obtained in 66% yield. It was crystallised from acetonitrile, m.p. 123.8 °C (Found: C, 48.7; H, 8.8; N, 24.3%; M^+ 688. $C_{28}H_{60}N_{12}P_4$ requires C, 48.8; H, 8.8; N, 24.4%; *M* 688).

(*c*) *With an excess of pyrrolidine using triethylamine as solvent.* Compound (**3**) (0.60 g, 1.2 mmol) was dissolved in triethylamine (10 cm^3) and pyrrolidine (3.40 g, 4.80 mmol) was added. The mixture was boiled under reflux (12 h). The excess of amines was removed, and the ^{31}P n.m.r. spectrum of the residue was recorded in $CDCl_3$. The ratio of monocycle:bicycle was 95:5.

(*d*) Diethylamine (15.0 g, 205 mmol), (**3**) (3.20 g, 6.4 mmol) in chloroform (250 cm^3) and triethylamine (10.4 g, 102 mmol) were allowed to react and worked-up as in (*a*). The ^{31}P n.m.r. spectrum of the product showed it to consist of bicycle (90%, δ 16—20 p.p.m.) and monocycle (10%, δ 2—5 p.p.m.). An oil was obtained, which solidified on washing with acetonitrile. It failed to crystallise from light petroleum (b.p. 40—60 °C), benzene, ether, methylene chloride, acetonitrile, or a mixture of the last two. 2,4,4,8,8-*Pentakis*(*diethylamino*)-2,6-*epimino*-9-*ethyl*-6-*ethylaminocyclotetraphosphazatetraene*, m.p. 79.2 °C, yield 1.48 g (37%) (Found: C, 45.8; H, 9.8; N, 24.2%; M^+ 627. $C_{24}H_{61}N_{11}P_4$ requires C, 46.0; H, 9.7; N, 24.6%; *M* 627). The ^{31}P n.m.r. spectrum in $CDCl_3$ changed with time. The solid, however, appeared to be stable. The monocycle $N_4P_4(NEt_2)_6(NHEt)_2$ was not isolated from the above or from a reaction in acetonitrile, where again the ratio of yields of bicycle to monocycle was 90:10.

(*e*) Piperidine (21.8 g, 256 mmol), (**3**) (3.2 g, 6.4 mmol) in chloroform and triethylamine (10.4 g, 102 mmol) were allowed to react and worked-up as in (*a*). The ratio of yields of bicycle to monocycle was 70:30. 2,6-*Bis*(*ethylamino*)-2,4,4,6,8,8-*hexakis*(*piperidino*)*cyclotetraphosphazatetraene* crystallised from hexane and was recrystallised from acetonitrile, m.p. 176.6 °C, yield 1.11 g (23%) (Found: C, 53.0; H, 9.6; N, 21.7%; M^+ 772. $C_{34}H_{72}N_{12}P_4$ requires C, 52.9; H, 9.4; N, 21.8%; *M* 772). This compound was also prepared in acetonitrile [procedure as in (*b*)] in 72% isolated yield. The bicycle was obtained as an oil, which became coloured on attempts to crystallise it from acetonitrile, or a mixture of light petroleum (b.p. 40—60 °C) and methylene chloride.

(*f*) Morpholine (20.0 g, 233 mmol), (**3**) (3.2 g, 6.4 mmol) in chloroform and triethylamine (10.4 g, 102 mmol) were allowed to react and worked-up as in (*a*). Relative yields of bicycle to monocycle were 87:13. 2,6-*Bis*(*ethylamino*)-2,4,4,6,8,8-*hexakis*(*morpholino*)*cyclotetraphosphazatetraene* crystallised from benzene and was recrystallised from acetonitrile, m.p. 230—295 °C (decomp.), yield 3.1 g (62%) (Found: C, 42.6; H, 7.8; N, 21.2%; M^+ 784. $C_{28}H_{60}N_{12}O_6P_4$ requires C, 42.9; H, 7.7; N, 21.2%; *M* 784). The bicyclic compound failed to crystallise from ether, methylene chloride, or light petroleum (b.p. 40—60 °C). It was purified by preparative t.l.c. on fluorescent silica gel using benzene–ethyl acetate (7:1) as eluant. Two bands were observed, scraped off, and extracted on a Soxhlet apparatus. The fast-moving one was the above monocycle, the slow one was 2,6-*epimino*-9-*ethyl*-6-*ethylamino*-2,4,4,8,8-*pentakis*(*morpholino*)*cyclotetraphosphazatetraene*, m.p. 152 °C, from benzene–ethanol (3:1), yield 10% (Found: C, 41.6; H, 7.4; N, 21.8; P, 18.0. $C_{24}H_{51}N_{11}O_5P_4$ requires C, 41.3; H, 7.3; N, 22.1; P, 17.8%).

(*g*) Compound (**3**) (3.2 g, 64 mmol) and triethylamine (10.4 g, 102 mmol) in chloroform (250 cm^3) were cooled to *ca.* −70 °C. An excess of dimethylamine was passed through the solution for 2 h and then the temperature slowly raised to ambient. The mixture was then boiled under reflux (5 h) using a solid carbon dioxide condenser at *ca.* −70 °C. The separation procedure was similar to that in (*a*). The bicyclic compound was crystallised from light petroleum (b.p. 40—60 °C), m.p. 123.5 °C (lit.,[3] 124 °C), yield 2.27 g (73%) (Found: M^+ 487. Calc. for $C_{14}H_{41}N_{11}P_4$: *M* 487). The monocycle crystallised from acetonitrile, m.p. 143 °C (lit.,[3] 139—140 °C), yield 0.53 g (16%) (Found: M^+ 532. Calc. for $C_{16}H_{48}N_{12}P_4$: *M* 532). This compound was also prepared in ether and isolated as in (*b*). Isolated yield 71%.

(*h*) Freshly distilled anhydrous cyclopropylamine (1.8 g, 31.2 mmol) in alcohol-free chloroform (15 cm^3) was cooled to 0 °C and added dropwise to a stirred solution of compound (**3**) (3 g, 6.24 mmol) and triethylamine (6.9 g, 68.5 mmol) in chloroform (150 cm^3) cooled to *ca.* −5 °C. The reaction mixture was stirred (9 h), and then allowed to attain room temperature. After removal of amine hydrochlorides and of solvent, the residual oil was digested with hot benzene and filtered through activated carbon. The products were column chromatographed [benzene–ethyl acetate (7:1)] and the first 100 cm^3 were subjected to preparative-scale t.l.c. [*cf.* (*f*)]. The fast-moving band was 2,4,4,6,8,8-*hexakis*(*cyclopropylamino*)-2,6-*bis*(*ethylamino*)*cyclotetraphosphazatetraene*, m.p. 130 °C [from benzene–ethanol (3:1)], yield 0.3 g (14%) (Found: C, 43.4; H, 7.8; N, 27.4; P, 20.1. $C_{22}H_{48}N_{11}P_4$ requires C, 43.7; H, 7.9; N, 27.8; P, 20.5%). The slow-moving band gave 2,4,4,8,8-*pentakis*(*cyclopropylamino*)-2,6-*epimino*-9-*ethyl*-6-*ethylaminocyclotetraphosphazatetraene*, m.p. 147 °C, yield 1.9 g (53%) (Found: C, 41.0; H, 7.5; N, 28.0; P, 22.2. $C_{19}H_{48}N_{11}P_4$ requires C, 41.7; H, 7.5; N, 28.2; P, 22.7%). In diethyl ether the monocycle was obtained in 67% isolated yield.

Reactions of Octachlorocyclotetraphosphazatetraene, (**1**).—(*i*) *With an excess of ethylamine in chloroform.* Compound (**1**) (4.64 g, 10 mmol), triethylamine (10.4 g, 102 mmol), and ethylamine (14.4 g, 640 mmol) in chloroform were allowed to react as in (*a*). After column chromatography [*cf.* (*a*)], the bicyclic compound $N_4P_4(NHEt)_6(NEt)$ was extracted with hot n-hexane and crystallised from benzene, m.p. 193.6 °C (lit.,[3] 184—185 °C), yield 2.84 g (58%) (Found: M^+ 487. Calc. for $C_{14}H_{41}N_{11}P_4$: *M* 487). The monocycle $N_4P_4(NHEt)_8$ was crystallised from a benzene–methylene chloride mixture, m.p. 121.5 °C (lit.,[51] 116, 122 °C), yield 0.98 g (18%) (Found: M^+ 532. Calc. for $C_{16}H_{48}N_{12}P_4$: *M* 532). This compound was also isolated from a reaction in acetonitrile [as in (*b*)] in 62% yield.

(*j*) *With an excess of methylamine in chloroform.* Compound (**1**) (4.64 g, 10 mmol) and triethylamine (18.3 g, 182 mmol) were allowed to react in chloroform with an excess of methylamine by procedure (*g*). The ^{31}P n.m.r. spectrum of the mixture consisted of an intense singlet at δ 10.1 p.p.m. (30%) from the monocycle $N_4P_4(NHMe)_8$ and a group of symmetrical signals at δ 16—19 p.p.m. (70%) from the bicycle $N_4P_4(NHMe)_6(NMe)$. The monocycle was crystallised from chloroform, m.p. 203 °C (lit.,[51] 206 °C), yield 0.84 g (20%) (Found: M^+ 420. Calc. for $C_8H_{32}N_{12}P_4$: *M* 420). The bicyclic compound was obtained as

an oil. This was boiled under reflux (3 h) (condenser at *ca.* −70 °C) in chloroform (100 cm^3) with an excess of methylamine. The ^{31}P n.m.r. spectrum showed only the presence of the monocycle, which was isolated from the mixture. This compound was also prepared in ether, isolated yield 55%.

(*k*) *With an excess of cyclopropylamine in chloroform.* An excess of anhydrous, freshly distilled cyclopropylamine (18.24 g, 0.32 mmol) was added to a solution of compound (**1**) (9.28 g, 0.02 mmol) in chloroform (170 cm^3), cooled to *ca.* −5 °C. The reaction mixture was stirred (6 h), the amine hydrochloride filtered off, and the solvent removed. The residue was subjected to preparative t.l.c. [*cf.* (*f*)]. The fast-moving band was *octakis(cyclopropylamino)cyclotetraphosphazatetraene*, m.p. 138 °C [from benzene–ethanol (3:1)], yield 2.4 g (19%) (Found: C, 45.8; H, 7.7, N, 26.1; P, 19.4. $C_{24}H_{48}N_{12}P_4$ requires C, 45.9; H, 7.6; N, 26.8; P, 19.7%). The slow-moving band gave 9-*cyclopropyl*-2,4,4,6,8,8-*hexakis(cyclopropylamino)*-2,6-*epimino-cyclotetraphosphazatetraene*, m.p. 149 °C [from benzene–n-hexane (3:1)], yield 4.3 g (38%) (Found: C, 44.5; H, 7.3; N, 26.4; P, 21.1. $C_{21}H_{41}N_{11}P_4$ requires C, 44.1; H, 7.2; N, 27.0; P, 21.7%). The monocycle was obtained in diethyl ether in 48% isolated yield.

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References

1 Part 49, T. Demir and R. A. Shaw, *J. Chem. Soc., Perkin Trans. 1*, 1987, 1547.
2 T. S. Cameron, Kh. Mannan, S. S. Krishnamurthy, A. C. Sau, A. R. Vasudeva Murthy, R. A. Shaw, and M. Woods, *J. Chem. Soc., Chem. Commun.*, 1975, 975.
3 S. S. Krishnamurthy, A. C. Sau, A. R. Vasudeva Murthy, R. A. Shaw, M. Woods, and R. Keat, *J. Chem. Res.*, 1977, (*S*) 70, (*M*) 0860—0844.
4 S. S. Krishnamurthy, K. Ramachandran, and M. Woods, *J. Chem. Res.*, 1979, (*S*) 92, (*M*) 1258—1266.
5 S. S. Krishnamurthy, K. Ramachandran, A. C. Sau, R. A. Shaw, A. R. Vasudeva Murthy, and M. Woods, *Inorg. Chem.*, 1979, **18**, 2010.
6 P. M. Sundaram, S. S. Krishnamurthy, A. R. Vasudeva Murthy, R. A. Shaw, and M. Woods, *Phosphorus Sulfur*, 1980, **8**, 373.
7 S. S. Krishnamurthy, P. M. Sundaram, and M. Woods, *Inorg. Chem.*, 1982, **21**, 406.
8 P. Ramabrahmam, K. S. Dhathathreyan, S. S. Krishnamurthy, and M. Woods, *Indian J. Chem., Sect. A*, 1983, **22**, 1.
9 S. R. Contractor, Ph.D. Thesis, University of London, 1983.
10 P. Y. Narayanaswamy, K. S. Dhathathreyan, and S. S. Krishnamurthy, *Inorg. Chem.*, 1985, 24, 640.
11 N. Gündüz, T. Gürdüz, E. Kılıç, S. G. Öztas, L. S. Shaw (née Gözen), R. A. Shaw, and M. Tüzün, *J. Chem. Soc., Dalton Trans.*, 1987, 925.
12 P. J. Argent, J. D. Healy, E. H. Ibrahim, R. A. Shaw, and M. Woods, *Phosphorus Sulfur*, 1981, **12**, 95.
13 J. D. Healy, E. H. M. Ibrahim, R. A. Shaw, T. S. Cameron, K. D. Howlett, and C. K. Prout, *Phosphorus*, 1971, **1**, 153.
14 M. Hasan, R. A. Shaw, and M. Woods, *J. Chem. Soc., Dalton Trans.*, 1975, 2202.
15 B. Capon, K Hills, and R. A Shaw, *J. Chem. Soc.*, 1965, 4059.
16 J. M. E. Goldschmidt and E. Licht, *J. Chem. Soc. A*, 1971, 2429.
17 J. M. E. Goldschmidt and E. Licht, *J. Chem. Soc., Dalton Trans.*, 1972, 728.
18 J. M. E. Goldschmidt and E. Licht, *J. Chem. Soc., Dalton Trans.*, 1972, 732.
19 J. M. E. Goldschmidt and E. Licht, *J. Chem. Soc., Dalton Trans.*, 1979, 1012.
20 J. M. E. Goldschmidt and E. Licht, *J. Chem. Soc., Dalton Trans.*, 1981, 107.
21 J. M. E. Goldschmidt and R. Goldstein, *J. Chem. Soc., Dalton Trans.*, 1981, 1283.
22 S. S. Krishnamurthy and P. M. Sundaram, *Inorg. Nucl. Chem. Lett.*, 1979, **15**, 367; *J. Chem. Soc., Dalton Trans.*, 1982, 67.
23 K. V. Katti and S. S. Krishnamurthy, *Phosphorus Sulfur*, 1983, **14**, 157.
24 K. V. Katti and S. S. Krishnamurthy, *J Chem. Soc., Dalton Trans.*, 1985, 285.
25 S. S. Krishnamurthy, P. Ramabrahmam, R. A. Shaw, A. R. Vasudeva Murthy, and M. Woods *Z. Anorg. Allg. Chem.*, 1985, **522**, 226.
26 C. Lensink, B. de Ruiter, and J. C. van de Grampel, *J. Chem. Soc., Dalton Trans.*, 1984, 1521.
27 S. K. Das, R. Keat, R. A. Shaw, and B. C. Smith, *J. Chem. Soc.*, 1965, 5032.
28 Z. Gabay and J. M. E. Goldschmidt, *J. Chem. Soc., Dalton Trans.*, 1981, 1456.
29 See, for example, R. A. Shaw, *Z. Naturforsch., Teil B*, 1976, **31**, 641.
30 V. B. Desai, R. A. Shaw, and B. C. Smith, *J. Chem. Soc. A*, 1970, 2023.
31 S. S. Krishnamurthy, A. C. Sau, A. R. Vasudeva Murthy, R. Keat, R. A. Shaw, and M. Woods, *J. Chem. Soc., Dalton Trans.*, 1976, 1405.
32 S. S. Krishnamurthy, A. C. Sau, A. R. Vasudeva Murthy, R. Keat, R. A. Shaw, and M. Woods, *J. Chem. Soc., Dalton Trans.*, 1977, 1980.
33 D. Millington and D. B. Sowerby, *J. Chem. Soc., Dalton Trans.*, 1972, 2035.
34 G. J. Bullen and P. A. Tucker, *J. Chem. Soc., Dalton Trans.*, 1972, 2437.
35 G. J. Bullen and P. E. Dann, *J. Chem. Soc., Dalton Trans.*, 1973, 1453.
36 G. J. Bullen and P. E. Dann, *J. Chem. Soc., Dalton Trans.*, 1974, 705.
37 T. T. Bamgboye, M. J Begley, and D. B. Sowerby, *J. Chem. Soc., Dalton Trans.*, 1975, 2617.
38 M. J. Begley, T. J. King, and D. B. Sowerby, *J. Chem. Soc., Dalton Trans.*, 1977, 149.
39 M. J. Begley and D. B. Sowerby, *J. Chem. Soc., Dalton Trans.*, 1978, 1094.
40 R. Das, R. A. Shaw, B. C. Smith, and M. Woods, *J. Chem. Soc., Dalton Trans.*, 1973, 709.
41 T. S. Cameron and Kh. Mannan, *Acta Crystallogr., Sect. B*, 1977, **33**, 443.
42 T. S. Cameron, R. E. Cordes, and F. A. Jackson, *Acta Crystallogr., Sect. B*, 1979, **35**, 980.
43 T. S. Cameron, R. A. Cordes, and B. R. Vincent, *Acta Crystallogr., Sect. C*, 1986, **42**, 1242.
44 M. B. Hursthouse, Z. Kılıç, L. S. Shaw (née Gözen), and R. A Shaw, unpublished work.
45 K. S. Dhathathreyan, S. S. Krishnamurthy, A. R. Vasudeva Murthy, R. A. Shaw, and M. Woods, *J. Chem. Soc., Dalton Trans.*, 1982, 1549.
46 K. S. Dhathathreyan, S. S. Krishnamurthy, A. R. Vasuvera Murthy, R. A. Shaw, and M Woods, *J. Chem. Soc., Dalton Trans.*, 1981, 1928.
47 A. H. Alkubaisi, W. F. Deutsch, M. B. Hursthouse, H. G. Parkes, L. S. Shaw (née Gözen), and R. A. Shaw, Abstracts, 4th International Symposium on Inorganic Ring Systems, Université Paris-Sud, 1985, p. 30; *Phosphorus Sulfur*, 1986, **28**, 229.
48 W. F. Deutsch, M. B. Hursthouse, Z. Kılıç, H. G. Parkes, L. S. Shaw (née Gözen), and R. A. Shaw, unpublished work.
49 J. K. Fincham, M. B. Hursthouse, H. G. Parkes, L. S. Shaw (née Gözen), and R. A. Shaw, *Acta Crystallogr., Sect. B*, 1986, **42**, 462.
50 H. G. Parkes and R. A. Shaw, unpublished work.
51 R. Keat and R. A. Shaw, 'Organic Phosphorus Compounds,' eds. G. M. Kosolapoff and L. Maier, New York and London, 1973, vol. 6, p. 833—940.

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