Aziridinolysis Patterns of $(NPCl_2)_3$ and $(NPCl_2)_4$; Crystal Structures of *trans*-$N_3P_3(NC_2H_4)_2Cl_4$ and 2,*trans*-4-$N_4P_4(NC_2H_4)_2Cl_6$†

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The secondary amine aziridine (HNC_2H_4) shows a peculiar competition between geminal and non-geminal substitution in its reactions with both $(NPCl_2)_3$ and $(NPCl_2)_4$. This is demonstrated by the formation of the complete series of (isomeric) derivatives $N_3P_3(NC_2H_4)_nCl_{6-n}$ (n = 1—6) and $N_4P_4(NC_2H_4)_nCl_{8-n}$ (n = 1—3). Structures are assigned based on ^{31}P and ^1H n.m.r. data supported by the crystal-structure determinations of two key compounds, *trans*-$N_3P_3(NC_2H_4)_2Cl_4$ and 2,*trans*-4-$N_4P_4(NC_2H_4)_2Cl_6$.

The synthesis of aziridinyl cyclophospha(thia)zenes as potential antitumour agents is a current subject of our investigations.[1–5] The utility of aziridinyl–chloro derivatives as precursors for compounds with specific stereochemical requirements prompted us to a detailed investigation on the aziridinolysis of $(NPCl_2)_3$ (**1**) and $(NPCl_2)_4$ (**2**).

In a preliminary study[2] we reported the reactions of aziridine with (**1**) to follow a partly geminal substitution pattern. Unlike earlier investigations,[6–8] a number of non-geminally substituted compounds was detected by ^{31}P n.m.r. In this paper the isolation of all possible derivatives $N_3P_3(az)_nCl_{6-n}$ (n = 1—6) and $N_4P_4(az)_nCl_{8-n}$ (n = 1—3) [az = aziridin-1-yl (NC_2H_4)] is described. Furthermore, a number of these compounds were studied individually in subsequent reactions with aziridine under various conditions. The corresponding substitution stages of the two N–P ring systems, which appear to be similar, will be discussed with reference to earlier reported aminolysis reactions with the closely related dimethylamine.[9,10] This leads to a provisional rationalization of the reaction patterns observed.

Structures were assigned mainly by ^{31}P and ^1H n.m.r.; for the key compounds *trans*-$N_3P_3(az)_2Cl_4$ (**4**) and 2,*trans*-4-$N_4P_4(az)_2Cl_6$ (**18**), *X*-ray structure determinations are described.

Results

Aziridinolysis of $(NPCl_2)_3$ (**1**).—The analysis of the successive aziridinolysis stages of (**1**) has shown a rather complicated reaction system featuring both geminal and non-geminal aziridinyl–chloro derivatives.

As reported previously,[6] $N_3P_3(az)Cl_5$ (**3**) can be easily isolated from the product of the 1:2 reaction of (**1**) with aziridine in various solvents, *i.e.* n-hexane, benzene, or diethyl ether. Reactions in more polar solvents like tetrahydrofuran or acetonitrile were hampered by the formation of side-products, arising from the opening of the three-membered aziridinyl rings by hydrogen chloride formed in the reaction.

† 2,*trans*-4-Bis(aziridin-1-yl)-2,4,6,6-tetrachlorocyclotri-(phosphazene) and 2,*trans*-4-bis(aziridin-1-yl)-2,4,6,6,8,8-hexachlorocyclotetra(phosphazene) respectively.

Supplementary data available (No. SUP 56494, 5 pp.): thermal parameters, least-squares planes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Relative amounts (%) of the isomers of $N_3P_3(az)_2Cl_4$, as formed in the 1:4 reactions of (**1**) with aziridine at 5—25 °C (mean values of several experiments)

Solvent	*trans*-$N_3P_3(az)_2Cl_4$ (**4**)	*cis*-$N_3P_3(az)_2Cl_4$ (**5**)	*gem*-$N_3P_3(az)_2Cl_4$ (**6**)
n-Hexane	35	15	50
Benzene	40	20	40
Diethyl ether	20	15	65

Table 2. Relative amounts (%) of the isomers of $N_3P_3(az)_3Cl_3$, as formed in the 1:2 reactions of (**4**)—(**6**) with aziridine

Precursor solvent	*trans*-$N_3P_3(az)_3Cl_3$ (**7**)	*cis*-$N_3P_3(az)_3Cl_3$ (**8**)	*gem*-$N_3P_3(az)_3Cl_3$ (**9**)
(**4**) n-Hexane	10		90
(**4**) Benzene	10		90
(**4**) Diethyl ether	10		90
(**5**) n-Hexane	30	5	65
(**5**) Benzene	40	5	55
(**5**) Diethyl ether	40	≤5	55
(**6**) n-Hexane			100
(**6**) Benzene			100
(**6**) Diethyl ether			100

A mixture of six components was found as a result of the 1:4 reaction of (**1**) with aziridine. These compounds were identified as (**3**), three isomers of $N_3P_3(az)_2Cl_4$ (**4**)—(**6**), *trans*-$N_3P_3(az)_3Cl_3$ (**7**), and *gem*-$N_3P_3(az)_3Cl_3$ (**9**). The relative amounts of the isomeric bis(aziridinyl) derivatives formed in different solvents (Table 1) indicate a random geminal and non-geminal substitution up to this stage.The data in Table 1 should be interpreted, however, with some caution as in a separate experiment the aziridinolysis of an equimolar mixture of the three isomers has shown the following sequence in reactivity: *trans*-(**4**) > *cis*-(**5**) > *gem*-(**6**).

The 1:6 reactions of (**1**) with aziridine afforded very complex mixtures of bis-, tris-, and tetrakis-(aziridinyl) derivatives, *gem*-$N_3P_3(az)_3Cl_3$ (**9**) being predominant. More information could be gained from the individual conversion of (**4**), (**5**), and (**6**) into tris(aziridinyl) derivatives using two equivalents of aziridine. The reactions were carried out in different solvents and standardized with respect to temperature and concentration. Apart from the isomers $N_3P_3(az)_3Cl_3$ (Table 2) the reaction mixtures contained small amounts of starting material and

Table 3. Relative yields (%) of the products isolated from the 1:4 reactions of (**2**) with aziridine (mean values of several experiments)

Product	Diethyl ether or benzene	n-Hexane
(**15**) $N_4P_4(az)Cl_7$	15	24
(**16**) 2,*trans*-6-$N_4P_4(az)_2Cl_6$	23	13
(**17**) 2,*cis*-6-$N_4P_4(az)_2Cl_6$	13	7
(**18**) 2,*trans*-4-$N_4P_4(az)_2Cl_6$	7	13
(**19**) 2,*cis*-4-$N_4P_4(az)_2Cl_6$	14	10
(**20**) 2,2-$N_4P_4(az)_2Cl_6$	3	5
(**21**)—(**25**) $N_4P_4(az)_3Cl_5$	25	28

tetrasubstituted derivatives, as estimated by ^{31}P n.m.r. and h.p.l.c. According to the data in Table 2 the reactions with the non-geminal isomers $N_3P_3(az)_2Cl_4$ followed different courses. The *trans*-isomer (**4**) gives (**9**) as the main product, whereas *cis*-$N_3P_3(az)_2Cl_4$ (**5**) yields, besides (**9**), considerable amounts of (**7**) and minor quantities of *cis*-$N_3P_3(az)_3Cl_3$ (**8**).

Derivatives $N_3P_3(az)_4Cl_2$ could also be obtained in three isomeric forms (**10**)—(**12**). The 1:8 reactions of (**1**) with aziridine afforded *gem*-$N_3P_3(az)_4Cl_2$ (**12**) as the major product. Because the compounds $N_3P_3(az)_nCl_{6-n}$ (n = 4—6) are hardly soluble in n-hexane, only diethyl ether and benzene were used as reaction media. No significant differences were found between reaction mixtures obtained in these solvents.

The 1:2 reactions of *trans*-$N_3P_3(az)_3Cl_3$ (**7**) gave both *trans*-$N_3P_3(az)_4Cl_2$ [(**10**) 45%] and *cis*-$N_3P_3(az)_4Cl_2$ [(**11**) 55%]. Using *gem*-$N_3P_3(az)_3Cl_3$ (**9**) as starting material, the 1:2 reactions afforded relative yields of 90% of (**12**) and 10% of about equal amounts of (**10**) and (**11**), together with considerable amounts of starting material. Generally, the geminal derivatives $N_3P_3(az)_nCl_{6-n}$ (n = 2—4) were found to be less reactive towards aziridinolysis reactions than their non-geminal isomers.

Three products resulted from the 1:10 reaction of (**1**) with aziridine, *viz.* (**12**), $N_3P_3(az)_5Cl$ (**13**), and the completely substituted product (**14**). The presence of (**12**) as the only tetrakis(aziridinyl) derivative might be an indication of its low reactivity as compared with (**10**) and (**11**). Probably due to this low reactivity the completion of the reaction to (**14**) required a large excess of aziridine and elevated temperatures.

Aziridinyl Derivatives of $(NPCl_2)_4$ (**2**).—Applying the same solvents as described for the aziridinolysis of the trimer, the first three substitution stages of (**2**) were studied in detail. Preliminary studies to higher substitution stages indicated that derivatives $N_4P_4(az)_nCl_{8-n}$ (n = 4—7) can also be prepared. The use of an excess of aziridine leads to $N_4P_4(az)_8$ as reported previously by Rätz *et al.*[8]

$N_4P_4(az)Cl_7$ (**15**) was prepared by the reaction of (**2**) with aziridine, using a molar ratio of 1:2 or 1:3.

The analogous 1:4 reaction gave a complex mixture of at least 11 components. A combined h.p.l.c. and mass spectrometric analysis of the reaction mixture revealed the presence of (**15**) [M^+ (^{35}Cl) = 467], five isomers of $N_4P_4(az)_2Cl_6$ (**16**)—(**20**) [M^+ (^{35}Cl) = 474], and three isomers of $N_4P_4(az)_3Cl_5$ (**21**)—(**23**) [M^+ (^{35}Cl) = 481]. ^{31}P N.m.r. spectra also showed the presence of the other two isomers of $N_4P_4(az)_3Cl_5$, (**24**) and (**25**). Whereas no detectable difference was found between reactions carried out in diethyl ether or benzene, notable changes were observed when using n-hexane. As shown in Table 3, 2,6-disubstitution is preferred in the first two solvents. In n-hexane about equal amounts of 2,6- and 2,4-disubstituted derivatives are formed, preferably the *trans*-isomers (**16**) and (**18**). Only small amounts of the geminal isomer (**20**) were isolated in both cases.

Table 4. Relative yields (%) of the isomers $N_4P_4(az)_3Cl_5$ (**21**)—(**25**) resulting from the 1:2 reactions of the isomers $N_4P_4(az)_2Cl_6$ (**16**)—(**20**) with aziridine

Precursors $N_4P_4(az)_2Cl_6$	$N_4P_4(az)_3Cl_5$ (**21**)	(**22**)	(**23**)	(**24**)	(**25**)
(**16**)	80		20		
(**17**)	35	65			<1
(**18**)		10	25	65	
(**19**)			55	5	40
(**20**)	95			5	

Similar results were obtained with reactions of (**15**) with aziridine using varying molar ratios (1:0.5—2.5), see Experimental section. As the relative yields of the bis(aziridinyl) isomers (**16**)—(**20**) hardly vary in these reactions, they appear to be comparably reactive towards further reaction. Only the 2,*trans*-4-derivative (**18**) tended to be somewhat less persistent than the other isomers.

The 1:6 reaction of (**2**) with aziridine gave an extremely complicated mixture of compounds $N_4P_4(az)_nCl_{8-n}$ (n = 2—5) according to h.p.l.c. and mass spectrometric data. The main products were 2,2,6-$N_4P_4(az)_3Cl_5$ (**21**) and 2,*cis*-4,*trans*-6-$N_4P_4(az)_3Cl_5$ (**23**). More informative were the experiments in which the individual isomers $N_4P_4(az)_2Cl_6$ (**16**)—(**20**) were treated with two equivalents of aziridine in diethyl ether or n-hexane. The relative yields of the trisubstituted products, given in Table 4, and the analytical h.p.l.c. chromatograms (Figure 1) clearly illustrate the various reaction patterns. A salient feature is the relative increase of geminal substitution as compared with the second stage. This is particularly pronounced when using the *trans* isomers (**16**) and (**18**) as precursors. The geminal isomer (**20**) preferentially gave the 2,2,6-substituted product with only minor amounts of the 2,2,4-isomer. From Table 4 and Figure 1 it can be argued that the structures assigned to precursors and products are in conformity with the substitution pathways followed.

Discussion

In Table 5 the product ratios observed and those expected on statistical grounds are listed for reactions of (**1**) with aziridine and dimethylamine[9] in diethyl ether. The number of aminolysis steps is restricted to five cases, *viz.* those starting from the mono(amino), the *trans*- and *cis*-bis(amino), and the *trans*- and *gem*-tris(amino) derivatives. Whereas dimethylamine generally affords ratios of non-geminal to geminal products exceeding the corresponding statistical ratios, aziridine tends to give geminal products. Assuming the aziridinolysis to proceed *via* a bimolecular mechanism, like the dimethylaminolysis, this tendency might be due to the relatively weaker electron-donating capacity and the smaller size of the aziridinyl group.

Data on the dimethylaminolysis of (**2**) are rather scarce, hardly allowing a similar comparison as the one described above. Referring to the study of Millington and Sowerby,[10] again dimethylamine gives relatively smaller amounts of geminal products than aziridine. *gem*-$N_4P_4(az)_2Cl_6$ (**20**) may be formed in smaller amounts compared with its trimeric analogue (**6**) in the reaction with (**1**) but this can mainly be ascribed to a lower statistical probability of geminal disubstitution in the tetrameric case. Another difference concerns the preferential 2,6-disubstitution observed with dimethylamine[10] which appears to be less pronounced with

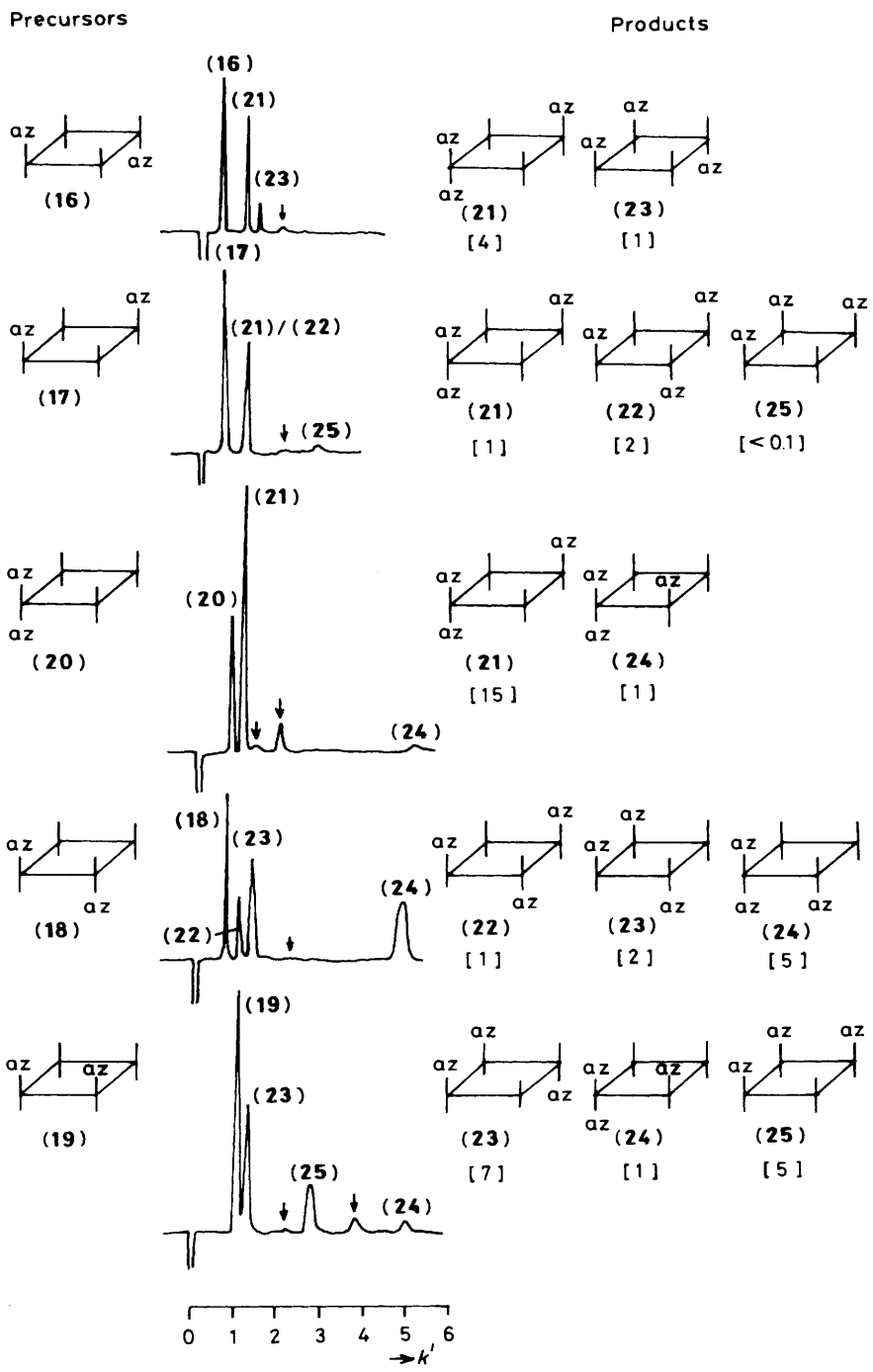

Figure 1. Conversion of $N_4P_4(az)_2Cl_6$ into $N_4P_4(az)_3Cl_5$ in diethyl ether (relative amounts in square brackets); the tetrameric ring systems are diagrammed as parallelograms, the corners indicating the positions of the P atoms, chloro ligands being omitted. H.p.l.c. chromatograms concern the crude reaction mixtures [eluant: diethyl ether–n-hexane (1:1)], negative peaks represent solvent, peaks indicated by an arrow are probably due to compounds $N_4P_4(az)_4Cl_4$; k' represents the capacity factor, taken relative to the solvent peak

aziridine (Table 3). As invoked by Krishnamurthy *et al.*[11] the presence of an electron-releasing substituent at P(2) will deactivate the adjacent phosphorus atoms P(4) and P(8) to a larger extent than P(6), leading to mainly 2,6-disubstituted products although 2,4-disubstitution is statistically favoured. The presence of a second aziridinyl group at P(2) apparently reinforces the deactivation of P(4) and P(8), as *gem*-$N_4P_4(az)_2Cl_6$ (**20**) shows preferential substitution at P(6), giving 2,2,6-$N_4P_4(az)_3Cl_5$ (**21**) and only minor amounts of the 2,2,4-isomer (*cf.* Table 4 and Figure 1).

Returning to the reactions of the trimer, a general preponderance of *trans*-isomers can be discerned in the formation of non-geminal bis- and tris-(amino) derivatives (Table 5). The kinetic studies with dimethylamine and piperidine by Goldschmidt and Goldstein[12] have shown the *trans*-isomers to be kinetically favoured. This is ascribed to the so-called

Table 5. Isomer ratios (%) of selected substitution steps of (1) with aziridine or dimethylamine[a]

Precursors	Product	Isomer ratio[b] *trans*	*cis*	*gem*	Statistical isomer ratio *trans*	*cis*	*gem*
(3) $N_3P_3(az)Cl_5$	Bis	20	15	65	40	40	20
$N_3P_3(NMe_2)Cl_5$		65	30	⩽5			
(4) *trans*-$N_3P_3(az)_2Cl_4$	Tris	10		90	50		50
trans-$N_3P_3(NMe_2)_2Cl_4$		55		45			
(5) *cis*-$N_3P_3(az)_2Cl_4$	Tris	40	⩽5	55	25	25	50
cis-$N_3P_3(NMe_2)_2Cl_4$		80	⩽5	15			
(7) *trans*-$N_3P_3(az)_3Cl_3$	Tetrakis	45	55		67	33	
trans-$N_3P_3(NMe_2)_3Cl_3$			100				
(9) *gem*-$N_3P_3(az)_3Cl_3$	Tetrakis	⩽5	⩽5	90	33	33	33
gem-$N_3P_3(NMe_2)_3Cl_3$			100				

[a] Data from ref. 9. [b] Reactions in diethyl ether.

Table 6. ^{31}P and ^1H n.m.r. data[a] for $N_3P_3(az)_nCl_{6-n}$ (n = 1—6)

Compound	^{31}P N.m.r. δ[P(az)$_2$]	δ[P(az)Cl]	δ(PCl$_2$)	$^2J_{PP}$	^1H N.m.r. δ[P(az)$_2$]	$^3J_{PH}$	δ[P(az)Cl]	$^3J_{PH}$
(3) $N_3P_3(az)Cl_5$		31.2	22.2	39.0			2.35	22.0
(4) *trans*-$N_3P_3(az)_2Cl_4$		34.7	25.0	38.0			2.34	22.0
(5) *cis*-$N_3P_3(az)_2Cl_4$		34.1	24.9	38.2			2.32	22.0
(6) *gem*-$N_3P_3(az)_2Cl_4$	34.2		21.9	30.0	2.20	17.5		
(7) *trans*-$N_3P_3(az)_3Cl_3$		38.3/37.9		34.0			2.29[b]	22.0
(8) *cis*-$N_3P_3(az)_3Cl_3$		37.2					2.23	22.0
(9) *gem*-$N_3P_3(az)_3Cl_3$	35.8	35.8	24.9	[c]	2.18	17.5	2.24	22.0
					2.15	17.5		
(10) *trans*-$N_3P_3(az)_4Cl_2$	37.6	40.0		29.4	2.17	17.0	2.23	22.0
(11) *cis*-$N_3P_3(az)_4Cl_2$	37.6	39.4		30.3	2.18	16.5	2.22	21.0
					2.12	16.5		
(12) *gem*-$N_3P_3(az)_4Cl_2$	35.6		25.5	29.3	2.13	17.0		
(13) $N_3P_3(az)_5Cl$	37.0	42.3		29.3	2.12	16.5	2.15	21.0
					2.11	16.5		
(14) $N_3P_3(az)_6$	37.0				2.00	15.5		

[a] Chemical shifts (p.p.m.) positive in low-field direction; coupling constants in Hz; solvent $CDCl_3$. [b] Unresolved spectrum; two doublets of ratio 1:2 were observed in C_6D_6. [c] Deceptively simple AA'X spectrum (ref. 19) with multiplet splitting of 34.0 Hz.

Table 7. ^{31}P Spin systems and ^1H n.m.r. data[a] for $N_4P_4(az)_nCl_{8-n}$ (n = 1—3)

Compound	^{31}P Spin system	Solvent $CDCl_3$ δ[N(CH$_2$)$_2$][b]	$^3J_{PH}$	Solvent C_6D_6 δ[N(CH$_2$)$_2$][b]	$^3J_{PH}$
(15) $N_4P_4(az)Cl_7$	AM_2X	2.35	22.4		
(16) 2,*trans*-6-$N_4P_4(az)_2Cl_6$	A_2X_2	2.32	22.2		
(17) 2,*cis*-6-$N_4P_4(az)_2Cl_6$	A_2X_2	2.32	22.2		
(18) 2,*trans*-4-$N_4P_4(az)_2Cl_6$	AA'XX'	2.30	22.4		
(19) 2,*cis*-4-$N_4P_4(az)_2Cl_6$	AA'XX'	2.29	22.3		
(20) 2,2-$N_4P_4(az)_2Cl_6$	AX_2Y	2.26	16.5		
(21) 2,2,6-$N_4P_4(az)_3Cl_5$	AMX_2	2.26 (1)	2.22	1.99 (1)	17.7
		2.20 (2)	17.7	1.97 (1)	17.7
				1.80 (1)	22.4
(22) 2,*trans*-4,*cis*-6-$N_4P_4(az)_3Cl_5$	AM_2X	2.24 (2)	21.9	1.91 (1)	21.7
		2.23 (1)	21.6	1.85 (2)	22.0
(23) 2,*cis*-4,*trans*-6-$N_4P_4(az)_3Cl_5$	ABCX	2.24 (2)	21.8	1.90 (1)	21.5
		2.21 (1)	21.5	1.89 (1)	21.9
				1.87 (1)	21.9
(24) 2,2,4-$N_4P_4(az)_3Cl_5$	AMXY	2.23 (1)	21.1	2.01 (1)	17.5
		2.21 (1)	17.4	1.97 (1)	17.5
		2.19 (1)	17.5	1.80 (1)	22.1
(25) 2,*cis*-4,*cis*-6-$N_4P_4(az)_3Cl_5$	AM_2X	2.27 (2)	21.7	1.86 (1)	21.3
		2.24 (1)	21.3	1.81 (2)	21.6

[a] Chemical shifts (p.p.m.) positive in low-field direction; coupling constants in Hz. [b] Peak ratio in parentheses.

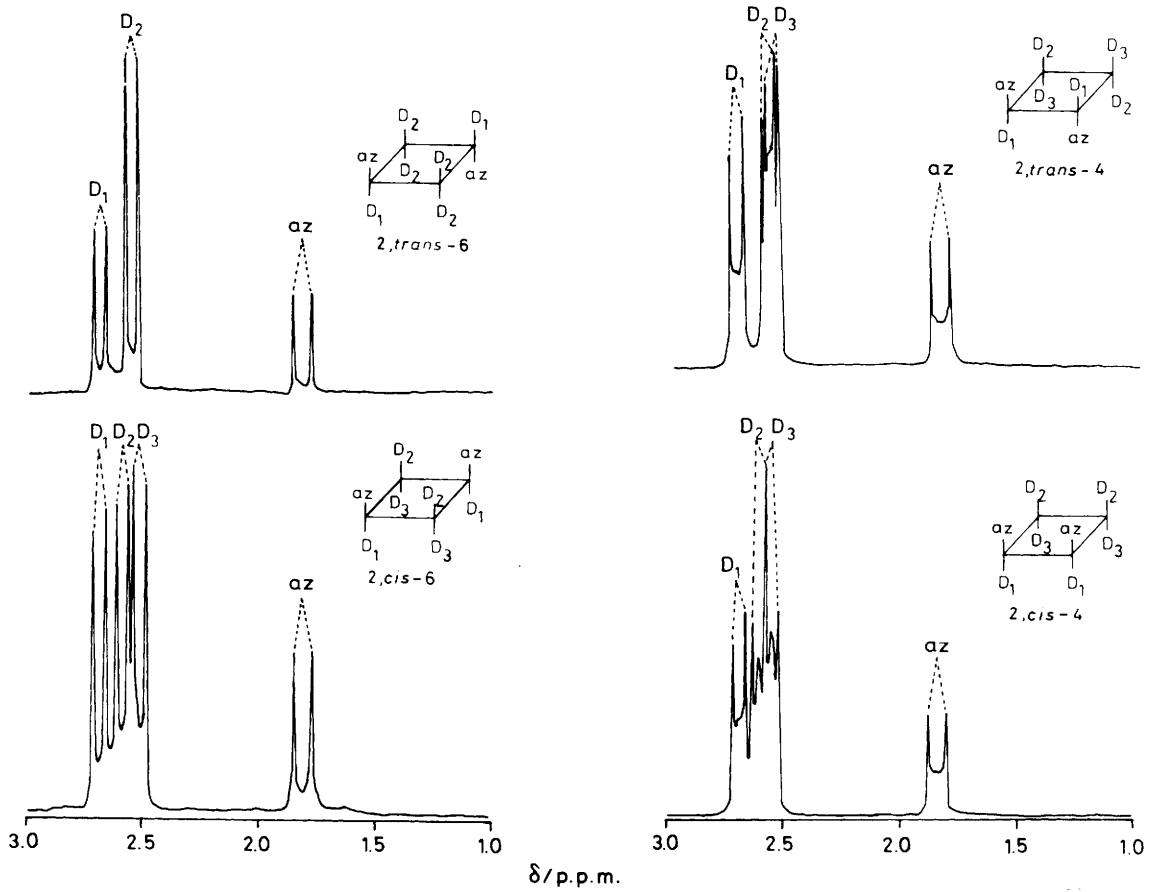

Figure 2. Schematic representations and 200-MHz ^{1}H n.m.r. spectra (1—3 p.p.m.) of the non-geminal isomers of $N_4P_4(az)_2(NMe_2)_6$

substituent solvating effect (s.s.e.) which implies the formation of H-bridged intermediates as described in ref. 12.

The data in Table 5 show a relative increase of *trans–cis* ratios on going from the second to the third stages of substitution, the latter using the *cis*-bis(amino) derivatives as precursors. Probably, the presence of two amino substituents in *cis*-positions statistically enhances the s.s.e., rendering a more pronounced *trans*-preference. Also the preferential reaction of the *trans*-tris(amino) to *cis*-tetrakis(amino) derivatives might be associated with this enhanced s.s.e.

Although not established by kinetic measurements the selective formation of *trans*-bis(amino) derivatives of the tetramer reported in the literature[13,14] also suggests an important role of the s.s.e. in the case of the tetramer.

In our experiments the 2,6-disubstitution also shows *trans–cis* ratios indicative of the s.s.e. (see Table 3). Probably, the flexibility of the eight-membered ring enables 2,6-interactions as evidenced by the recently reported formation of transannular-bridged tetrameric derivatives.[15,16] In the interpretation of the *trans–cis* ratios found for 2,4-disubstitution (Table 3) one should take account of the higher reactivity of the 2,*trans*-4-isomer (**18**) compared with the other bis(aziridinyl) isomers. This difference in reactivity seems to affect the apparent ratio of 2,6- to 2,4-disubstitution. An increase of this difference on going from n-hexane to diethyl ether may explain the observed decrease of the ratio (**18**)/(**19**) and the observed relative increase of 2,6-disubstitution. A similar increasing amount of 2,6- relative to 2,4-disubstituted products was reported for *N*-methylaniline[11] and dibenzylamine.[16]

It should be noted that the third stages of the substitution of the trimeric and the tetrameric ring systems show a strong resemblance (*cf.* Tables 2 and 4). Generally, precursors with a *trans*-structure preferably react to give geminal products. On the other hand, precursors with a *cis*-structure tend to give merely non-geminal derivatives $N_3P_3(az)_3Cl_3$ and $N_4P_4(az)_3Cl_5$. Again these stereoselective differences point to the operation of an enhanced s.s.e. if two amino groups are in *cis*-configuration.

The relative amounts of non-geminal products resulting from the tetrameric *cis*-precursors clearly show a *trans*-preference (see Table 4 and Figure 1) in accordance with the trimeric case mentioned before. Thus (**17**) reacts preferentially to (**22**) with minor amounts of (**25**), whereas (**19**) affords (**23**) and (**25**) in a 7:5 ratio.

Summarizing, it can be stated that the corresponding substitution stages of the trimer and the tetramer show a parallel behaviour of aziridine towards the two ring systems. This indicates the operation of similar reaction mechanisms.

N.M.R. Spectra.—The structures of the compounds isolated were assigned unambiguously by a combination of ^{31}P and ^{1}H n.m.r. spectroscopy.

In the case of the isomeric forms of $N_3P_3(az)_2Cl_4$ (**4**)—(**6**), compound (**6**) obviously has a geminal structure due to the relatively low value of $^3J_{PH}$ of 17.5 Hz, compared with 22.0 Hz for (**4**) and (**5**). The difference in $^3J_{PH}$ values is probably caused by σ-inductive effects, by analogy with known P^V-bonded dimethylamino derivatives.[17] Additionally, the AX_2 ^{31}P n.m.r. spectrum of (**6**) shows a triplet at 34.2 p.p.m. [$P(az)_2$] and a doublet at 21.9 p.p.m. (PCl_2), whereas the A_2X spectra of (**4**) and

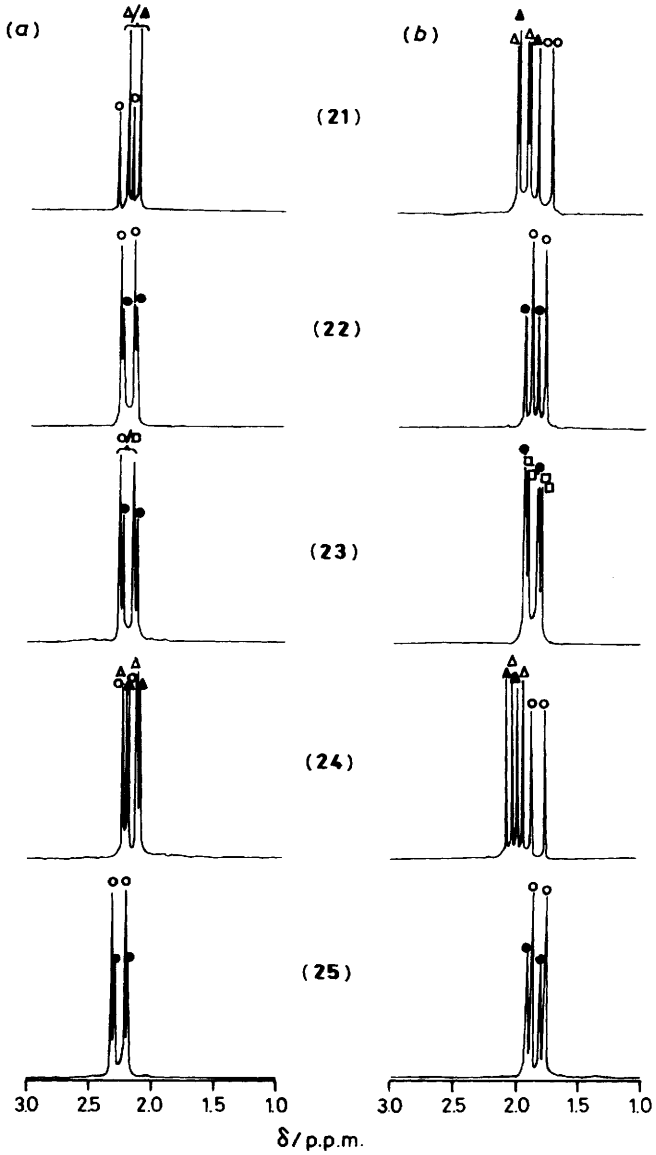

Figure 3. 200-MHz ^1H n.m.r. spectra (1—3 p.p.m.) of the isomers $N_4P_4(az)_3Cl_5$ (**21**)—(**25**), taken in $CDCl_3$ (*a*) and C_6D_6 (*b*); P(az)Cl signals (○, ●, □), $P(az)_2$ signals (△, ▲)

(**5**) are almost mirrored with respect to this: doublets at 34.7 and 34.1 p.p.m. [P(az)Cl] and triplets at 25.0 and 24.9 p.p.m. (PCl_2), respectively. Based on the higher mutual shielding of the aziridinyl groups in the ^1H n.m.r. spectrum of (**5**) compared with that in (**4**) (see Table 6) the former compound was assigned a *cis*-structure. A similar method has been reported for bis-(dimethylamino) derivatives of (**1**).[18] The *trans*-structure of (**4**) was confirmed by a crystal-structure determination, see later.

The number of non-equivalent aziridinyl groups, present as doublets with splitting $^3J_{PH}$ in the ^1H n.m.r. spectra, served as a tool for assigning structures to the isomeric tris- and tetrakis-(aziridinyl) derivatives of (**1**). The structures of the isomers $N_3P_3(az)_3Cl_3$, *viz.* (**7**) (*trans*; two doublets, ratio 1:2), (**8**) (*cis*; one doublet), and (**9**) (*gem*; three doublets of equal intensity), do match with the values of $^3J_{PH}$, corresponding to either $P(az)_2$ groups (15.5—17.5) or P(az)Cl groups (21.0—22.0 Hz). This also holds for the isomers $N_3P_3(az)_4Cl_2$, *viz.* (**10**) (*trans*; two doublets of equal intensity), (**11**) (*cis*; three doublets of ratio 2:1:1), and (**12**) (*gem*; one doublet). Also the ^{31}P n.m.r. data

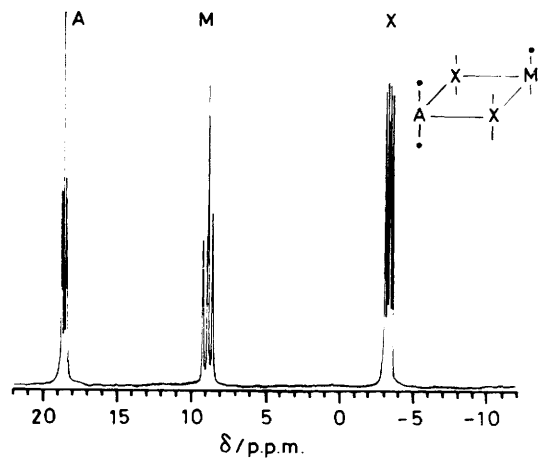

Figure 4. 80.9-MHz $^{31}P-\{^1H\}$ n.m.r. spectrum of 2,2,6-$N_4P_4(az)_3Cl_5$ (**21**)

Table 8. ^1H N.m.r. data* for the non-geminal isomers $N_4P_4(az)_2(NMe_2)_6$

Compound	δ(az)	$^3J_{PH}$	δ(D_1)	$^3J_{PH}$	δ(D_2)	$^3J_{PH}$	δ(D_3)	$^3J_{PH}$
(**26**)	1.82	15.3	2.69	10.6	2.55	10.5		
(**27**)	1.81	15.3	2.69	10.6	2.59	10.1	2.52	11.0
(**28**)	1.85	15.8	2.72	11.0	2.59	10.8	2.57	11.0
(**29**)	1.84	15.7	2.69	10.9	2.61	10.8	2.55	11.1

* Chemical shifts (p.p.m.) positive in low-field direction; coupling constants in Hz.

(Table 6) are in line with the structures assigned. In the case of *gem*-$N_3P_3(az)_3Cl_3$ a 'deceptively simple' ABX spectrum is encountered, consisting of a 'doublet' [$P(az)_2$, P(az)Cl; 35.8 p.p.m.] and a 'triplet' (PCl_2; 24.9 p.p.m.). Under certain conditions[19] these types of spectra (essentially AA'X) are known to possess an A_2X shape. A similar ^{31}P n.m.r. spectrum has been observed with the analogous compound *gem*-$N_3P_3(NMe_2)_3Cl_3$.[20] As found for other amino-substituted cyclophospha(thia)zenes[20–23] the values of δ[*P*$(az)_2$], δ[*P*(az)Cl], and δ(PCl_2) all tend to shift in a low-field direction with increasing degree of substitution.

Amongst the five isomers $N_4P_4(az)_2Cl_6$ (**16**)—(**20**) only (**20**) has an asymmetric AX_2Y type ^{31}P n.m.r. spectrum, which is expected for a geminal structure. Analogous with the trimeric case (*cf.* Table 7) the geminal structure is accompanied by a relatively small value of $^3J_{PH}$. Although the ^{31}P n.m.r. spectra of (**16**)—(**19**) allow the determination of 2,6- or 2,4-structures (giving A_2X_2 or AA'XX' spectra, respectively), no *trans*- or *cis*-structures can be assigned regarding the ^1H n.m.r. spectra (data in Table 7). However, the ^1H n.m.r. spectra of the compounds $N_4P_4(az)_2(NMe_2)_6$ derived from (**16**)—(**19**) allow an unambiguous structure assignment. As in all cases the substitution reactions afford single isomers the structures can be directly related to the chloro precursors.

Amongst the possible non-geminal structures of the derivatives $N_4P_4(az)_2(NMe_2)_6$ the 2,*trans*-6-isomer contains two chemically non-equivalent dimethylamino (D) groups (ratio 1:2) against three for the other isomers (ratio 1:1:1) (Figure 2). Therefore, the structures of the two 2,6-isomers, *i.e.* *trans*-(**26**) and *cis*-(**27**), can be easily assigned as well as those of their precursors, *i.e.* (**16**) and (**17**), respectively (*cf.* Figure 2). A closer examination of the ^1H n.m.r. spectra of the 2,4-isomers (**28**) and (**29**) provides a tentative *trans*–*cis* assignment. Referring to the

Table 9. ^{31}P N.m.r. data* for the tetrameric derivatives (**15**)—(**29**)

	$\delta(^{31}P)$				$^2J_{PP}$				
Compound	δ[P(2)]	δ[P(4)]	δ[P(6)]	δ[P(8)]	J_{24}	J_{46}	J_{68}	J_{28}	$^4J_{PP}$
(**15**)	8.6	−4.7	−7.2	−4.7	27.6	30.6	30.6	27.6	
(**16**)	8.4	−1.9	8.4	−1.9	27.9	27.9	27.9	27.9	
(**17**)	8.7	−2.6	8.7	−2.6	28.4	28.4	28.4	28.4	
(**18**)	11.8	11.8	−4.9	−4.9	27.6	25.4	31.1	25.4	−0.9
(**19**)	10.3	10.3	−5.0	−5.0	29.2	27.1	32.7	27.1	−0.8
(**20**)	18.8	−5.9	−6.5	−5.9	11.6	26.1	26.1	11.6	
(**21**)	18.5	−3.4	8.9	−3.4	13.9	26.4	26.4	13.9	
(**22**)	12.1	14.9	12.1	−2.5	27.0	27.0	26.5	26.5	
(**23**)	10.3	13.7	11.7	−1.8	28.9	27.6	24.7	26.9	
(**24**)	19.6	11.3	−4.4	−6.8	22.8	25.6	27.9	12.0	
(**25**)	10.3	12.2	10.3	−3.5	29.4	29.4	27.8	27.8	
(**26**)	12.8	9.6	12.8	9.6	38.3	38.3	38.3	38.3	
(**27**)	13.9	9.6	13.9	9.6	39.8	39.8	39.8	39.8	
(**28**)	14.0	14.0	8.6	8.6	31.7	38.9	43.6	38.9	−0.4
(**29**)	12.5	12.5	8.3	8.3	33.0	39.9	43.5	39.9	−0.1

* Chemical shifts (p.p.m.) positive in low-field direction; coupling constants in Hz.

Table. 10. Crystallographic data for $N_3P_3(az)_2Cl_4$ (**4**) and $N_4P_4(az)_2Cl_6$ (**18**)*

Complex	(**4**)	(**18**)
Formula	$C_4H_8Cl_4N_5P_3$	$C_4H_8Cl_6N_6P_4$
M	360.88	476.76
Space group	Monoclinic $C2/c$	Monoclinic $P2_1/n$
T/K	293	293
a/Å	14.869(5)	8.522(1)
b/Å	7.596(4)	12.707(5)
c/Å	14.046(5)	16.623(4)
β/°	117.06(2)	104.75(2)
U/Å^3	1 412.7	1 740.9
Z	4	4
D_c/g cm^{-3}	1.697	1.819
μ(Mo-K_α)/cm^{-1}	11.6	13.5
F(000)	720	944
Crystal size/mm	0.3 × 0.35 × 0.4	0.4 × 0.35 × 0.3
Number of reflections	1 546 (1 < 2θ < 54°)	2 245 (1 < 2θ < 44°)
R	0.047	0.046
R' (w = 1)	0.059	0.058
Number of reflections [$I > 3\sigma(I)$]	1 153	1 803

* Details for both complexes: data collection: Nonius CAD-4F diffractometer, interfaced to a PDP-11/23, graphite-monochromated Mo-K_α radiation, ω—2θ scan; corrections; correction for Lorentz polarization, no absorption correction; solution and refinement: direct methods (P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J. P. Declerq, and M. M. Woolfson, 'Multan 82, a system of computer programs for the automatic solution of crystal structures from X-ray diffraction data,' Universities of York and Louvain, 1982), full-matrix refinement of positional and anisotropic thermal parameters, no attempts were made to locate the H atoms.

Table 11. Positional parameters for $N_3P_3(az)_2Cl_4$ (**4**) (estimated standard deviations in parentheses)

Atom	x	y	z
Cl(1)	−0.218 7(1)	0.031 5(3)	0.137 5(1)
Cl(2)	0.077 5(1)	0.574 0(2)	0.205 9(1)
P(1)	−0.081 2(1)	0.095 2(2)	0.149 7(1)
P(2)	0.000	0.406 9(3)	0.250
N(1)	0.000	−0.004 2(9)	0.250
N(2)	−0.076 1(3)	0.304 3(6)	0.148 1(4)
N(3)	−0.078 0(3)	0.021 0(7)	0.043 0(3)
C(1)	−0.166 4(5)	0.014(1)	−0.063 8(5)
C(2)	−0.118 8(5)	−0.152 6(9)	−0.004 4(5)

spectra of (**26**)—(**29**) the signals at lowest field [$\delta(^1H)$ = 2.69—2.72 p.p.m.] can generally be ascribed to the dimethylamino groups D_1, geminal to the groups az (see Figure 2), which implies that the shielding contributions of the groups az have to be significantly smaller than those of the groups D. On these grounds it can be argued that the shielding of the dimethylamino substituents increases in the order $D_1 < D_2 < D_3$ (see Figure 2). Applying this order of shielding constants the following can be derived for these two isomers: $[\delta(D_2) - \delta(D_3)]_{2,cis\text{-}4} > [\delta(D_2) - \delta(D_3)]_{2,trans\text{-}4}$. From the data in Table 8 it appears that for (**28**), $\delta(D_2) - \delta(D_3)$ = 0.02 p.p.m. and for (**29**), $\delta(D_2) - \delta(D_3)$ = 0.06 p.p.m.

This small, but significant difference between (**28**) and (**29**) indicates a 2,*trans*-4-conformation of aziridinyl groups in (**28**) and the precursor (**18**), whereas a 2,*cis*-4-structure can be ascribed to (**29**) and the precursor (**19**). This structure assignment was confirmed by a crystal structure determination of (**18**), see later.

In the ^{31}P n.m.r. spectra of the isomers $N_4P_4(az)_3Cl_5$ (**23**) and (**24**) four non-equivalent phosphorus nuclei (Table 9) are observed. Only two isomers meet this condition, *viz.* the 2,*cis*-4,*trans*-6- and 2,2,4-isomers. In the ^1H n.m.r. spectra of both (**23**) and (**24**) (see Table 7 and Figure 3) three non-equivalent aziridinyl groups can be distinguished, which is in line with the structures proposed. The data in Table 7 for the spectra taken in C_6D_6 solution show values of $^3J_{PH}$ of 21.5, 21.9, and 21.9 Hz for (**23**) and 17.5, 17.5, and 22.1 Hz for (**24**). As smaller values of $^3J_{PH}$ can be expected in a $P(az)_2$ grouping rather than in P(az)Cl, (**24**) is most probably the 2,2,4-isomer and, consequently, (**23**) has the 2,*cis*-4,*trans*-6-structure.

The values of $^3J_{PH}$ found for isomer (**21**) (Table 7) also indicate a geminal structure; the AMX_2 ^{31}P n.m.r. spectrum (Figure 4) is in agreement with a 2,6-geminal structure. As shown in Table 9, both the geminal isomers (**21**) and (**24**) show the low-field ^{31}P chemical shift, characteristic of $P(az)_2$ centres.

The symmetrically substituted 2,*trans*-4,*cis*-6- and 2,*cis*-4,*cis*-6-isomers cannot be distinguished on the basis of their n.m.r. spectra. In both cases AM_2X ^{31}P n.m.r. spectra are encountered, whereas the ^1H n.m.r. spectra (Table 7, Figure 3) show the expected 1:2 ratio of two inequivalent types of aziridinyl groups with $^3J_{PH}$ values characteristic of non-geminal substitution. The only argument for the structure assignment of

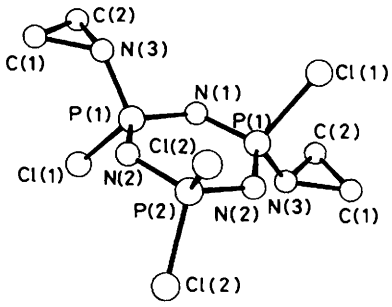

Figure 5. Molecular structure of *trans*-$N_3P_3(az)_2Cl_4$ (**4**)

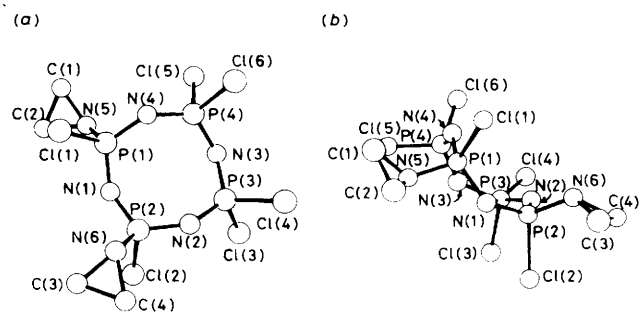

Figure 6. Molecular structure of 2,*trans*-4-$N_4P_4(az)_2Cl_6$ (**18**), upper view (*a*) and side view (*b*)

Table 12. Positional parameters for $N_4P_4(az)_2Cl_6$ (**18**) (estimated standard deviations in parentheses)

Atom	*x*	*y*	*z*
Cl(1)	0.740 7(3)	0.249 7(2)	0.173 0(1)
Cl(2)	0.146 3(2)	0.355 2(2)	0.231 8(2)
Cl(3)	0.225 2(3)	0.263 4(2)	0.450 3(1)
Cl(4)	0.551 4(4)	0.365 0(2)	0.542 9(1)
Cl(5)	0.676 2(3)	−0.017 0(2)	0.426 0(1)
Cl(6)	0.879 8(3)	0.178 1(2)	0.499 8(1)
P(1)	0.595 1(2)	0.184 7(2)	0.238 9(1)
P(2)	0.391 9(2)	0.355 6(2)	0.268 0(1)
P(3)	0.448 9(3)	0.290 3(2)	0.437 5(1)
P(4)	0.678 4(2)	0.138 5(2)	0.412 3(1)
N(1)	0.440 5(7)	0.254 6(5)	0.226 4(4)
N(2)	0.444 2(7)	0.369 5(5)	0.365 8(3)
N(3)	0.526 7(7)	0.177 9(5)	0.439 0(4)
N(4)	0.713 5(7)	0.170 1(6)	0.328 5(4)
N(5)	0.536 8(7)	0.070 7(5)	0.197 9(4)
N(6)	0.455 2(7)	0.462 1(5)	0.230 7(4)
C(1)	0.638(1)	−0.001 8(7)	0.162 7(6)
C(2)	0.490(1)	0.047 3(7)	0.107 7(6)
C(3)	0.371(1)	0.511 6(7)	0.152 5(5)
C(4)	0.376(1)	0.566 7(6)	0.233 4(6)

(**25**) is that this isomer was prepared from 2,*cis*-4-$N_4P_4(az)_2Cl_6$ (see Experimental section). Hence, assuming that no isomerization takes place, (**25**) should have the 2,*cis*-4,*cis*-6-structure.

In Table 9 the ^{31}P n.m.r. data on the tetrameric derivatives (**15**)—(**29**) are listed. For most compounds these data were verified by spectrum simulation.

Crystal Structure Determinations.—Structural data. In order to establish the structure assignments based on n.m.r. data, two so-called key compounds, *viz.* $N_3P_3(az)_2Cl_4$ (**4**) and $N_4P_4(az)_2Cl_6$ (**18**) were investigated by *X*-ray methods. Crystal data of these compounds as well as the experimental details on the structure determinations are compiled in Table 10. The final fractional atomic co-ordinates are given in Tables 11 and 12.

Molecular structures of $N_3P_3(az)_2Cl_4$ (**4**) *and* $N_4P_4(az)_2Cl_6$ (**18**). As shown in Figures 5 and 6 the aziridinyl groupings in $N_3P_3(az)_2Cl_4$ (**4**) and $N_4P_4(az)_2Cl_6$ (**18**) are in 2,*trans*-4-positions. These findings agree with the previous structure assignments based on n.m.r. data and can be considered as a justification of the procedures followed.

In the unit cell of the trimer the molecule $N_3P_3(az)_2Cl_4$ is located on a two-fold axis through the atoms P(2) and N(1). The six-membered N–P ring is slightly twisted, P(1) and N(2) being positioned 0.04 Å out of the mean plane of the ring.

The eight-membered phosphazene ring of (**18**) has a saddle-like conformation with the atoms P(1), P(2), P(3), and P(4) almost situated in one plane, the maximum deviation from planarity being 0.09 Å.

Table 13. Bond distances (Å) and angles (°) in *trans*-$N_3P_3(az)_2Cl_4$ (**4**) (estimated standard deviations in parentheses)

Cl(1)–P(1)	2.031(2)	P(2)–N(2)	1.570(5)
Cl(2)–P(2)	1.993(2)	N(3)–C(1)	1.479(7)
P(2)–N(1)	1.571(3)	N(3)–C(2)	1.477(8)
P(1)–N(2)	1.590(5)	C(1)–C(2)	1.501(10)
P(1)–N(3)	1.622(4)		
Cl(1)–P(1)–N(1)	107.1(1)	N(2)–P(2)–N(2)	120.4(3)
Cl(1)–P(1)–N(2)	106.8(2)	P(1)–N(1)–P(1)	122.5(4)
Cl(1)–P(1)–N(3)	106.9(2)	P(1)–N(2)–P(2)	120.1(3)
N(1)–P(1)–N(2)	118.1(3)	P(1)–N(3)–C(1)	124.3(4)
N(1)–P(1)–N(3)	109.1(2)	P(1)–N(3)–C(2)	123.2(4)
N(2)–P(1)–N(3)	108.2(3)	C(1)–N(3)–C(2)	61.1(4)
Cl(2)–P(2)–N(2)	108.2(3)	N(3)–C(1)–C(2)	59.4(4)
Cl(2)–P(2)–Cl(2)	100.8(1)	N(3)–C(2)–C(1)	59.5(4)

Apart from the N–P ring shape the molecular structures of (**4**) and (**18**) are quite similar. In a PCl_2 group the P–Cl bonds are positioned symmetrically with respect to the adjacent $P(N_{endo})_2$ plane. The same holds for the $P–N_{exo}$ and P–Cl bonds in a P(az)Cl group, whereas the aziridinyl planes are almost parallel to their corresponding $P(N_{endo})_2$ planes. The exocyclic nitrogens possess a pyramidal character, the distances from the PCC planes being 0.596 [N(3)] in (**4**), 0.582 [N(5)] and 0.611 Å [N(6)] in (**18**) {*cf.* 0.69 Å in $N_3P_3(az)_6$;[24] 0.68 and 0.71 Å in $[NP(az)_2]_2NSO(az)$[25]}. This is in sharp contrast with corresponding dimethylamino derivatives in which the $PNMe_2$ groups approach planarity.[26–31]

The sequences of endocyclic bond lengths and bond angles (Tables 13 and 14) are comparable with those found in analogous systems, *e.g.* *trans*-$N_3P_3(NMe_2)_2Cl_4$[31] and 2,*trans*-4-$N_4P_4(NMePh)_2Cl_6$.[32] The difference in N–P bond lengths in a PCl_2–N–P[(az)Cl] unit can be explained from a difference in electronegativity of the phosphorus centres.

Replacement of a chloro ligand in a PCl_2 moiety by an aziridinyl group leads to a lengthening of the remaining P–Cl bond, reflecting an increase of the ionic character of the bond by the electron-donating character of the aziridinyl group {mean values of P–Cl bond lengths: 2.031 [P(az)Cl] and 1.993 Å (PCl_2) in (**4**); 2.027 [P(az)Cl] and 1.998 Å (PCl_2) in (**18**)}.

Experimental

General.—All experiments were carried out under dry nitrogen. Aziridine and dimethylamine were distilled prior to use over KOH pellets. $(NPCl_2)_3$ and $(NPCl_2)_4$ (Otsuka Ltd., Japan) were recrystallized once from n-hexane. Solvents were purified and dried according to conventional methods. **CAUTION**: aziridine is a suspected carcinogen; use only in a well ventilated hood.

Table 14. Bond distances (Å) and angles (°) in 2,*trans*-4-$N_4P_4(az)_2Cl_6$ (**18**) (estimated standard deviations in parentheses)

Cl(1)–P(1)	2.029(2)	P(2)–N(6)	1.636(4)
Cl(2)–P(2)	2.025(2)	P(3)–N(2)	1.553(4)
Cl(3)–P(3)	2.002(2)	P(3)–N(3)	1.574(4)
Cl(4)–P(3)	1.988(2)	P(4)–N(3)	1.550(4)
Cl(5)–P(4)	1.990(2)	P(4)–N(4)	1.550(4)
Cl(6)–P(4)	2.010(2)	N(5)–C(1)	1.474(7)
P(1)–N(1)	1.558(4)	N(5)–C(2)	1.457(7)
P(1)–N(4)	1.582(4)	N(6)–C(3)	1.442(7)
P(1)–N(5)	1.622(4)	N(6)–C(4)	1.485(7)
P(2)–N(1)	1.563(4)	C(1)–C(2)	1.463(8)
P(2)–N(2)	1.585(4)	C(3)–C(4)	1.461(8)
Cl(1)–P(1)–N(1)	108.0(2)	Cl(5)–P(4)–N(3)	104.7(2)
Cl(1)–P(1)–N(4)	103.1(2)	Cl(5)–P(4)–N(4)	111.6(2)
Cl(1)–P(1)–N(5)	107.6(2)	Cl(6)–P(4)–N(3)	109.5(2)
N(1)–P(1)–N(4)	120.5(5)	Cl(6)–P(4)–N(4)	105.3(2)
N(1)–P(1)–N(5)	107.1(2)	N(3)–P(4)–N(4)	122.5(2)
N(4)–P(1)–N(5)	109.9(2)	P(1)–N(1)–P(2)	136.0(3)
Cl(2)–P(2)–N(1)	103.7(2)	P(2)–N(2)–P(3)	131.2(3)
Cl(2)–P(2)–N(2)	107.7(2)	P(3)–N(3)–P(4)	131.9(3)
Cl(2)–P(2)–N(6)	107.9(2)	P(1)–N(4)–P(4)	131.0(3)
N(1)–P(2)–N(2)	120.7(2)	P(1)–N(5)–C(1)	125.9(4)
N(1)–P(2)–N(6)	111.1(2)	P(1)–N(5)–C(2)	125.3(4)
N(2)–P(2)–N(6)	105.1(2)	C(1)–N(5)–C(2)	59.9(4)
Cl(3)–P(3)–Cl(4)	101.8(1)	P(2)–N(6)–C(3)	123.8(4)
Cl(3)–P(3)–N(2)	110.7(2)	P(2)–N(6)–C(4)	122.5(4)
Cl(3)–P(3)–N(3)	104.7(2)	C(3)–N(6)–C(4)	59.9(4)
Cl(4)–P(3)–N(2)	106.5(2)	N(5)–C(1)–C(2)	59.5(4)
Cl(4)–P(3)–N(3)	109.5(2)	N(5)–C(2)–C(1)	60.6(4)
N(2)–P(3)–N(3)	122.0(2)	N(6)–C(3)–C(4)	61.5(4)
Cl(5)–P(4)–Cl(6)	101.3(1)	N(6)–C(4)–C(3)	58.6(4)

Purification by h.p.l.c. was carried out using a Waters system consisting of two 6000 A pumps, combined with a R401 RI detector. Separations were performed on Lichrosorb Si 60/10 columns (outside diameter 22 mm, length 30 cm).

Elemental analyses (Table 15) were performed under the supervision of Mr. A. F. Hamminga. Mass spectra were recorded on an AEI M.S.9 mass spectrometer as a routine purity check (Mr. A. Kiewiet, Department of Organic Chemistry, University of Groningen).

All n.m.r. spectra were taken of $CDCl_3$ solutions unless stated otherwise. Proton n.m.r. spectra were recorded either at 60 MHz with a JEOL C-60-HL spectrometer or at 200 MHz with a Nicolet 283 A FT spectrometer in 5-mm tubes using $SiMe_4$ as internal reference. $^{31}P-\{^1H\}$ N.m.r. spectra were taken with a Nicolet 283 AFT spectrometer in 10-mm tubes at 80.9 MHz; $(NPCl_2)_3$ was used as external reference (19.9 p.p.m.); the ^2H resonance line of the solvent was used for field-frequency lock. Chemical shifts are positive to low field.

Work-up Procedure for all Reactions.—The reactions described afforded considerable amounts of hydrochloride salt precipitates. The use of aziridine as a hydrogen chloride scavenger resulted in the aziridinium chloride salt, which is rather unstable[33] and polymerizes subsequently.

Precipitated (polymeric) salts were removed by filtration. After thorough washing with solvent the combined filtrates containing the N–P ring compounds were evaporated *in vacuo*. Crude products were chromatographed by h.p.l.c. and/or recrystallized from an appropriate solvent.

Preparation of $N_3P_3(az)_nCl_{6-n}$ (n = 1—6) (**3**)—(**14**).— (*i*) $N_3P_3(az)Cl_5$ (**3**). To a stirred solution of (**1**) (5.2 g, 15 mmol) in diethyl ether (100 cm^3), cooled at −20 °C, was added dropwise aziridine (1.55 cm^3, 30 mmol) in diethyl ether (50 cm^3). After warming to room temperature and a total reaction time of 20 h the reaction mixture was worked-up according to the general procedure. The resulting white solid was recrystallized from diethyl ether to yield several crops of white crystals. Yield: 3.0 g (56.5%) of pure (**3**), m.p. 67—68.5 °C (lit.,[6] 69—70 °C).

(*ii*) *trans-, cis-, and gem*-$N_3P_3(az)_2Cl_4$ (**4**)—(**6**). A solution of aziridine (12.4 cm^3, 240 mmol) in benzene (100 cm^3) was added slowly to a vigorously stirred solution of (**1**) (20.8 g, 60 mmol) in benzene (200 cm^3) cooled at 6 °C. Warming slowly to room temperature and stirring for a further 18 h, followed by the general work-up procedure, yielded a white, waxy material. Residual polymeric side products and a small amount of $N_3P_3(az)_4Cl_2$ were removed over a silica column with n-hexane–diethyl ether (3:2) as eluant. Five fractions were isolated by h.p.l.c., using n-hexane–diethyl ether (2:1) as eluant. Further experimental data are listed in Table 16.

(*iii*) *trans-, cis-, and gem*-$N_3P_3(az)_3Cl_3$ (**7**)—(**9**). Using (**5**) (2.0 g, 5.5 mmol) as starting material, a reaction under the conditions described for the preparation of (**4**)—(**6**) was carrried out with a (**5**):aziridine molar ratio of 1:2. The crude product obtained was chromatographed by h.p.l.c. using n-hexane–diethyl ether (2:3) as eluant, containing 2% of acetonitrile. Four fractions were isolated (Table 16).

(*iv*) *trans- and cis*-$N_3P_3(az)_4Cl_2$ (**10**) *and* (**11**). Using (**7**) (0.3 g, 0.81 mmol) as starting material, a reaction under the conditions described for the preparation of (**4**)—(**6**) was carried out with a (**7**):aziridine molar ratio of 1:2. The crude product obtained was chromatographed by h.p.l.c. using n-hexane–acetone (2:1) as eluant. Three fractions were collected (Table 16).

(*v*) *gem*-$N_3P_3(az)_4Cl_2$ (**12**) *and* $N_3P_3(az)_5Cl$ (**13**). A reaction under the conditions described for (**4**)—(**6**) with a (**1**):aziridine molar ratio of 1:10 afforded a white solid. This material, consisting of (**12**), (**13**), and (**14**), was subjected to h.p.l.c., using acetone as eluant. Three fractions were collected (Table 16).

(*vi*) $N_3P_3(az)_6$ (**14**). Several procedures have been described for preparing this particular derivative.[6,8,34] A solution of

Table 15. Elemental analysis[a] (%)

Compound	C	H	N	Cl
(**3**)	6.95 (6.80)	1.10 (1.15)	15.60 (15.80)	49.60 (50.05)
(**4**)	13.25 (13.30)	2.25 (2.25)	19.55 (19.40)	39.00 (39.30)
(**5**)	13.35 (13.30)	2.30 (2.25)	19.20 (19.40)	39.55 (39.30)
(**6**)	13.40 (13.30)	2.10 (2.25)	19.30 (19.40)	39.55 (39.30)
(**7**)	19.80 (19.60)	3.25 (3.30)	22.80 (22.85)	29.00 (28.95)
(**8**)	21.30 (19.60)	3.55 (3.30)	23.15 (22.85)	*b* (28.95)
(**9**)	19.60 (19.60)	3.20 (3.30)	22.75 (22.85)	28.70 (28.95)
(**10**)	25.70 (25.70)	4.30 (4.30)	26.30 (26.20)	18.90 (18.95)
(**11**)	26.00 (25.70)	4.35 (4.30)	26.15 (26.20)	18.90 (18.95)
(**12**)	25.95 (25.70)	4.35 (4.30)	26.05 (26.20)	18.60 (18.95)
(**13**)	31.60 (31.55)	5.30 (5.30)	28.90 (29.45)	9.15 (9.30)
(**14**)	37.30 (37.20)	6.25 (6.25)	32.50 (32.55)	
(**15**)	5.05 (5.10)	0.85 (0.85)	14.85 (14.90)	52.60 (52.80)
(**16**)	10.10 (10.10)	1.60 (1.70)	17.55 (17.65)	44.65 (44.60)
(**17**)	10.10 (10.10)	1.60 (1.70)	17.65 (17.65)	44.65 (44.60)
(**18**)	10.20 (10.10)	1.70 (1.70)	17.75 (17.65)	44.30 (44.60)
(**19**)	10.45 (10.10)	1.65 (1.70)	17.45 (17.65)	44.55 (44.60)
(**20**)	10.00 (10.10)	1.60 (1.70)	17.55 (17.65)	44.95 (44.60)
(**21**)	14.95 (14.90)	2.50 (2.50)	20.35 (20.30)	36.85 (36.65)
(**22**)	14.75 (14.90)	2.45 (2.50)	20.35 (20.30)	36.45 (36.65)
(**23**)	14.70 (14.90)	2.55 (2.50)	20.40 (20.30)	36.95 (36.65)
(**24**)	14.90 (14.90)	2.50 (2.50)	20.35 (20.30)	36.70 (36.65)
(**25**)	14.90 (14.90)	2.50 (2.50)	20.35 (20.30)	36.35 (36.65)
(**26**)	36.35 (36.35)	8.35 (8.40)	31.45 (31.80)	
(**27**)	36.50 (36.35)	8.40 (8.40)	32.25 (31.80)	
(**28**)	36.55 (36.35)	8.60 (8.40)	32.20 (31.80)	

[a] Calculated values in parentheses. [b] No chlorine analysis; impure sample (see text).

Table 16. Data on experiments (*ii*)—(*v*); mean values of several experiments

Experiment	Fraction	Amount (g)	Compound	Recrystallization solvent	Yield (%)	M.p. (°C)[a]
(*ii*)	1	3.00	(**3**)			
	2	3.74	(**4**)	$n\text{-}C_6H_{14}$	14	66.5—68
	3	3.71	(**6**)	$n\text{-}C_6H_{14}$–Et_2O	13	105.5—107 (104—105.5)
	4	2.97	(**5**)	$n\text{-}C_6H_{14}$	10	65.5—67
	5	1.68	(**9**)			
(*iii*)	1	0.46	(**5**)			
	2	0.43	(**7**)	$n\text{-}C_6H_{14}$–Et_2O	14	95.5—97
	3	0.64	(**9**)	$n\text{-}C_6H_{14}$–Et_2O	16	61.5—63 (69—70)
	4	0.12	(**8**)	Et_2O	1.5	>200[b]
(*iv*)	1	0.06	(**7**)			
	2	0.10	(**10**)	$n\text{-}C_6H_{14}$–Et_2O	23	102.5—104
	3	0.12	(**11**)	Et_2O	30	116—118
(*v*)	1	7.70	(**12**)	Et_2O	27	131 (131)
	2	7.80	(**13**)	Et_2O	23	122—122.5 (122)
	3[c]					

[a] Literature melting points (ref. 6 and 7) in parentheses. [b] According to elemental analysis and ^{31}P n.m.r. data the recrystallized material was contaminated with traces of $N_3P_3(az)_4Cl_2$. [c] Indeterminable product, probably due to the reaction of (**14**) with the column material in the acetone eluant applied.

Table 17. Experimental data on the separation of (**15**)—(**23**) by h.p.l.c.; mean values of several experiments

Fraction	Amount (g)	Compound	Recrystallization solvent	Yield (%)	M.p. (°C)
1	2.00	(**15**)	Et_2O–$n\text{-}C_6H_{14}$	17	68.5—70
2	1.13	(**16**)	Et_2O–$n\text{-}C_6H_{14}$	6	103—104
3	0.61	(**17**)	Et_2O–$n\text{-}C_6H_{14}$	4	122.5—123.5
4	1.06	(**18**)	Et_2O–$n\text{-}C_6H_{14}$	8	91—92
5	0.48	(**20**)	$n\text{-}C_6H_{14}$	2	39.5—40.5
6	0.81	(**19**)	Et_2O–$n\text{-}C_6H_{14}$	6	68—70
7	1.16	(**21**)/(**22**)	*	—	—
8	1.19	(**23**)	Et_2O–$n\text{-}C_6H_{14}$	9	84.5—86.5

* Additional separation required.

aziridine (7.7 cm^3, 150 mmol) in benzene (30 cm^3) was added slowly to a stirred solution of (**1**) (1.75 g, 5 mmol) in benzene (30 cm^3), cooled at 5—10 °C. After completion of the addition the temperature was raised to 50 °C for 20 h. The general work-up procedure gave a white solid. Recrystallization from tetrahydrofuran gave (**14**) as a tetrahydrofuran adduct. An amount [1.45 g (75%)] of pure (**14**), m.p. 151.5—153 °C (lit.,[6,8] 149—150 °C) was obtained by keeping the adduct under vacuum (1 mmHg) for *ca.* 8 h.

Preparation of $N_4P_4(az)_nCl_{8-n}$ (n = 1—3) (**15**)—(**25**).—(*i*) $N_4P_4(az)Cl_7$ (**15**). To a stirred solution of (**2**) (5.0 g, 10.8 mmol) in diethyl ether (300 cm^3), cooled at −20 °C, was added slowly a solution of aziridine (1.4 cm^3, 27.0 mmol) in diethyl ether (150 cm^3). The reaction mixture was warmed slowly to room temperature and left to stir for 18 h. The general work-up procedure afforded a waxy oil, which upon separation by h.p.l.c. using diethyl ether–n-hexane (1:3) as eluant gave a white solid. Recrystallization from diethyl ether–n-hexane yielded 2.28 g (45%) of (**15**), m.p. 68.5—70 °C.

(*ii*) $N_4P_4(az)_2Cl_6$ (**16**)—(**20**). To a stirred solution of (**2**) (10.0 g, 21.6 mmol) in n-hexane (300 cm^3), cooled at 0 °C, was added slowly a solution of aziridine (4.5 cm^3, 86.4 mmol) in n-hexane (100 cm^3). A procedure, similar to that described for (**15**) yielded a viscous oil. Separation by h.p.l.c. using diethyl ether–n-hexane (1:3) as eluant afforded eight fractions. Further experimental data are listed in Table 17.

(*iii*) $N_4P_4(az)_3Cl_5$ (**21**)—(**23**). An additional separation by h.p.l.c. using diethyl ether–n-hexane (15:85) as eluant, containing 1.5% of acetonitrile, was carried out with fraction 7 of the h.p.l.c. experiment described in (*ii*). Two fractions were obtained: 0.68 g of (**21**) and 0.20 g of (**22**). Recrystallizations from diethyl ether–n-hexane mixtures yielded 0.5 g (5%) of (**21**), m.p. 84—85 °C, and 0.1 g (1%) of (**22**), m.p. 82—82.5 °C. Fraction 8 (Table 17) afforded (**23**) by recrystallization from diethyl ether–n-hexane, yield 1.19 g (9%), m.p. 84.5—86.5 °C.

(*iv*) $N_4P_4(az)_3Cl_5$ (**24**). A procedure similar to that applied for the synthesis of (**15**) using (**18**) (0.8 g, 1.7 mmol) as starting material yielded an oil. By h.p.l.c. separation using diethyl ether–n-hexane (3:1) as eluant, containing 1% of acetonitrile, 0.18 g of (**24**) was obtained as the main product. Recrystallization from diethyl ether–n-pentane afforded 0.12 g (15%) of (**24**), m.p. 52—54 °C.

(*v*) $N_4P_4(az)_3Cl_5$ (**25**). A procedure similar to that applied for the synthesis of (**15**) using (**19**) (0.5 g 1.1 mmol) as starting material yielded an oil. By h.p.l.c. separation using diethyl ether–n-hexane (3:1) as eluant, 0.07 g of (**25**) was obtained as one of the fractions. Recrystallization from diethyl ether–n-hexane afforded 0.03 g (6%) of (**25**), m.p. 61—63 °C.

Preparation of $N_4P_4(az)_2(NMe_2)_6$ (**26**)—(**29**).—To a stirred solution of $N_4P_4(az)_2Cl_6$ (**16**)—(**19**) (0.5 g, 1 mmol) in diethyl ether (25 cm^3), cooled at 0 °C, was added dropwise 15 cm^3 of a 3 mol dm^{-3} solution of dimethylamine in diethyl ether. After warming to room temperature and a reaction time of 18 h the general work-up procedure yielded an oily material in all cases. This was dissolved in diethyl ether (25 cm^3) and refluxed overnight after adding 10 cm^3 of a 3 mol dm^{-3} solution of dimethylamine in diethyl ether. The general work-up procedure yielded a white solid [starting material (**16**)] or a viscous oil [starting materials (**17**)—(**19**)]. The solid was crystallized from n-hexane, yielding 0.38 g (68%) of (**26**), m.p. 198—200 °C. The oils were recrystallized several times from n-hexane at −70 °C, giving either waxy crystals [(**27**) and (**28**)] or an oily substance (**29**). In this way we obtained 0.18 g (32%) of (**27**), m.p. 192—195 °C, 0.13 g (24%) of (**28**), m.p. >200 °C (decomp.), and 0.17 g (30%) of (**29**) (oil). The purity of (**29**) remained unsatisfactory, probably by inclusion of solvent; mass and n.m.r. spectra were in agreement with the completely aminolysed product (**29**).

Investigation of Separate Substitution Steps and Reactivity.— In order to study the various substitution steps of the trimer and the tetramer a number of reactions were carried out under standardized conditions using a phosphazene:aziridine molar ratio of 1:2. To a stirred solution of phosphazene (0.2 mmol) in 10 cm^3 of solvent, cooled at 5 °C, was added dropwise 9.0 cm^3 of a 0.05 mol dm^{-3} solution of aziridine. After warming to room temperature and a reaction time of 18 h the general work-up procedure gave the crude, salt-free, product, which was stored at −30 °C under dry nitrogen. Solvents used were diethyl ether, benzene, or n-hexane. Similar reactions with equimolar mixtures of the isomeric bis-, tris-, and tetrakis-(aziridinyl) derivatives of (**1**) allowed a comparison between the reactivities of these compounds. For this purpose the relative peak areas in the ^{31}P n.m.r. spectra and h.p.l.c. chromatograms were determined, before and after the reactions. Also, reactions with (**15**) in diethyl ether with varying molar ratios (1:0.5—2.5) were performed according to analogous procedures. This also holds for the 1:8—14 reactions with (**2**).

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