Phosphorus–Nitrogen Compounds. Part 54.[1] The Reactions of Geminal $N_3P_3(NH_2)_2Cl_4$ and of $N_3P_3(NH_2)Cl_5$ with Alkoxide Ions in Alcohols. The Geminal $\equiv P(NH_2)_2$ to Non-geminal $\equiv P(NH_2)(OR)$ Rearrangement. The Crystal Structures of *trans*-$N_3P_3(NH_2)_2(OPr^n)_4$, *cis*-$N_3P_3(NH_2)_2(OMe)_4$, and Geminal $N_3P_3(NH_2)_2(OMe)_4$†‡

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Geminal $N_3P_3(NH_2)_2Cl_4$ has been allowed to react with alkoxide ions in alcohol to give rearranged *cis*- and *trans*-$N_3P_3(NH_2)_2(OR)_4$ (R = Me, Et, Pr^n, or Bu^n), as well as unrearranged geminal $N_3P_3(NH_2)_2(OR)_4$ (R = Me). The ^1H, ^{13}C, and ^{31}P n.m.r. spectra are reported. The crystal structures of *trans*-$N_3P_3(NH_2)_2(OPr^n)_4$, geminal and *cis*-$N_3P_3(NH_2)_2(OMe)_4$ are presented, the last two being present in a 1 : 1 ratio in the same unit cell.

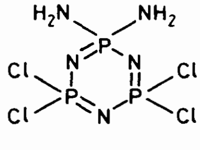
The reversible *cis* $\rightleftharpoons$ *trans* isomerisation of non-geminal aminochlorocyclotriphosphazatrienes[2–6] and the irreversible rearrangement alkoxycyclophosphazene $\longrightarrow$ *N*-alkyl-*P*-oxo-cyclophosphazane are now well established.[7–14] The geminal $\equiv P(NH_2)_2$ to non-geminal $\equiv P(NH_2)(OR)$ migration is described here.

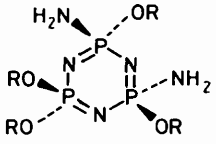
The structure of diaminotetrachlorocyclotriphosphazatriene, $N_3P_3(NH_2)_2Cl_4$ (**1**), has been controversial. Non-geminal and geminal structures have been proposed, with the latter predominating.[15–25] Three derivatives of (**1**), *viz.* $N_3P_3(NH_2)_2F_4$ (**2**),[26] $N_3P_3(NPPh_3)_2Cl_4$ (**3**),[27] and $N_3P_3(NPPh_3)(NH_2)Cl_4$ (**4**),[28,29] have been examined by *X*-ray crystallography and found to have a geminal disposition of the two nitrogen-containing substituents. ^{31}P N.m.r. investigations with and without proton coupling at room temperature and at −80 °C did not yield totally unambiguous results.[22] The recent crystal structure determination of compound (**1**) proved conclusively its geminal nature.[29]

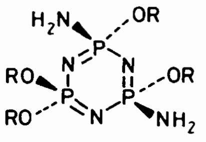
We have investigated the reactions of (**1**) with sodium alkoxide in refluxing alcohols to obtain fully alcoholysed products [equation (1)].[20,22] Initially we obtained the *trans*-

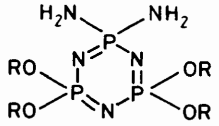
$$(1) + NaOR-ROH \longrightarrow N_3P_3(NH_2)_2(OR)_4 \quad (1)$$

non-geminal derivatives, $N_3P_3(NH_2)_2(OR)_4$ (R = Me, Et,[20,22] Pr^n,[20,22] or Bu^n [20,22]) (**5**), which are the major products. We also isolated smaller yields of the *cis* isomers, $N_3P_3(NH_2)_2(OR)_4$ (R = Me, Et, Pr^n, or Bu^n) (**6**), and (for R = Me only) also the unrearranged geminal derivative, $N_3P_3(NH_2)_2(OR)_4$ (**7**). The three isomers having R = Me, (**5**)—(**7**), were eventually separated by high-performance liquid chromatography (h.p.l.c.), the *trans* derivative being only sparingly soluble in most organic solvents except alcohols. Initially, the *trans* isomer, because of its insolubility, was overlooked and fractional crystallisation yielded well shaped crystals, which gave an A_2B ^{31}P n.m.r. spectrum at room temperature. Crystallographic examination showed that these crystals contained geminal and *cis* isomers in a 1:1 ratio. Subsequently, low-temperature ^{31}P n.m.r. spectroscopy showed the existence of two A_2B spectra.


(**1**)


(**5**) (*trans*)
R = Me, Et,
Pr^n, or Bu^n


(**6**) (*cis*)
R = Me, Et,
Pr^n, or Bu^n


(**7**)
R = Me

The monoamino-derivative $N_3P_3(NH_2)Cl_5$ (**8**) was prepared and fully alcoholysed under similar conditions to give $N_3P_3(NH_2)(OR)_5$ (**9**; R = Me). The parent hexa-alkoxy derivatives, $N_3P_3(OR)_6$ (**10**; R = Me or Et), were also reprepared for spectroscopic comparison.

Results and Discussion

Crystallography.—Compounds (**5**; R = Pr^n) (**6**; R = Me), and (**7**; R = Me) were investigated crystallographically. The positional parameters and bond lengths and angles are listed in Tables 1 and 2 for (**5**), 3 and 4 for (**6**) and (**7**) and Figures 1, 2, and 3 show the averaged bond lengths and angles for (**5**), (**6**),

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‡ 2-*trans*-4-Diamino-2,4,6,6-tetra-n-propoxo-, 2-*cis*-4-diamino-2,4,6,6-tetramethoxo-, and 2,2-diamino-4,4,6,6-tetramethoxo-cyclotri(λ^5-phosphazene).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Fractional atomic co-ordinates (× 10^4) (non-hydrogen atoms), (× 10^3) (hydrogen atoms) for $N_3P_3(NH_2)_2(OPr^n)_4$

Atom	*x*	*y*	*z*
P(2A)	2 446(1)	6 393(3)	8 629(2)
P(6A)	1 558(1)	5 561(3)	8 627(1)
P(4A)	1 778(1)	7 008(2)	9 416(2)
N(1A)	2 096(4)	5 620(8)	8 431(5)
N(3A)	2 297(4)	7 064(8)	9 143(4)
N(5A)	1 428(3)	6 233(7)	9 141(4)
O(2A1)	2 964(3)	5 986(10)	8 834(6)
O(2A2)	2 592(5)	6 958(10)	8 062(5)
O(6A)	1 447(3)	4 550(6)	8 834(4)
N(6A)	1 175(4)	5 688(8)	8 024(5)
O(4A)	1 502(4)	7 962(7)	9 339(5)
N(4A)	1 849(4)	6 933(9)	10 147(5)
P(2B)	982(1)	3 802(3)	6 634(1)
P(4B)	501(1)	3 827(3)	5 477(1)
P(6B)	43(1)	4 448(3)	6 486(1)
N(1B)	518(3)	4 199(7)	6 909(4)
N(3B)	950(3)	3 556(7)	5 942(4)
N(5B)	54(3)	4 294(7)	5 773(4)
O(2B1)	1 390(3)	4 509(7)	6 807(4)
O(2B2)	1 189(3)	2 973(8)	7 038(4)
O(4B)	324(4)	2 947(7)	5 124(4)
N(4B)	670(4)	4 468(8)	4 948(5)
O(6B)	−86(3)	5 478(6)	6 596(4)
N(6B)	−417(4)	3 905(8)	6 734(4)
H(6A1)	125(4)	531(7)	766(3)
H(6A2)	87(3)	602(8)	811(6)
H(4A1)	152(2)	710(9)	1 028(6)
H(4A2)	218(2)	717(9)	1 029(7)
H(4B1)	99(3)	442(10)	475(6)
H(4B2)	44(3)	491(6)	474(5)
H(6B1)	−40(4)	422(7)	715(2)
H(6B2)	−78(2)	402(13)	666(10)

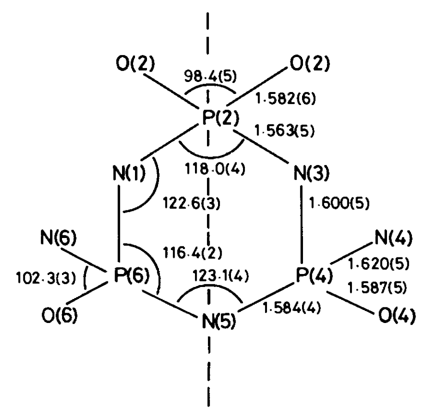

Figure 1. Averaged bond lengths (Å) and angles (°) (across dashed line) for *trans*-$N_3P_3(NH_2)_2(OPr^n)_4$

Table 2. Bond lengths (Å) and bond angles (°) for $N_3P_3(NH_2)_2(OPr^n)_4$

N(1A)–P(2A)	1.541(10)	N(3A)–P(2A)	1.578(11)
O(2A1)–P(2A)	1.594(12)	O(2A2)–P(2A)	1.574(12)
N(1A)–P(6A)	1.589(9)	N(5A)–P(6A)	1.563(9)
O(6A)–P(6A)	1.593(9)	N(6A)–P(6A)	1.645(11)
N(3A)–P(4A)	1.608(10)	N(5A)–P(4A)	1.589(10)
O(4A)–P(4A)	1.603(11)	N(4A)–P(4A)	1.603(10)
N(1B)–P(2B)	1.579(9)	N(3B)–P(2B)	1.554(9)
O(2B1)–P(2B)	1.566(10)	O(2B2)–P(2B)	1.592(10)
N(3B)–P(4B)	1.603(9)	N(5B)–P(4B)	1.602(8)
O(4B)–P(4B)	1.569(10)	N(4B)–P(4B)	1.593(10)
N(1B)–P(6B)	1.599(9)	N(5B)–P(6B)	1.581(1)
O(6B)–P(6B)	1.581(9)	N(6B)–P(6B)	1.637(10)
N(3A)–P(2A)–N(1A)	117.9(5)	O(2A1)–P(2A)–N(1A)	109.9(8)
O(2A1)–P(2A)–N(3A)	108.4(6)	O(2A2)–P(2A)–N(1A)	111.4(7)
O(2A2)–P(2A)–N(3A)	109.3(7)	O(2A2)–P(2A)–O(2A1)	98.1(8)
N(5A)–P(6A)–N(1A)	115.7(5)	O(6A)–P(6A)–N(1A)	109.6(7)
O(6A)–P(6A)–N(5A)	109.1(5)	N(6A)–P(6A)–N(1A)	110.1(6)
N(6A)–P(6A)–N(5A)	109.5(6)	N(6A)–P(6A)–O(6A)	101.9(6)
N(5A)–P(4A)–N(3A)	116.0(5)	O(4A)–P(4A)–N(3A)	110.6(7)
O(4A)–P(4A)–N(5A)	108.4(5)	N(4A)–P(4A)–N(3A)	109.1(7)
N(4A)–P(4A)–N(5A)	110.8(5)	N(4A)–P(4A)–O(4A)	100.8(8)
P(6A)–N(1A)–P(2A)	123.6(7)	P(4A)–N(3A)–P(2A)	121.7(7)
P(4A)–N(5A)–P(6A)	124.1(5)	O(2B1)–P(2B)–N(1B)	105.1(5)
N(3B)–P(2B)–N(1B)	118.1(5)	O(2B2)–P(2B)–N(1B)	110.1(5)
O(2B1)–P(2B)–N(3B)	112.2(5)	O(2B2)–P(2B)–O(2B1)	98.7(6)
O(2B2)–P(2B)–N(3B)	110.8(5)	O(4B)–P(4B)–N(3B)	107.9(6)
N(5B)–P(4B)–N(3B)	116.2(5)	N(4B)–P(4B)–N(3B)	110.5(6)
O(4B)–P(4B)–N(5B)	109.3(5)	N(4B)–P(4B)–O(4B)	103.3(6)
N(4B)–P(4B)–N(5B)	108.8(5)	O(6B)–P(6B)–N(1B)	108.6(5)
N(5B)–P(6B)–N(1B)	117.5(4)	N(6B)–P(6B)–N(1B)	109.2(5)
O(6B)–P(6B)–N(5B)	108.0(5)	N(6B)–P(6B)–O(6B)	103.0(5)
N(6B)–P(6B)–N(5B)	109.4(5)	P(4B)–N(3B)–P(2B)	123.1(6)
P(6B)–N(1B)–P(2B)	121.9(5)		
P(6B)–N(5B)–P(4B)	122.4(5)		

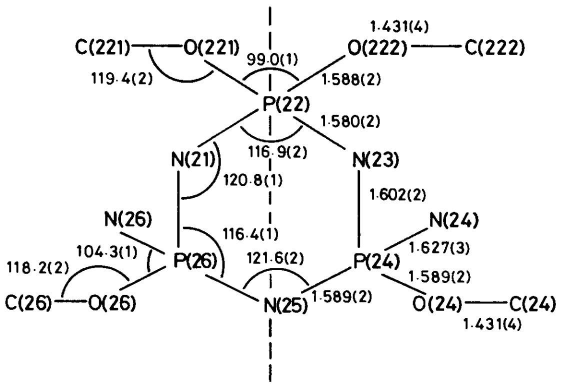

Figure 2. Averaged bond lengths (Å) and angles (°) (across dashed line) for *cis*-$N_3P_3(NH_2)_2(OMe)_4$

and (7) respectively, the last two compounds crystallising together and occupying the same unit cell in a 1 : 1 ratio.

Compound (5; R = Pr^n) was the first rearranged compound to be isolated and the first crystal structure of its type to be determined.[20,22] High thermal motions of the n-propyl groups prevented us from obtaining a good structure (*R* = 0.10). The structure is stabilised by extensive hydrogen bonding and within that framework the alkyl chains can take up different orientations. Little else can be added to the description which appeared in the preliminary publication.[20]

Compounds (6; R = Me) and (7; R = Me) gave much better data, *R* = 0.045. It has been shown earlier in compounds of the type geminal $N_3P_3X_2Cl_4$ (where X are nitrogen-containing substituents) that a very considerable lengthening of the P–N ring bond adjacent to X_2P and very considerable shortening of the ring bond adjacent to Cl_2P occurs (for recent summaries see refs. 29 and 30). We call this Δ(P–N). For X = amino groups, Δ(P–N) ranges from 0.04 to 0.07 Å.[29] A similar, but lesser effect, is observed when X = alkoxy groups, Δ(P–N) = 0.02—0.03 Å.[30] For the geminal compound $N_3P_3(NH_2)_2(OMe)_4$, Δ(P–N) is of the order of 0.03 Å, with the bonds adjacent to $(H_2N)_2P$ being the longer ones (Figure 3).

For non-geminal $\equiv PCl(NR_2)$ groupings Δ(P–N) is 0.03—0.04 Å and part of the back donation of the lone pair of the

Table 3. Fractional atomic co-ordinates (× 10^4) (non hydrogen atoms), (× 10^3) (hydrogen atoms) for $N_3P_3(NH_2)_2(OMe)_4$

Atom	*x*	*y*	*z*
P(12)	−45(1)	7 425(1)	−1 105(1)
P(14)	3 304(1)	7 797(1)	171(1)
P(16)	2 050(1)	5 872(1)	−32(1)
N(11)	177(4)	6 394(3)	−681(3)
N(13)	1 472(4)	8 167(3)	−580(3)
N(15)	3 470(4)	6 720(3)	527(3)
N(161)	2 695(6)	4 730(3)	−910(4)
N(162)	1 981(5)	5 451(3)	946(3)
O(141)	3 902(4)	8 784(2)	1 205(2)
O(142)	4 842(4)	7 698(3)	−346(3)
O(121)	−302(5)	6 940(3)	−2 395(3)
O(122)	−1 848(4)	8 202(3)	−1 098(3)
C(121)	−654(8)	7 655(5)	−3 053(4)
C(122)	—2 117(7)	9 023(4)	−75(4)
C(141)	2 826(6)	9 267(4)	1 965(4)
C(142)	4 863(7)	6 861(4)	−1 367(4)
P(22)	1 083(1)	7 356(1)	3 918(1)
P(24)	2 928(1)	9 110(1)	5 178(1)
P(26)	4 535(1)	7 185(1)	3 920(1)
N(21)	2 617(4)	6 850(3)	3 315(3)
N(23)	1 242(4)	8 506(3)	4 818(3)
N(25)	4 631(4)	8 356(3)	4 816(3)
O(221)	817(4)	6 514(2)	4 458(2)
O(222)	−740(3)	7 384(2)	3 031(2)
N(24)	2 378(5)	10 214(3)	4 758(3)
O(24)	3 422(4)	9 578(3)	6 463(2)
N(26)	5 481(6)	7 012(4)	2 968(4)
O(26)	5 711(4)	6 303(2)	4 549(2)
C(221)	521(7)	5 417(4)	3 793(4)
C(222)	−1 086(6)	7 998(4)	2 265(4)
C(24)	3 883(8)	8 830(6)	7 097(5)
C(26)	5 834(7)	5 140(4)	3 923(5)
H(161)	224(7)	470(5)	−143(4)
H(162)	364(8)	439(5)	−68(4)
H(163)	199(6)	594(4)	158(4)
H(164)	145(6)	499(4)	79(4)
H(244)	319(6)	1 068(4)	495(4)
H(245)	133(7)	1 057(4)	478(4)
H(264)	481(7)	700(4)	232(4)
H(265)	636(6)	726(4)	313(4)

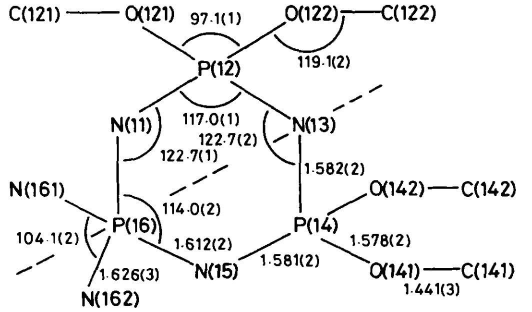

Figure 3. Averaged bond lengths (Å) and angles (°) (across dashed line) for *gem*-$N_3P_3(NH_2)_2(OMe)_4$

Table 4. Bond lengths (Å) and bond angles (°) for $N_3P_3(NH_2)_2(OMe)_4$ (**6**, **7**; R = Me)

N(11)–P(12)	1.575(3)	N(13)–P(12)	1.583(3)
O(121)–P(12)	1.603(3)	O(122)–P(12)	1.559(3)
N(13)–P(14)	1.580(3)	N(15)–P(14)	1.587(3)
O(141)–P(14)	1.572(3)	O(142)–P(14)	1.577(3)
N(11)–P(16)	1.608(3)	N(15)–P(16)	1.615(3)
N(161)–P(16)	1.636(4)	N(162)–P(16)	1.616(4)
C(141)–O(141)	1.441(5)	C(142)–O(142)	1.435(5)
C(121)–O(121)	1.417(6)	C(122)–O(122)	1.470(5)
N(21)–P(22)	1.591(3)	N(23)–P(22)	1.569(3)
O(221)–P(22)	1.592(3)	O(222)–P(22)	1.582(3)
N(23)–P(24)	1.603(3)	N(25)–P(24)	1.594(3)
N(24)–P(24)	1.625(4)	O(24)–P(24)	1.583(3)
N(21)–P(26)	1.601(3)	N(25)–P(26)	1.584(3)
N(26)–P(26)	1.629(4)	O(26)–P(26)	1.595(3)
C(221)–O(221)	1.427(5)	C(222)–O(222)	1.434(5)
C(24)–O(24)	1.413(6)	C(26)–O(26)	1.448(5)
H(161)–N(161)	0.67(5)	H(162)–N(161)	0.83(5)
H(163)–N(162)	0.88(5)	H(164)–N(162)	0.75(5)
H(244)–N(24)	0.89(4)	H(245)–N(24)	0.95(5)
H(264)–N(26)	0.88(5)	H(265)–N(26)	0.79(5)
N(13)–P(12)–N(11)	117.4(2)	O(121)–P(12)–N(11)	106.1(2)
O(121)–P(12)–N(13)	110.2(2)	O(122)–P(12)–N(11)	113.9(2)
O(122)–P(12)–N(13)	108.9(2)	O(122)–P(12)–O(121)	98.7(2)
N(15)–P(14)–N(13)	116.5(2)	O(141)–P(14)–N(13)	111.5(2)
O(141)–P(14)–N(15)	109.7(2)	O(142)–P(14)–N(13)	110.5(2)
O(142)–P(14)–N(15)	111.1(2)	O(142)–P(14)–O(141)	95.5(2)
N(15)–P(16)–N(11)	114.0(2)	N(161)–P(16)–N(11)	105.6(2)
N(161)–P(16)–N(15)	113.4(2)	N(162)–P(16)–N(11)	114.8(2)
N(162)–P(16)–N(15)	104.7(2)	N(162)–P(16)–N(161)	104.1(2)
P(16)–N(11)–P(12)	122.2(2)	P(14)–N(13)–P(12)	122.7(2)
P(16)–N(15)–P(14)	123.1(2)	C(141)–O(141)–P(14)	118.8(3)
C(142)–O(142)–P(14)	117.0(3)	C(121)–O(121)–P(12)	121.3(3)
C(122)–O(122)–P(12)	119.4(3)	N(23)–P(22)–N(21)	116.9(2)
O(221)–P(22)–N(21)	112.0(2)	O(221)–P(22)–N(23)	107.1(2)
O(222)–P(22)–N(21)	108.7(2)	O(222)–P(22)–N(23)	111.8(2)
O(222)–P(22)–O(221)	99.0(1)	N(25)–P(24)–N(23)	116.2(2)
N(24)–P(24)–N(23)	109.1(2)	N(24)–P(24)–N(25)	110.4(2)
O(24)–P(24)–N(23)	107.4(2)	O(24)–P(24)–N(25)	108.4(2)
O(24)–P(24)–N(24)	104.5(2)	N(25)–P(26)–N(21)	116.5(2)
N(26)–P(26)–N(21)	106.4(2)	N(26)–P(26)–N(25)	114.3(2)
O(26)–P(26)–N(21)	110.1(2)	O(26)–P(26)–N(25)	104.7(2)
O(26)–P(26)–N(26)	104.1(2)	P(26)–N(21)–P(22)	119.6(2)
P(24)–N(23)–P(22)	122.0(2)	P(26)–N(25)–P(24)	121.6(2)
C(221)–O(221)–P(22)	118.7(3)	C(222)–O(222)–P(22)	120.1(2)
C(24)–O(24)–P(24)	119.5(3)	C(26)–O(26)–P(26)	116.9(3)
H(161)–N(161)–P(16)	114(5)	H(162)–N(161)–P(16)	115(4)
H(162)–N(161)–H(161)	128(6)	H(163)–N(162)–P(16)	118(3)
H(164)–N(162)–P(16)	117(3)	H(164)–N(162)–H(163)	116(4)
H(244)–N(24)–P(24)	120(3)	H(245)–N(24)–P(24)	115(3)
H(245)–N(24)–H(244)	113(4)	H(264)–N(26)–P(26)	118(3)
H(265)–N(26)–P(26)	119(3)	H(265)–N(26)–H(264)	115(4)

amino substituent causes significant shortening of the exocyclic P–N bond and significant lengthening of the P–Cl bond. This is also reflected in much higher ^{35}Cl n.q.r. frequencies for $\equiv PCl_2$ groups than for $\equiv PCl(NR_2)$ groups.[31–34]

As in the non-geminal systems mentioned above one might expect a considerably smaller exocyclic transfer in a ≡PCl(OR) group. Few data are available on compounds of this type. The spiro-ansa (ansa means a difunctional ligand bridging two different phosphorus atoms in the same molecule) derivative, $N_3P_3[O(CH_2)_3O]_2Cl_2$, has the moiety ≡PCl(OR).[35] No significant changes were detected between the $\equiv P(OR)_2$ and ≡PCl(OR) groups. It must be pointed out, however, that the *trans*-annular bridge has introduced a considerable strain into this molecule,[36] and this may have effects, which could obscure differences noticeable in unstrained structures.

Again only a small exocyclic transfer might be expected in a non-geminal $\equiv P(NH_2)(OR)$ moiety. In the present system this is obscured by hydrogen-bonding effects, which as we have shown elsewhere have profound effects on bond lengths and angles.[29] In the present structures we note that NH_2 substituents forming two hydrogen bonds have somewhat shorter P–N bonds than those which form only one and this effect appears to be more pronounced than the differences between geminal and non-geminal amino alkoxy structures.

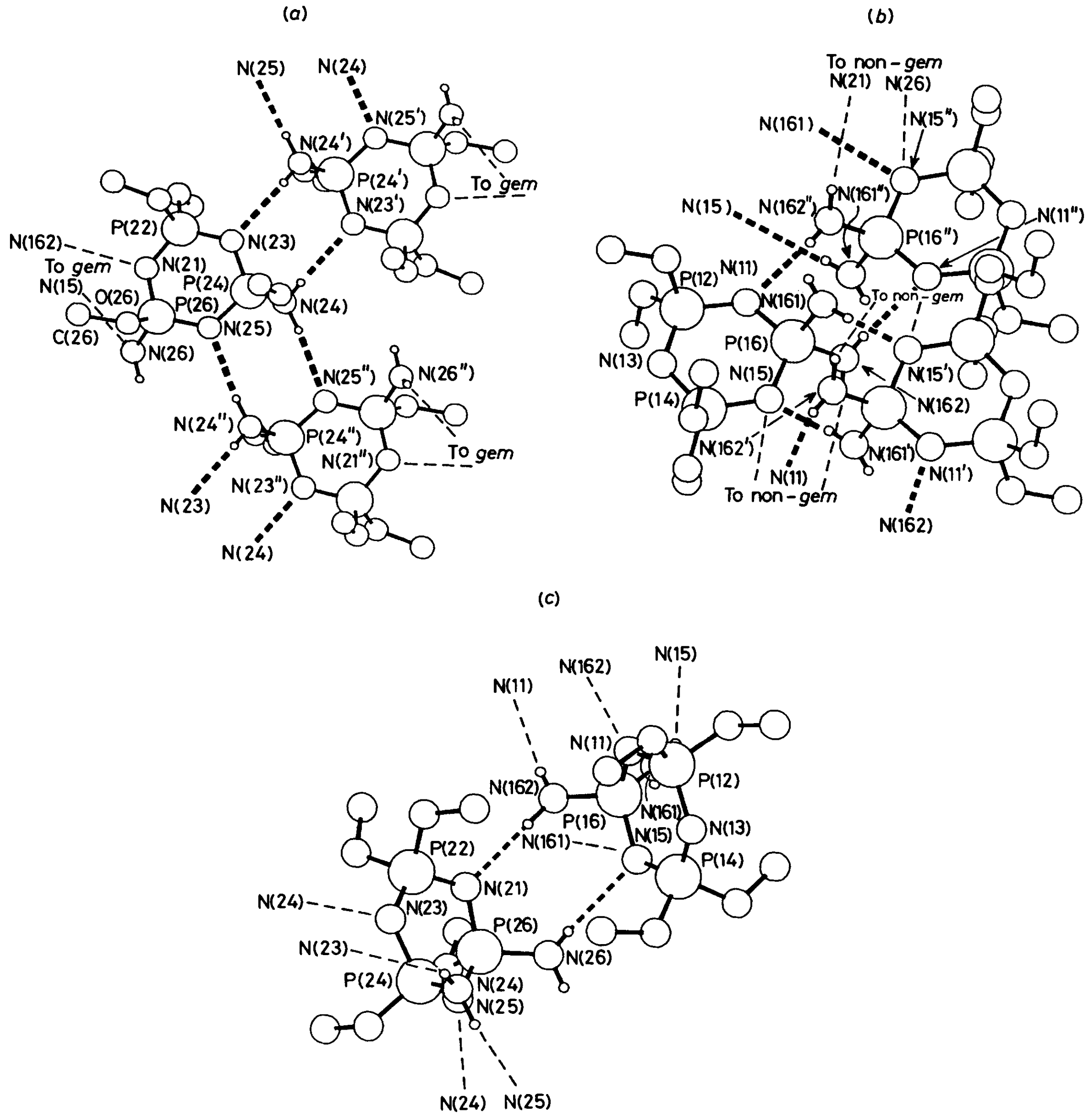

Figure 4. Hydrogen-bonded network of the 1 : 1 complex between *cis*- and *gem*-$N_3P_3(NH_2)_2(OMe)_4$: (*a*) between *cis*-units [primed and double primed atoms are related to unprimed atoms by symmetry operations (−*x*, 2.0 − *y*, 1.0 − *z*) and (1.0 − *x*, 2.0 − *y*, 1.0 − *z*) respectively; N(23′) ··· N(24) 3.118 and N(25″)... N(24) 3.206 Å]; (*b*) between geminal units [primed and double primed atoms are related to unprimed atoms by symmetry operations (1.0 − *x*, 1.0 − *y*, −*z*) and (−*x*, 1.0 − *y*, −*z*) respectively; N(15′) ··· N(161) 3.198 and N(11″) ··· N(162) 3.160 Å]; and (*c*) between *cis* and geminal units [N(26) ··· N(15) 3.121 and N(162) ··· N(21) 3.041 Å]

It has been shown elsewhere,[37,38] that in general, bond-angle changes provide a more reliable guide than bond-length changes relating to electron donor–acceptor properties. In particular, the endocyclic bond angle α (the one adjacent to the two substituents in question) shows a decrease with increased electron-donor capacity.[29,30,38] Thus, in the geminal isomer $N_3P_3(NH_2)_2(OMe)_4$ the α angle adjacent to the $\equiv P(NH_2)_2$ moiety is 114.0(2)°, whilst the averaged α angle for the $\equiv P(OMe)_2$ group is 117.0(1)°, showing clearly the greater electron-releasing capacity of the former. In the non-geminal *cis*-isomer the differences are very much less pronounced. The α angle adjacent to $\equiv P(OMe)_2$ is 116.9(2)°, virtually identical with that of the geminal isomer, whilst that adjacent to $\equiv P(NH_2)(OMe)$ has an average value of 116.4(1)°, indicating only a marginally greater electron density here.

The exocyclic bond angles vary substantially. In the geminal isomer NPN is 104.1(2)° and thus much larger than the average OPO angles of 97.1(1)°, again indicative of the greater π-back bonding capacity of the former. In the *cis*-non-geminal isomer, the OPO angle of 99.0(1)° is larger than its counterpart in the geminal isomer, but the OPN exocyclic bond angles, which average 104.3(1)°, are almost identical to the exocyclic NPN angle in the geminal isomer.

As mentioned above, anticipated bond-length changes in this non-geminal grouping giving rise to a shortened exocyclic P–N bond and lengthened P–O bond, compared to those in the geminal $P(NH_2)_2$ and $P(OMe)_2$ groupings, are obscured by hydrogen-bonding effects. The rather more sensitive bond-angle changes reveal, however, that the considerable size of the OPN angle is probably associated with back donation of the NH_2 lone pair. This, in turn, would imply a lesser back donation from the oxygen lone pair and this is just noticeable in the decreased POC bond angles in the non-geminal isomer, average 118.2(2)° compared to 119.4(2) and 119.1(2)° in the geminal moieties of

Table 5. ^{31}P N.m.r. data in $CDCl_3$ at room temperature (recorded at field strengths 24.15 MHz and 80.98 MHz)

Compound	δ/p.p.m.					Coupling constants, Hz,
	PCl_2	$PCl(NH_2)$	$P(NH_2)_2$	$P(NH_2)(OR)$	$P(OR)_2$	^2J(P–P)
$N_3P_3(NH_2)_2Cl_4$	21.1		8.26			50.0
$N_3P_3(NH_2)Cl_5$	22.2	18.9				49.0
gem-$N_3P_3(NH_2)_2(OMe)_4$			19.69		20.78	52.3
trans-$N_3P_3(NH_2)_2(OMe)_4$				23.80	20.10	66.9
cis-$N_3P_3(NH_2)_2(OMe)_4$				23.58	19.70	68.4
trans-$N_3P_3(NH_2)_2(OEt)_4$				21.30	16.30	66.7
cis-$N_3P_3(NH_2)_2(OEt)_4$				21.90	16.80	65.5
trans-$N_3P_3(NH_2)_2(OPr^n)_4$				21.40	16.50	66.4
cis-$N_3P_3(NH_2)_2(OPr^n)_4$				22.35	17.30	65.8
trans-$N_3P_3(NH_2)_2(OBu^n)_4$				21.50	16.50	66.4
cis-$N_3P_3(NH_2)_2(OBu^n)_4$				22.28	17.44	65.9
$N_3P_3(NH_2)(OMe)_5$				24.86	20.98	69.4
$N_3P_3(OMe)_6$					21.56	
$N_3P_3(OEt)_6$					18.26	

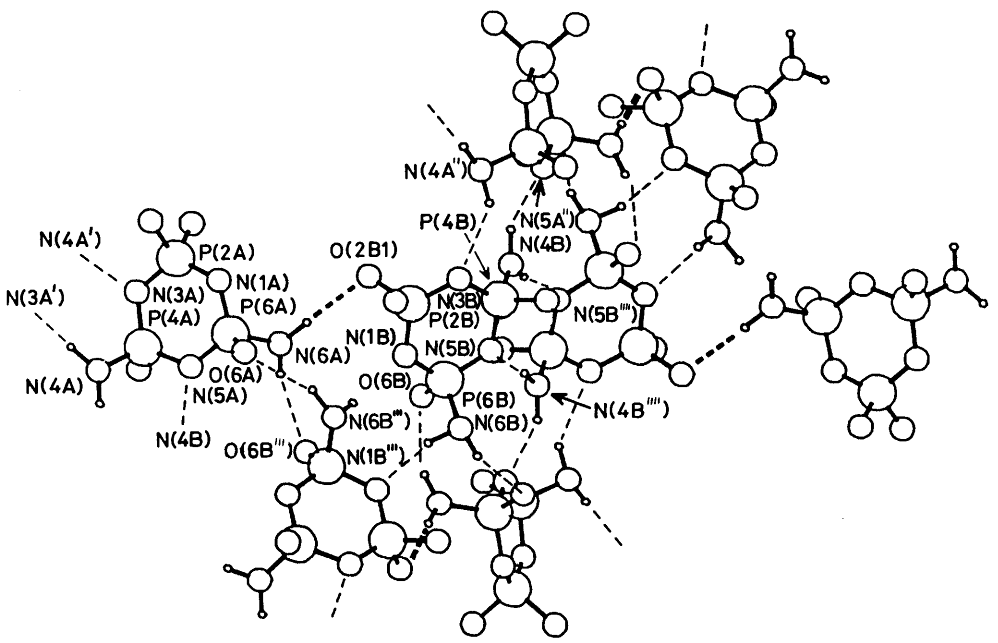

Figure 5. Hydrogen-bonded network of *trans*-$N_3P_3(NH_2)_2(OPr^n)_4$ (all carbon atoms are deleted for clarity). Thick dashes denote hydrogen bonds between molecules A and B, thin dashes denote hydrogen bonds amongst molecules A or B. Primed, double-, triple-, and quadruple-primed atoms are related to unprimed atoms by symmetry operations $(0.5 - x, 1.5 - y, 2.0 - z)$, $(x, 1.0 - y, -0.5 + z)$, $(-x, y, 1.5 - z)$, $(-x, 1.0 - y, 1.0 - z)$ respectively. N(3A')···N(4A) 3.113, N(5A'')···N(4B) 3.036, N(6A)···O(6B''') 3.220, O(6A)···N(6B''') 3.183, N(1B''')···N(6B) 3.038, N(4A'')···N(3B) 3.238, N(5B'''')···N(4B) 3.068, and N(6A)···O(2B1) 3.276 Å

the two isomers. A similar conclusion can be drawn from the ^{1}H and ^{13}C n.m.r. spectra of these compounds (see below).

Similar trends, as for non-geminal *cis*-$N_3P_3(NH_2)_2(OMe)_4$, can be observed in the bond-length and -angle data for non-geminal *trans*-$N_3P_3(NH_2)_2(OPr^n)_4$.

Parallel to these crystallographic results, we note that in basicity studies amino substituents are rather more electron releasing than alkoxy substituents, substituent constant values (α_R) for the former being 5.2—6.2, for the latter 3.6—4.0; chlorine the reference standard has a value of zero.[39]

Hydrogen Bonding.—The $N_3P_3(NH_2)_2(OMe)_4$ isomers form a complex three-dimensional hydrogen-bonded network, involving eight-membered rings. The geminal and the *cis*-non-geminal isomers form hydrogen-bonded strands amongst themselves, and additionally bond to each other, as shown in Figure 4(*a*), (*b*), and (*c*)[40] respectively. A complex hydrogen-bonded pattern also exists in *trans*-$N_3P_3(NH_2)_2(OPr^n)_4$ (Figure 5), but because of the low accuracy of the structure any discussion would be less meaningful.

N.M.R. Spectroscopy.—The ^{31}P n.m.r. spectra of the compounds prepared in this study are given in Table 5. All the two-bond coupling constants are high (50—70 Hz). The chemical shifts of the PCl_2 group are relatively small, whilst those of the $P(NH_2)_2$ and $P(NH_2)(OR)$ moieties are considerably affected by the nature of the substituents on adjacent phosphorus atoms. Both of them seem to become about 6 p.p.m. more positive on replacement of one PCl_2 group by a $P(OR)_2$ group. With the exception of the methoxy derivatives the chemical shifts of the *cis* isomers (**6**) appear to be somewhat more positive than those of the *trans* isomers (**5**) and the coupling constants of the former slightly larger than those of the latter.

Carbon-13 n.m.r. spectroscopy proved an extremely useful

Table 6. ^{13}C N.m.r. spectroscopic data in $CDCl_3$ at room temperature (recorded at field strengths 50.10 MHz and 100.577 MHz)

		δ/p.p.m.				Coupling constants, Hz,	
Compound	Environment	α-C	β-C	γ-C	δ-C	J(C–P)	Multiplicity
(7)	$P(OMe)_2$	52.5				5.4	triplet *
(5)	$P(OMe)_2$	52.5				6.0	doublet
	$P(NH_2)(OMe)$	52.0				6.2	triplet *
(6)	$P(OMe)_2$	52.6				5.9	doublet
		52.5				5.4	doublet
	$P(NH_2)(OMe)$	52.0				6.4	triplet *
(5)	$P(OEt)_2$	61.53				6.0	doublet
			16.13			8.0	doublet
	$P(NH_2)(OEt)$	61.0				6.0	triplet *
			16.16			8.8	triplet *
(6)	$P(OEt)_2$	61.5				5.6	doublet
			16.13			7.9	doublet
			16.08			8.4	doublet
	$P(NH_2)(OEt)$	60.93				6.2	triplet *
			16.18			8.4	triplet *
(5)	$P(OPr^n)_2$	66.96				6.0	doublet
			23.42			8.0	doublet
				10.02		—	singlet
	$P(NH_2)(OPr^n)$	66.48				6.0	triplet *
			23.45			8.4	triplet *
				10.07		—	singlet
(6)	$P(OPr^n)_2$	67.17				5.9	doublet
		67.11				5.3	doublet
			23.64			8.1	doublet
			23.59			8.6	doublet
				10.31		—	singlet
				10.22		—	singlet
	$P(NH_2)(OPr^n)$	66.96				6.4	triplet *
			23.68			8.6	triplet *
				10.27		—	singlet
(5)	$P(OBu^n)_2$	64.91				5.9	doublet
			32.38			8.0	doublet
				18.92		—	singlet
					13.69	—	singlet
	$P(NH_2)(OBu^n)$	65.37				5.9	triplet *
			32.27			7.8	triplet *
				18.98		—	singlet
					13.69	—	singlet
(6)	$P(OBu^n)_2$	65.39				5.9	doublet
			32.39			8.1	doublet
				18.94		—	singlet
					13.69	—	singlet
	$P(NH_2)(OBu^n)$	64.90				6.2	triplet *
			32.43			8.3	triplet *
				19.00		—	singlet
					13.72	—	singlet
(9)	$P(OMe)_2$	52.60				5.3	triplet *
		52.50				5.3	triplet *
	$P(NH_2)(OMe)$	52.00				6.2	doublet
(10)	$P(OMe)_2$	52.88				5.6	quartet *
(10)	$P(OEt)_2$	61.55				5.6	quartet *
			16.04			8.4	quartet *

* Denotes environments where virtual coupling is observed.

tool to determine the number of different chemical environments present and hence the structure of the compounds. The data are given in Table 6. An interesting inversion of chemical shifts between the α- and β-carbon nuclei of the $\equiv P(OR)_2$ and $\equiv P(NH_2)(OR)$ moieties was observed. This is exemplified by the spectrum of *trans*-$N_3P_3(NH_2)_2(OPr^n)_4$ (Figure 6). The α-carbon nuclei (doublet) of the $\equiv P(OR)_2$ group absorb at lower field than those (triplet) of the $\equiv P(NH_2)(OR)$ groups, whilst the reverse is observed for the β nuclei.

The α-carbon nuclei in the non-geminal groups $\equiv P(NH_2)(OR)$ are always somewhat more shielded than in their geminal counterparts $\equiv P(OR)_2$, indicating that some of the electron density from the lone-pair back donation of the NH_2 group is transferred to the alkoxy group in keeping with the crystallographic findings (see above).

The two-bond coupling constants ^2J(P–C) 5.4—6.4 Hz are about 2 Hz smaller than the corresponding three-bond constants, ^3J(P–C) 7.8—8.8 Hz.

The ^1H n.m.r. data are given in Table 7. The protons on the α-carbon atoms are more shielded in the $\equiv P(NH_2)(OR)$ moieties than in the $\equiv P(OR)_2$ groups in keeping with ^{13}C n.m.r. and crystallographic data (see above).

Table 7. ^1H N.m.r. data in $CDCl_3$ at room temperature (recorded at 199.5 MHz, 250.48 MHz, and 399.95 MHz)

		δ/p.p.m.				Coupling constant, Hz		Multiplicity[a]	
Compound	Environment	Hα	Hβ	Hγ	Hδ	^3J(P–H)	^3J(H–H)	^{31}P coupled	^{31}P decoupled
(7)	$P(OMe)_2$	3.66				12.7[b]	—	d[c]	s
(5)	$P(OMe)_2$	3.68				12.1	—	d	s
	$P(NH_2)(OMe)$	3.63				13.3[b]	—	t	s
(6)	$P(OMe)_2$	3.68				12.0	—	d	s
		3.66				13.4	—	d	s
	$P(NH_2)(OMe)$	3.63				13.1[b]	—	t	s
(5)	$P(OEt)_2$	4.02				7.8	10.0[d]	2q[e]	4q
		3.99[d]							
			1.32			1.0[f]	7.0	d[g]	t
	$P(NH_2)(OEt)$	3.84				8.0[b]	7.0	t[e]	q
			1.30			—	7.0	s[g]	t
(6)	$P(OEt)_2$	4.03				7.6	10.0[d]	2q[e](2 × 2q)[h]	4q(2 × 4q)[h]
		3.99[d]				8.0			
			1.32			1.0[f]	7.0	d[g]	t
			1.31			1.0[f]	7.0	d[g]	t
	$P(NH_2)(OEt)$	3.97				8.3[b]	7.0	t[e]	q
			1.30			—	7.0	s[g]	t
(5)	$P(OPr^n)_2$	3.89				7.0	10.0[d]	2q[e]	3q
		3.87[d]							
			1.68			1.0[f]	7.0	2t[i]	4t
				0.94		—	7.0	s[e]	t
	$P(NH_2)(OPr^n)$	3.84				7.5[b]	7.0	t[e]	t
			1.69				7.0	2t[i]	4t
				0.95		—	7.0	s[e]	t
(6)	$P(OPr^n)_2$	3.88				7.0	10.0[d]	2q[e](2 × 2q)[h]	3q(2 × 3q)[h]
		3.90[d]				7.0			
			1.68			—	7.0	2t[i]	4t
			1.68			—	7.0	2t[i]	4t
				0.94		—	7.0	s[e]	t
				0.93		—	7.0	s[e]	t
	$P(NH_2)(OPr^n)$	3.85				7.6[b]	7.0	t[e]	t
			1.69			—	7.0	2t[i]	4t
				0.92		—	7.0	s[e]	t
(5)	$P(OBu^n)_2$	3.90				—	7.0	c(2q[e])[h]	t(3q)[h]
		3.88				—	7.0	c	t
	$P(NH_2)(OBu^n)$		1.62			—	—	c	c
				1.36		—	—	c	c
					0.92	—	7.0	t	t
(6)	$P(OBu^n)_2$	3.92				7.7[b]	7.0	2q[e](2 × 2q)[h]	t(2 × 3q)[h]
		3.87				7.0	7.0	t[e]	t
	$P(NH_2)(OBu^n)$		1.64			—	—	7 lines[g]	24 lines[j]
				1.41		—	—	12 lines[j]	12 lines[j]
					0.92	—	7.0	s	t
(9)	$P(OMe)_2$	3.67				12.5[b]	—	d[c]	s
		3.68				12.5[b]	—	d[c]	s
	$P(NH_2)(OMe)$	3.63				12.5	—	d	s
(10)	$P(OMe)_2$	3.67				12.7[b]	—	d[c]	s
(10)	$P(OEt)_2$	4.00				8.0[b]	7.1	q[g]	q
			1.31			—	7.1	t	t

[a] s = Singlet, d = doublet, t = triplet, and q = quartet. [b] Denotes environments where long range virtual coupling is observed. [c] Signal also contains virtual coupling hump. [d] OCH_2 groups where intrinsic asymmetry occurs: J_{H-H} denotes H_A–H_B coupling. [e] β protons decoupled. [f] Observed ^4J(P–H) coupling. [g] α Protons decoupled. [h] Theoretical multiplicities are given in parentheses. [i] γ protons decoupled. [j] Multiplicity too complex to distinguish the different environments.

Intrinsic asymmetry of the α-methylene protons is observed in the $\equiv P(OR)_2$, but not in the $\equiv P(NH_2)(OR)$ groupings. Three-bond coupling constants ^3J(P–H) are in the expected range, 12.0—13.4 Hz for CH_3 and 7.0—8.3 Hz for CH_2 protons. Some four-bond coupling, ^4J(P–H) 1.0 Hz, is also observed.

Conclusions

It would be premature to have a detailed discussion on the reaction mechanism of these amino group migrations. We note, however, the following points. The fact that both *trans* and *cis* isomers are formed points to an intermolecular process. The migration might well be preceded by chelated hydrogen bonding from the pair of geminal amino groups to the alkoxide ion. Preliminary work suggests that this rearrangement does not occur when the alcoholysis is carried out by alcohols in the presence of a tertiary base. Further work to determine the scope of this rearrangement is in progress. At this point it should be stressed that the existence of this rearrangement, and the possibility of others, not yet observed, make structure determinations based on derivatisation somewhat suspect.

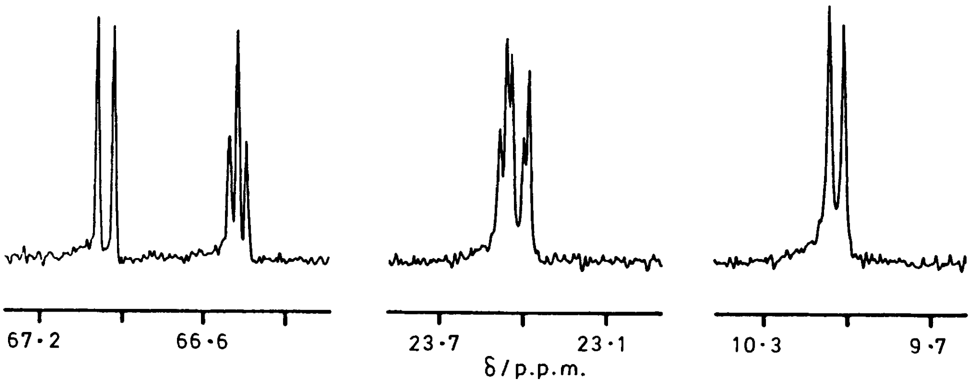

Figure 6. The ^{13}C n.m.r. spectrum of *trans*-$N_3P_3(NH_2)_2(OPr^n)_4$

Experimental

Crystallography.—Both crystals were colourless and block shaped, 0.30 × 0.25 × 0.20 and 0.40 × 0.20 × 0.20 mm respectively. Unit-cell parameters were determined by least-squares refinement of the setting angles for 25 reflections [$16 < \theta(Mo\text{-}K_\alpha) < 17°$] automatically centred on an Enraf-Nonius CAD-4 diffractometer. Intensity data were recorded on the same instrument at 295(2) K, using Mo-K_α radiation (λ = 0.710 69 Å; graphite monochromatised) in the ω—2θ scan mode, in a manner previously described in detail,[41] with a θ range of 1.5—25° and ω scan width of 0.80 + 0.35tanθ. Data for both compounds were corrected for Lorentz and polarisation effects.

Crystal data. $N_3P_3(NH_2)_2(OPr^n)_4$ (**5**; R = Pr^n), M = 403.3, monoclinic, space group $C2/c$, a = 27.842(4), b = 14.730(3), c = 21.912(5) Å, β = 94.36(2)°, U = 8960.5 Å^3, Z = 16, D_c = 1.196 g cm^{-3}, $\mu(Mo\text{-}K_\alpha)$ = 2.44 cm^{-1}, $F(000)$ = 3 456; $N_3P_3(NH_2)_2(OMe)_4$ (**6**, **7**; R = Me), M = 291.1, triclinic, space group $P\bar{1}$, a = 8.130(2), b = 12.930(4), c = 13.542(2) Å, α = 110.10(2), β = 108.65(3), γ = 75.62(2)°, U = 1 251.3 Å^3, Z = 4, D_c = 1.545 g cm^{-3}, $\mu(Mo\text{-}K_\alpha)$ = 4.21 cm^{-1}, $F(000)$ = 608.

Structure analysis and refinement. Both structures were solved by direct methods applying SHELX 84[42] and refined by least squares.

There are two crystallographically independent molecules of (**5**; R = Pr^n) in the asymmetric unit, both having *trans*-non-geminal arrangements of the NH_2 groups. There are no significant structural differences between the two molecules. Hydrogen atoms of the NH_2 groups were located experimentally and included with individual U_{iso} values (N–H fixed at 1.01 Å), but those on carbon atoms were not included, since all the carbon atoms have high thermal parameters. All the non-carbon atoms were refined anisotropically and the carbon atoms isotropically with O–C and C–C distances fixed at 1.461 and 1.500 Å respectively, giving a final R value of 0.10 and R' = 0.11 for 3 263 unique reflections with $I > 1.5\sigma(I)$. Total unique data: 8 091. Maximum shift-to-error ratio in final least-squares cycle: 1.22 (345 parameters). Weighting scheme: $w = [\sigma^2(F_o) + 0.004F_o^2]^{-1}$. Residual electron density: 0.8 e Å^{-3}. Maximum h, k, l: ±33, 17, 26.

There are two crystallographically independent and chemically different molecules of (**6**, **7**; R = Me) in the asymmetric unit. Although all hydrogen atoms (32) were located from a Fourier difference synthesis, only the eight nitrogen hydrogen atoms were refined freely. All others were restricted to idealised positions (C–H 1.08 Å) in the refinement, giving a final R value of 0.045 and R' = 0.046 (H-atoms isotropic, others anisotropic), for 3 237 unique reflections with $I > 1.5\sigma(I)$. Total unique data: 4 394. Maximum shift-to-error ratio: 0.06 (329 parameters). Weighting scheme: $w = [\sigma^2(F_o) + 0.0004F_o^2]^{-1}$. Residual electron density: 0.9 e Å^{-3}. Maximum h, k, l: ±9, 15, ±16.

The calculations were performed on a DEC VAX11/750 computer using the SHELX 84[42] and SHELX 76[43] program systems. Neutral scattering factors were taken from refs. 44 and 45 for the non-hydrogen and hydrogen atoms respectively. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

Spectroscopy.—Alcohols and sodium metals were obtained from BDH Chemicals Ltd. Solvents were dried by conventional methods.

All reactions were monitored by using Kieselgel 60 (silica gel) precoated t.l.c. plates and developed with ninhydrin (0.5% w/v) in butanol solution. Products (**5**), (**6**) (R = Et, Pr^n, or Bu^n), and (**9**) were separated by column chromatography using Kieselgel 60 (silica gel). Products (**5**)—(**7**) (R = Me), which could not be separated by column chromatography, were separated by h.p.l.c. on a 10 cm × 4.5 mm I.D. + 2 × 25 cm × 7 mm I.D. column system using 5-μm Lichrosorb silica gel, 12.5% methanol in ethyl acetate as the mobile phase, refractive index detection, and a flow rate of 2 cm^3 min^{-1}. The order of elution was *trans*, *cis*, *gem*.

Melting points were measured on a Reichert-Kofler micro heating stage fitted with a polarising microscope.

Proton n.m.r. spectra were recorded using JEOL FX-200 (operating at 199.5 MHz), Bruker WH250 (operating at 250.48 MHz; Kings College, London), and Varian XL400 spectrometers (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, $SiMe_4$ as internal reference, and sample concentrations of 15—20 mg cm^{-3}. Phosphorus-31 n.m.r. spectra were recorded using JEOL JNM FX-60 (operating at 24.15 MHz) and Varian XL-200 spectrometers (operating at 80.98 MHz; University College, London) with 85% H_3PO_4 used as an external reference. Carbon-13 n.m.r. spectra were recorded using JEOL FX-200 (operating at 50.10 MHz) and Varian XL 400 spectrometers (operating at 100.577 MHz; University College, London), with $SiMe_4$ as an internal reference. Mass spectra were recorded using a VG 7070H mass spectrometer and a Finnigan INCOS data system at University College, London.

Materials.—The starting materials $N_3P_3(NH_2)_2Cl_4$ (**1**) and $N_3P_3(NH_2)Cl_5$ (**8**) were prepared by the methods of Feistel and Moeller,[19] although compound (**1**) was recrystallised from

Table 8. Experimental details (all products were recrystallised from a 4:1 dichloromethane:benzene mixture)

Compound	Reactants (g)	Reactants (mmol)	Solvent[a] (cm^3)	Chromatographic eluant ratios	Product ratios
(**1**)	5.0	16	methanol(80)	4thf:1MeOH[b]	(**5**) *trans*: 2 (**6**) *cis*: 1 (**7**) *gem*: 1
(**1**)	5.0	16	ethanol(80)	2CH$_2$Cl$_2$:1thf	(**5**) *trans*: 4 (**6**) *cis*: 1
(**1**)	5.0	16	propanol(80)	2CH$_2$Cl$_2$:1thf	(**5**) *trans*: 4 (**6**) *cis*: 1
(**1**)	5.0	16	butanol[c](80)	2CH$_2$Cl$_2$:1thf	(**5**) *trans*: 4 (**6**) *cis*: 1
(**8**)	1.0	3	methanol(40)	4thf:1MeOH	(**9**)[d]

[a] All reactions were refluxed for 1 h in the parent alcohol containing a slight excess of its sodium alkoxide. [b] Three isomers were separated by h.p.l.c. using 12.5% methanol: 87.5% ethyl acetate. [c] Sodium chloride precipitate removed by centrifugation. [d] A small amount of mono-amino tris- and tetrakis methoxy mixture was also obtained.

Table 9. Analytical data

Formula	Compound	M.p. (°C)	Found (%) C	Found (%) H	Found (%) N	Found (%) P	Found M^+	Required (%) C	Required (%) H	Required (%) N	Required (%) P	Required M
$C_4H_{16}N_5O_4P_3$	(**5**)	153	16.1	5.3	23.9	31.6	291	16.5	5.5	24.1	32.0	291
$C_4H_{16}N_5O_4P_3$	(**6**)	125—126	16.8	5.6	23.8	31.7	291	16.5	5.5	24.1	32.0	291
$C_4H_{16}N_5O_4P_3$	(**7**)	78	16.2	5.0	23.8	31.7	291	16.5	5.5	24.1	32.0	291
$C_8H_{24}N_5O_4P_3$	(**5**)	94—96	27.2	6.8	19.8	26.3	347	27.6	6.9	20.2	26.8	347
$C_8H_{24}N_5O_4P_3$	(**6**)	55	27.8	6.9	20.0	26.2	347	27.6	6.9	20.2	26.8	347
$C_{12}H_{32}N_5O_4P_3$	(**5**)	124	35.5	8.0	17.6	23.0	403	35.7	7.9	17.4	23.1	403
$C_{12}H_{32}N_5O_4P_3$	(**6**)	64—66	35.4	8.0	17.3	23.0	403	35.7	7.9	17.4	23.1	403
$C_{16}H_{40}N_5O_4P_3$	(**5**)	176—178	20.7	11.9	21.0	27.2	459	21.2	11.8	20.7	27.4	459
$C_{16}H_{40}N_5O_4P_3$	(**6**)	93	21.0	11.6	20.8	27.2	459	21.2	11.8	20.7	27.4	459
$C_5H_{17}N_4O_5P_3$	(**9**)	52—54	19.4	5.7	18.1	30.3	306	19.6	5.5	18.3	30.4	306

dichloromethane at room temperature. The hexa-alkoxy derivatives, $N_3P_3(OR)_6$ (**10**) were prepared by the method of Fitzsimmons and Shaw.[46] One experiment is described in detail and the remainder were prepared in a similar manner. Experimental details are summarised in Table 8 and the analytical data in Table 9.

Preparation of 2-trans-4- *and* 2-cis-4-*diamino*-2,4,6,6-*tetraethoxycyclotriphosphazatriene*. Sodium (1.5 g, 65 mmol) was dissolved in ethanol (80 cm^3) and the diamino compound (**1**) (5 g, 16 mmol) added. The reaction mixture was then refluxed for 1 h. After cooling, the white precipitate of sodium chloride was filtered off and the solvent removed under vacuum. The resulting colourless oil was extracted with light petroleum (b.p. 40—60 °C) and then benzene. The benzene extract gave a solid–oil mixture; the solid crystals were removed and washed with diethyl ether to give the *trans* isomer (1.2 g, 21%), m.p. 94—96 °C. Using column chromatography, the oil was separated into a further amount of the *trans* isomer (1.5 g, 27%) and a smaller amount of the *cis* isomer (0.6 g, 8%), m.p. 55 °C. Both isomers were recrystallised from dichloromethane–benzene (4:1).

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