A Phosphorus-31 Nuclear Magnetic Resonance Study of Amino-derivatives of the Chlorocyclophosphazenes, $N_3P_3Cl_6$ and $N_4P_4Cl_8$

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The proton decoupled ^{31}P n.m.r. spectra of an extensive series of primary and secondary amine derivatives of $N_3P_3Cl_6$ and $N_4P_4Cl_8$ have been recorded and analysed. ^1H-$\{^{31}P\}$ INDOR studies show that *P*–N–*P* coupling constants for *cis*-$N_3P_3Cl_3(NMe_2)_3$, $N_3P_3(NMe_2)_6$, and $N_4P_4(NMe_2)_8$ are positive. Trends in ^{31}P chemical shifts and *P*–N–*P* coupling constants are discussed and compared with similar data for chloro(phenyl)- and amino(phenyl)-cyclophosphazenes. The appearance of ' virtual coupling ' effects in the ^1H spectra of some of these derivatives and the origins of broadening effects in the ^{31}P spectra are discussed.

THE application of broad band ^1H decoupling has greatly improved the quality and usefulness of ^{31}P n.m.r. data, not least on the cyclophosphazenes, but recent reviews [1,2] of data for these compounds show that this technique has been little applied. We now report an extensive compilation of new ^{31}P n.m.r. data, obtained with (and without) complete ^1H decoupling for amino-derivatives of $N_3P_3Cl_6$ and $N_4P_4Cl_8$ and discuss some of the trends observed. The nomenclature used is a shortened form of that described some time ago,[3] and the sign convention used for ^{31}P chemical shifts is that positive δ-values indicate a shift to low field of the external reference, 85% H_3PO_4.

Secondary Amine Derivatives.—Chemical shifts for secondary amine derivatives of known structure are collected in Table 1. It is clear that the overall trend is to low field with increasing amino-group substitution of chlorine atoms, and this is less pronounced for the diethylamino- and piperidino-derivatives. The result, with the bispiperidino-derivatives, is that it is difficult to make structural assignments to geometrical isomers. For example, in the bispiperidino-derivatives, $\equiv PClNC_5H_{10}$ and $\equiv PCl_2$ groups are not distinguishable. In general, the ^{31}P shifts of the $\equiv PClNR_2$ and $\equiv P(NR_2)_2$ groups lie to high field of the range bracketed by $N_3P_3Cl_6$ and the hexakisamino-derivatives (δ 19.3—24.6) so that ^{31}P shifts are not additive for a given substituent. There is, however, a reasonable correlation between the chemical shift for the $\equiv PClNR_2$ group and the degree of

[1] R. Keat and R. A. Shaw, ' Organic Phosphorus Compounds ' eds. G. M. Kosolapoff and L. Maier, Interscience, New York, 1973, vol. 6, ch. 17.

[2] R. Keat in ' Organophosphorus Chemistry ' ed. S. Trippett, The Chemical Society, London, 1972–75, vols. 3—6.

[3] R. A. Shaw, B. W. Fitzsimmons, and B. C. Smith, *Chem. Rev.*, 1962, **62**, 247.

TABLE 1

^{31}P N.m.r. data for secondary amine derivatives of $N_3P_3Cl_6$

Compound	M.p. (θ_c/°C)	Structure	δ_{PCl_2}	δ_{PClR}	δ_{PR_2}	J_{P-N-P}/Hz	
$N_3P_3Cl_6$	113		19.3				
$N_3P_3Cl_5{\cdot}NMe_2$	12—14	2,2,4,4,6:6	20.5	21.6		49.1	48.4 [b]
$N_3P_3Cl_4(NMe_2)_2$	103	2,2,4-*trans*-6:4,6	21.5	25.2		44.4	48.4 [b]
$N_3P_3Cl_4(NMe_2)_2$	86	2,2,4-*cis*-6:4,6	21.6	24.9		46.3	48.4 [b]
$N_3P_3Cl_3(NMe_2)_3$	105	2-*trans*-4,6:2,4,6		27.7(2), 28.3(1)[a]		41.4	46.0 [b]
$N_3P_3Cl_3(NMe_2)_3$	152	2-*cis*-4-*cis*-6:2,4,6		27.5			
$N_3P_3Cl_3(NMe_2)_3$	71	2,2,4:4,6,6	21.7	27.3	21.7	44.8 [c]	48.4 [b] 44.2 [b]
$N_3P_3Cl_2(NMe)_4$	104	2-*cis*-4:2,4,6,6		32.2	24.8	38.4	43.5 [b]
$N_3P_3(NMe_2)_6$	104				24.6	*d*	41.2 [b]
$N_3P_3Cl_3(NEt_2)_3$	43	2-*trans*-4,6:2,4,6		24.4			
$N_3P_3(NEt_2)_6$	205				22.5		
$N_3P_3Cl_5{\cdot}NC_5H_{10}$	68	2,2,4,4,6:6	20.8	18.7		48.0	
$N_3P_3Cl_4(NC_5H_{10})_2$	104—105	2,2,4-*trans*-6:4,6,	21.2				
$N_3P_3Cl_4(NC_5H_{10})_2$	129	2,2,4-*cis*-6:4,6	21.6				
$N_3P_3Cl_3(NC_5H_{10})_3$	114	2-*trans*-4,6:2,4,6		24.3(2), 25.2(1)[a]		40.5	
$N_3P_3Cl_2(NC_5H_{10})_4$	111—112	2-*cis*-4,6,6:2,4		26.4	18.0	37.4	
$N_3P_3(NC_5H_{10})_6$	266				21.2		
$N_3P_3Cl_5{\cdot}N(CH_2Ph)_2$	112	2,2,4,4,6:6	19.6				
$N_3P_3Cl_4[N(CH_2Ph)_2]_2$	108	2,2,4,6:4,6	20.0	21.9		50.6	
$N_3P_3Cl_2(NC_4H_8)_4$	122	2,4:2,4,6,6		26.4	14.6	36.5	

[a] Measured at 40.5 MHz on a Varian XL-100 spectrometer; figures in parentheses denote relative intensities. [b] Calculated, see text. [c] Equal couplings to $\equiv PClNMe_2$. [d] See text.

substitution, n, in the series, $N_3P_3Cl_{6-n}(NR_2)_n$: this is illustrated for dimethylamino- and piperidino-derivatives in Figure 1. The pentakisamino-derivatives would, therefore, be expected to show the lowest field shift for the $\equiv PClNR_2$ group. Non-additive ^{31}P shift influences have previously been recognised in compounds containing acyclic P–N–P fragments,[4,5] as well as in mononuclear phosphorus compounds.[6] The effect is

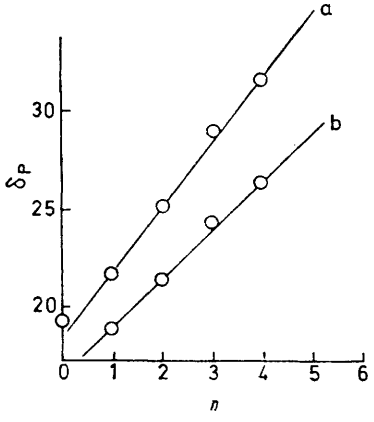


FIGURE 1 Graph of δ_P for $\equiv PClNR_2$ signals against n in the series (a) $N_3P_3Cl_{6-n}(NMe_2)_n$ and (b) $N_3P_3Cl_{6-n}(NC_5H_{10})_n$. Where isomeric forms have been measured, the mean $\equiv PClNR_2$ shift has been used

most marked for $\equiv PClNR_2$ groups, and can be illustrated by the ^1H-decoupled ^{31}P spectrum of the geminal trisdimethylamino-derivative, $N_3P_3Cl_3(NMe_2)_3$, which comprises an AB_2 spin system (Figure 2). ^1H-{^{31}P} double resonance experiments, which rely on previous ^1H spectral assignments,[7] showed that the A signal at δ 27.3 could be assigned to the $\equiv PClNMe_2$ group and, surprisingly, that the B signals arise from $\equiv PCl_2$ and $\equiv P(NMe_2)_2$

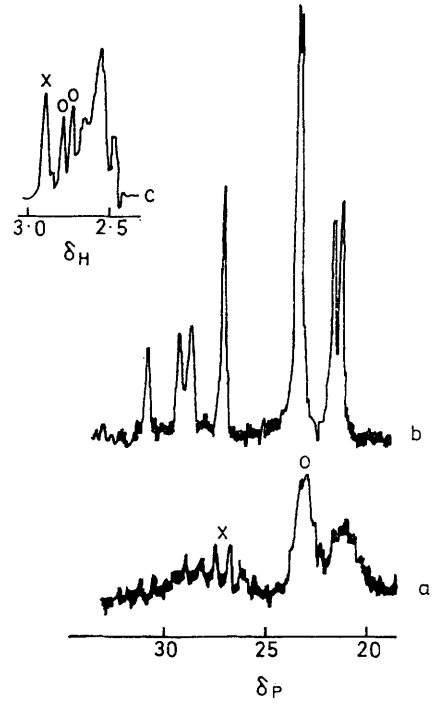


FIGURE 2 ^{31}P N.m.r. spectrum of geminal $N_3P_3Cl_3(NMe_2)_3$ (a) single resonance spectrum, (b) with ^1H decoupling, and (c) shows the ^1H spectrum at 60 MHz with connection between major peaks established by ^1H-{^{31}P} experiments

groups with experimentally indistinguishable chemical shifts. The influence of aromatic solvents on ^1H chemical shifts has been used as an aid to spectral

[4] G. Hägele, R. K. Harris, M. I. M. Wazeer, and R. Keat, *J.C.S. Dalton*, 1974, 1985.

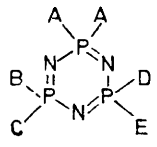
[5] A. Schmidpeter, H. Brecht, and J. Ebeling, *Chem. Ber.*, 1968, **101**, 3902.

[6] J. H. Letcher and J. R. Van Wazer, *Topics Phosphorus Chem.*, 1967, **5**, 75.

[7] R. Keat, S. K. Ray, and R. A. Shaw, *J. Chem. Soc.*, 1965, 7193.

assignments,[8] but a few selected experiments on this and other dimethylamino-derivatives suggest that any effect of benzene, relative to chloroform or methylene chloride, on ^{31}P chemical shifts is within the limits of experimental error. More significant chemical-shift effects are apparent using protic solvents,[9] or where hydrogen halide adducts may be formed (see below).

The coupling constants, J_{P-N-P}, have been subjected to closer scrutiny [10,11] than ^{31}P chemical shifts, and it has been noted [12] that they are dependent on the electronegativity of the substituent X in derivatives of the type, $N_3P_3Cl_5X$. Further, an expression, $J_{P-N-P} = [\lambda_B + \lambda_C] \times [\lambda_D + \lambda_E]$, has been developed [13] for compounds of



(I)

structure (I), where λ_B to λ_E are substituent parameters for groups B—E, assuming that the couplings are positive. The coupling constants calculated for the dimethylamino-derivatives (Table 1) show that, although the correct trend is established with J_{P-N-P} decreasing with increasing degree of aminolysis, variations occur depending on the relative orientations of the substituents (*cis*- and *trans*-isomers) and, perhaps more important, the nature of the substituents on the third phosphorus atom.

The same points have recently been made for fluoro- [14] and fluoro(phenyl)-cyclophosphazenes.[15] Possibly, a better general set of calculated values could be obtained by inclusion of smaller λ' values for the substituents at the third phosphorus atom, but the correlation would become very unwieldy, and even then fail to cope with results such as that for geminal $N_3P_3Cl_3(NMe_2)_3$. For geometrical isomers there are not yet enough data to make generalisations on the relative magnitudes of J_{P-N-P}, which are significantly different in the nongeminal forms of $N_3P_3Cl_4(NMe_2)_2$.

Primary Amine Derivatives.—A feature of this group (Table 2) is that ≡PClNHR and ≡P(NHR)$_2$ signals are generally shifted upfield relative to the ≡PCl_2 signals.

TABLE 2

^{31}P N.m.r. data for primary amine derivatives of $N_3P_3Cl_6$

Compound	M.p. (θ_c/°C)	Structure	$\delta_{\equiv PCl_2}$	$\delta_{\equiv PClR}$	$\delta_{\equiv PR_2}$	J_{P-N-P}/Hz
$N_3P_3Cl_5{\cdot}NH_2$ [a]	138—139	2,2,4,4,6:6	20.4	19.0		46.5
$N_3P_3Cl_4(NH_2)_2$ [a]	164	2,2,4,4:6,6	18.3		9.0	48.5
$N_3P_3(NH_2)_6$ [b]	220(decomp.)				15.3	
$N_3P_3(NHMe)_6$ [c]	259				21.5	
$N_3P_3Cl_5{\cdot}NHEt$	33—34	2,2,4,4,6:6	20.3	18.7		43(±2)
$N_3P_3Cl_4(NHEt)_2$	98	2,2,4,6:4-*cis*-6		20.8		
$N_3P_3(NHEt)_6$	118—119				18.0	
$N_3P_3Cl_5{\cdot}NHPr^i$	54—55	2,2,4,4,6:6	20.8	17.5		46.0
$N_3P_3Cl_2(NHPr^i)_4$	126	2,2:4,4,6,6	22.2		9.4	49.4
$N_3P_3(NHPr^i)_6$	81				12.6	
$N_3P_3Cl_5{\cdot}NHBu^t$	−10	2,2,4,4,6:6	16.0	−5.3		40.6
$N_3P_3Cl_4(NHBu^t)_2$	120—122	2,2,4,4:6,6	17.5		0.7	44.7
$N_3P_3Cl_2(NHBu^t)_4$	156	2,2:4,4,6,6	19.7		3.9	52.6
$N_3P_3Cl_4(NHPh)_2$ [d]	207.5 —208.5	2,2,4,4:6,6	20.4		2.3	48
$N_3P_3Cl_5{\cdot}NHCH_2Ph$	61	2,2,4,4,6:6	21.3	18.1		46.6
$N_3P_3Cl_4(NHCH_2Ph)_2$	70	2,2,4,6:4,6		21.1		
$N_3P_3Cl_4(NHCH_2Ph)_2$	110	2,2,4,4:6,6	21.0		9.4	44.4

[a] G. R. Feistel and T. Moeller, *J. Inorg. Nuclear Chem.*, 1967, **29**, 2731. [b] T. Moeller, unpublished results referred to in *Topics Phosphorus Chem.*, 1967, **5**, 406. [c] Chemical shifts, but not coupling constants have been reported for the series, $N_3P_3Cl_{6-n}(NHMe)_n$ (n = 1,2,6) (ref. 16). [d] H. F. Lederle, G. F. Ottmann, and E. H. Kober, *Inorg. Chem.*, 1966, **2**, 1818.

The values reported by Lehr [16] for methylamino-derivatives are exceptions. The trend appears to be unique to the cyclophosphazenes, for both primary and secondary amine derivatives of phosphoryl chloride display low-field shifts relative to the parent compound (R = Cl),[17] as illustrated below:

$Cl_2P(O){\cdot}R$ =	Cl	NHMe	NHEt	$NHPr^i$	$NHBu^t$
^{31}P shift: δ =	3	18	16	13	10

The most complete series of derivatives is that obtained with t-butylamine, $N_3P_3Cl_{6-n}(NHBu^t)_n$ (n = 1, 2, or 4), and here apparently erratic changes in shifts of the ≡P(NHBu^t)$_2$ group accompany unit changes in n. It is peculiar to find that the ≡PCl_2 shifts approach the value for $N_3P_3Cl_6$ with increasing degree of aminolysis.

Changes in electronegativity, π-bonding, and bond angles are known to affect ^{31}P chemical shifts,[6] but in most cases it is difficult to isolate these parameters. It is worth noting that a so-called 'γ effect' has been recognised [18] for the ^{31}P chemical shifts of alkylphosphine

[8] R. Keat and R. A. Shaw, *J. Chem. Soc.* (*A*), 1968, 703.
[9] R. Keat and R. A. Shaw, unpublished results.
[10] E. G. Finer and R. K. Harris, *Progr. in N.M.R. Spectroscopy*, 1970, **6**, 86.
[11] K. Schumann and A. Schmidpeter, *Phosphorus*, 1973, **3**, 51.
[12] F. Heatley and S. M. Todd, *J. Chem. Soc.* (*A*), 1966, 1152.
[13] E. G. Finer, *J. Mol. Spectroscopy*, 1967, **23**, 104.
[14] P. Clare, D. B. Sowerby, R. K. Harris, and M. I. M. Wazeer, *J.C.S. Dalton*, 1975, 625.
[15] C. W. Allen, *J. Magnetic Resonance*, 1971, **5**, 435.
[16] W. Lehr, *Z. anorg. Chem.*, 1967, **352**, 27.
[17] G. Bulloch and R. Keat, *J.C.S. Dalton*, 1974, 2010.
[18] L. D. Quin and J. J. Breen, *Org. Magnetic Resonance*, 1973, **5**, 17.

oxides. This shows that the introduction of methyl-groups in a γ-position relative to phosphorus results in an additive upfield ^{31}P chemical shift. This effect may also be important for the alkylamino-derivatives described here, for increasing methyl-group substitution at the γ-position from Me to Bu^t, for example in the series $N_3P_3(NHR)_6$ (R = Me, Et, and Pr^i), results in a progressive upfield shift.

The fact that primary and secondary amine residues tend to shift ^{31}P signals in opposite directions relative to that for $N_3P_3Cl_6$ means that structural and coupling constant data are readily obtained for mixed amine derivatives (Table 3). Indeed, the relative shifts in these cases are often greater than when secondary amine residues and chlorine are present. However, the interpretation of variations in these coupling constants where phosphorus is bonded to a primary amine residue is difficult.[10] Thus in Table 2 we find that monoamino-derivatives, $N_3P_3Cl_5$·NHR, have smaller couplings than $N_3P_3Cl_5$·NMe_2, but that increasing replacement of chlorine atoms (in geminal compounds) increases J_{P-N-P} relative to the value for dimethylamino-derivatives, especially when R = Pr^i or Bu^t. This latter trend implies that primary amine residues are less effective in supplying electron density to phosphorus than secondary amine residues, if the previously established electronegativity relationship [12] is valid here. This contention is supported by recent ^{35}Cl n.q.r. measurements,[19] which suggest that the P–Cl bond in the ≡PClNHR grouping is less polar than the same bond in the ≡PClNR$_2$ grouping. Basicity measurements, on the other hand,[20] show that the primary amine derivatives have higher pK_a' values than secondary amine derivatives, but in this case the phosphazene ring is perturbed by nitrogen protonation. It would, therefore, have been interesting to compare coupling constants for hydrogen halide adducts, but only one of these was available (Table 3). In this case J_{P-N-P} was much reduced in $N_3P_3(NMe_2)_2(NHEt)_4$·HCl relative to the free base; this result might be anticipated if the coupling is dominated by the Fermi contact term,[10] because ring protonation is known [21,22] to lengthen the endocyclic P–N bonds relative to those in the free base.

Amino-derivatives of $N_4P_4Cl_8$.—Very little ^{31}P n.m.r. data have been reported for derivatives of $N_4P_4Cl_8$, and in those cases where structural assignments have been sought,[23,24] ambiguities arise because of $^1H \cdots {}^{31}P$ spin-coupling effects. The ^1H spectra of these derivatives are generally of limited use in distinguishing isomers with structures such as (II), (III), and (IV).

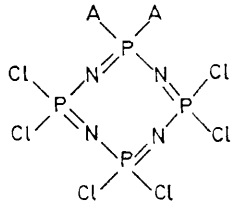
The ^{31}P n.m.r. spectra of these isomers † would be of the types AB_2C, AA'BB', and A_2B_2 respectively, which are readily recognised, except that it is not easy to distinguish AA'BB' and A_2B_2 spin systems when J/δ_{AB} becomes relatively small.

TABLE 3

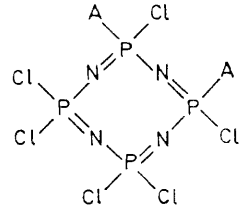
^{31}P N.m.r. data for mixed amine derivatives of $N_3P_3Cl_6$

Compound	M.p.(θ_c/°C)	Structure	$\delta_{\equiv PR_2}$ or $\delta_{\equiv PRR'}$		J_{P-N-P}/Hz
$N_3P_3(NH_2)_2(NMe_2)_4$	155	2,2:4,4,6,6	19.2	26.0 [a]	41.5
$N_3P_3(NMe_2)_2(NHEt)_4$	117	2-*trans*-4:2,4,6,6	18.9	22.8	42.1
$N_3P_3(NMe_2)_2(NHEt)_4$·HCl	155—157	2-*trans*-4:2,4,6,6	12.3	17.3	30.0
$N_3P_3(NMe_2)_4(NHEt)_2$	126	2,2,4-*cis*-6:4,6	26.6 [a]	22.8	42.2
$N_3P_3(NMe_2)_2(NHPr^i)_4$	42	2,2:4,4,6,6	25.8 [a]	14.2	45.7
$N_3P_3(NMe_2)_4(NHPr^i)_2$	76—78	2,2,4,6:4,6	24.8 [a]	20.0	41.9
$N_3P_3(NMe_2)_5(NHPr^i)$	74—75	2,2,4,4,6:6	25.4 [a]	20.2	43.7
$N_3P_3(NMe_2)_2(NHBu^t)_4$	67	2,2:4,4,6,6	22.4 [a]	8.2	45.2
$N_3P_3(NMe_2)_2(NHBu^t)_4$	106	2,4:2,4,6,6	19.1	12.0	49.1

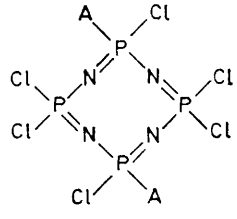
[a] ≡P(NMe_2)$_2$.



(II)



(III)



(IV)

(A = amino-group)

Structural assignments based on the recognition of these spin systems assume that possible differences in ring conformations are small and do not affect the ^{31}P spectra. Examples of A_2B_2 spectra are provided by the isomers $N_4P_4Cl_6R_2$ (R = NMe_2, NHEt, and NHBu^t) and

† Isomeric hexakisamino-derivatives, $N_4P_4Cl_2A_6$, have the same overall symmetry, and may, therefore, be distinguished in the same way.

[19] W. H. Dalgleish, R. Keat, A. L. Porte, D. A. Tong, M-Ul-Hasan, and R. A. Shaw, *J.C.S. Dalton*, 1975, 309.

[20] D. Feakins, S. N. Nabi, R. A. Shaw, and P. Watson, *J. Chem. Soc.* (*A*), 1969, 2468.

[21] N. V. Mani and A. J. Wagner, *Acta Cryst.*, 1971, **B27**, 51; W. Polder and A. J. Wagner, personal communication to R. A. Shaw.

[22] H. R. Allcock, E. C. Bissell, and E. T. Shawl, *Inorg. Chem.*, 1973, **12**, 2963; S. J. Rettig and J. Trotter, *Canad. J. Chem.*, 1973, **51**, 1295.

[23] K. John, T. Moeller, and L. F. Audrieth, *J. Amer. Chem. Soc.*, 1960, **82**, 5616.

[24] G. Mattogno and A. Monaci, *Ricerca sci.*, 1965, **3**, 1139.

$N_4P_4Cl_2(NMe_2)_6$ listed in Table 4 and these are easily analysed.[25] The ^{31}P spectrum of $N_4P_4Cl_6(NMe_2)_2$, m.p. 170 °C, is shown in Figure 3; the A_2B_2 spectrum establishes a 2,4,4,6,8,8 : 2,6 structure, but not the relative orientations of the amino-groups. An example of an AA'BB' spectrum has been reported elsewhere [26] [2,4-$N_4P_4Cl_6(NMePh)_2$, m.p. 105—106 °C] but its full analysis has not yet been completed.

It has already been observed [11] that decreased coupling constants are obtained when one of the phosphorus atoms in a cyclotriphosphazene ring is replaced by a carbon atom and a modified set of λ_L values has been devised to take account of this. This decrease appears to be related to a decrease in the angles at nitrogen and phosphorus in the ring. By the same token one might expect that the larger ring angles in the tetramer relative

TABLE 4

^{31}P N.m.r. data for selected amino-derivatives of $N_4P_4Cl_8$

Compound	M.p.(θ_c/°C)	Structure	$\delta_{\equiv PCl_2}$	$\delta_{\equiv PClR}$	$\delta_{\equiv PR_2}$	J_{P-N-P}/Hz
$N_4P_4Cl_8$	123		−6.7			
$N_4P_4Cl_6(NMe_2)_2$	170	2,4,4,6,8,8:2-*trans*-6	−3.7	−0.2		39.7
$N_4P_4Cl_4(NMe_2)_4$	200	2,4,6,8:2-*cis*-4-*trans*-6-*trans*-8		5.2		
$N_4P_4Cl_2(NMe_2)_6$	168	2-*trans*-6:2,4,4,6,8,8		4.4	9.9	47.1
$N_4P_4(NMe_2)_8$	220—238 (d)				9.6	
$N_4P_4Cl_6(NMePh)_2$	145	2,4,4,6,8,8:2,6		5.3 [a]		
$N_4P_4Cl_6(NHEt)_2$	115	2,4,4,6,8,8:2,6	−3.4	−4.9		46.0
$N_4P_4(NHEt)_8$	116				4.3	
$N_4P_4Cl_6(NHBu^t)_2$	170—171	2,4,4,6,8,8:2,6	−6.3	−10.8		39.7
$N_4P_4(NHBu^t)_8$	180—200 (d)				−3.1	

[a] An alternative geminal structure is possible, but we consider that a singlet is very unlikely to be observed when $\equiv PCl_2$ and $\equiv P(NMePh)_2$ groups are present.

The replacement of chlorine by amino-groups in $N_4P_4Cl_8$ generally results in a downfield ^{31}P shift, but with $N_3P_3Cl_6$ this is only true for secondary amine or

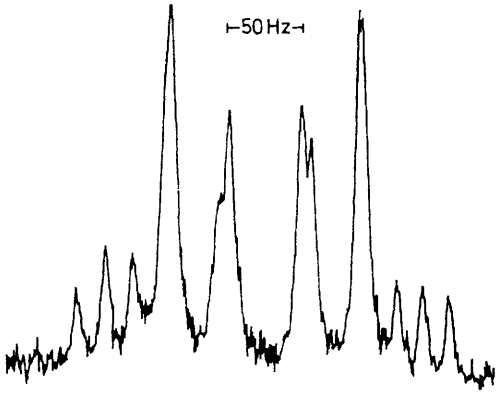


FIGURE 3 ^1H-Decoupled ^{31}P n.m.r. spectrum of $N_4P_4Cl_6(NMe_2)_2$, m.p. 170 °C

methylamine derivatives. It is still a general observation though, that primary amine derivatives give ^{31}P signals upfield of secondary amine derivatives. There is a relatively large difference in shifts between $N_4P_4Cl_8$ and $N_4P_4(NMe_2)_8$ (16.3 p.p.m.) compared to a mere 4.1 p.p.m. in the analogous trimeric compounds. However, when the t-butylamino-derivatives are considered, the range for the tetramer is 7.7 p.p.m. compared with 23.6 p.p.m. for the trimer. It is tempting to suggest that these differences may be associated with the known greater deviations from planarity of the tetramer relative to the trimer ring, but this remains to be established.

[25] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Resonance Spectroscopy,' Pergamon, Oxford, 1965, vol. 1.

[26] R. Keat, S. S. Krishnamurthy, A. C. Sau, R. A. Shaw, M. N. Sudheendra Rao, A. R. Vasudeva Murthy, and M. Woods, *Z. Naturforsch.*, 1974, **29b**, 701.

to the trimer derivatives [*e.g.* $P\hat{N}P = 121.4(4)$ in $N_3P_3Cl_6$,[27] and 133.6, 137.6(8)° in $N_4P_4Cl_8$ [28]] might be paralleled by larger coupling constants. This does not appear to be the case with the bis(dimethylamino)-derivatives, $N_3P_3Cl_4(NMe_2)_2$ and $N_4P_4Cl_6(NMe_2)_2$ (Tables 1 and 4), where the latter has a considerably smaller coupling. Comparisons of this coupling constant in the bis-t-butylamino-derivatives (Tables 2 and 4) are hampered by the occurrence of geminal and non-geminal isomers, but here also the tetramer-derivative has the smaller value.

The data in Table 5 are included to show the effects of substituting phenyl groups for chlorine atoms on ^{31}P n.m.r. parameters. Whereas the chemical shifts are broadly in the ranges anticipated, there are several surprising changes in J_{P-N-P}. For example, variations of this parameter within the series, $N_3P_3Cl_{6-n}Ph_n$ ($n = 2$, 3, or 4) show little relation to those predicted (see Table 5), especially for the *trans*-triphenyl derivative. There is also a marked reduction in J_{P-N-P} in passing from the trimer to tetramer series which was not apparent in the amino-derivatives, and the dimethylamino(phenyl)-derivatives always have considerably larger coupling constants than their precursors, the chloro(phenyl)-derivatives. Evidently the factors which determine J_{P-N-P} in the tetramer series are more complex than in the trimer series.

Relative Signs of Coupling Constants.—In making the foregoing comparisons of $P-N-P$ coupling constants we have assumed that there is no change of sign. Analysis shows that J_{P-N-P} is of opposite sign to J_{P-F} in $N_3P_3Cl_5F$,[12] geminal $N_3P_3Cl_4F_2$,[29] and a series of fluorocyclotriphosphazatrienes with chloro-, bromo-, and dimethylamino-

[27] G. J. Bullen, *J. Chem. Soc.* (*A*), 1971, 1450.

[28] A. J. Wagner and A. Vos, *Acta Cryst.*, 1968, **B24**, 707.

[29] M. L. Heffernan and R. F. M. White, *J. Chem. Soc.*, 1961, 1382.

substituents.[14] These findings show that J_{P-N-P} is positive. Attempts to obtain the magnitude of J_{P-N-P} from the ^1H n.m.r. spectra of aminocyclophosphazenes, or even to simulate lineshapes, have so far only proved moderately successful. However, it has recently been shown [31,32] that the magnitudes and signs of P · · · P coupling constants can be obtained from the ^1H spectra of diphosphorus compounds whose spectra represent examples of $[AX_n]_2$ spin systems (X = H, A = P) in which $J_{X \ldots X'}$ is zero. This method takes advantage of the fact that transitions which give rise to the outer sharp lines in the ^1H spectrum (the N doublet), often enclosing an unresolved set of transitions, have energy

TABLE 5

^{31}P N.m.r. data for phenyl and amino(phenyl) derivatives

Compound	M.p. (θ_c/°C)	Structure	$\delta_{\equiv PCl_2}$	$\delta_{\equiv P(NMe_2)_2}$	$\delta_{\equiv PPh_2}$	J_{P-N-P}/Hz [e]
$N_3P_3Cl_4Ph_2$	95	2,2,4,4:6,6	17.1		19.5	12.1 (16.8)
$N_3P_3(NMe_2)_4Ph_2$	122	2,2,4,4:6,6		24.1	16.1	21.9
$N_3P_3Cl_3Ph_3$	158—159	2-*trans*-4,6:2,4,6			30.2(2), 32.8(1)[a]	5.4 (22.6)
$N_3P_3Cl_3Ph_3$	191—192	2-*cis*-4-*cis*-6:2,4,6			29.6 [d]	
$N_3P_3Cl_2Ph_4$	142—143	2,2:4,4,6,6	14.8		17.1 [b]	9.3 (16.8)
$N_3P_3(NMe_2)_2Ph_4$	145	2,2:4,4,6,6		21.0	15.5	16.0
$N_4P_4Cl_4Ph_4$	135	2,2,4,4:6,6,8,8	−4.5 [c]		5.9 [c]	<2
$N_4P_4Cl_4Ph_4$	212.5	2,2,6,6:4,4,8,8	−3.1 [c]		2.9 [c]	<2
$N_4P_4(NMe_2)_4Ph_4$	178	2,2,6,6:4,4,8,8		15.6 [d]	0.3	17.5
$N_4P_4Ph_8$	318—319				5.2	

[a] Figures in parentheses indicate relative intensities; these are for ≡PClPh groups. [b] For $N_3P_3Ph_6$, δ = 15.2, see ref. 1. [c] Singlets with ^1H decoupling. [d] Checked by ^1H-{^{31}P} double resonance. [e] Calculated [13] values in parentheses.

levels in common with weak outer lines in the ^{31}P spectrum. The appearance and separation of these outer lines, which were located by monitoring the components of the N-doublet in ^1H-{^{31}P} INDOR experiments, gave the relative sign and magnitude of $J_{P \ldots P}$. We have

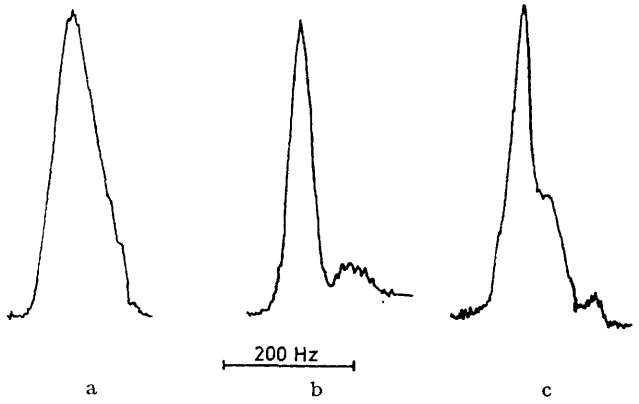


FIGURE 4 ^1H-{^{31}P} INDOR spectra of (a) *cis*-$N_3P_3Cl_3(NMe_2)_3$, (b) $N_3P_3(NMe_2)_6$, and (c) $N_4P_4(NMe_2)_8$. All spectra were obtained monitoring the high frequency component of the 'N doublet'. Mirror-image spectra were obtained by monitoring the low-frequency component. The frequency scale is common to (a), (b), and (c)

carried out the same experiment on the symmetrical dimethylamino-derivatives, *cis*-$N_3P_3Cl_3(NMe_2)_3$, $N_3P_3(NMe_2)_6$, and $N_4P_4(NMe_2)_8$ and obtained the positions of the outer lines in the ^{31}P spectrum (Figure 4). The outer lines were not identifiable in the single-resonance ^{31}P spectra. Unfortunately, expressions for the transition frequencies of $(AX_n)_{3 \text{ or } 4}$ systems have not been calculated (although expressions for some of the X frequencies are known [33]), but it is likely that the separation of the outer lines from the central multiplet will give an upper limit to J_{P-N-P}. In $N_3P_3(NMe_2)_6$, the separation of the two groups of outer lines was 120 ± 5 Hz, and in *cis*-$N_3P_3Cl_3(NMe_2)_3$ it was of a similar order (Figure 4). This separation would appear to be about 3 J_{P-N-P}, for the data in Table 1 suggests that J_{P-N-P} would be *ca.* 40 Hz in these derivatives. It is worth noting that the simpler $(AX)_3$ spin system will include two ab_2 subspectra,[34] which, when $\delta/J_{ab} \longrightarrow 0$, will consist of an intense central line with two symmetrically placed outer lines of separation 3 J_{ab}. The results imply that the INDOR experiment locates the ^{31}P ab_2 subspectra in the more complex $(AX_n)_3$ spin systems. Any further conclusions regarding the magnitude of J_{P-N-P} will require a detailed consideration of the A(^{31}P) spectra. This is especially true of the INDOR spectra of $N_4P_4(NMe_2)_8$, in which two multiplets were located on either side of the more intense central multiplet. An important aspect of these INDOR experiments is that the high-field component of the N doublet is always connected with the low frequency (high field) set of outer lines in the ^{31}P spectrum. In the $(AX_n)_2$ system it is known [32,33] that this type of behaviour indicates that J_{P-N-P} and N (see below) have the same relative sign, and we assume that this is also true of the more complex $(AX_{12})_{3,4}$ systems. Thus J_{P-N-P} has the same sign as N (= $J_{P-N-C-H}$ + 2 $J_{P-N-P-N-C-H}$) in the trimeric system, and, since $J_{P-N-P-N-C-H}$ is likely to be small or zero, the same sign as $J_{P-N-C-H}$, known to be positive.[35] We may, therefore, be fairly confident that J_{P-N-P} has a positive sign in all amino- and aminochloro-cyclotriphosphazatrienes and cyclotetraphosphazatetraenes. It might perhaps be prudent to carry out relative sign determinations on

[30] E. G. Finer, R. K. Harris, M. R. Bond, R. Keat, and R. A. Shaw, *J. Mol. Spectroscopy*, 1970, **33**, 72.
[31] W. McFarlane and D. S. Rycroft, *J.C.S. Faraday II*, 1974, 377.
[32] R. J. Goodfellow and B. F. Taylor, *J.C.S. Dalton*, 1974, 1676.
[33] E. G. Finer and R. K. Harris, *J. Chem. Soc.* (*A*), 1969, 1972.
[34] P. Diehl, R. K. Harris, and R. G. Jones, *Progr. N.M.R. Spectroscopy*, 1967, **3**, 1.
[35] R. D. Bertrand, F. B. Ogilvie, and J. G. Verkade, *J. Amer. Chem. Soc.*, 1970, **92**, 1908.

cyclophosphazenes with relatively small $J_{P\text{-}N\text{-}P}$ values, such as those with phenyl or thioalkoxy-substituents [1] before further generalisations are made with regard to the sign of this parameter.

'Virtual Coupling' Effects.—The ^{31}P n.m.r. parameters for the dimethylaminocyclophosphazenes are consistent with the conditions [36] for the appearance of the so called 'virtual coupling' effects in the ^{1}H spectra of these compounds, which generally take the form of a 'hump' between the components of the sharp doublet, previously described. These conditions are that (*a*) $|N| \leq |J_{P\text{-}N\text{-}P}|$, and (*b*) the chemical shift between the ^{31}P nuclei giving rise to these effects is small or zero. For example, the monodimethylamino-derivative, $N_3P_3Cl_5 \cdot NMe_2$, shows virtual coupling because the shift between the ^{31}P signals is *ca.* 1 p.p.m., but this is not the case in geminal $N_3P_3(NMe_2)_2(NHBu^t)_4$, where the ^{31}P shift is larger (*ca.* 12 p.p.m.), even though $J_{P\text{-}N\text{-}P}$ is of a similar order in both compounds (49.1 and 45.2 Hz respectively). Inspection of Table 1 shows that the chlorodimethylamino-derivatives least likely to show these effects are geminal $N_3P_3Cl_3(NMe_2)_3$ ([$\equiv$PClNMe$_2$] signals) and *cis*-$N_3P_3Cl_2(NMe_2)_4$([$\equiv$P(NMe$_2$)$_2$] signals) where the ^{31}P shift differences are 5.6 and 7.4 p.p.m. respectively. The effect is illustrated by the 220 MHz ^{1}H spectrum of geminal $N_3P_3Cl_3(NMe_2)_3$ (Figure 5) where the only

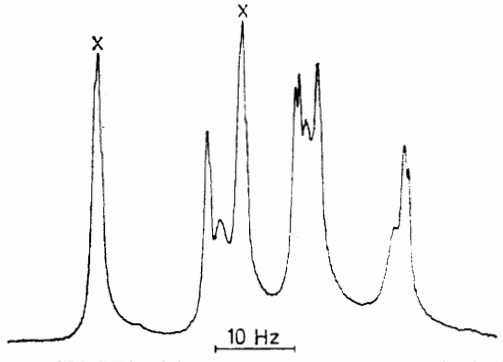


FIGURE 5 220 MHz ^{1}H n.m.r. spectrum of geminal $N_3P_3Cl_3(NMe_2)_3$. The low-field doublet marked X arises from the $\equiv$PClNMe$_2$ group

'clean' doublet is that at low field and associated with the $\equiv$PClNMe$_2$ group.

The effect of differences in ^{31}P chemical shifts on virtual coupling effects has been used to advantage in distinguishing positional isomers of dimethylaminocyclophosphazenes.[37-39] For example, the geminal (2,2,6,6 : 4,4,8,8-isomer) of $N_4P_4(NMe_2)_4Ph_4$ (Table 5) is distinguished from the 2,2,4,4 : 6,6,8,8-isomer by the absence of virtual coupling effects in the former derivative,[38] where the ^{31}P shift is now shown to be 15.3 p.p.m. The non-appearance of virtual coupling effects in this isomer also implies that $J_{P\text{-}N\text{-}P\text{-}N\text{-}P}$ is small (*ca.* <10 Hz).

[36] R. K. Harris and E. G. Finer, *Bull. Soc. chim. France* 1968, 2805.
[37] S. K. Das, R. Keat, R. A. Shaw, and B. C. Smith, *J. Chem. Soc.* (*A*), 1966, 1677.
[38] G. J. Bullen, P. E. Dann, V. B. Desai, R. A. Shaw, B. C. Smith, and M. Woods, *Phosphorus*, 1973, **3**, 67.

Other Coupling Effects.—It is a general observation that the line widths of the ^{31}P signals of cyclophosphazenes are greater than those observed for phosphorus compounds where nitrogen is not adjacent to phosphorus.

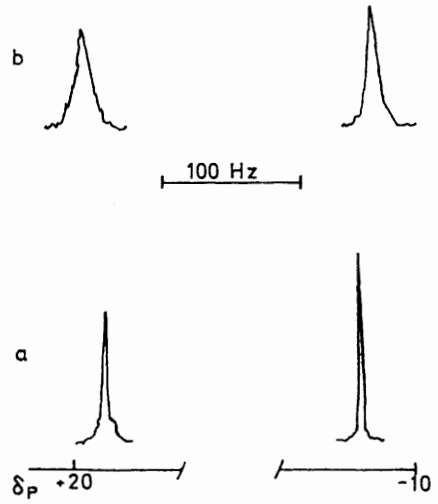


FIGURE 6 ^{31}P N.m.r. spectra of a mixture of $N_3P_3Cl_6$ and $N_4P_4Cl_8$ in chlorobenzene solution (a) at *ca.* 20 °C, (b) at 130 °C

The line widths of the ^{31}P signals of $N_3P_3Cl_6$ and $N_4P_4Cl_8$ (Figure 6) at half peak height are *ca.* 8 and 4 Hz respectively at 20 °C. The ^{31}P signals of both compounds broaden as the temperature is raised, which suggests the operation of an ^{14}N coupling effect. It is to be expected that the rate of ^{14}N quadrupole relaxation will be slower at higher temperatures and so increased coupling effects will be observed.[40] Unfortunately we have not been able to confirm this suggestion because the ^{31}P spectra are unaffected by power irradiation over a wide range of frequencies in the ^{14}N region, even at higher temperatures. There was no discernible increase or decrease in these broadening effects when chlorine was replaced by amino-groups, which leads us to discount the possibility that broadening might be caused by coupling with $^{35}Cl/^{37}Cl$ quadrupolar nuclei. It is worth noting that the ^{31}P spectrum of $Cl_3P{=}N{-}P(O)Cl_2$ shows [41] a broader $Cl_3P{=}$ signal than $-P(O)Cl_2$ signal, a result also interpretable in terms of a larger coupling between ^{14}N and ^{31}P nuclei through a formal double-bond than through a formal single-bond.

EXPERIMENTAL

Cyclotriphosphazatrienes and phenylcyclotetraphosphazatetraenes were synthesised by literature methods,[1] and the preparation of most of the aminochlorocyclotetraphosphazatetraenes (Table 4) will be described in future publications. ^{31}P N.m.r. spectra were recorded on a JEOL C60HL spectrometer at 24.3 MHz in the external-lock field-sweep mode using methylene chloride solutions. A JEOL SDHC

[39] M. Biddlestone, S. S. Krishnamurthy, R. A. Shaw, M. Woods, G. J. Bullen, and P. E. Dann, *Phosphorus*, 1973, **3**, 179.
[40] J. D. Roberts, *J. Amer. Chem. Soc.*, 1956, **78**, 4495.
[41] G. Bulloch and R. Keat, unpublished results.

unit was used for ^{1}H power/noise irradiation. Charts were calibrated by observation of the shifts produced by changes in the ^{31}P frequencies, which were measured on a frequency counter. Coupling constants should, in general, be accurate to ± 1 Hz, except where otherwise stated. ^{1}H-{^{31}P} experiments were carried out on the same spectrometer, and INDOR spectra obtained using a voltage ramp to drive synchronously the interpolation unit of a Schomandl ND100M Frequency Synthesiser and the *X*-axis of an X-Y recorder. ^{14}N Frequencies were derived from the frequency synthesiser and amplified using the SDHC unit.

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