Studies of Phosphazenes. Part 25.† Synthesis, Nuclear Magnetic Resonance Spectroscopy, and Mode of Formation of (Aziridino)(triphenylphosphazenyl)-cyclotriphosphazenes. *X*-Ray Crystal Structure and Enzyme-inhibiting Activity of $N_3P_3(NPPh_3)(NC_2H_4)_5$‡

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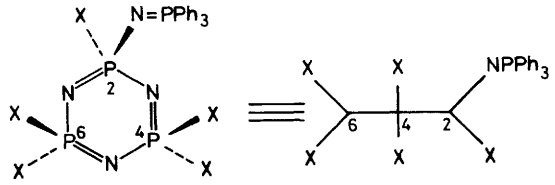
Aziridine (HNC_2H_4) reacts with the triphenylphosphazenyl derivative $N_3P_3(NPPh_3)Cl_5$ (**1**) to yield the compounds $N_3P_3(NPPh_3)(NC_2H_4)_nCl_{5-n}$ [n = 1—5; (**3**)—(**9**)], the structures of which are elucidated by ^1H and ^{31}P n.m.r. spectroscopy. The fluoro-analogue, $N_3P_3(NPPh_3)F_5$ (**2**), is unreactive even under drastic conditions. The chlorine replacement pattern and the associated mechanistic aspects are discussed. The *X*-ray crystal structure analysis of $N_3P_3(NPPh_3)(NC_2H_4)_5$ (**9**) shows a novel conformation of the $-NPPh_3$ substituent in which one of the phenyl groups lies in a plane nearly perpendicular and in close proximity to the $-NC_2H_4$ group at the $\equiv P(NPPh_3)(NC_2H_4)$ site. The n.m.r. [^1H, ^{13}C, and ^{31}P] parameters of (**9**) are discussed in relation to its structure. The enzyme-inhibiting activity of (**9**) is compared with that of $N_3P_3(NC_2H_4)_6$.

The burgeoning interest in the syntheses and structures of (aziridino)cyclophosphazenes is due to three reasons: (*i*) the wide-spectrum antitumour activity exhibited by some of these derivatives,[1–3] (*ii*) the structural modifications as shown by *X*-ray crystallography,[4–6] and (*iii*) the behaviour of aziridine as a secondary amino nucleophile.[2,3,7,8] We have investigated the 'aziridinolysis' of $N_3P_3(NPPh_3)X_5$ [X = Cl (**1**) or F (**2**)] in order to assess the role of the $-NPPh_3$ substituent and the leaving group in these reactions. The results are discussed in this paper. The *X*-ray crystal structure of $N_3P_3(NPPh_3)(NC_2H_4)_5$ (**9**) and the correlation of its n.m.r. parameters (^1H, ^{13}C, ^{31}P) with the conformation of the $-NPPh_3$ group are described. Finally, we give a brief account of the relative enzyme (Reverse Transcriptase) inhibiting activities of compound (**9**) and $N_3P_3(NC_2H_4)_6$.

Experimental

The conditions for n.m.r. spectroscopic measurements were as described previously.[9] I.r. spectra were recorded on a Carl Zeiss UR-10 spectrophotometer using KBr or KCl pellets. Mass spectra were obtained from a JEOL OX 300 or a Varian MAT CH5 spectrometer. Elemental analyses were obtained from (*i*) National Chemical Laboratory, Poona (India), (*ii*) Mikroanalytisches Labor, Beller, Göttingen (W. Germany), or (*iii*) Vikram Sarabhai Space Centre, Trivandrum (India). The compound $N_3P_3(NC_2H_4)_6$ was prepared by the method reported previously.[10] The trifluoroethoxy derivative, $N_3P_3(NPPh_3)(OCH_2CF_3)_5$, was obtained from the reaction of (**1**) with an excess of sodium 2,2,2-trifluoroethoxide in methyl cyanide.

The reactions of aziridine with $N_3P_3(NPPh_3)Cl_5$ (**1**)[11] were carried out by varying the stoicheiometry of the reactants using



X = Cl (**1**) or F (**2**)

benzene or diethyl ether as the solvent. Use of methyl cyanide as the reaction medium led to the formation of products in which the aziridine ring underwent cleavage, in addition to the formation of the partially substituted aziridino-derivatives. To obtain good yields of $N_3P_3(NPPh_3)(NC_2H_4)_nCl_{5-n}$ ($n \geq 2$), it was necessary to use more aziridine than the required stoicheiometric quantity. The formation of products other than those isolated could not be detected by t.l.c. or ^1H n.m.r. spectra of the reaction mixtures. The details of experiments are summarised in Table 1. Two typical reactions are described below.

(*a*) *Reaction of* $N_3P_3(NPPh_3)Cl_5$ (**1**) *with Two Equivalents of Aziridine in Benzene.*—Aziridine (0.30 g, 6.9 mmol) in benzene (50 cm^3) was added dropwise to a solution of compound (**1**) (2.0 g, 3.4 mmol) in benzene (150 cm^3) over a period of 40 min at 25 °C with continuous stirring. After 24 h, a t.l.c. (silica gel; benzene as eluant) examination of the reaction mixture showed the presence of three components with R_f values 0.85 [(**1**)], 0.50 [$N_3P_3(NPPh_3)(NC_2H_4)Cl_4$ (**3**)], and 0.48 [$N_3P_3(NPPh_3)(NC_2H_4)Cl_4$ (**4**)] in the intensity ratio 4:2:1. In addition, two faint spots at R_f values 0.25 [$N_3P_3(NPPh_3)(NC_2H_4)_2Cl_3$ (**5**)] and 0.22 [$N_3P_3(NPPh_3)(NC_2H_4)_2Cl_3$ (**6**)] were observed. Aziridine hydrochloride formed in the reaction adhered to the bottom of the flask. The reaction mixture was decanted into a separating funnel and was washed with water (2 × 50 cm^3). The organic layer was dried over anhydrous sodium sulphate and the solvent was evaporated to obtain a white solid (1.85 g) which was subjected to column chromatography over silica gel (25 g); the products isolated are shown in Table 1.

A similar reaction in methyl cyanide showed the formation of an additional component with a t.l.c. R_f of 0.60 (benzene eluant).

† Part 24: K. V. Katti and S. S. Krishnamurthy, *Indian J. Chem., Sect. A*, in the press.

‡ 2,4,4,6,6-Pentakis(aziridino)-2-(2′,2′,2′-triphenylphosphazen-1′-yl)-cyclotriphosphazatriene.

Supplementary data available (No. SUP 56253, 9 pp.): H-atom co-ordinates, anisotropic thermal parameters, least-squares planes, full list of all bond lengths and angles for non-hydrogen atoms. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Non-S.I. unit employed: Torr = 133 Pa.

Table 1. Experimental details for the reaction of aziridine with $N_3P_3(NPPh_3)Cl_5$ (1)[a]

Stoicheiometry[b]	Solvent (cm^3)	Product(s)[c]	Yield[d] (%)
1:2	Benzene (200)	(1)	31
		(3)	18
		(4) [3] + (5) [1]	13
		(6)	3
1:2	Et_2O (200)	(1)	50
		(3)	13
		(3) [1] + (4) [3] + (5) [1]	9
		(6)	3
1:1[e]	Et_2O (100)	(1)	50
		(3)	10
		(4) [1] + (5) [1]	10
		(6)	2
1:4	Benzene (200)	(1)	6
		(3)	13
		(4) [1] + (5) [2]	13
		(5) [4] + (6) [1]	10
		(6)	22
1:6	Benzene (200)	(1) [1] + (3) [4] + (4) [2] + (5) [2]	19
		(5) [4] + (6) [1]	8
		(6)	16
		(7)	6
1:8	Benzene (200)	(3) [2] + (4) [1] + (5) [2] + (6) [1]	38
		(7)	13
1:16[f]	Benzene (200)	(7)	75
		(8)	6
1:(32 × 3)[g]	Benzene (200)	(9)	56

[a] Aziridine was added to a solution (or slurry) of phosphazene over a period of 35—40 min; reactions were carried out for 24 h at 25 °C unless otherwise stated. [b] Amount of phosphazene used was 2.0 g (3.4 mmol) unless stated otherwise. [c] The structures of the compounds (3)—(9) are shown in Figure 1; the numbers in square brackets refer to the relative proportions. [d] These are the yields obtained after column chromatography and crystallization. [e] Amount of phosphazene used was 1.0 g (1.7 mmol); an equivalent amount of triethylamine was used as base. [f] + NaOH pellets (1.0 g); the reaction temperature was *ca.* 45 °C and reaction time 72 h. [g] See Experimental section for details.

This component was isolated as an oil and contained *ca.* 10% of (3) + (4). The ^1H n.m.r. spectrum (60 MHz) of the oil showed broad peaks in the range δ 2.8—3.8 ($-NCH_2$) and a triplet centred at δ 3.5 [$^3J(H-H) \approx 4$ Hz] ($-CCH_2$) which indicate the presence of a $\equiv P(NHCH_2CH_2Cl)$ group. The i.r. spectrum (neat) showed strong bands at 1 190, 1 210, and 1 265 cm^{-1} [ν(P=N)]. The intensity ratio of phenyl protons to those at δ 2.8—3.8 was 15:4.2. Thus, this derivative could be a product of the type $N_3P_3(NPPh_3)(NHCH_2CH_2Cl)Cl_4$; no further characterization was attempted.

(*b*) *Preparation of the Pentakis(aziridino) Derivative* $N_3P_3(NPPh_3)(NC_2H_4)_5$ (9).—Aziridine (1.2 g, 27.9 mmol) in benzene (20 cm^3) was added to a solution of (1) (1.0 g, 1.7 mmol) in benzene (100 cm^3) at 25 °C with continuous stirring. A few pellets of sodium hydroxide (1.0 g) and water (5 cm^3) were also added. The resulting heterogeneous mixture was stirred at *ca.* 45 °C for 48 h, decanted to another flask, and a further 1.2 g (27.9 mmol) of aziridine was added; stirring at *ca.* 45 °C was continued for 48 h. The contents were decanted to a third flask; more aziridine (1.2 g, 27.9 mmol) and sodium hydroxide (1.0 g) were added. Stirring at *ca.* 45 °C was continued for 48 h. T.l.c. examination at this stage showed a spot at R_f 0.10 (acetone eluant) corresponding to $N_3P_3(NPPh_3)(NC_2H_4)_5$ (9). The reaction mixture was filtered, the filtrate washed with water (5 × 30 cm^3) and the organic layer was dried over anhydrous sodium sulphate. The solvent was evaporated *in vacuo* and the solid obtained was recrystallized from dichloromethane–light petroleum (b.p. 60–80 °C) (1:1) to obtain the pure compound (9) (0.6 g, 56%), m.p. 202 °C (decomp.). These crystals were used for *X*-ray crystallographic studies (see below).

An analogous reaction with the fluoro-compound, $N_3P_3(NPPh_3)F_5$ (2)[11] resulted in the recovery of the starting material (2) quantitatively.

Difficulties encountered in the Elemental Analyses and Mass Spectra of the Aziridino-derivatives (3)—(9).—For all the aziridinyl derivatives isolated in the present study, it was not possible to obtain satisfactory elemental analyses. As a typical example, the values obtained for compound (9) were [Found: C, 31.7; H, 5.1; N, 29.4 (Göttingen); C, 51.7; H, 5.4 (Trivandrum). $C_{28}H_{35}N_9P_4$ requires C, 54.1; H, 5.6; N, 20.3%]. Such large deviations from the expected values are probably a result of the polymerization involving the strained aziridino-rings. Indeed, the aziridino-derivatives (3)—(9) melt with decomposition (polymerization). In particular, the compound $N_3P_3(NPPh_3)(NC_2H_4)_3Cl_2$ (7) was melted (175 °C) and cooled. A t.l.c. examination of the resulting solid [eluant benzene–ethyl acetate (1:5)] showed the absence of the starting material (7). This solid did not melt even at 200 °C and its i.r. spectrum showed only broad bands (800—1 400 cm^{-1}, 2 800—3 100 cm^{-1}). This product also had a very low solubility in dichloromethane. Analysis of nitrogen for (7) by a wet method (Kjeldal) gave N, 14.9% ($C_{24}H_{27}Cl_2N_7P_4$ requires N, 16.1%); large quantities of samples (~200 mg) were needed to obtain reasonably accurate values by this method.

Attempts to obtain good mass spectra for the aziridino-derivatives (3)—(9) were also unsuccessful. The mass spectra seem to depend upon the temperature at which the compounds were sublimed into the 'source' of the spectrometer. The compound $N_3P_3(NPPh_3)(NC_2H_4)_2Cl_3$ (6) did not sublime. The mass spectrum (Varian MAT EI CH5) of (7) was recorded at 100, 200, and 300 °C (10^{-6} Torr). The spectra recorded at 100

or 300 °C did not show peaks beyond m/z 106. The spectrum at 200 °C showed the following peaks (M = 607): m/z 488 (40%, $M - 2NC_2H_4 - {}^{35}Cl$), 481 (75, $M - 3NC_2H_4$), 447 (35, $M - 3NC_2H_4 - {}^{35}Cl + H$), 198 [5, (H–N=$PPh_2$) – 2H], 183 (45, $PPh_2 - 2H$), and 122 (10, N=PPh).

In view of the above difficulties, ^1H n.m.r. integrated intensity ratio (C_6H_5:NC_2H_4), ^{31}P n.m.r., and t.l.c. were used as criteria for ascertaining the purity of the above aziridino-derivatives.

Other physical data are as follows. (**3**), m.p. 138—140 °C (decomp.); i.r., 1 215vs and 1 185vs $(P=N)_{ring}$, 1 310s and 1 280s cm^{-1} $(P=N)_{exo}$. (**4**), m.p. 148 °C (decomp.); i.r., 1 210vs and 1 170vs $(P=N)_{ring}$, 1 280m and 1 255m cm^{-1} $(P=N)_{exo}$. (**5**) [mixture containing (**5**) and (**6**); ratio 4:1], m.p. 138—143 °C (decomp.); i.r., 1 200vs and 1 170s $(P=N)_{ring}$, 1 250s cm^{-1} $(P=N)_{exo}$. (**6**), m.p. 160 °C (decomp.); i.r., 1 220vs and 1 185s $(P=N)_{ring}$, 1 270s cm^{-1} $(P=N)_{exo}$. (**7**), m.p. 175 °C (decomp.); i.r., 1 220vs and 1 180vs $(P=N)_{ring}$, 1 265s cm^{-1} $(P=N)_{exo}$. (**8**), m.p. 148 °C (decomp.); i.r., 1 210vs and 1 175vs $(P=N)_{ring}$, 1 260s cm^{-1} $(P=N)_{exo}$. (**9**), m.p. 202 °C (decomp.); i.r., 1 205vs and 1 185vs $(P=N)_{ring}$, 1 320s and 1 260s cm^{-1} $(P=N)_{exo}$.

Crystal Structure of $N_3P_3(NPPh_3)(NC_2H_4)_5$ (**9**).—*Crystal data.* $C_{28}H_{35}N_9P_4$, M = 621, triclinic, a = 9.336(2), b = 11.427(3), c = 14.922(3) Å, α = 100.47(3), β = 93.11(2), γ = 94.74(2)°, U = 1 556 Å^3, D_m = 1.34 g cm^{-3}, Z = 2, D_c = 1.33 g cm^{-3}, $F(000)$ = 652, space group $P\bar{1}$, λ(Mo-K_α) = 0.7107 Å, μ = 2.31 cm^{-1}.

Intensity data, structure determination, and refinement. Intensity data were collected on a CAD-4 diffractometer by the ω–2θ scan technique with a constant scan speed of 1° min^{-1} to a maximum of 2θ = 47° using Mo-K_α radiation. Of the 5 052 reflections measured, 4 286 reflections were above the threshhold [$I \geqslant 3\sigma(I)$]. Intensities were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by direct methods and refined by full-matrix least-squares techniques using anisotropic thermal parameters for non-hydrogen atoms. All hydrogen atoms except one [at an aziridinyl carbon, C(6), whose position was fixed from geometrical considerations] were located from a difference Fourier synthesis. The contributions from H atoms with $B_{iso.} = B(C) + 1.5$ Å^2 were introduced in further cycles of refinement, but no attempt was made to refine any of the parameters. Final R ($= \Sigma||F_o|-|F_c||/\Sigma|F_o|$) and R' $\{=[\Sigma w(F_o-|F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}\}$ values are 0.056 and 0.053 respectively. The weighting scheme used in the refinement was $w = 1.0/(\sigma_F^2 + 0.0025|F|^2)$. Details of the programs and computer used, and sources of scattering factor data are given in ref. 12.

Results and Discussion

Structures and Spectroscopic Features of the Aziridino-derivatives (**3**)—(**9**).—The structural elucidation of the derivatives $N_3P_3(NPPh_3)(NC_2H_4)_nCl_{5-n}$ (n = 1—4) is based on criteria described previously.[9] Figure 1 shows the structures of the compounds (**3**)—(**9**) along with the ^1H n.m.r. data for the aziridino-protons; the ^{31}P-{^1H} n.m.r. data are summarised in Table 2.

The ^1H n.m.r. spectrum (60 MHz) of the compound $N_3P_3(NPPh_3)(NC_2H_4)Cl_4$ (**3**) shows a simple doublet centred at δ 2.24 with a $^3J(P-H)$ value of 21.4 Hz; the high $^3J(P-H)$ value is indicative of the presence of a $\equiv P(NC_2H_4)Cl$ group.[13] The ^{31}P-{^1H} n.m.r. spectrum (Figure 2) shows four distinct phosphorus environments which confirm the non-geminal (with respect to the $-NPPh_3$ group) disposition of the $-NC_2H_4$ group. A '2-*trans*-4' structure * is assigned for compound (**3**) on the basis of the high ^1H n.m.r. chemical shift value for the $-NC_2H_4$ protons.

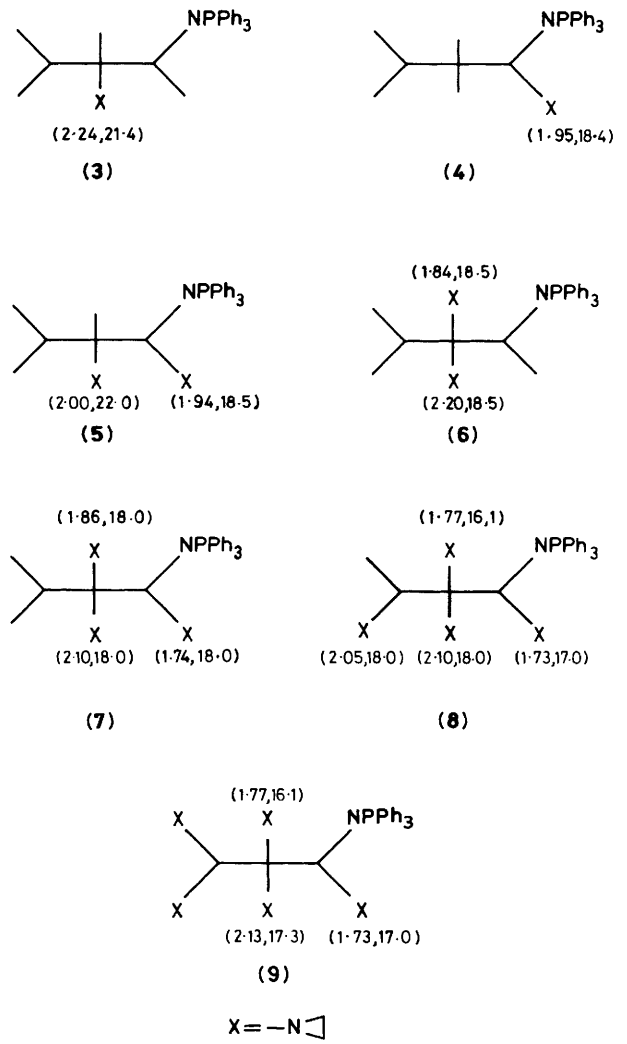


Figure 1. Structures of the aziridino-derivatives (**3**)—(**9**) and ^1H n.m.r. data for the $-NC_2H_4$ protons; chemical shifts (δ/p.p.m.) and $^3J(P-H)$/Hz values are given in parentheses (chlorine atoms not shown)

The other mono(aziridino)-derivative, $N_3P_3(NPPh_3)(NC_2H_4)Cl_4$ (**4**), shows a doublet at δ 1.95 with a $^3J(P-H)$ value of 18.4 Hz. The low $^3J(P-H)$ value is suggestive of a geminal structure [$\equiv P(NPPh_3)(NC_2H_4)$ group].[7,13] The ^{31}P-{^1H} n.m.r. spectrum of this compound [as a mixture with compound (**5**) in the ratio 3:1] shows three sets of signals centred at δ 18.09 [$\equiv PCl_2$], 14.43 [$=PPh_3$], and 10.32 [$\equiv P(NPPh_3)(NC_2H_4)$] in the intensity ratio 2:1:1 which confirm the geminal structure for compound (**4**).

The bis(aziridino)-derivative $N_3P_3(NPPh_3)(NC_2H_4)_2Cl_3$ (**5**) has been obtained only as a mixture [with (**4**) or with the isomeric compound (**6**)]. The ^1H n.m.r. chemical shifts and $^3J(P-H)$ values suggest the presence of $\equiv P(NPPh_3)(NC_2H_4)$ and $\equiv P(NC_2H_4)Cl$ groups. The aziridinyl group at the $\equiv P(NC_2H_4)Cl$ site is *trans* to the $-NPPh_3$ substituent; the slight upfield shift of these protons compared to those of compound (**3**) is due to shielding by the other $-NC_2H_4$ group. The ^{31}P-{^1H} n.m.r. spectrum of a mixture of (**5**) and (**6**) (ratio 4:1) is shown in Figure 3.

* The disposition of the $-NC_2H_4$ groups is defined with respect to the $-NPPh_3$ substituent; the phosphorus bearing the $-NPPh_3$ group is P(2) by this nomenclature.

Table 2. The $^{31}P-\{^1H\}$ n.m.r. spectroscopic data for the derivatives $N_3P_3(NPPh_3)(NC_2H_4)_nCl_{5-n}$ [n = 1—5; (3)—(9)][a]

	Chemical shifts (δ/p.p.m.)[b]					Coupling constants, ^2J(PP)/Hz						
Compound	P_A	P_B	P_C	P_D	P_E	AB	BC	BD	BE	CD	CE	DE
(1)[c]	15.40	0.20	20.30			27.8	47.5					
(3)	14.63	5.54	23.81	34.38	—	27.4	46.7	40.8	—	46.7	—	—
(4)	14.43	10.32	18.09	—	—	24.7	34.2	—	—	—	—	—
(5)	11.63	13.17	21.38	33.84	—	26.2	33.5	33.2	—	36.9	—	—
(6)	13.02	8.75	24.63	—	35.28	29.4	49.4	—	34.1	—	39.0	—
(7)	10.06	13.71	23.01	—	35.04	23.4	36.5	—	36.5	—	36.5	—
(8)	7.87	16.66	—	41.61	37.10	25.0	—	35.3	35.1	—	—	35.5
(9)	7.77	18.69	—	—	37.38	19.5	—	—	34.7	—	—	—

[a] Spectra recorded at 109.4 MHz in $CDCl_3$ solutions with 85% H_3PO_4 as an external standard. For all the compounds except (6), ^4J(PP) < 1.0 Hz; for compound (6), $^4J[P_AP_C]$ = 4.8, $^4J[P_AP_E]$ = 3.0 Hz. [b] P_A = PPh_3, P_B = $P(NPPh_3)X$, P_C = PCl_2, P_D = $P(NC_2H_4)Cl$, P_E = $P(NC_2H_4)_2$. [c] From ref. 29.

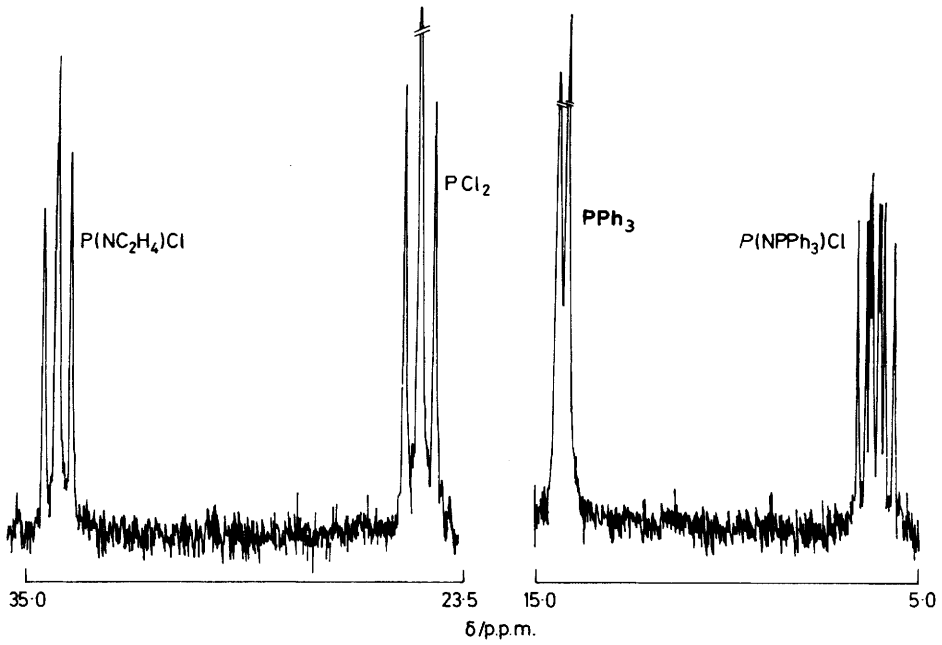


Figure 2. The $^{31}P-\{^1H\}$ n.m.r. spectrum (109.4 MHz) of $N_3P_3(NPPh_3)(NC_2H_4)Cl_4$ (3)

Since isomer (6) is obtained in a pure state, signals due to this isomer can be easily identified. Thus for isomer (5), four sets of peaks centred at δ 11.63, 13.17, 21.38, and 33.84 are observed. The peaks at δ 11.63 and 13.17 are easily assigned to the $=PPh_3$ and $\equiv P(NPPh_3)(NC_2H_4)$ groups on the basis of the multiplet pattern. The downfield signal at δ 33.84 is assigned to a $\equiv P(NC_2H_4)Cl$ group.[7,8] The remaining set at δ 21.38 is then attributable to the $\equiv PCl_2$ group.

A structure with a $\equiv P(NC_2H_4)_2$ group (Figure 1) is assigned for the bis(aziridino)-derivative (6) from the following considerations. (*i*) Low $^3J(P-H)$ values (18.5 Hz) in the ^1H n.m.r. spectrum are observed for both the $-NC_2H_4$ groups. (*ii*) In the $^{31}P-\{^1H\}$ n.m.r. spectrum, the signals centred at δ 24.63 (Table 2) are due to $\equiv PCl_2$ since $\equiv P(NC_2H_4)Cl$ and $\equiv P(NC_2H_4)_2$ appear much downfield (δ 30—40). (*iii*) The chemical shifts of the ring phosphorus $\delta[P(NPPh_3)X]$ can be expected to appear more downfield when X = NC_2H_4 than when X = Cl;[2,7,8] also, the value of $^2J(PCl_2) - {}^2J[P(NPPh_3)X]$ is expected to be lower when X = NC_2H_4 than when X = Cl.[14] By comparing these values for compounds (4), (5), and (7) with those for (1), (3), and (6) it can be concluded that compound (6) contains the $\equiv P(NPPh_3)Cl$ group. The most downfield signal, centred at δ 35.28, for (6) is therefore attributable only to $\equiv P(NC_2H_4)_2$.

Six isomers are possible for the tris(aziridino)-derivative (7). The geminal structure (Figure 1) is assigned because of the low $^3J(P-H)$ values for all the three $-NC_2H_4$ groups. The $^{31}P-\{^1H\}$ n.m.r. spectrum (Figure 4) shows four phosphorus environments [at δ 10.06, 13.71, 23.01, and 35.04] in the intensity ratio 1:1:1:1 and confirms the structural assignment. Any other structure should exhibit signals corresponding to two phosphorus nuclei in the range δ 31—43 [two $\equiv P(NC_2H_4)Cl$ groups or a $\equiv P(NC_2H_4)Cl$ and a $\equiv P(NC_2H_4)_2$ group].

For the tetrakis(aziridino)-derivative (8), the structure with a $\equiv P(NC_2H_4)Cl$ group (NC_2H_4 *trans* to $NPPh_3$) follows from its ^1H and ^{31}P n.m.r. spectroscopic data (Figure 1 and Table 2).

The trends in phosphorus chemical shifts shown in Figure 5 for derivatives (1) and (3)—(9) are also useful for structural elucidation. The effect of substitution of –Cl by the $-NC_2H_4$ group is quite significant. The chemical shifts of PCl_2 and $P(NPPh_3)X$ for (1), (3), and (6) (X = Cl) follow a downfield trend and those for (4), (5), and (7)—(9) (X = NC_2H_4) follow a different but parallel trend. The phosphorus shifts of PPh_3 move

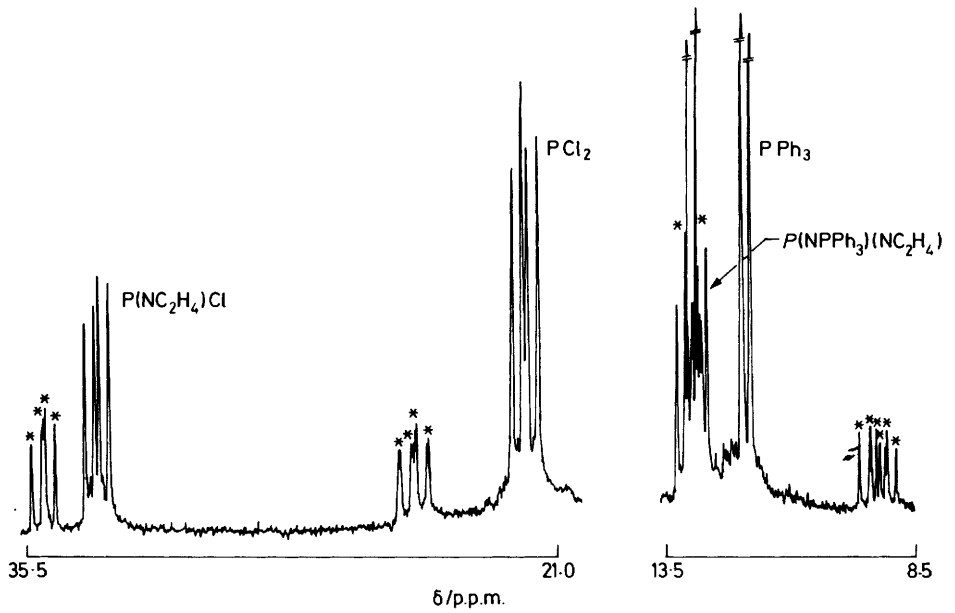


Figure 3. The $^{31}P-\{^1H\}$ n.m.r. spectrum (109.4 MHz) of $N_3P_3(NPPh_3)(NC_2H_4)_2Cl_3$ [(**5**) + (**6**) in the ratio 4:1]; peaks marked with an asterisk are due to (**6**)

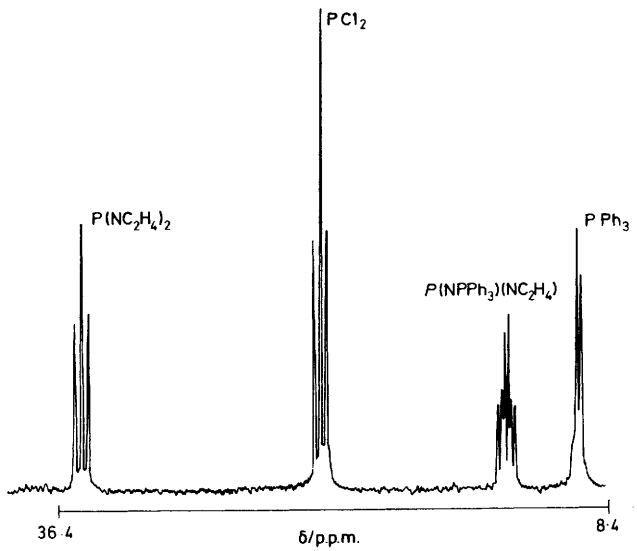


Figure 4. The $^{31}P-\{^1H\}$ n.m.r. spectrum (109.4 MHz) of $N_3P_3(NPPh_3)(NC_2H_4)_3Cl_2$ (**7**)

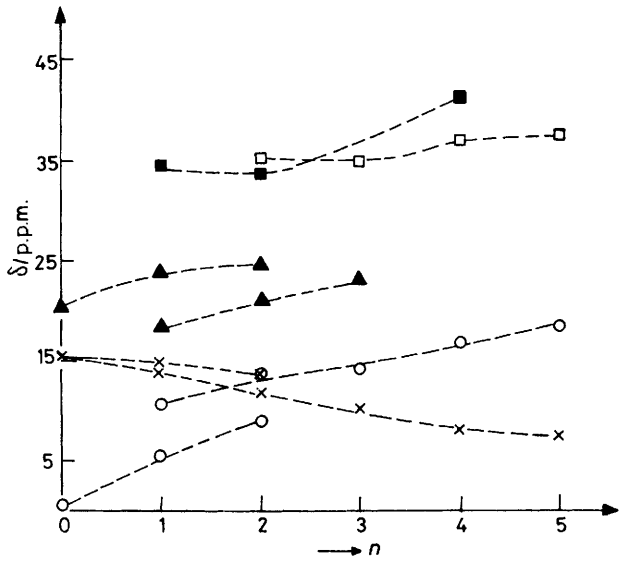
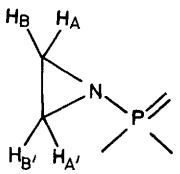


Figure 5. Trends in ^{31}P chemical shifts for the compounds $N_3P_3(NPPh_3)(NC_2H_4)_nCl_{5-n}$ [n = 0—5; (**1**), (**3**)—(**9**)]: (▲) PCl_2, (×) PPh_3, (○) $P(NPPh_3)X$, (■) $P(NC_2H_4)Cl$, (□) $P(NC_2H_4)_2$

upfield upon progressive substitution probably as the result of a decreased participation of the lone pair on the nitrogen of the exocyclic $-NPPh_3$ group in π-bonding with the ring phosphorus atom.

An interesting feature of the ^1H n.m.r. spectra of the aziridino-compounds isolated in the present study is that the high-field (270 MHz) spectra of many of these derivatives show an AA'BB' type of non-equivalence for the aziridino-protons at room temperature. Compound (**3**) exhibits one AA'BB'X spectrum (H-atom labelling given) whereas the derivative (**6**) exhibits two sets. The ^1H n.m.r. spectrum of (**3**) is illustrated in Figure 6. The significance of this observation is that most of the phosphorus compounds containing $P-NC_2H_4$ groups do not show non-equivalence even at very low temperatures;[15,16] the protons in the compound $N_3P_3(NC_2H_4)_6$ also are not distinguishable even at −55 °C. These results show that the $-NPPh_3$ substituent renders the aziridino-protons non-equivalent by hindering the pyramidal inversion at the aziridino-nitrogen atom or the rotation around the P–N bond.



Halogen Replacement Pattern and Mechanistic Implications.— Three important observations emerge from the present study of the aziridinolysis of $N_3P_3(NPPh_3)Cl_5$ (**1**). (*i*) At the mono and bis stages of chlorine replacement, the derivatives (**3**) and (**6**) are

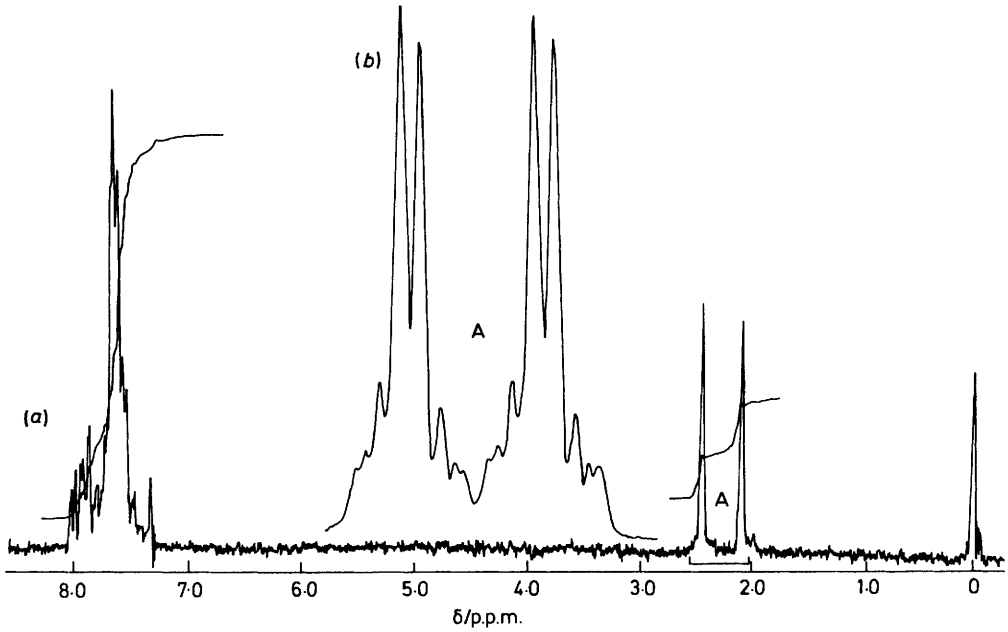


Figure 6. The ^{1}H n.m.r. spectrum of $N_3P_3(NPPh_3)(NC_2H_4)Cl_4$ (**3**): (*a*) at 60 MHz and (*b*) the NC_2H_4 region (marked A) at 270 MHz showing the non-equivalence of aziridino-protons

Table 3. Final positional parameters ($\times 10^4$) with estimated standard deviations (e.s.d.s) for non-hydrogen atoms

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
P(1)	3 261(1)	2 263(1)	2 008(1)	P(4)	4 137(2)	−56(1)	2 438(1)
P(2)	1 648(1)	4 035(1)	2 904(1)	N(9)	3 625(5)	1 220(4)	2 533(3)
P(3)	4 531(1)	4 612(1)	2 659(1)	C(11)	3 614(6)	−654(5)	3 423(4)
N(1)	1 760(4)	2 744(3)	2 323(3)	C(12)	3 204(10)	130(6)	4 168(5)
N(2)	3 021(4)	4 962(3)	3 015(3)	C(13)	2 825(12)	−292(8)	4 947(5)
N(3)	4 570(3)	3 295(3)	2 097(2)	C(14)	2 866(11)	−1 461(8)	4 990(5)
N(4)	3 098(4)	1 644(3)	889(2)	C(15)	3 254(10)	−2 240(6)	4 264(5)
N(5)	187(4)	4 558(3)	2 445(4)	C(16)	3 630(8)	−1 845(5)	3 477(4)
N(6)	1 167(7)	4 080(5)	4 008(4)	C(21)	6 081(6)	−47(5)	2 413(4)
N(7)	5 133(4)	5 652(3)	2 073(3)	C(22)	6 869(7)	1 002(5)	2 337(4)
N(8)	5 762(4)	4 943(3)	3 553(2)	C(23)	8 355(7)	1 072(6)	2 319(5)
C(1)	2 289(5)	2 228(5)	260(3)	C(24)	9 056(7)	87(8)	2 398(6)
C(2)	1 693(5)	1 077(5)	461(4)	C(25)	8 291(8)	−978(7)	2 469(6)
C(3)	69(6)	5 847(5)	2 655(5)	C(26)	6 784(7)	−1 073(6)	2 474(5)
C(4)	410(6)	5 269(5)	1 745(5)	C(31)	3 387(6)	−1 110(5)	1 435(4)
C(5)	1 834(8)	3 293(5)	4 499(4)	C(32)	4 116(6)	−1 259(5)	637(4)
C(6)	374(9)	3 115(8)	4 269(5)	C(33)	3 465(7)	−1 966(6)	−157(4)
C(7)	4 671(6)	5 465(5)	1 102(4)	C(34)	2 085(8)	−2 499(6)	−173(4)
C(8)	6 170(6)	5 372(4)	1 384(3)	C(35)	1 361(7)	−2 366(6)	619(5)
C(9)	5 899(6)	4 004(5)	4 104(4)	C(36)	2 009(6)	−1 677(5)	1 420(4)
C(10)	7 050(5)	4 284(5)	3 533(4)				

the major products (>65%); compounds (**4**) and (**5**) are the minor products (<30%). (*ii*) The geminal compound, $N_3P_3(NPPh_3)(NC_2H_4)_3Cl_2$ (**7**) is formed exclusively at the tris stage of chlorine replacement. (*iii*) It has not been possible to maximize the yield of the tetrakis(aziridino)-derivative, (**8**). The reaction of (**7**) with aziridine leads mainly to the fully substituted derivative (**9**); only a small quantity of (**8**) could be isolated.

It is reasonable to assume that the formation of compound (**3**) occurs *via* an $S_N2(P)$ mechanism.[17] Since aziridine is a weaker base than dimethylamine and methylamine,[7,18] it is likely that the substituent constant α[19] (which is a measure of the electron-releasing power of the substituent) for the $-NC_2H_4$ group is less than that for an $-NMe_2$ group. [This hypothesis is supported by the fact that the π-bonding of the lone pair of electrons on aziridino-nitrogen atoms is less effective than of those on dimethylamino-nitrogen atoms as shown by the longer P–N(amino) bonds and the pyramidal character of amino-nitrogens in $N_3P_3(NC_2H_4)_6$[4] when compared to those in $N_3P_3(NMe_2)_6$[20] (see *X*-ray section).] In view of these considerations, it is unlikely for an $S_N1(P)$ mechanism[17] to be operative in the formation of (**6**) which contains a $\equiv P(NC_2H_4)_2$ group. The insufficient electron release by the $-NC_2H_4$ group causes lesser deactivation (or more activation) for the attack at a $\equiv P(NC_2H_4)Cl$ centre by an $S_N2(P)$ mechanism, thus favouring the formation of (**6**). The formation of significant quantities of geminal products in the aziridinolysis of $N_3P_3Cl_6$,[3,8,13,18] the isolation of a stable pentakis(aziridinyl) derivative $N_3P_3(NC_2H_4)_5Cl$,[8,13,18] and the preferential attack by aziridine at a $\equiv P(NC_2H_4)Cl$ centre than at a $\equiv P(R)Cl$ centre in its reactions

Table 4. Selected bond distances (Å) and angles (°) with e.s.d.s for $N_3P_3(NPPh_3)(NC_2H_4)_5$ (**9**)

P(1)–N(1)	1.610(4)	P(1)–N(4)	1.684(3)	N(5)–C(3)	1.464(7)	C(7)–C(8)	1.457(8)
P(1)–N(3)	1.609(3)	P(2)–N(5)	1.695(5)	N(5)–C(4)	1.448(9)	N(8)–C(9)	1.475(7)
P(2)–N(1)	1.585(4)	P(2)–N(6)	1.724(7)	C(3)–C(4)	1.463(10)	N(8)–C(10)	1.468(7)
P(2)–N(2)	1.576(4)	P(3)–N(7)	1.678(4)	N(6)–C(5)	1.419(9)	C(9)–C(10)	1.458(8)
P(3)–N(2)	1.589(4)	P(3)–N(8)	1.680(4)	N(6)–C(6)	1.403(11)	P(4)–C(11)	1.803(6)
P(3)–N(3)	1.588(3)	N(4)–C(1)	1.460(7)	C(5)–C(6)	1.377(11)	P(4)–C(21)	1.816(6)
P(1)–N(9)	1.589(1)	N(4)–C(2)	1.471(6)	N(7)–C(7)	1.461(7)	P(4)–C(31)	1.810(5)
P(4)–N(9)	1.557(5)	C(1)–C(2)	1.473(8)	N(7)–C(8)	1.462(7)		

N(1)–P(1)–N(2)	114.0(2)	C(1)–N(4)–C(2)	60.3(3)	P(3)–N(7)–C(7)	117.3(3)
N(1)–P(2)–N(2)	117.6(2)	P(2)–N(5)–C(3)	117.8(4)	P(3)–N(7)–C(8)	120.1(3)
N(2)–P(3)–N(3)	116.7(2)	P(2)–N(5)–C(4)	117.7(3)	C(7)–N(7)–C(8)	59.8(3)
P(1)–N(1)–P(2)	123.2(2)	C(3)–N(5)–C(9)	60.3(4)	P(3)–N(8)–C(9)	115.8(3)
P(2)–N(2)–P(3)	122.7(2)	P(2)–N(6)–C(5)	115.9(5)	P(3)–N(8)–C(10)	118.9(3)
P(1)–N(3)–P(3)	123.8(2)	P(2)–N(6)–C(6)	122.0(5)	C(9)–N(8)–C(10)	59.4(4)
P(1)–N(4)–C(1)	118.7(3)	C(5)–N(6)–C(6)	58.4(5)	P(1)–N(9)–P(4)	145.3(1)
P(1)–N(4)–C(2)	119.9(3)				

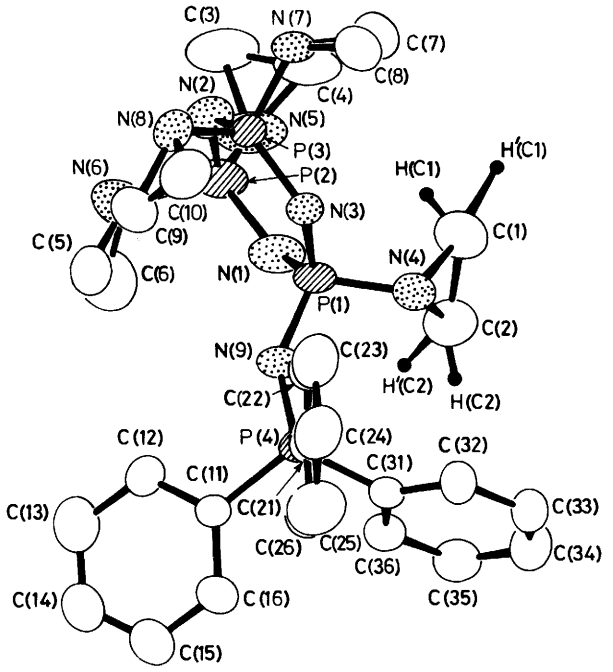
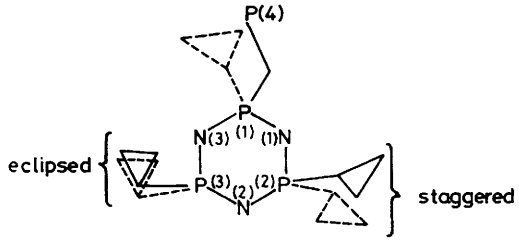


Figure 7. A view of the molecule of $N_3P_3(NPPh_3)(NC_2H_4)_5$ (**9**) down the *a* axis



(I)

with $N_3P_3(R)Cl_5$ [R = morpholino, piperidino, or pyrrolidino],[7] can all be rationalised using the above guidelines and by postulating an $S_N2(P)$ mechanism operating in these reactions.

At the tris stage of chlorine replacement in the aziridinolysis of compound (**1**), the combined electron release by the $-NPPh_3$ and two $-NC_2H_4$ groups is sufficient for a dissociative mechanism [$S_N1(P)$] to operate;[17] the formation of (**7**) as the sole tris(aziridino)-derivative is thus explained. A fast $S_N1(P)$ mechanism in the replacement of the last chlorine atom from (**8**) explains the low yield of this compound.

The reluctance of the fluoro-compound, $N_3P_3(NPPh_3)F_5$ (**2**) to undergo reaction with aziridine may be attributed to the deactivation caused by the presence of the $-NPPh_3$ group and the sluggish reactivity of aziridine. The difficulty of replacing fluorine from an (amino)fluorophosphazene has also been noted elsewhere.[21,22]

X-Ray Crystal Structure of (**9**): *Conformational Effects on N.M.R. Spectroscopy.*—A view of the molecule of compound (**9**) down the *a* axis with numbering of non-hydrogen atoms is shown in Figure 7. The final atomic co-ordinates for the non-hydrogen atoms are listed in Table 3. The important bond lengths and bond angles are listed in Table 4. The P–N endocyclic bonds at the phosphorus bearing the $-NPPh_3$ group [P(1)] (mean 1.609 Å) are slightly longer than the other endocyclic P–N bonds (mean 1.584 Å) but are shorter than those observed in *gem*-$N_3P_3(NPPh_3)_2Cl_4$ (1.632 Å)[23] and *gem*-$N_3P_3(NPPh_3)(NEt_2)Cl_4$ (1.64 Å).[24] Electron-releasing substituents [$-NPPh_3$, $-NEt_2$, or $-NC_2H_4$] at P(1) increase the endocyclic bond lengths at this phosphorus centre;[25] this effect may be annulled by the presence of electron-releasing groups ($-NC_2H_4$) at P(2) and P(3) in the present structure.

The average bond angle (123.2°) at the ring nitrogens in (**9**) is the highest value reported for the cyclotriphosphazene series.[25] The average value of the endocyclic bond angle at phosphorus is low (116.1°) but is greater than that observed recently by Labarre and co-workers[26] in $N_3P_3[NH(CH_2)_3NH]_3 \cdot 2H_2O$ (115°). These features may also be a consequence of electron-donating groups on all endocyclic phosphorus atoms; in the present compound, the most important contribution arises from the $-NPPh_3$ substituent.[19] The bond angle at the exocyclic nitrogen, P(4)–N(9)–P(1) (145.3°) is the largest observed for (triphenylphosphazenyl)cyclotriphosphazenes; the widening of this angle may be attributed to a combination of steric[27] and conformational effects (see below). The P–N(aziridino) bond lengths (mean 1.692 Å) are close to those reported for $N_3P_3(NC_2H_4)_6$[4] (mean 1.676 Å) but are much longer than P–N(dimethylamino) bond lengths in $N_3P_3(NMe_2)_6$[20] (mean 1.652 Å). The aziridino-nitrogens have pronounced pyramidal character; the sum of bond angles around these nitrogen atoms range from 294.1 to 298.9° (mean

296°). The corresponding average of sum of the bond angles at N atoms in $N_3P_3(NC_2H_4)_6$ is 300°[4] and in $N_3P_3(NMe_2)_6$ it is 353°.[20] These observations on the bond lengths and bond angles at aziridino-nitrogen atoms show that the participation of the lone pair of electrons of aziridino-groups in π-bonding to the ring phosphorus atoms is much less than that for a dimethylamino-group.

There are short intramolecular contacts between atoms of the aziridino-groups at the $\equiv P(NPPh_3)(NC_2H_4)$ site and one of the phenyl groups. These interatomic distances are as follows: N(4) ··· P(4) 3.433, N(9) ··· C(2) 3.474, N(4) ··· C(31) 3.418, C(2) ··· C(31) 3.540, N(4) ··· C(32) 3.483, C(2) ··· C(32) 3.675 Å. These values suggest that the aziridino-group at the $\equiv P(NPPh_3)(NC_2H_4)$ site would be affected by the conformation of the $-NPPh_3$ substituent (see below).

The phosphazene ring is almost planar [maximum deviation: P(1), 0.076 Å] with a slight deviation towards the chair conformation. The two aziridino-rings attached to P(2) are staggered with respect to each other whereas those attached to P(3) are in eclipsed conformation [structure (**I**)] when the molecule is viewed perpendicular to the plane of the phosphazene ring. This feature may be contrasted with those observed in $N_3P_3(NC_2H_4)_6$,[4] $N_3P_3(NC_2H_4)_6 \cdot 3CCl_4$[5] and $[N_3P_3(NC_2H_4)_6]_2 \cdot C_6H_6$[5] where all the rings have either staggered or eclipsed conformation. The conformations of these aziridino-rings may have relevance to the antitumour activity of these compounds.[1]

The torsion angles which define the conformation of the $-NPPh_3$ substituents are as follows: N(1)–P(1)–N(9)–P(4) 133.9(1), N(3)–P(1)–N(9)–P(4) −98.1(1), N(4)–P(1)–N(9)–P(4) 14.9(1)°. The last torsion angle shows that the $-NPPh_3$ group has nearly a Type II conformation.[19] An interesting consequence of this conformation is that one of the phenyl groups [containing C(31)] is in close proximity to the aziridino-group at the $\equiv P(NPPh_3)(NC_2H_4)$ site (see above: intramolecular contacts). This aziridino-group lies in a plane approximately perpendicular to that of the phenyl ring containing C(31). The large value of the bond angle at N(9) [145.3(1)°] may also be a result of this conformation.

The following features in the n.m.r. spectra can be explained on the basis of the above conformation of the $-NPPh_3$ substituent.

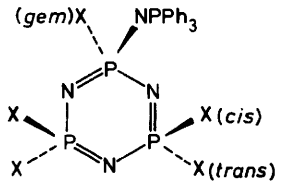
Hydrogen-1 n.m.r. The ^1H n.m.r. chemical shifts (δ p.p.m.) of some fully substituted (triphenylphosphazenyl)cyclotriphosphazenes, $N_3P_3(NPPh_3)X_5$ (**II**), are given in Table 5.

The upfield shift of the aziridino-protons (δ 1.73) at the $\equiv P(NPPh_3)(NC_2H_4)$ site when compared to that of protons of even the *cis*-NC_2H_4 group (δ 1.77) can be contrasted with the chemical shifts for the protons of *cis* and *gem* groups in the other three compounds. This feature can be attributed to the shielding of the geminal $-NC_2H_4$ protons by one of the phenyl rings in (**9**).

Carbon-13 n.m.r. The ^{13}C n.m.r. data for a large number of (triphenylphosphazenyl)cyclotriphosphazenes have been compiled.[28] The spectra for $N_3P_3(NPPh_3)X_5$ [X = F, Cl, NMe_2, OCH_3, OCH_2CF_3, or NC_2H_4] and *gem*-$N_3P_3(NPPh_3)(Ph)Cl_4$ have also been recorded. The magnitude of $^2J(P\text{–}C_{ortho})$ for the phenyl carbons of (**9**) (14.7 Hz) is markedly higher than that observed for all other compounds (12.6 Hz). Such a difference probably arises due to the conformation of the $-NPPh_3$ group in compound (**9**).

Phosphorus-31 n.m.r. The four-bond P–P coupling constants [^4J(P–P)] for a few selected compounds along with the conformations [defined by the torsion angle P′–N–P–X in structure (**III**)] adopted by the $-NPPh_3$ substituent are shown in Table 6.

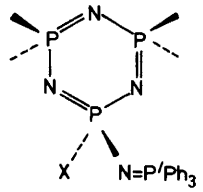
Table 5. Hydrogen-1 n.m.r. chemical shifts for $N_3P_3(NPPh_3)X_5$ (**II**)



(**II**)

X	*cis*	*gem*	*trans*	Ref.
NMe_2	2.38	2.46	2.59	*a*
OCH_3	3.30	3.56	3.69	*b*
OCH_2CF_3	3.84	4.10	4.20	*c*
NC_2H_4	1.77	1.73	2.13	*c*

[a] M. Biddlestone and R. A. Shaw, *J. Chem. Soc., Dalton Trans.*, 1973, 2740. [b] K. C. Kumara Swamy and S. S. Krishnamurthy, *Phosphorus Sulphur*, 1983, **18**, 241. [c] This work.



(**III**)

It has been suggested by Biddlestone *et al.*[29] that the smaller or least positive ^4J(P–P) values may be correlated with the preferred conformation in which the plane containing the exocyclic P–N–P unit is approximately perpendicular to the plane containing the phosphazene ring (*i.e.* Type II conform-

Table 6. Conformations of the $-NPPh_3$ group and their correlation with ^4J(P–P) values for a few (triphenylphosphazenyl)cyclotriphosphazenes

Compound	X	Torsion angle P′–N–P–X(°)	^4J(P–P)/Hz	Ref.
$N_3P_3(NPPh_3)Cl_5$ (**1**)	Cl	−83 (Type I)	+3.4	*a, b*
gem-$N_3P_3(NPPh_3)(Ph)Cl_4$	Ph	−178 (Type II)	−0.4	*a, c*
gem-$N_3P_3(NPPh_3)(NEt_2)Cl_4$	NEt_2	154 (Type II–III)	<1	*d, e*
trans-$N_3P_3(NPPh_3)(NEt_2)Cl_4$	Cl	65 (Type I)	5.7, 2.9	*e, f*
$N_3P_3(NPPh_3)(NC_2H_4)_5$	NC_2H_4	15 (Type II)	<1	*g*

[a] Ref. 29. [b] Y. S. Babu, T. S. Cameron, S. S. Krishnamurthy, H. Manohar, and R. A. Shaw, *Z. Naturforsch., Teil B*, 1976, **31**, 999; Y. S. Babu, H. Manohar, and R. A. Shaw, *Acta Crystallogr. Sect. B*, 1979, **35**, 1410. [c] M. Biddlestone, R. A. Shaw, G. J. Bullen, and P. E. Dann, *J. Chem. Soc., Chem. Commun.*, 1974, 56. [d] Ref. 24. [e] P. Ramabrahmam, S. S. Krishnamurthy, A. R. Vasudeva Murthy, R. A. Shaw, and M. Woods, *Z. Anorg. Allg. Chem.*, in the press. [f] V. Chandrasekhar, M. Damodara Poojary, S. S. Krishnamurthy and H. Manohar, unpublished work. [g] This work.

ation). The relatively inefficient electron supply to the cyclophosphazene ring in this conformation would be consistent with a reduced Fermi contribution to $^4J(P\text{–}N\text{–}P\text{–}N\text{–}P)$.[29] The low $^4J(P\text{–}P)$ values for compounds having Type II conformation agree with the above explanation.

Enzyme-activity Inhibition by $N_3P_3(NPPh_3)(NC_2H_4)_5$ (**9**) *and* $N_3P_3(NC_2H_4)_6$.—Many aziridinocyclophosphazenes exhibit antitumour activity and this behaviour is attributed to the alkylating ability of these compounds by the facile opening of aziridino-rings.[1,2] Electron-releasing substituents on phosphorus would increase the electron density within the phosphazene ring as well as within the three-membered aziridino-rings. The resulting higher basicity of the endocyclic and exocyclic N atoms leads to easier nucleophilic attack (which might be the rate-determining step in the opening of aziridino-rings[15]) and promotes the alkylating ability of these compounds.[2] Because of the powerful electron-releasing $-NPPh_3$ group, compound (**9**) is expected to be a more effective antitumour agent than Myko 63 [$N_3P_3(NC_2H_4)_6$, 'Apholate'].[1,2] Hence a preliminary comparative study of the inhibition of the activity of the enzyme Reverse Transcriptase (present in the virus *Avian myeloblastosis* which can cause leukaemia in chicks)[30] has been carried out. By using solutions containing 10 μg of the aziridino-derivatives in dimethyl sulphoxide (dmso) and adopting the procedure given by Vasudevachari and Antony[30] it is found that the enzyme-inhibiting activity of (**9**) (62%) is much higher than that of $N_3P_3(NC_2H_4)_6$ (27%) as expected. The main disadvantage of (**9**) is its low solubility in dmso (or water).

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