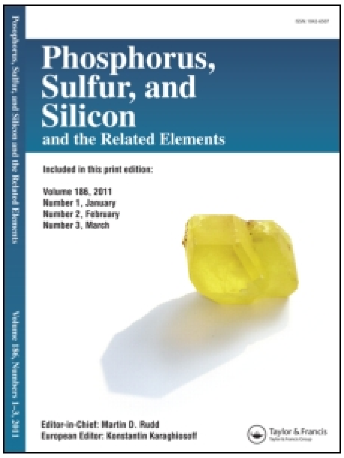


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

PHOSPHORUS-NITROGEN COMPOUNDS. PART 47[1]. CONFORMATIONS AND PHOSPHORUS-PHOSPHORUS SPIN-SPIN COUPLING CONSTANTS IN PHOSPHAZENYLCYCLOPHOSPHAZENES

Malcolm Biddlestone[a]; Rodney Keat[bc]; Harold G. Parkes[a]; Hans Rose[d]; David S. Rycroft[b]; Robert A. Shaw[a]
[a] Department of Chemistry, Birkbeck College (University of London), London, U.K [b] Department of Chemistry, University of Glasgow, Glasgow, U.K. [c] Chemdata Ltd., Helston, Cornwall, U.K. [d] Lehrstuhl für Anorganische Chemie I der Ruhr-Universität, Bochum-Querenburg, Postfach, B.D.R.

To cite this Article Biddlestone, Malcolm , Keat, Rodney , Parkes, Harold G. , Rose, Hans , Rycroft, David S. and Shaw, Robert A.(1985) 'PHOSPHORUS-NITROGEN COMPOUNDS. PART 47[1]. CONFORMATIONS AND PHOSPHORUS-PHOSPHORUS SPIN-SPIN COUPLING CONSTANTS IN PHOSPHAZENYLCYCLOPHOSPHAZENES', Phosphorus, Sulfur, and Silicon and the Related Elements, 25: 1, 25 — 31

To link to this Article: DOI: 10.1080/03086648508074253

URL: http://dx.doi.org/10.1080/03086648508074253

Phosphorus and Sulfur, 1985, Vol. 25, pp. 25–31
0308-664X/85/2501-0025/$15.00/0

PHOSPHORUS-NITROGEN COMPOUNDS. PART 47[1]. CONFORMATIONS AND PHOSPHORUS-PHOSPHORUS SPIN–SPIN COUPLING CONSTANTS IN PHOSPHAZENYLCYCLOPHOSPHAZENES

MALCOLM BIDDLESTONE,[a] RODNEY KEAT,[b†]
HAROLD G. PARKES,[a] HANS ROSE,[c] DAVID S. RYCROFT[b]
and ROBERT A. SHAW[a*]

[a]*Department of Chemistry, Birkbeck College (University of London), Malet Street, London WC1E 7HX, U.K.*

[b]*Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, U.K.*

[c]*Lehrstuhl für Anorganische Chemie I der Ruhr-Universität, Bochum, D-463 Bochum-Querenburg, Postfach 2148, B.D.R.*

(*Received January 28, 1985; in final form April 4, 1985*)

$^4J_{PP}$ Spin–spin coupling constants have been measured in a series of phosphazenylcyclophosphazenes. They can be correlated with the conformations adopted by the phosphazenyl substituents in the solid state, which are also believed to be the predominant ones in solution. The conformations are depicted by suitable orthographic projections based on published X-ray crystallographic data.

We have shown earlier[2] that four-bond spin–spin coupling constants $^4J_{PP}$, in triphenylphosphazenylcyclophosphazenes fall into two distinct classes: those in the range 3.3 to 5.7 Hz, and those close to zero. (For the sign of these coupling constants, see ref. 2). Further examples of this spin–spin phenomenon are now reported, and these are compared with the results of recent[3–9] X-ray crystallographic studies (see Figure 1). The crystal structures of phosphazenylcyclophosphazenes show that the phosphazenyl-substituent, $R_3P{=}N{-}$ (R = Ph), generally exhibits two different types of conformation with respect to the local N—P—N segment of the cyclophosphazene ring. In one of these, the P—N bond of the substituent is almost parallel to the plane containing the local N—P—N phosphazene ring segment [type (I)], and in the other, the substituent P—N bond is rotated through 90° [type (II)]. Type (III), mainly observed for dialkylamino groups NR_2, and for phenyl groups, Ph, represents a conformation approximately half-way between types (I) and (II). Making these definitions crystallographically more precise, we can define the di-

---

[†] Present address: Chemdata Ltd., Grambla, Wendron, Helston, Cornwall TR13 ONQ, U.K.
[*] Author to whom all correspondence should be addressed.

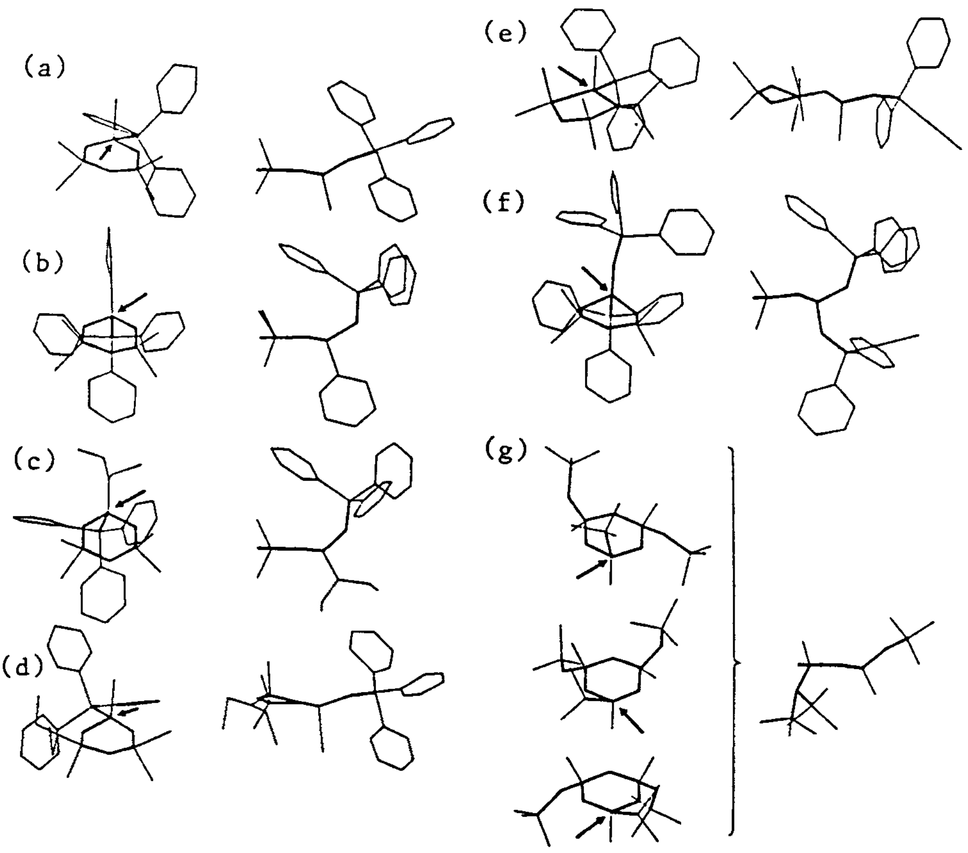
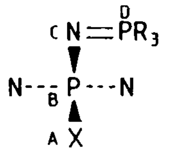


FIGURE 1 Solid-state conformational features of phosphazenylcyclophosphazenes. Bolder lines show the P—N skeletal detail, except that for the P—NEt_2 bonds. The left-hand column shows a projection along the first *exo* P—N bond (arrowed), and the right-hand column shows a projection across the cyclophosphazene ring approximately perpendicular to the same P—N bond.

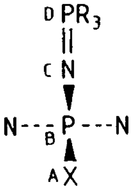
a $N_3P_3Cl_5(N{=}PPh_3)$[3]
b $N_3P_3Cl_4Ph(N{=}PPh_3)$ (geminal)[4]
c $N_3P_3Cl_4(NEt_2)(N{=}PPh_3)$ (geminal)[5]
d $N_3P_3Cl_4(NEt_2)(N{=}PPh_3)$ (nongeminal)[6]
e $N_4P_4Cl_7(N{=}PPh_3)$[7]
f $N_3P_3Cl_4(N{=}PPh_3)_2$ (geminal)[8]
g $N_3P_3F_3(N{=}PMe_3)_3$ (nongeminal,[9] all three projections shown)
Orthographic projections produced by Chemdata Ltd., System MGB.

hedral angle ABCD (see Diagram) as ±90° for type (I), 180° or 0° for type (II), and ±45, ±135 for type (III). The $^4J_{PP}$ coupling constants in type (I) are an average of the *syn* and *anti* couplings. These conformations (see Diagram), and some of their implications for chemical properties have been discussed elsewhere.[10]

Where both the structure of the solid and the spin–spin coupling data in solution are available, it is clear that a type (I) conformation gives rise to a relatively large four-bond spin–spin coupling, $^4J_{PP}$ (3.3 to 5.7 Hz), whilst those compounds which exhibit a type (II) conformation have $^4J_{PP}$ close to zero. This suggests that the conformations in the solid state and the predominant conformations in solution are



Type (I)



Type (II)

similar. For those compounds where only N.M.R. data were at first available, common structural features allowed a prediction of conformation, which was largely borne out by subsequent crystallographic findings. Thus, with two possible exceptions, the phosphazenylcyclophosphazenes conform to two rules:

1. In compounds where a phosphazenyl-group is geminal to a halogen atom, the expected relatively large $^4J_{PP}$ spin–spin coupling in solution and crystallographic type (I) conformation in the solid are observed. An exception is found in the 2-*trans*-4,6-trifluorotris(trimethylphosphazenyl)cyclotriphosphazatriene, $N_3P_3F_3(N{=}PMe_3)_3$, where an X-ray crystallographic investigation[9] shows that two of the $Me_3P{=}N{-}$ substituents exhibit the expected type (I) conformation, whilst the third has a type (II) conformation (Figure 1, g). The two substituents in the former conformation have a *trans*-arrangement, whilst the third, in the type (II) conformation, is *cis* to one of the type (I) substituents. This raises the question of whether two substituents *cis* to one another, which, individually, might exhibit a type (I) conformation, can do so in the presence of each other, or whether steric or other factors prevent this. Our inability, so far, to satisfactorily decouple ^{19}F nuclei whilst observing the ^{31}P spectrum of this compound prevents us from discussing the solution behaviour of this compound.

2. In compounds where a phosphazenyl-group is geminal to a nitrogeneous-group, such as an amino-group or another phosphazenyl-substituent, or if a phenyl-group is the geminal partner, type (II) behaviour with some slight deviations is observed. An apparent exception to this is $N_3P_3Cl_4(N{=}PCl_3)_2$, for which a geminal structure has been proposed.[11] No crystallographic data is available for this compound. The $^4J_{PP}$ spin coupling (Table I) for this compound is less than half of that for $N_3P_3Cl_5(N{=}PCl_3)$. It is worth noting that the $Cl_3P{=}N{-}$ group is likely to be a much weaker π-donor to the ring phosphorus atom than the other $R_3P{=}N{-}$ groups described here and, as such, may not be subject to the same type of conformational constraints as are imposed by the bonding scheme described below. An alternative explanation may be that the difference in $^4J_{PP}$ between type (I) and type (II) conformations is 3 to 5 Hz, which for R = Ph gives coupling constants for the former conformations of the order of 3.3 to 5.7 Hz, for the latter close to zero, whilst for R = Cl the corresponding values of 9.5 and 4.2 Hz represent a similar decrease.

Most of the examples in Table I have triphenylphosphazenyl substituents, $R_3P{=}N{-}$ (R = Ph). A more limited range of examples where R = Cl, NMe_2 and Me is also available. Only one example of a type (II) conformation, where R is other than Ph, is evident viz. $[N_3P_3F_3(N{=}PMe_3)_3]$.[9] The N=P segment of the substituent adjacent to the ring in $N_3P_3Cl_5[N{=}PPh(N{=}PPh_3)_2]$[12] is expected to have a type (I)

TABLE I

^{31}P N.M.R. data[a] for phosphazenylcyclophosphazenes

Compound[b]	$\delta\underline{P}Cl_2$	$\delta\underline{P}ClR$	$\delta\underline{P}(R)N{=}PR_3$	$\delta\underline{P}R_3$	$^2J_{PP}$/Hz		$^4J_{PP}$/Hz[c]
					endo	*exo*	
$N_3P_3Cl_5(N{=}PPh_3)$[d]	20.3	—	0.2	15.4	47.5	27.8	3.4
$N_3P_3Cl_5(N{=}PPh_2Me)$[d]	20.4	—	1.6	17.1	45.8	23.4	5.4
$N_3P_3Cl_5(N{=}PPhMe_2)$[e]	21.2	—	2.0	21.7	45.6	21.1	6.4
$N_3P_3Cl_5(N{=}PMe_3)$[d]	20.9	—	1.1	25.4	44.5	16.0	7.5
$N_3P_3Cl_5[N{=}P(NMe_2)_3]$[e]	21.1	—	−6.8	23.3	48.0	61.7	5.2
$N_3P_3Cl_5[N{=}PPh(N{=}PPh_3)_2]$[d]	19.7	—	−10.5	−4.9[f]	40.9	15.3 3.8	7.7
$N_3P_3Cl_5(N{=}PCl_3)$[g]	20.5	—	−2.2	−3.3	58.4	40.0	9.5
2,4-$N_3P_3Cl_4(NMe_2)(N{=}PPh_3)$[d]	21.4	26.4	4.4	14.6	42.8[j] 57.0 57.4	26.2	5.5[h] 3.3
2,4-$N_3P_3Cl_4(NEt_2)(N{=}PPh_3)$[d]	20.7	22.1	4.3	14.3	42.8[k] 47.0	26.3	5.7[h] −2.9
2-*trans*-6-$N_4P_4Cl_6(N{=}PPh_3)_2$ [d]	−12.2	—	−16.8	13.8	29.0	23.2	4.6
2,2-$N_3P_3Cl_4Ph(N{=}PPh_3)$[e]	16.6	—	3.4	14.8	21.9	5.7	< 0.2
2,2-$N_3P_3Cl_4(NH_2)(N{=}PPh_3)$[i]	17.1	—	−1.7	12.2	44.0	27.2	< 0.2
2,2-$N_3P_3Cl_4(NMe_2)(N{=}PPh_3)$[e]	17.7	—	5.1	14.1	36.8	28.4	< 0.2
2,2-$N_3P_3Cl_4(NEt_2)(N{=}PPh_3)$[e]	16.7	—	1.9	13.6	37.1	27.6	< 0.2
2,2-$N_3P_3Cl_4(NC_5H_{10})(N{=}PPh_3)$[e]	17.6	—	2.6	14.1	36.2	27.0	< 0.2
2,2-$N_3P_3Cl_4(OEt)(N{=}PPh_3)$[d]	18.5	—	−1.6	13.5	49.5	39.0	0.9
2,2-$N_3P_3Cl_4(N{=}PPh_3)_2$ [e]	14.2	—	−10.4	6.6	35.3	20.5	< 0.2
2,2-$N_3P_3Cl_4(N{=}PCl_3)_2$[g]	17.5	—	−20.4	−13.5	61.0	35.5	4.2
2,2 : 4,6-$N_3P_3Cl_2Ph(N{=}PPh_3)(NMe_2)_2$[d]	—	20.6 20.8	5.7	9.3	30.1[l] 32.6	11.1	< 0.2

[a] In $CDCl_3$ solution at *ca*.25 C, chemical shifts in p.p.m. referenced to 85% phosphoric acid.

[b] For isomer numbering scheme, see R. A. Shaw, B. W. Fitzsimmons and B. C. Smith, *Chem Rev*., **62**, 247, (1962). Numbering refers in this Table to non-chlorine substituents.

[c] See ref. 2 for relative sign determination.

[d] Obtained on a Varian XL-100 at 40.5 MHz.

[e] Obtained on a Varian XL-200 at 80.984 MHz.

[f] Chemical shift of $\underline{P}Ph_3$ 7.2 p.p.m.

[g] Data from ref. 11.

[h] Coupling to $\underline{P}Cl_2$.

[i] Obtained on a JEOL FX-60 at 24.15 MHz.

[j] $J\underline{P}Cl_2PClNMe_2$ 42.8 Hz, $J\underline{P}Cl_2\underline{P}ClNPPh_3$ 57.4 Hz and $J\underline{P}ClNMe_2\underline{P}ClNPPh_3$ 57.0 Hz.

[k] $J\underline{P}Cl_2\underline{P}ClNPPh_3$ 47.0 Hz, $J\underline{P}ClNEt_2\underline{P}ClNPPh_3$ 42.8, Hz only two coupling constants observed.

[l] Couplings not assigned.

conformation, analogous to that of $N_3P_3Cl_5(N{=}PPh_3)$ and a value of $^4J_{PP}$ *exo-endo* of 7.7 Hz has been observed in this former compound. $^4J_{PP}$ (*exo*) in the acyclic fragment, $NPPh(NPPh_3)_2$, is zero, presumably because the $—N{=}PPh_3$ group is geminal to the substituents $—N{=}PPh_3$ and Ph, both of which give rise to a type (II) conformation when geminally substituted. This finding suggests that a similar conformational behaviour will be observed in acyclic phosphazenes, although more data will be required to test this hypothesis. As Table I shows, there appears to be no obvious relationship between $^2J_{PP}$ and $^4J_{PP}$, only the latter being of value for identification of conformations.

It has been found[13] that P—O multiple bonding effects are largely attributable to an interaction between the oxygen lone-pairs and the anti-bonding orbitals that are associated with the other bonds to phosphorus. This $n_O \rightarrow \sigma^*_{P-X}$ interaction imposes conformational constraints not associated with $n_O \rightarrow 3d$ [(2p–3d)π] bonding because the oxygen lone-pair and the P—X bond must lie in the same plane. Since the σ*-orbital will be lowered in energy by relatively electronegative substituents, X, the $n_O \rightarrow \sigma^*_{P-X}$ interaction will be most important when X = oxygen or halogen. If these conclusions are applied to $N_3P_3Cl_5(N{=}PPh_3)$, then this interaction will be between a lone-pair on the phosphazenyl-group (perpendicular to the P_{exo}—N—P_{endo} plane) and the σ^*_{P-Cl} orbital and will only occur in a type (I) conformation. Replacement of chlorine by other less electro-negative groups will mean that the conformation observed is the result of competition for the σ*-orbitals at *endo*-phosphorus by the *exo*-π-donor(s). The presence of competing π-donors such as the NMe_2 group, or another $Ph_3P{=}N$—group, will also mean that interaction with a single σ*-orbital will be less decisive, and that steric effects may be more important in determining the conformations observed. A consideration of the structures[14] of $N_3P_3Cl_{6-n}(NMe_2)_n$ (n = 2–6) suggests that similar arguments can be applied to the conformations of the dimethylamino-groups, or indeed any amino-group where steric constraints are not excessive.

Figure 1 shows the relationship between the $R_3P{=}N$-- groups and the N_3P_3/N_4P_4 rings in all the relevant crystal structures. The particular projections chosen highlight two other aspects of the crystallographic work. Firstly, type (II) conformations can, and do, exist in two forms, where the $Ph_3P{=}N$— groups bend towards the N_3P_3-ring and the other in the opposite direction. The latter conformation, observed for one $NPPh_3$ substituent in geminal $N_3P_3Cl_4(NPPh_3)_2$, is, to date, unique. It may be the result of steric effects, as the N_3P_3 ring has a pronounced pucker (Figure 1, f). Secondly, in those compounds with type (I) conformations, for example nongeminal, $N_3P_3Cl_4(NR'_2)(N{=}PPh_3)$, the phosphazenyl-group can be directed towards the $\equiv PCl_2$ or the $\equiv PCl(NR'_2)$ groups. In the crystal structure of the compound where R′ = Et, the former is the case. Two different $^4J_{PP}$ coupling constants were obtained for this compound where R′ = Me, (the larger to the PCl_2-phosphorus), and it may be pointed out that the conformation associated with the $(Cl_2)P_{endo}$—N—P—N—P_{exo} skeleton is that of an approximate "W" shape, a form linked with relatively large proton–proton couplings in H—C—C—C—H fragments.

Recently, two $^4J_{PP}$ coupling constants, differing by 2–3 Hz have been observed in a number of triphenylphosphazenylcyclotriphosphazatriene derivatives.[15] All of these have the common structural features of (i) a $\equiv PCl(NPPh_3)$ grouping [probably in type (I) conformation], and (ii) two differently substituted ring phosphorus atoms. Similarly, one would anticipate two different coupling constants in structures like the above, but with $\equiv PR'(NPPh_3)$ (R′ = NR_2, Ph, $NPPh_3$) groupings [and presumably type (II) conformations], but as $^4J_{PP}$ in type (II) tends to zero, such differences have not been observed.

The data in Table I allow some further relationships to be drawn. The ^{31}P N.M.R. chemical shifts of the $\underline{P}Cl_2$ groups in the monophosphazenylpentachlorocyclotriphosphazatrienes, as well as in their nongeminal mono-amino derivatives range from 20.3 to 21.4 p.p.m. By contrast, $\delta\underline{P}Cl_2$ in the geminal 2,2-derivatives lie more up-field [14.2–17.7, (or 14.2–18.5 p.p.m. if the ethoxy derivative is included)]. This may point to some dependence of the $\underline{P}Cl_2$ chemical shift on the conformation of the phosphazenyl substituent. It is noteworthy that the ethoxy-derivative gives a $^4J_{PP}$

value intermediate between those of types (I) and (II), and this compound may be worthy of an X-ray crystallographic examination.

In cyclotetraphosphazatetraene derivatives the $\underline{P}Cl_2$ chemical shift in the parent compound, $N_4P_4Cl_8$, (-6.7 p.p.m.) generally moves down-field on aminolysis.[16] In the case of 2-*trans*-6-$N_4P_4(NPPh_3)_2Cl_6$ it moves, however, up-field to -12.2 p.p.m.

$\delta\underline{P}R_3$ values in $N_3P_3Cl_5(NPR_3)$ show a steady downfield trend (15.4–25.4 p.p.m.) on replacing step-wise R = Ph by R = Me. In the same series $^4J_{PP}$ increases from 3.4 to 7.5 Hz and $^2J_{PP}$ (*exo*) decreases from 27.8 to 16.0 Hz. The last mentioned parameter, $^2J_{PP}$, seems highly sensitive to changes in R as well as in the substitution of the N_3P_3 ring and the values reported here range from 3.8 to 61.7 Hz. For a discussion of prior work on $^2J_{PP}$ see ref. 16 and references noted therein.

In compounds of the general formula, $N_3P_3Cl_4R'(NPR_3)$ the chemical shifts of the junction phosphorus $\underline{P}R'(NPR_3)$ (R′ = NPR_3 or different) cover a larger range (5.1 to -20.4 p.p.m.) whilst the chemical shift of the $NPPh_3$ group is little affected by many substituents (Cl, NH_2, NMe_2, NEt_2, NC_5H_{10}, Ph, OEt) on the phosphorus atom to which it is attached (12.2–15.4 p.p.m.), it experiences a considerable up-field shift when this substituent is another $NPPh_3$ group (6.6–7.2 p.p.m.). The pronounced effect on chemical shift of geminal phosphazenyl substituents appears to be more general, viz. for the $NPCl_3$ substituent in $N_3P_3Cl_5(NPCl_3)$ (-3.3 p.p.m.) and in gem.-$N_3P_3Cl_4(NPCl_3)_2$ (-13.5 p.p.m.).

We also note the effect of dimethylamino substituents on the chemical shift of the phosphorus in the $NPPh_3$ group and on the related junction phosphorus atom. Replacement of chlorine atoms of the cyclotriphosphazatriene ring by dimethylamino groups causes progressive shielding of the $N\underline{P}Ph_3$ group and progressive shielding of the junction phosphorus, both being approximately linear with the number of chlorine atoms replaced by dimethylamino groups (this work and ref. 15). The latter effect has been observed earlier[16] for $PCl(NR_2)$ groups ($NR_2 = NMe_2$ or NC_5H_{10}) in cyclotriphosphazatrienes.

The results described in this paper highlight the beneficial interaction between solid state crystallographic and solution N.M.R. findings.

We are grateful to Dr. G. J. Bullen, University of Essex, and Professor H. Manohar, Indian Institute of Science, Bangalore, for providing us with information prior to publication.

REFERENCES

1. Part 46, P. J. Argent, J. D. Healy, E. H. Ibrahim, R. A. Shaw and M. Woods, *Phosphorus and Sulfur*, **12**, 95, (1981).
2. M. Biddlestone, R. Keat, H. Rose, D. S. Rycroft and R. A. Shaw, *Z. Naturforsch*, **31b**, 1001 (1976).
3. Y. S. Babu, H. Manohar and T. S. Cameron, *Acta Cryst.*, **B35**, 1410 (1979).
4. M. Biddlestone, R. A. Shaw, G. J. Bullen and P. E. Dann, *J. Chem. Soc. Chem. Commun.*, 1974, 56.
5. Y. S. Babu, H. Manohar and R. A. Shaw, *J. Chem. Soc. Dalton Trans.*, 1981, 599.
6. V. Chandrasekhar, P. Ramabrahmam and H. Manohar, personal communication.
7. Y. S. Babu and H. Manohar, *Acta Cryst.*, **B35**, 2363 (1979).
8. M. Krishnaiah, L. Ramamurthy, P. Ramabrahmam and H. Manohar, *Z. Naturforsch.*, **36b**, 765 (1981); H. Manohar, personal communication.
9. G. J. Bullen and K. O. Tam, personal communication.
10. R. A. Shaw, *Phosphorus and Sulfur*, **5**, 363 (1979).
11. G. R. Feistel and T. Moeller, *J. Inorg. Nucl. Chem.*, **29**, 2731 (1967); W. Lehr, *Z. Anorg. Allg. Chem.*, **350**, 18 (1967).
12. M. Biddlestone and R. A. Shaw, *J. Chem. Soc. (A)*, 1971, 2715.

13. *e.g.*, see J.-M. Lehn and G. Wipff, *J. Chem. Soc. Chem. Commun.*, 1975, 800.
14. F. R. Ahmed and S. Fortier, *Acta Cryst.*, **B31**, 1028 (1975); F. R. Ahmed and D. R. Pollard, *ibid.*, **B28**, 513 (1972), *idem*, *ibid.*, **B28**, 3530 (1972); F. R. Ahmed and E. J. Gabe, *ibid.*, **B31**, 1028 (1975); S. J. Rettig and J. Trotter, *Canad. J. Chem.*, **51**, 1295 (1973).
15. S. S. Krishnamurthy, P. Ramabrahmam, R. A. Shaw, A. R. Vasudeva Murthy and M. Woods, *Z. Anorg. Allg. Chem.*, in the press.
16. R. Keat, R. A. Shaw and M. Woods, *J. Chem. Soc. Dalton Trans.*, 1976, 1582.