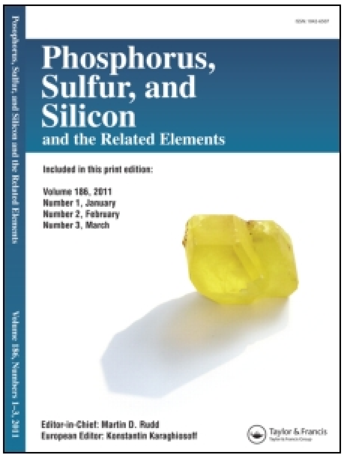

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PHOSPHORUS-NITROGEN COMPOUNDS. PART 61[1]. THE REACTIONS OF OCTACHLOROCYCLOTETRA-PHOSPHAZATETRAENE WITH ETHANEDIOL, 1,3-PROPANEDIOL AND 1,4-BUTANEDIOL. SYNTHETIC AND NUCLEAR MAGNETIC RESONANCE SPECTROSCOPIC INVESTIGATIONS

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PHOSPHORUS-NITROGEN COMPOUNDS. PART 61[1]. THE REACTIONS OF OCTACHLOROCYCLOTETRA-PHOSPHAZATETRAENE WITH ETHANEDIOL, 1,3-PROPANEDIOL AND 1,4-BUTANEDIOL. SYNTHETIC AND NUCLEAR MAGNETIC RESONANCE SPECTROSCOPIC INVESTIGATIONS

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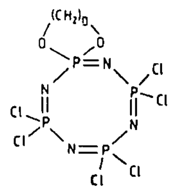
The reactions of octachlorocyclotetraphosphazatetraene, $N_4P_4Cl_8$, with ethane diol did not yield any characterised products. Those with 1,3-propanediol and 1,4-butanediol gave the following isolated and characterised derivatives, $N_4P_4Cl_{8-2x}[O(CH_2)_nO]_x$: $x = 1$, $n = 3, 4$; $x = 2$, $n = 3, 4$ (2 isomers of each); $x = 3$, $n = 3,4$; $x = 4$, $n = 4$. ^{31}P, ^1H and ^{13}C n.m.r. spectroscopic investigations showed all derivatives to have spiro structures. The isomeric bis derivatives have 2,2,4,4- and 2,2,6,6-structures.

The reactions of the eight-membered ring system, $N_4P_4Cl_8$ (**1**) with monofunctional reagents[2a] have received much less attention than those of its lower homologue, $N_3P_3Cl_6$, (**2**). The octachloride, (**1**), is more reactive than the hexachloride (**2**); the former can also, in principle, give rise to a much larger number of products, and hence structure determination is also more difficult. The same pertains, with even greater force to the less investigated difunctional reagents and little is known about this system. Only two derivatives of (**1**), $N_4P_4Cl_6[NMe(CH_2)_2NMe]$,[3,4] and $N_4P_4Cl_6[NH(CH_2)_3NH]$,[4] have been isolated as such, two further ones, $N_4P_4(NMe_2)_6[O(CH_2)_2NMe]$,[4] and $N_4P_4(OMe)_6$-$[O(CH_2)_3O]$[4], only on derivatisation. Only resinous material was obtained from the reactions with ethylene glycol and diaminoethane.[4]

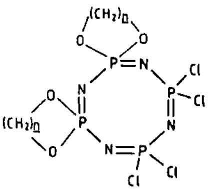
We have recently reported detailed studies of the reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, (**2**) with ethylene diol, 1,3-propanediol (**3**), and 1,4-butanediol (**4**). Spiro, ansa, bridging and dangling derivatives were characterised.[5] We now describe reactions of the diols ethane glycol, 1,3-propanediol, (**3**), and 1,4-butanediol, (**4**), with the next higher homologue, octachlorocyclotetraphosphazatetraene, $N_4P_4Cl_8$, (**1**).

In keeping with earlier work,[4] we found the reaction products of the octachloride, (**1**), with ethylene glycol too unstable to be isolated. Indeed, we were unable to identify with certainty, any products in the reaction mixture. This instability was also noticed, although to a lesser extent, with the homologous diol, (**3**). This too had been noted earlier,[4] but we were able to isolate derivatives. 1,4-Butanediol (**4**) gave stable derivatives.

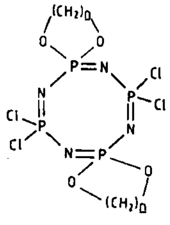
From the reactions of 1,3-propanediol, (**3**), we isolated one mono-, $N_4P_4Cl_6[O(CH_2)_3O]$, (**5**), two isomeric bis-, $N_4P_4Cl_4[O(CH_2)_3O]_2$, (**6** and **7**), and one tris-derivative, $N_4P_4Cl_2[O(CH_2)_3O]_3$, (**8**). In spite of repeated attempts, we failed to obtain the tetrakis-derivative, $N_4P_4[O(CH_2)_3O]_4$. The homologous diol, (**4**), yielded one mono-, $N_4P_4Cl_6[O(CH_2)_4O]$, (**9**), two isomeric bis-, $N_4P_4Cl_4[O(CH_2)_4O]_2$, (**10** and **11**), one tris-, $N_4P_4Cl_2[O(CH_2)_4O]_3$, (**12**), and a tetrakis-derivative, $N_4P_4[O(CH_2)_4O]_4$, (**13**). Initially, the ^{31}P n.m.r. spectrum of compound (**11**), a single line reminiscent of an A_4 system, suggested erroneously a bis ansa structure (**11A**) or (**11B**). A 2,6:4,8 double *trans*-annular bridged structure is known for a metallocene derivative of octafluorocyclotetraphosphazatetraene.[6] Ansa structures of type (**11B**) are known in the trimer system.[5] However, a detailed comparative analysis of the ^{31}P spectra of the derivatives reported here, as well as of earlier ones,[1,7,8] together with ^1H[1,7,8] and ^{13}C data[1,7,8] showed convincingly that this compound had a 2,2,6,6-bis spiro structure (**11C**). N.m.r. spectroscopy proved to be a powerful tool to deduce the structures of the derivatives prepared in this study.



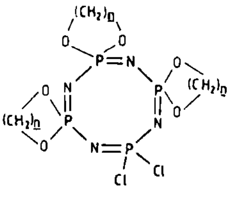
(5, n = 3;
9, n = 4)



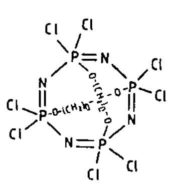
(6, n = 3;
10, n = 4)



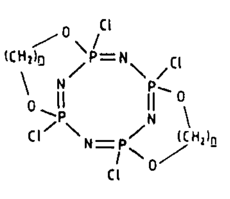
(7, n = 3;
11C, n = 4)



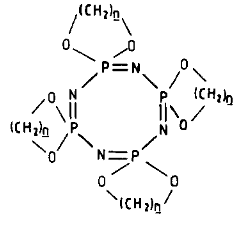
(8, n = 3;
12, n = 4)



(11A, n = 4)



(11B, n = 4)



(13, n = 4)

^{31}P n.m.r. SPECTRA

The spectra of the derivatives of the tetramer, (**1**) with four spins are obviously more complicated than those of the trimer (**2**) with only three spins. There is also the possibility that, in addition to two-bond $^2\underline{J}(\underline{PP})$, four-bond coupling $^4\underline{J}(\underline{PP})$ might further complicate the spectra. We did not observe any of the latter in our analyses; examples of it are, however, known.[4,9]

In this study, we observed spectra of four types: A_2MX (A_2BX), $AA'XX'$($AA'BB'$), A_2X_2(A_2B_2), and A_4.

$A_2MX(A_2BX)$

Compounds (**5**, **8**, **9**, and **12**) show spectra of this type, establishing that these mono- and tris-derivatives are all spiro compounds. Proton coupled spectra allow unambiguous assignments to ≡Pspiro and $\equiv PCl_2$ moieties. A spectrum of the A_2MX type, viz. that of compound (**9**) is shown in Figure 1.

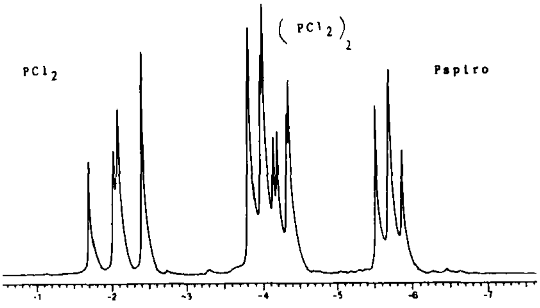


FIGURE 1 $^{31}P\{^1H\}$ n.m.r. spectrum of compound (**9**) in $CDCl_3$ (85% phosphoric acid external reference) at 162.0 MHz (room temperature).

AA'XX'(AA'BB')

Compounds (**6** and **10**) are of this type. This establishes them clearly as 2,2,4,4-bis spiro derivatives. The spectrum of the latter (**10**) is shown in Figure 2.

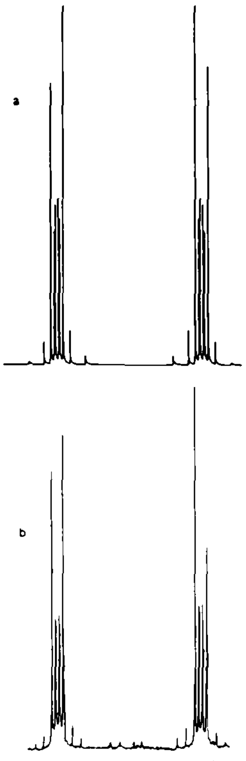


FIGURE 2 $^{31}P\{^1H\}$ n.m.r. spectrum of compound (**10**) in $CDCl_3$ at 162.0 MHz (room temperature) (a) simulated (b) experimental.

$A_2X_2(A_2B_2)$

Compound (**7**) exhibiting two triplets is thus shown to have a 2,2,6,6-bis-spiro structure.

A_4

Compounds (**11** and **13**) show only a singlet. This is, what one would have expected of a tetrakis-spiro derivative (**13**). More surprising is its occurrence in the bis-derivative (**11**).

A graphical representation of all the ^{31}P n.m.r. shifts (Table I) of the compounds discussed here, showed that replacement of a spiro propanedioxy by a spiro butanedioxy group causes a deshielding of the ≡Pspiro nucleus, which brings it into the region of absorption for the $\equiv PCl_2$ nuclei and thus gives rise to an accidental isochrony. Such close chemical shifts led us originally to assign on spectroscopic grounds an erroneous structure to $N_3P_3Cl_2(NHBu^t)_2[O(CH_2)_3O]$[10]; the correct structure was subsequently deduced by X-ray crystallography.[10] A detailed comparison of the graph suggested that a 2,2,6,6-bis spiro butanedioxy derivative (**11C**) should have ^{31}P n.m.r. absorptions for both the $\equiv PCl_2$ and the ≡Pspiro nuclei around −1 p.p.m., and these might well be isochronous. (Change of solvent to C_6D_6 allows these two environments to be resolved.) Furthermore this graph allows a prediction of chemical shift of also approximately −1 p.p.m. for the, so far unknown, tetrakis spiro propanedioxy derivative, $N_4P_4[O(CH_2)_3O]_4$.

TABLE I

^{31}P n.m.r. data of diol derivatives

Compound	δPspiro[a]	δPCl_2[a]	$^2J(\underline{P}spiro\text{-}\underline{P}Cl_2)$[b]	$^2J(\underline{P}X_2\text{-}\underline{P}X_2)$[b]
(**1**)		−6.5		
(**5**)	−10.5	−5.5(1)[c] −4.3(2)	59.0	29.9 (X = Cl)
(**6**)	−6.6	−4.7	58.2	82.85 (X_2 = spiro)
(**7**)	−9.6	−2.3	57.9	36.5 (X = Cl)
(**8**)	−2.1(1) −5.7(2)	−2.6	53.7	79.4 (X_2 = spiro)
(**9**)	−2.05	−5.7(1) −4.1(2)	62.5	29.3 (X = Cl)
(**10**)	1.4	−2.6	60.7	89.2 (X_2 = spiro)
(**11**)	−1.0[d]	−1.0[d]		
(**12**)	5.5(1) 2.2(2)	−0.2	54.2	39.9 (X = Cl) 86.1 (X_2 = spiro)
(**13**)	7.1			

[a] In p.p.m., [b] in Hz, [c] relative number of nuclei in brackets [d] accidental isochrony

^1H n.m.r. DATA

As for derivatives of the lower homologue, $N_3P_3Cl_6$, (**2**)[5,7] the present series shows that the $^3J(\underline{P}OC\underline{H}_2)$ values are lower (13.0–13.5 Hz) for the spiro

TABLE II

^{1}H *n.m.r. data of diol derivatives*

Compound	δ OC$\underline{H}_2$[a]	δ CC$\underline{H}_2$[a]	$^3\underline{J}(\underline{P}OC\underline{H}_2)$[b]	$^3\underline{J}(C\underline{H}_2C\underline{H}_2)$[b]
(5)	4.48	2.05	13.5	5.3
(6)	4.49	1.98	c	c
(7)	4.46	2.04	13.4	5.45
(8)	4.38	1.97	13.1	5.0
(9)	4.18	1.96	18.0	2.45
(10)	4.16	1.92	18.6	c
(11)	4.20	1.93	18.7	2.4
(12)	4.10	1.83	17.55	c
(13)	4.09	1.83	18.0	2.4

[a] Mean value in p.p.m., [b] in Hz., [c] complex overlap of lines.

derivatives of propanediol (**3**) than for those of the butanediol (**4**) analogues (17.5–18.7 Hz). The value of 18.7 Hz for compound (**11**) clearly demonstrates a seven-membered spiro ring, whilst bridging compounds, viz. $(N_3P_3Cl_5)_2$-$[O(CH_2)_4O]$, have $^3\underline{J}(POC\underline{H}_2)$ values of around 9 Hz.[5,7] The data are presented in Table II.

^{13}C n.m.r. DATA

Again, as with the data for the N_3P_3 derivatives[5,7] there is a distinct chemical shift difference for the $C\underline{C}H_2$ nuclei between the six- and seven-membered spiro derivatives.[5,7,11] Ansa and bridging derivatives absorb at different values.[5,7] Most pronounced are the differences in three bond coupling constants, $^3\underline{J}(\underline{P}OC\underline{C})$. The six-membered spiro compounds have values of 6–8 Hz, the seven-membered rings show no coupling. We have shown crystallographically that the dihedral angles, POCC, in the latter are close to 90°,[12] and thus a value of close to zero would be expected from a Karplus relationship. By contrast, we note that a butanedioxy bridge has a $^3\underline{J}(\underline{P}OC\underline{C})$ value of 9 Hz.[5,7] These data are presented in Table III.

TABLE III

^{13}C n.m.r. data for diol derivatives

Compound	δ O$\underline{C}$H$_2$[a]	δ C$\underline{C}$H$_2$[a]	$^2\underline{J}(\underline{P}O\underline{C})$[b]	$^3\underline{J}(\underline{P}OC\underline{C})$[b]
(5)	68.0(d)[c]	26.1(d)	5.9	7.0
(6)	67.5(t)	26.2(t)	5.4	6.45
(7)	67.7(t)	26.2(t)	5.9	7.0
(8)	67.3(2)[d](t)	26.35(2)(t)	5.5	6.1
	66.9(1)(d)	26.4(1)(d)	5.5	5.5
(9)	67.8(d)	29.05(s)	5.1	0.0
(10)	66.9(t)	29.05(s)	4.8	0.0
(11)	67.3(t)	29.0(s)	4.3	0.0
(12)	66.4(s)(t)	29.1(2)(s)	4.8	0.0
	66.0(1)(d)	29.15(1)(s)	4.8	0.0
(13)	65.6(qui)	29.2(s)	4.8	0.0

[a] In p.p.m., [b] in Hz, [c] s = singlet, d = doublet, t = triplet, qui = quintet, [d] numbers in brackets refer to relative numbers of nuclei.

Noteworthy are the inversions of chemical shifts δ POÇ and POCÇ in each of the tris-derivatives (**8** and **12**). The more deshielded POÇ signals arise from the two spiro groups, which are flanked on one side by the $\equiv PCl_2$ moiety. These same groups have more shielded POCÇ nuclei. We have reported one earlier observation of this inversion phenomenon.[13] The tetrakis derivative (**13**) shows a quintet signal for the POÇ nuclei due to virtual coupling with four ^{31}P nuclei. A similar quintet has been reported for the *ipso*-carbon of $N_4P_4(OPh)_8$[14,15] and for α- and β-carbon nuclei of $N_4P_4(OR)_8$ (R = Me, Et, Pr^i).[15] It is clear from the above ^1H and ^{13}C data that these too point definitely to the 2,2,6,6-bis spiro structure (**11C**) for the butanedioxy derivative (**11**).

Comparing the results of the present study with our earlier one on the lower homologue (**2**),[5] we note that the octachloride (**1**) is more reactive than the hexachloride (**2**) towards the diols investigated. The instability of the products with a given diol is considerably greater for the cyclotetraphosphazatetraene system than for its lower homologue. This is most pronounced for the reaction products with ethylene glycol and least for those with 1,4-butanediol. The five-membered spiro rings are somewhat unstable in the N_3P_3 system. We, in keeping with earlier observations,[4] were unable to isolate any based on N_4P_4 rings. The six-membered spiro rings are stable with the lower homologue (**2**), but rather unstable (when P-Cl bonds are present)[4] in the higher homologue (**1**). The seven-membered spiro derivatives appear to be stable in both systems. In keeping with the above, resin formation is considerably greater for the N_4P_4 than for the N_3P_3 system.

Finally we make the following empirical observations. Monofunctional nucleophilic reagents, which on disubstitution of the trimer (**2**), give rise to nongeminal products, tend to give in the tetramer system on disubstitution only 2,6-derivatives.[2] Those reagents, which with the trimer give geminal bis derivatives, have a tendency with the tetramer to give 2,4-, as well as 2,6-derivatives.[2] The diols (**3**) and (**4**) give predominantly (though not exclusively) spiro derivatives with the N_3P_3 system.[5] In keeping with the above empirical rule, they give rise to 2,2,4,4-, as well as, 2,2,6,6-derivatives in the N_4P_4 system.

EXPERIMENTAL

Chemicals were obtained as follows: Light Petroleum (b.p. 40–60°C) (May & Baker Ltd), tetrahydrofuran (Fluka-Garantie 99.5%), acetonitrile, deuteriated solvents for n.m.r. spectroscopy, propane-1,3-diol, butane-1,4-diol (Aldrich Chem. Co. Ltd.), pyridine, ethanediol (B.D.H. Chemical Co. Ltd.,) octachlorocyclotetraphosphazatetraene (Shin Nisso Kako Co. ltd.). Solvents were dried by conventional methods.

All reactions were monitored by using Kieselgel 60 F-254 (silica gel) precoated t.l.c. plates and sprayed with ninhydrine (0.5 w/v%) in butanol solution and developed at approx. 130°C. Separations of products were carried out by column chromatography using Kieselgel 60. Melting points were determined on a Reichert-Kofler micro heating stage fitted with a polarising microscope.

^1H n.m.r. spectra were recorded using a JEOL FX-200 spectrometer (operating at 199.5 MHz), a Bruker WH 250 spectrometer (operating at 250.48 MHz, Kings College, London), and a Varian XL 400 spectrometer (operating at 399.95 MHZ, University College, London). Samples were dissolved in $CDCl_3$ and placed in 5 mm n.m.r. tubes. Measurements were carried out using a $CDCl_3$ lock, TMS as internal reference and sample concentrations of 15–20 mg/cm^3. ^{31}P n.m.r. spectra were recorded using a JEOL JNM FX-60 spectrometer (operating at 24.15 MHz), a Varian XL-200 spectrometer (operating at 80.98 MHz, University College, London), a Bruker WH 400 spectrometer (operating at 162.0 MHz, Queen Mary College,) and a Varian VXR-400 spectrometer (operating at 162.0 MHz, University College, London). 85% H_3PO_4 was used as an external reference. ^{13}C n.m.r. spectra were recorded using a JEOL FX-200 spectrometer (operating at 50.10 MHz) and a Varian VXR 400 spectrometer (operating at 100.577 MHz, University College, London), TMS was used as an internal reference.

Mass spectra were recorded using a VG 7070H mass spectrometer with Finnigan INCOS data system at University College, London and a VGZAB IF mass spectrometer at the School of Pharmacy.

The reactions of $N_4P_4Cl_8$ (**1**) with different equivalents of ethylene glycol and pyridine gave after a few minutes precipitates of white resinous materials. T.l.c. of the filtrate revealed the absence of mobile compounds.

Reactions with 1,3-*propanediol* (**3**). To $N_4P_4Cl_8$, (**1**), (10 g, 21 mmol) in acetonitrile (250 cm^3) were added with stirring eight equivalents of anhydrous pyridine (13.62 g, 172 mmol) at room temperature. The 1,3-propane diol (3.27 g, 43 mmol) in acetonitrile (10 cm^3) was added with stirring (0.5 hr) and the mixture was allowed to boil under reflux (1 hr). A white precipitate was formed 15–20 minutes after the addition of the diol. After 48 hrs t.l.c. showed the completion of the reaction. On attaining room temperature the pyridine hydrochloride was removed by filtration and the filtrate was concentrated to 25 cm^3. One half of the filtrate was column chromatographed using 60 g of silica gel and eluted with light petroleum/dichloromethane (2:1). Four major components were obtained in the following order. (**5**), m.p. 79°C, (0.4 g, 8%); (**7**), m.p. 218°C, (0.45 g, 9%); (**6**), m.p. 107°C, (0.4 g, 8%); and (**8**), m.p. 149–151°C (0.75 g, 15%).

Reactions with 1,4-*butanediol* (**4**). (a) Two equivalents of (**4**). Following the same procedure as in the reaction with (**3**), the reaction of $N_4P_4Cl_8$ (**1**) (10 g, 21.5 mmol) with (**4**), (3.9 g, 43 mmol) gave three major components. These were eluted with light petroleum/dichloromethane (1:1) in the following order: (**9**), m.p. 62–64°C, (1.55 g, 31%); (**11**), m.p. 194°C, (0.65 g, 13%); and (**10**), m.p. 136–138°C, (0.55 g, 11%).

(b) Four equivalents of (**4**). Anhydrous pyridine (6.1 g, 77 mmol) was added to a stirred solution of $N_4P_4Cl_8$ (**1**) (3 g, 6.4 mmol) in acetonitrile (100 cm^3). The diol (**4**) (2.32 g, 25.6 mmol) in acetonitrile (10 cm^3) was added slowly. After refluxing (3 hr), stirring was continued (12 hr). T.l.c. monitored the completion of the reaction. The pyridine hydrochloride was removed and the filtrate was concentrated (15 cm^3) and column chromatographed using 30 g of silica gel and eluted with tetrahydrofuran/dichloromethane (1:9). Two major products were obtained: (**12**), m.p. 108–110°C, (0.51 g, 17%) and (**13**), m.p. 220°C (dec.) (0.80 g, 28%).

Elemental analyses and mass spectrometric molecular weights are given in Table IV.

TABLE IV

Characterization details for the diol derivatives of $N_4P_4Cl_8$ (**1**)

	M		Elemental analysis/percentage composition					
			Calc.			Found		
Compound	Calc.[a]	Obs.	C	H	N	C	H	N
(**5**)	464	464	7.7	1.3	12.0	7.8	1.1	11.9
(**6**)	468	468	15.3	2.55	11.9	15.5	2.5	12.0
(**7**)	468	468	15.3	2.55	11.9	15.1	2.5	11.5
(**8**)	472	472	22.85	3.8	11.8	23.05	3.8	11.7
(**9**)	478	478	10.0	1.7	11.65	10.2	1.4	11.8
(**10**)	496	496	19.3	3.2	11.25	19.3	3.2	11.3
(**11**)	496	496	19.3	3.2	11.25	19.2	3.15	11.2
(**12**)	514	514	28.0	4.65	10.9	28.2	5.9	10.5
(**13**)	532	532	36.1	6.0	10.5	35.6	5.9	10.5

[a] Based on the mass of the most abundant isotope.

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REFERENCES

1. Part 60. H. A. Al-Madfa and R. A. Shaw, *Phosphorus Sulfur*, **45**, 1 (1989).
2. (a) cf. K. C. Kumara Swamy, S. S. Krishnamurthy, A. R. Vasudeva Murthy, R. A. Shaw and M. Woods, *Ind. J. Chem. (A)*., **25**, 1004 (1986) and references therein. (b) For summaries see R. A. Shaw, *Z. Naturforsch.*, **31b**, 641 (1976); H. R. Allcock, Phosphorus-Nitrogen Compounds, Academic Press, New York, 1972; S. S. Krishnamurthy, A. C. Sau and M. Woods, *Adv. Inorg. Chem. Radiochem.*, **21**, 41 (1978).
3. T. Chivers and R. Hedgeland, *Canad. J. Chem.*, **50**, 1017 (1972).
4. V. Chandrasekhar, S. Karthikeyan, S. S. Krishnamurthy and M. Woods, *Ind. J. Chem.*, **24A**, 379 (1985).
5. A. H. Alkubaisi, H. G. Parkes and R. A. Shaw, *Heterocycles*, 1989, in the press.
6. K. D. Lavin, G. H. Riding, M. Parvez and H. R. Allcock, *J. Chem. Soc., Chem. Commun.*, 1986, 117.
7. A. H. Alkubaisi, H. G. Parkes and R. A. Shaw, unpublished results.
8. H. A. Al-Madfa, personal communication.
9. M. Biddlestone, R. Keat, H. Rose, D. S. Rycroft and R. A. Shaw, *Z. Naturforsch.*, **31b**, 1001 (1976). M.Biddlestone, R. Keat, H. G. Parkes, H. Rose, D. S. Rycroft and R. A. Shaw, *Phosphorus Sulfur*, **25**, 25 (1985).
10. W. F. Deutsch, N. Gündüz, T. Gündüz, M. B. Hursthouse, E. Kilic, H. G. Parkes, L. S. Shaw (née Gözen), R. A. Shaw and M. Tüzün, *Phosphorus Sulfur*, **28**, 253 (1986).
11. A. H. Alkubaisi, W. F. Deutsch, M. B. Hursthouse, H. G. Parkes, L. S. Shaw (née Gözen) and R. A. Shaw, *Phosphorus Sulfur*, **28**, 229 (1986).
12. S. R. Contractor, M. B. Hursthouse, L. S. Shaw (née Gözen), R. A. Shaw and H. Yilmaz, *Acta Crystallogr.*, **B41**, 122 (1985); L. S. Shaw, personal communication.
13. J. K. Fincham, M. B. Hursthouse, H. G. Parkes, L. S. Shaw (née Gözen) and R. A. Shaw, *J. Chem. Soc., Dalton Trans.*, 1169 (1988).
14. J. Reuben, *Magn. Reson. Chem.*, **25**, 1049 (1987).
15. J. K. Fincham, personal communication.