PHOSPHORUS-NITROGEN COMPOUNDS. PART 62.[1] THE REACTIONS OF 2,2-DIAMINO-4,4,6,6,8,8-HEXACHLORO- AND 2,6-DIAMINO-2,4,4,6,8,8-HEXACHLORO CYCLOTETRAPHOSPHAZATETRAENE WITH SODIUM METHOXIDE IN METHANOL. THE FIRST EXAMPLE OF AMINO GROUP MIGRATION IN THE TETRAMER SYSTEM. ^{31}P, ^{1}H, AND ^{13}C NUCLEAR MAGNETIC RESONANCE SPECTROSCOPIC INVESTIGATIONS OF THE PRODUCTS

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The reaction of octachlorocyclotetraphosphazatetraene with aqueous ammonia yields the geminal 2,2- and the nongeminal 2,6-diamides, $N_4P_4Cl_6(NH_2)_2$ as well as a trace of the monoamide, $N_4P_4Cl_7(NH_2)$. The reactions of 2,2-diamino-4,4,6,6,8,8-hexachloro- and 2,6-diamino-2,4,4,6,8,8-hexachloro-cyclotetraphosphazatetraene with sodium methoxide in methanol were studied. The former yields the geminal hexamethoxide, $N_4P_4(NH_2)_2(OMe)_6$, a rearranged 2,6-isomer (being the first example of an amino group migration in the tetramer system), and the heptamethoxide, $N_4P_4(NH_2)(OMe)_7$, whilst the latter gives rise to two isomeric 2,6-derivatives, $N_4P_4(NH_2)_2(OMe)_6$, together with the heptamethoxide. The ^{31}P, ^{1}H and ^{13}C nuclear magnetic resonance spectra of the products are reported.

The partial ammonolysis of the hexachloride, $N_3P_3Cl_6$, (1) yields only a bis-amino derivative, $N_3P_3Cl_4(NH_2)_2$, (2), whose structure long controversial, has now been firmly established by X-ray crystallography to be geminal.[2] The mono amino compound, $N_3P_3Cl_5(NH_2)$, (3) has only been obtained by deamination of the diamide (2).[3]

Our understanding of the partial ammonolysis of the octachloride, $N_4P_4Cl_8$, (4) is less clear. De Ficquelmont[4] on passing ammonia gas through an ether solution of the octachloride (4), isolated a bis amino compound of m.p. 217–218°C and a tetra-amino derivative, m.p. 161–162°C. The reaction was repeated by Lehr and Pietschmann,[5] who established the structures of the above as 2,6(*cis* or *trans*)

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(5) and 2,2,6,6 (6), respectively. Ramabrahman *et al.*[6] on treatment of the octa-chloride (4) with aqueous ammonia obtained an isomeric diamide, m.p. 86–89°C, whose ^{31}P n.m.r. spectrum was of the A_2BC type and the geminal structure (7) was assigned to this.

The same conclusion was drawn from ^1H n.m.r. spectroscopy on derivatising compound (7) with dimethylamine to give the hexakis(dimethylamino) derivative, $N_3P_3(NH_2)_2(NMe_2)_6$.[6]

We now report a re-examination of the reaction of the octachloride (4) with aqueous ammonia. Three derivatives were isolated: (i) The geminal diamide (7), (ii) its nongeminal 2,6-isomer (5) (for structure see later) and the mono amide $N_4P_4Cl_7(NH_2)$, (8). The last was only obtained in trace yields. The absence of stereoisomeric products in nongeminal amino derivatives of the octachloride (4) has been noted earlier. The two isomeric diamides, (5), and (7), were treated with sodium methoxide in methanol. We have earlier shown that the analogous reaction of the trimeric diamide (2) gave both unrearranged (9) and rearranged tetramethoxides, $N_3P_3(NH_2)_2(OMe)_4$, (10A and 10B).[7,8,9] The structures of the geminal and of the *cis*-product were crystallographically determined.[9]

(5)

(7)

(11)

(13)
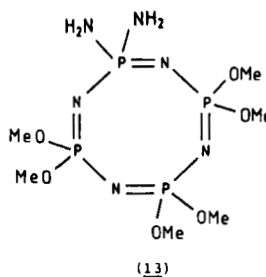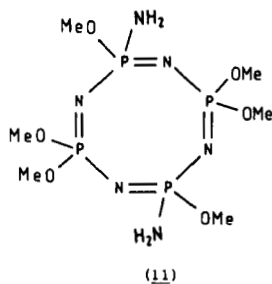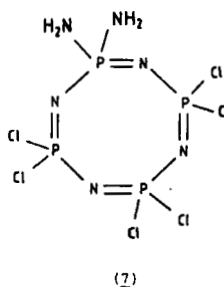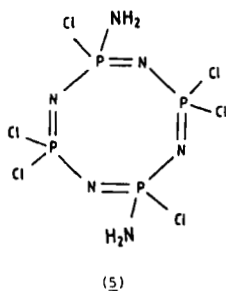
The reaction of the nongeminal diamide (5) yielded four fractions: (i) and (ii) were isomeric 2,6-bisamino-2,4,4,6,8,8-hexamethoxycyclotetraphos-phazatetraenes, $N_4P_4(NH_2)_2(OMe)_6$ (11A and 11B), fraction (iii) was the mono amino derivative $N_4P_4(NH_2(OMe)_7$, (12). The remaining fraction (iv) was an oil, not completely identified, with the same mass spectrometric molecular weight (398) as the isomers (11A and 11B). It could be a 2,4-isomer or a partially

rearranged product (OMe→NMe rearrangement). The occurrence of stereoisomeric products (**11A** and **11B**) is in keeping with similar findings in the trimer series.[9]

When the geminal diamide (**7**) was subjected to the same treatment as above. Three fractions were isolated. These were: (i) the unrearranged product, $N_4P_4(NH_2)_2(OMe)_6$, (**13**), and (ii) one of the isomeric rearranged products, m.p. 82–84°C (**11A**). The third component (iii) was the monoamide (**12**).

We now discuss the n.m.r. spectra of the above and their use in deducing the structures put forward.

Phosphorus-31 n.m.r. spectroscopy

Compound (**5**) has an A_2X_2 spectrum which clearly proves its 2,6-structure. By contrast its isomer, compound (**7**), has a much more complex spectrum of the A_2BX type (Figure 1a). A cross correlation spectrum (Figure 1b) allows the correct assignment of coupling constants.

The methanolysed derivatives (**11A** and **11B**) and (**13**) show the expected A_2X_2 and A_2BC type of spectra corresponding to 2,6- and 2,2-structures respectively. The data are collected in Table I together with those for the trimer systems. We note the following interesting features: (i) $\Delta\delta$, the chemical shift changes on passing from the six-membered (N_3P_3) to the eight-membered (N_4P_4) system varies systematically with the donor power of the substituants, $\Delta\delta$ PCl_2
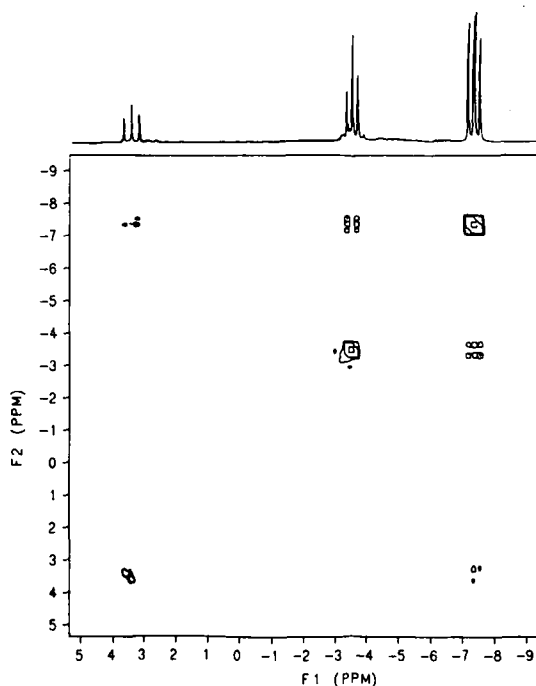

FIGURE 1   (a) ^{31}P {^1H} spectrum. (b) Cross correlation spectrum, both of (**7**) at room temperature in acetone at 162.0 MHz.

TABLE I

The ³¹P n.m.r. data of the aminochloro- and aminomethoxy-cyclophosphazenes[a]

Compound	Pattern	δPCl₂[b]	δP(NH₂)₂[b]	δPCl(NH₂)[b]	²J(PCl₂–P(NH₂)₂)[c]	²J(PCl₂–PCl(NH₂))[c]	²J(PCl₂–PCl₂)[c]
(4)	A₄	−6.7					
(5)	A₂X₂	−4.3					
(7)	A₂BX	−6.0(2)[d] −4.8(1)[d]		−1.4	33.6	38.5	28.0
(1)	A₃	19.9					
(2)	AX₂	21.1					
(3)	AB₂	22.2	8.26	18.9	50.0	49.0	

Compound	Pattern	δP(OMe)₂[b]	δP(NH₂)₂[b]	δP(OMe)(NH₂)[b]	²J[P(OMe)₂–P(NH₂)₂][c]	²J[P(OMe)₂–P(OMe)(NH₂)][c]	²J[P(OMe)₂–P(OMe)₂][c]
(11A)	A₂X₂	4.1		7.9			64.6
(11B)	A₂X₂	4.15		7.9			64.6
(13)	A₂BC	4.2[e]		7.6		f	f
(12)	A₂BC	4.0[e]		8.0			
N₄P₄(OMe)₈	A₄	3.9					
(9)	A₂B	20.8	19.7		52.3		
(10A) trans	A₂B	20.1		23.8			66.9
(10B) cis	A₂B	19.7		23.6			68.4
N₃P₃(NH₂)(OMe)₅	A₂B	21.0		24.9			69.4
N₃P₃(OMe)₆	A₃	21.6					

[a] In CDCl₃ at 80.98 and 162.0 MHz. (85% orthophosphoric acid as external reference) at room temperature. [b] in p.p.m. [c] in Hz. [d] numbers in brackets refer to relative number of nuclei in these environments. [e] Centre of A₂B signal. [f] Too complex to be analysed.

(24–28 p.p.m.) $> \Delta\delta$ PCl(NH$_2$) (21 p.p.m.) $> \Delta\delta$ P(OMe)$_2$ (16–18 p.p.m.) $> \Delta\delta$ P(OMe)(NH$_2$) (15–17 p.p.m.) $>$ P(NH$_2$)$_2$ (9–12 p.p.m.). If we use basicity substituent constants[10] α_R as a measure of donor power $\Sigma\alpha_R$ for Cl$_2$ (0.0) $<$ Cl(NH$_2$) (6.0) $<$ (OMe)$_2$ (7.6) $<$ (OMe)(NH$_2$) (9.6) $<$ (NH$_2$)$_2$ (12.0), we observe a nice proportionality, $\Delta\delta$ decreases as α_R increases.

A similar trend, though less uniform, can be observed for ΔJ, this being the difference in $^2J(PP)$ (N$_3$P$_3$) and $^2J(PP)$ (N$_4$P$_4$), where ΔJ decreases with increasing donor power of the substituents.

^1H n.m.r. spectroscopy

The data for the compounds described in this paper together with the corresponding trimer derivatives are summarised in Table II. Chemical shifts and coupling constants are fairly uniform, with perhaps $^3J(PH)$ marginally larger in

TABLE II

The ^{1}H n.m.r. data of the aminomethoxycyclophosphazenes[a]

Compound	δP(OCH$_3$)$_2$[b]	δP(OCH$_3$)P(NH$_2$)[b]	$^3J(PH)$[c,d]	$^3J(PH)$[c,e]	Multiplicity[g] ³¹P coupled [d]	[e]	³¹P decoupled [d]	[e]
(11A)	3.63	3.64	12.0	12.4	d	d	s	s
(11B)	3.64	3.65	12.0	12.3	d	d	s	s
(13)	3.64		12.0		m[f]		s	s
	3.66		12.0					
(12)	3.65	3.65	12.0	12.0	m[f]	m[f]	s	s
	3.64		12.0				s	
	3.64		12.0					s
	3.63		12.0				s	
N$_4$P$_4$(OMe)$_8$	3.67		12.4		qt[f]			
(10A) trans	3.68	3.63	12.1	13.3	d	t	s	s
(10B) cis	3.68	3.63	12.0	13.1	d	t	s	s
	3.66		13.4		d		s	
(9)	3.66		12.7		t[f]		s	
N$_3$P$_3$(NH$_2$(OMe)$_5$	3.67	3.63	12.5	12.5	d[f]	d	s	s
	3.68		12.5		d[f]		s	
N$_3$P$_3$(OMe)$_6$	3.67		12.7		qt	s		

[a] In CDCl$_3$ at 250.48 and 399.95 MHz. (TMS internal reference) at room temperature. [b] in p.p.m. [c] in Hz. [d] refers to P(OMe)$_2$. [e] refers to (P(OMe)(NH$_2$) [f] denotes the presence of second order effects. [g] s = singlet, d = doublet, t = triplet, q = quartet, qt = quintet, m = multiplet.

the trimer series. Multiplicities due to second order effects are greater in the tetramer series. Compound (12) has its five methoxy proton environments clearly resolved on decoupling of the phosphorus nuclei (Figure 2).

Carbon-13 n.m.r. spectra

These are in Table III together with those of the trimer derivatives. The values in the table are fairly uniform, except for the greater multiplicity (due to second order effects) in the tetramer series. As in the trimer system[9] the chemical shifts of the methoxy resonances in the P(NH$_2$)(OMe) groups are always somewhat more shielded than those of their geminal counterparts P(OMe)$_2$.
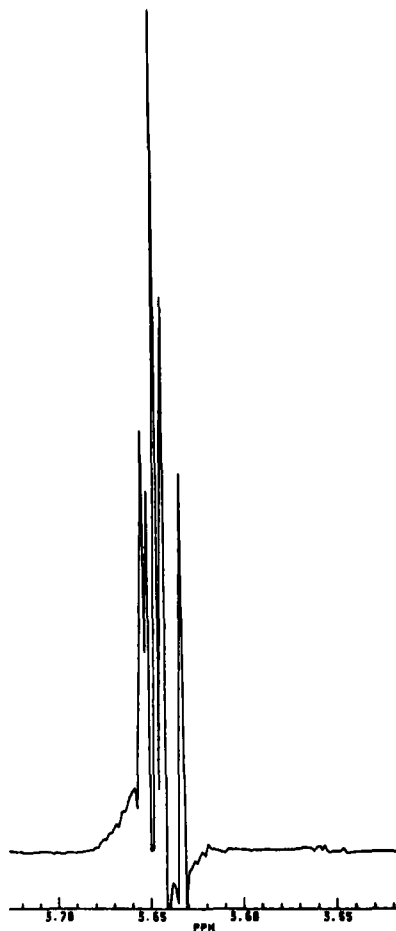
FIGURE 2 ^{1}H {^{31}P} spectrum of (12) at room temperature in CDCl$_3$ at 250.48 MHz.

Experimental

Chemicals were obtained as follows: benzene, light petroleum (b.p. 60–80°C), anhydrous diethyl ether (May and Baker Ltd.), tetrahydrofuran (Fluka-Garantie 99.5%), deuteriated solvents for n.m.r. spectroscopy (Aldrich Chem. Co. Ltd.), anhydrous sodium sulphate, pyridine, methanol, dichloromethane, ammonia solution, sodium metal (B.D.H. Chemical Ltd.), hexachlorocyclotriphosphaza-triene (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 Ninhydrin (0.5% w/v) in butanol solution, and developed at approximately 130°C. Separation of products were carried out by flash column chromatography[8] using Kieselgel 60. Melting points were deter-mined on a Reichert-Kofler microheating stage and a Mettler FB 82 hot stage connected to a FP 800 Central Processor both fitted with a polarising microscope. ^{1}H N.m.r. spectra were recorded using a Bruker WH 250 spectrometer (operating

TABLE III

The ^{13}C n.m.r. data of the aminomethoxycyclophosphazenes[a]

Compound	$\delta P(OCH_3)_2$[b]	$\delta P(OCH_3)(NH_2)$[b]	$^2J(PC)$[c,d]	$^2J(PC)$[c,e]	Multiplicity[g] d	e
(11A)	52.9	52.3	6.2	6.2	t[f]	t[f]
(11B)	52.8	52.2	6.2	6.2	t[f]	t[f]
(13)	52.9		~5.4		4 lines	
(12)	52.9	52.2	~5.4	6.3	5 lines d	
$N_4P_4(OMe)_8$	53.0			5.4	qt[f]	
(10A) trans	52.5	52.0	6.0	6.2	d	t[f]
(10B) cis	52.6	52.0	5.9	6.4	d	t[f]
	52.5		5.4		d	
(9)	52.5		5.4		t[f]	
$N_3P_3(NH_2(OMe)_5$	52.6	52.0	5.3	6.2	t[f]	d
	52.5		5.3		t[f]	
$N_3P_3(OMe)_6$	52.9		5.6		q[f]	

[a] In CDCl₃ at 50.10 and 100.577 MHz (TMS internal reference) at room temperature. [b] in p.p.m. [c] in Hz. [d] refers to P(OMe)₂. [e] refers to P(OMe)(NH₂). [f] denotes the presence of second order effects. [g] s = singlet, d = doublet, t = triplet, q = quartet, qt = quintet.

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 CDCl₃ and placed in 5 mm n.m.r. tubes. Measurements were carried out using a CDCl₃ lock, TMS as internal reference and sample concentrations of 15–20 mg/cm³.

^{31}P N.m.r. spectra were recorded using a Varian XL-200 spectrometer (operating at 80.98 MHz.—University College, London), and a Varian VXR 400 spectrometer (operating at 162.0 MHz.—University College, London), 85% H₃PO₄ was used as an external reference.

^{13}C N.m.r. spectra were recorded using a JEOL JNM FX-200 spectrometer (operating at 50.10 MHz.) and a Varian XL-400 spectrometer (operating at 100.577 MHz.—University College, London), TMS was used as an internal reference and CDCl₃ as a lock solvent.

The mass spectra were recorded using a VG 7070 H mass spectrometer with Finnigan INCOS Data System at University College, London and a VG ZAB IF mass spectrometer at the School of Pharmacy.

EXPERIMENTAL

The ammonolysis of the octachloride (4). Anhydrous sodium sulphate (75 g) was suspended in a solution of the tetramer (4) (5.6 g, 12 mmol) in diethyl ether (250 cm³) at 0°C. Whilst stirring vigorously, aqueous ammonia solution (3.5 cm³, 17 M, 48 mmol) in diethyl ether (50 cm³) was added dropwise over 1 h. The mixture was filtered and the solvent removed under vacuum, giving the crude product mixture. This was extracted with light petroleum (b.p. 60–80°C) (3 × 30 cm³) and the extract left to crystallise under anhydrous conditions to give 2,2-bisamino-4,4,6,6,8,8-hexachlorocyclotetraphosphazetetraene, (7), m.p. 86–89°C yield 1.0 g (20%). The residue was dissolved in diethyl ether and t.l.c. showed three spots, two major and a minor one. These were separated using dichloromethane/THF (2:1) as eluent [or light petroleum (b.p. 60–80°C)/diethyl ether (2:1)]. The first fraction gave 2,6-bisamino-2,4,4,6,8,8-hexachlorocyclotetraphosphazatetraene (5) m.p. 216–217°C [CH₂Cl₂/PhMe (5:1)], yield 0.66 g (12%). The second fraction gave an extra 0.26 g (5%) of the gem bisamino isomer (7). The last fraction, a minor product was the 2-monoamino-2,4,4,6,6,8,8-hepta-

TABLE IV

Analytical data

Formula	Compound	M.p. (°C)	Found (%)					Found[a] M^+	Required					Required M
			C	H	N	P	Cl		C	H	N	P	Cl	
$H_4N_6P_4Cl_6$	(7)	86–89	—	1.0	19.7	—	49.8	422	—	1.0	19.8	—	50.2	422
$H_4N_6P_4Cl_6$	(5)	216–217	—	1.0	19.9	—	50.4	422	—	1.0	19.8	—	50.2	422
$C_6H_{22}N_6O_6P_4$	(11A)[b]	82–84	18.3	5.6	21.3	31.1	—	398	18.1	5.5	21.1	31.2	—	398
$C_6H_{22}N_6O_6P_4$	(11B)	oil	18.0	5.7	21.0	31.2	—	398	18.1	5.5	21.1	31.2	—	398
$C_7H_{23}N_5O_7P_4$	(12)	oil	20.5	5.6	16.8	30.0	—	413	20.3	5.6	16.9	30.0	—	413
$C_6H_{22}N_6O_6P_4$	(13)	oil	18.4	5.3	20.9	31.3	—	398	18.1	5.5	21.1	31.2	—	398

[a] Based on the mass of the most abundant isotope. [b] Recrystallised from CH_2Cl_2/toluene mixture.

chlorocyclotetraphosphazatetraene (8) (Found: M^+ 441; $H_2N_5P_4^{35}Cl_7$ requires M^+ 441). Not enough product was obtained for microanalysis or ^{31}P n.m.r. spectroscopy.

Alcoholysis of the geminal bisamino compound (7) *using an excess of sodium methoxide in methanol.* Sodium (1.8 g, 78 mmol) was dissolved in methanol (80 cm^3) and the geminal bisamino compound (7) (5 g, 12 mmol) (7) added at 0°C with stirring. The reaction mixture was allowed to reach room temperature and left standing for 24 h in a desiccator. The reaction mixture was filtered and the solvent removed under vacuum. The resulting oil was dissolved in a minimum of dichloromethane and passed three times through a column to obtain good separation. Three out of the four fractions (four spots by t.l.c.) were isolated using CH_2Cl_2/THF (2:1) as eluent.

(i) 2-monoamino-2,4,4,6,6,8,8-heptamethoxycyclotetraphosphazatetraene (0.2 g, 4.1%) (12); (ii) 2,6-bisamino-2,4,4,6,8,8-hexamethoxycyclotetraphosphazetetraene (0.6 g, 12.3%) (11A); (iii) 2,2-bisamino-4,4,6,6,8,8-hexamethoxycyclotetraphosphazetetraene (0.32 g, 6.5%) (13). Analytical data are summarised in Table IV.

Alcoholysis of the non-geminal bisamino isomer (5) *using an excess of sodium methoxide in methanol.* Sodium (1.8 g, 78 mmol) was added to methanol (80 cm^3) and the non-geminal bisamino isomer (5) (5 g, 12 mmol) was added to the solution at 0°C with stirring. The reaction mixture was allowed to reach room temperature and stored in a desiccator for 48 h. The reaction mixture was filtered and the solvent removed under vacuum to give a colourless oil. The oil was dissolved in the minimum of dichloromethane and passed twice through a column using CH_2Cl_2/THF (1:1) as eluent. All four fractions were isolated (four spots by t.l.c.).

(i) Unidentified oil, trace amount M^+ 398; (ii) 2-monoamino-2,4,4,6,6,8,8-heptamethoxycyclotetraphosphazatetraene (0.1 g, 2.1%) (12); (iii) 2,6-bisamino-2,4,4,6,6,8,8-hexamethoxycyclotetraphosphazatetraene (0.5 g, 10.4%) (11A); 2,6-bisamino-2,4,4,6,8,8-hexamethoxycyclotetraphosphazatetraene (0.2 g, 4.2%) (11B).

Analytical data are summarised in Table IV.

ACKNOWLEDGEMENTS

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