Studies of Phosphazenes. Part 17.* Reaction of Hexachlorocyclotriphosphazatriene with *N*-Methylethanolamine: *X*-Ray Crystal Structure of a Dispirocyclotriphosphazatriene, $N_3P_3(NMeCH_2CH_2O)_2Cl_2$ †

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Hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, reacts with *N*-methylethanolamine to give the spirocyclic derivatives, $N_3P_3(NMeCH_2CH_2O)_nCl_{6-2n}$ (n = 1—3), whose structures have been elucidated by ^1H and ^{31}P n.m.r. spectroscopy. The structure of the dispiro compound, $N_3P_3(NMeCH_2CH_2O)_2Cl_2$, has been determined by *X*-ray crystallography; the exocyclic nitrogen atoms are in a '*cis*' configuration and the phosphazene and the two spiro rings are planar. The observed chlorine replacement pattern is discussed briefly. Variations in the ^{31}P chemical shifts of spirocyclic phosphorus nuclei with the size of the spiro ring are correlated with differences in structural features.

The reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$ (1), with aliphatic difunctional reagents have been investigated systematically only in recent years and several spirocyclic phosphazenes have been isolated and characterized.[1–4] In a study of the reactions of chlorocyclotriphosphazenes with ethylenediamine and ethanolamine, we have shown that the replacement of two chlorine atoms occurs readily to yield spirocyclic phosphazenes but that resin-forming intermolecular condensation reactions predominate thereafter. Some possible reasons for the observed mode(s) of chlorine replacement have been adduced.[1] We have now investigated the reaction of $N_3P_3Cl_6$ (1) with *N*-methylethanolamine with a view to elucidating the factors that influence the reaction pathways and the results are reported in this paper. The structure of $N_3P_3(NMeCH_2CH_2O)_2Cl_2$ (3) has been determined by *X*-ray crystallography. An attempt is made to correlate the structural features of cyclophosphazenes containing five- and six-membered spiro rings with the n.m.r. chemical shifts of the spiro phosphorus nuclei.

Experimental

The purification of starting materials and solvents, and details of the instrumental measurements are described in a previous paper.[5] *N*-Methylethanolamine (Fluka, Switzerland) was used as supplied.

Syntheses of (N-*Methylethanolamino*)*cyclotriphosphazatriene Derivatives*.—(a) 4,4,6,6-*Tetrachloro*-2,2-*spiro*(N-*methylethanolamino*)*cyclotriphosphazatriene*, (2). *N*-Methylethanolamine (2.55 g, 30 mmol) dissolved in tetrahydrofuran (thf) (20 cm^3) was added dropwise to a stirred solution of the hexachloride (1) (3.48 g, 10 mmol) in thf (230 cm^3) at 25 °C. The mixture was stirred for 10 h and filtered to remove *N*-methylethanolamine hydrochloride. Evaporation of the solvent from the filtrate afforded an oil which was dissolved in diethyl ether. The ether solution was washed with water and then dried ($CaCl_2$). Diethyl ether was removed *in vacuo* and the solid obtained was recrystallized from methylene chloride–light petroleum (b.p. 60—80 °C) (1 : 1) to give$N_3P_3(NMeCH_2CH_2O)Cl_4$ (2), m.p. 148 °C (yield 2.7 g, 72%) (Found: C, 10.9; H, 2.4; N, 15.6. $C_3H_7Cl_4N_4OP_3$ requires C, 10.3; H, 2.0; N, 16.0%); ^1H n.m.r. (270 MHz, $CDCl_3$, throughout); δ 4.40 (OCH_2), 3.41 (NCH_2), and 2.66 p.p.m. (NMe); apparent coupling constant $^3J^*(P-H)$ = 10.0, 11.4, and 12.2 Hz respectively.

(b) 6,6-*Dichloro*-2,2,4,4-*dispiro*(N-*methylethanolamino*)-*cyclotriphosphazatriene*, (3). A mixture of the hexachloride (1) (3.48 g, 10 mmol) and *N*-methylethanolamine (4.5 g, 60 mmol) in thf (250 cm^3) was stirred at 25 °C for 48 h. After filtration and removal of the solvent, the residual oil was dissolved in diethyl ether and the solution washed with water (2 × 25 cm^3). The ether solution was dried (Na_2SO_4) and removal of the solvent gave a crystalline product. After several recrystallizations from methylene chloride–light petroleum (b.p. 60—80 °C) (1 : 1), a solid of constant m.p. was obtained and was identified as the title compound, $N_3P_3(NMeCH_2CH_2O)_2Cl_2$ (3), m.p. 198 °C (yield 2.0 g, 60%) (Found: C, 20.6; H, 4.2; N, 20.6. $C_6H_{14}Cl_2N_5O_2P_3$ requires C, 20.5; H, 4.0; N, 19.9%). The mass spectrum showed the parent ion peak at *m/e* 351 ($C_6H_{14}{}^{35}Cl_2N_5O_2P_3$); some of the major fragments observed in the spectrum were as follows: [M – NMe] (*m/e* 322), [M – Cl] (*m/e* 316), [M – $NMeCH_2CH_2O$] (*m/e* 278), [M – NMe – $NMeCH_2CH_2O$] (*m/e* 249), and [M – $(NMeCH_2CH_2O)_2$] (*m/e* 205). ^1H N.m.r.: δ 4.32 (OCH_2), 3.36 (NCH_2), and 2.66 p.p.m. (NMe); $^3J^*(P-H)$ = 9.9, 12.2, and 12.0 Hz respectively.

Thin layer chromatographic examination of the mother-liquor after the removal of compound (3) showed the presence of another compound in small yield having an R_f value slightly less than that of compound (3). It was not possible to obtain a sufficiently pure sample of this compound for its adequate characterization.

(c) 2,2,4,4,6,6-*Trispiro*(N-*methylethanolamino*)*cyclotriphosphazatriene* (4). *N*-Methylethanolamine (9.0 g, 120 mmol), triethylamine (25.2 g, 250 mmol), and $N_3P_3Cl_6$ (1) (3.48 g, 10 mmol) were heated in boiling chloroform for 48 h. The reaction mixture was washed with water (2 × 25 cm^3) and the chloroform solution was then dried ($CaCl_2$). After evaporation of the solvent, a semi-solid was obtained which could be crystallized from dichloromethane–light petroleum (b.p. 60—80 °C) (1 : 1) to give a product, m.p. 220 °C (yield 1.75 g, 49%), which was characterised as *trans*-2,2,4,4,6,6-trispiro(*N*-

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* Part 16, P. Ramabrahmam, K. S. Dhathathreyan, S. S. Krishnamurthy, and M. Woods, *Indian J. Chem., Sect. A*, 1983, **22**, 1.

† 6,6-Dichloro-2,2,4,4-dispiro(*N*-methylethanolamino)cyclotriphosphazatriene.

Supplementary data available (No. SUP 23835, 24 pp.): structure factors, anisotropic thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Atomic co-ordinates with e.s.d.s in parentheses for $N_3P_3(NMeCH_2CH_2O)_2Cl_2$ (3)

Atom	*X/a*	*Y/b*	*Z/c*
Cl(1)	0.647 7(1)	0.136 8(1)	0.439 6(1)
Cl(2)	0.584 3(1)	0.294 1(1)	0.226 4(1)
P(1)	0.679 5(1)	0.137 6(1)	0.271 5(1)
P(2)	0.709 6(1)	−0.099 6(1)	0.147 4(1)
P(3)	0.879 6(1)	0.078 4(1)	0.195 7(1)
N(1)	0.635 0(3)	0.000 3(4)	0.220 4(3)
N(2)	0.826 8(3)	−0.051 6(4)	0.136 3(3)
N(3)	0.796 4(3)	0.181 8(4)	0.252 5(3)
N(4)	0.655 3(4)	−0.137 2(4)	0.026 6(3)
N(5)	0.962 4(3)	0.158 9(6)	0.113 8(4)
O(1)	0.704 5(3)	−0.251 9(3)	0.196 6(3)
O(2)	0.962 9(3)	0.031 8(4)	0.286 5(3)
C(1)	0.644 6(5)	−0.279 7(6)	0.007 3(4)
C(2)	0.657 6(4)	−0.350 4(5)	0.119 3(4)
C(3)	0.641 5(5)	−0.037 0(6)	−0.062 8(4)
C(4)	1.067 7(4)	0.158 1(7)	0.152 3(6)
C(5)	1.069 6(4)	0.070 0(9)	0.257 2(6)
C(6)	0.932 7(5)	0.231 4(8)	0.011 8(6)

methylethanolamino)cyclotriphosphazatriene, $N_3P_3(NMeCH_2CH_2O)_3$ (4a) (Found: C, 30.2; H, 6.1; N, 23.1. $C_9H_{21}N_6O_3P_3$ requires C, 30.5; H, 5.9; N, 23.7%). ^1H N.m.r. (relative intensities in parentheses): δ 4.26(2) and 4.14(1) (OCH_2), $^3J^*(P-H) = 9.9$ and 13.5 Hz; 3.3 (multiplet) (NCH_2); 2.70(1) and 2.62(2) (NMe), $^3J^*(P-H)$ 12.5 and 11.5 Hz. The hydrogen-1 and phosphorus-31 n.m.r. spectra indicated that the above product contained a small quantity of the '*cis*' isomer, $N_3P_3(NMeCH_2CH_2O)_3$ (4b) (see Discussion section).

(*d*) $N_3P_3(NMe_2)_4(NMeCH_2CH_2O)$ (5), $N_3P_3(OMe)_4(NMeCH_2CH_2O)$ (6), *and* $N_3P_3(NMe_2)_2(NMeCH_2CH_2O)_2$ (7). Treatment of compound (2) with an excess of dimethylamine [1] or sodium methoxide [5] in diethyl ether, or (3) with dimethylamine [1] in diethyl ether, yielded the following compounds (respectively): 4,4,6,6-tetrakis(dimethylamino)-2,2-spiro(*N*-methylethanolamino)cyclotriphosphazatriene, (5), m.p. 81 °C (yield 75%); ^1H n.m.r.: δ, 4.16 (OCH_2) and 3.32 (NCH_2), $^3J^*(P-H) = 9.5$ and 11.0 Hz respectively; 2.52 (NMe); 2.57 and 2.54 (NMe_2); $^3J^*(P-H) = 11.0$, 11.8, and 11.0 Hz respectively; 4,4,6,6-tetramethoxy-2,2-spiro(*N*-methylethanolamino)cyclotriphosphazatriene, (6), liquid (yield 74%), mass spectrum shows parent ion at *m/e* 332; ^1H n.m.r.: δ 4.20 (OCH_2), 3.53 and 3.51 (OMe), 3.22 (NCH_2), 2.60 (NMe); $^3J^*(P-H) = 10.0$, 12.0, 12.0, 11.0, and 11.0 Hz respectively; 6,6-bis(dimethylamino)-2,2,4,4-dispiro(*N*-methylethanolamino)cyclotriphosphazatriene, (7), m.p. 155 °C (yield 70%) (Found: C, 32.8; H, 6.6; N, 25.3. $C_{10}H_{26}N_7O_2P_3$ requires C, 32.5; H, 7.0; N, 23.8%); mass spectrum showed parent ion peak at *m/e* 369. ^1H N.m.r.: δ 4.25 (OCH_2), 3.30 (NCH_2), 2.66 (NMe_2 *trans* to NMe), 2.62 (NMe), 2.59 (NMe_2 *cis* to NMe), $^3J^*(P-H) = 9.5$, 12.1, 11.4, 11.8, and 11.4 Hz respectively.

Crystal Structure of the Dispiro Derivative, $N_3P_3(NMeCH_2CH_2O)_2Cl_2$ (3).—*Crystal data.* $C_6H_{14}Cl_2N_5O_2P_3$, $M = 352.02$, $a = 12.717(2)$, $b = 9.677(1)$, $c = 11.847(2)$ Å, $\beta = 89.46(1)°$, $D_m = 1.44$, $Z = 4$, $D_c = 1.57$ g cm^{-3}, $U = 1\,456$ Å^3, $F(000) = 720$, $\lambda = 0.7107$ Å, $\mu(Mo\text{-}K_\alpha) = 7.0$ cm^{-1}, space group $P2_1/c$.

Table 2. Bond distances (Å) and angles (°) for $N_3P_3(NMeCH_2CH_2O)_2Cl_2$ (3)

P(1)–Cl(1)	2.029(1)	P(1)–N(1)–P(2)	120.4(2)
P(1)–Cl(2)	2.014(2)	P(2)–N(2)–P(3)	127.0(4)
P(1)–N(1)	1.568(4)	P(3)–N(3)–P(1)	121.0(2)
P(1)–N(3)	1.561(4)	N(1)–P(2)–N(2)	115.2(2)
P(2)–N(1)	1.603(4)	N(2)–P(3)–N(3)	113.6(2)
P(2)–N(2)	1.565(4)	N(3)–P(1)–N(1)	121.5(2)
P(2)–N(4)	1.635(4)	Cl(1)–P(1)–Cl(2)	98.5(1)
P(2)–O(1)	1.587(3)	O(1)–P(2)–N(4)	95.7(2)
P(3)–N(2)	1.593(4)	O(2)–P(3)–N(5)	96.2(2)
P(3)–N(3)	1.600(4)	C(3)–N(4)–P(2)	123.1(4)
P(3)–N(5)	1.624(4)	C(1)–N(4)–P(2)	113.8(3)
P(3)–O(2)	1.582(4)	C(1)–N(4)–C(3)	121.7(4)
N(4)–C(1)	1.405(7)	C(4)–N(5)–C(6)	121.6(5)
N(4)–C(3)	1.448(6)	C(4)–N(5)–P(3)	114.5(4)
O(1)–C(2)	1.453(5)	C(6)–N(5)–P(3)	123.9(4)
N(5)–C(4)	1.419(7)		
N(5)–C(6)	1.450(7)		
O(2)–C(5)	1.446(6)		
C(1)–C(2)	1.503(7)		
C(4)–C(5)	1.507(9)		

Intensity data, structure determination, and refinement. Intensity data were collected on a CAD-4 diffractometer by the ω—2θ scan technique using monochromated Mo-K_α radiation. Of the 4 139 reflections measured, 2 968 reflections were considered observed [$I > 3\sigma(I)$]. The structure was solved by direct methods and refined by full-matrix least squares using anisotropic thermal parameters. The hydrogen atoms of the spirocyclic ring were included at the calculated positions but were not refined. The final $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for the observed reflections was 0.056. In the last cycle of refinement all the parameter shifts were less than 0.03σ. The weighting scheme used in the refinement was $w = 0.155/(\sigma_F^2 + 0.045|F|^2)$ where σ_F is the standard deviation associated with the '*F*' values. Scattering factors were from Cromer and Weber.[6]

Computations were carried out on a DEC 1090 computer system with program MULTAN [7] for structure solution and SHELX [8] for refinement. The final positional co-ordinates of the non-hydrogen atoms are given in Table 1. The bond lengths and bond angles are shown in Table 2.

Results and Discussion

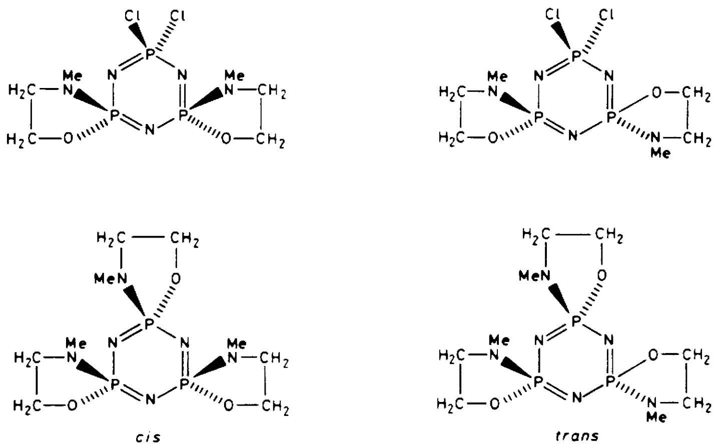
Structural Assignments for the (N-*Methylethanolamino*)-*cyclotriphosphazatrienes*.—Spirocyclic structures have been assigned to compounds (2), (3), and (4) on the basis of ^1H (see Experimental section) and ^{31}P n.m.r. data (Table 3). The ^{31}P-{^1H} n.m.r. spectra of the mono- and bis-(*N*-methylethanolamino) derivatives are of the AB_2 type. Since the difunctional reagent is asymmetrical there exists the possibility of geometrical isomerism for the di- and tri-spiro compounds (3) and (4) as shown in Figure 1. It is not possible to distinguish between the *cis* and *trans* structures for the dispiro derivative (3) from its n.m.r. data. *X*-Ray crystallography (see below for details) reveals that compound (3) has a *cis* orientation of the exocyclic nitrogen atoms and not a *trans* arrangement as tentatively suggested earlier.[2] The n.m.r. data for the methoxy- and dimethylamino-derivatives, (5)—(7), are consistent with the spirocyclic structures assigned to the chloro-precursors (2) and (3).

The ^{31}P-{^1H} n.m.r. spectrum of the trispiro derivative (4) is illustrated in Figure 2. It shows an AB_2 spectrum which can be assigned to the major *trans* component (4a). Additional strong lines at δ 35.2, 34.2, 33.5, 33.0, and 27.8 p.p.m. are also seen, which can be assigned to the *cis* isomer (4b). Although this isomer would be expected to show an A_3 type of ^{31}P n.m.r. spectrum, a slight non-equivalence of the phosphorus nuclei may result from the steric constraints and the consequent non-planarity of the cyclophosphazene ring. The preponderance of the *trans* isomer (4a) is confirmed by the ^1H n.m.r. spectrum. The $N-CH_3$ region consists of two doublets whose relative intensities are in the ratio of 1 : 2. Virtua

Table 3. Phosphorus-31 n.m.r. chemical shifts for some chloro(amino) and spirocyclic phosphazenes [a]

	Compound	$\delta(PCl_2)$/ p.p.m.	$\delta[P(NRR')_2]$/ p.p.m.	δ[P(spiro)]/ p.p.m.	$^2J(P\cdots P)$/ Hz	Ref.
	$N_3P_3(NHCH_2CH_2NH)Cl_4$	22.0		22.0		1
	$N_3P_3(NMe_2)_4(NHCH_2CH_2NH)$		26.7	35.5		1
	$N_3P_3(NHCH_2CH_2O)Cl_4$	23.3		23.3		1
	$N_3P_3(NHCH_2CH_2O)_2Cl_2$	29.0		29.0		1
(2)	$N_3P_3(NMeCH_2CH_2O)Cl_4$ [b]	25.1		22.4	53.9	This work
(3)	$N_3P_3(NMeCH_2CH_2O)_2Cl_2$	30.7		28.5	62.3	This work
(4a)	$N_3P_3(NMeCH_2CH_2O)_3$			33.6(1) [c] 25.4(2) [c]	58.6	This work
(5)	$N_3P_3(NMe_2)_4(NMeCH_2CH_2O)$		28.3	32.5	46.0	This work
(6)	$N_3P_3(OMe)_4(NMeCH_2CH_2O)$		21.9 [d]	33.7	67.5	This work
(7)	$N_3P_3(NMe_2)_2(NMeCH_2CH_2O)_2$		29.7	33.4	52.5	This work
	$N_3P_3[NH(CH_2)_3NH]Cl_4$	21.5		7.5	45.5	2
	$N_3P_3[NH(CH_2)_4NH]Cl_4$	21.2		12.8	46.0	2
	gem-$N_3P_3(NHPr^i)_2Cl_4$	19.8	6.2		45.5	14
	gem-$N_3P_3(NHPr^i)_4Cl_2$	22.2	9.4		49.4	9

[a] 36.43 MHz, $CDCl_3$ solution, 85% H_3PO_4 (external standard), upfield shifts negative. [b] Values previously reported[2] are incorrect. [c] Relative intensities in parentheses. [d] $\delta[P(OMe)_2]$/p.p.m.



cis *trans*

Figure 1. *cis* and *trans* isomers of $N_3P_3(NMeCH_2CH_2O)_2Cl_2$ and $N_3P_3(NMeCH_2CH_2O)_3$

coupling [9,10] is observed only for the doublet of higher intensity as expected for the *trans* isomer.[11]

Structural Features of the Dispiro Derivative, $N_3P_3(NMeCH_2CH_2O)_2Cl_2$ (3), *and Comparison with Related Cyclophosphazene Structures*.—*X*-Ray crystallography besides confirming the spirocyclic arrangement of the difunctional groups reveals the *cis* structure for the bis(*N*-methylethanolamino) derivative (3). A view of the molecule down the *a* axis is shown in Figure 3.

The bond lengths within the phosphazene ring (Table 2) are not equal. The P(1)–N(1) and the P(1)–N(3) distances (mean = 1.565 Å) are relatively short compared to the other ring distances. The P(2)–N(1) and P(3)–N(3) distances (mean = 1.602 Å) are the longest observed in this structure. These inequalities are consistent with the current theories of bonding in cyclophosphazenes.[10] The other two P–N bond distances, P(3)–N(2) and P(2)–N(2) (1.593 and 1.565 Å), are unequal contrary to expectation; the reasons for this inequality are not clear. Such bond length inequalities in apparently similar bond types are known, *e.g.* in the structure of 2-*cis*-4-*cis*-6-*trans*-8-tetrachloro-2,4,6,8-tetrakis(dimethylamino)cyclotetraphosphazatetraene, $N_4P_4(NMe_2)_4Cl_4$.[12] The exocyclic P–N bond distances observed in the present instance are unexceptional and are comparable to those found for (amino)cyclophosphazenes.[10]

The bond angles follow the general trend observed for many cyclophosphazenes; a decrease in the ring P–N bond lengths consequent upon the increasing electronegativity of the substituents is accompanied by a decrease in the angle subtended by the exocyclic substituents at phosphorus, an increase in the ring NPN angle, and a decrease in the ring PNP angle.[10] The exocyclic angles around the two spiro phosphorus atoms O(1)–P(2)–N(4) and O(2)–P(3)–N(5) are, however, smaller (95.7 and 96.2°) than usually observed.

The phosphazene ring is very nearly planar, the maximum deviation being 0.08 Å for P(3). The spirocyclic rings are also virtually planar; maximum deviation for C(1) is 0.1 Å and for C(5), 0.04 Å. The dihedral angles made by the spirocyclic rings attached to P(2) and P(3) with the phosphazene ring are 89.1 and 89.9°, respectively.

It is interesting to compare the structural parameters of the dispiro compound (3) with those of geminally substituted amino derivatives and other spiro phosphazenes whose structures have been reported. The relevant data are summarised in Table 4.

The exocyclic angle in the spirocyclic phosphazenes containing a five-membered spiro ring is smaller than that observed

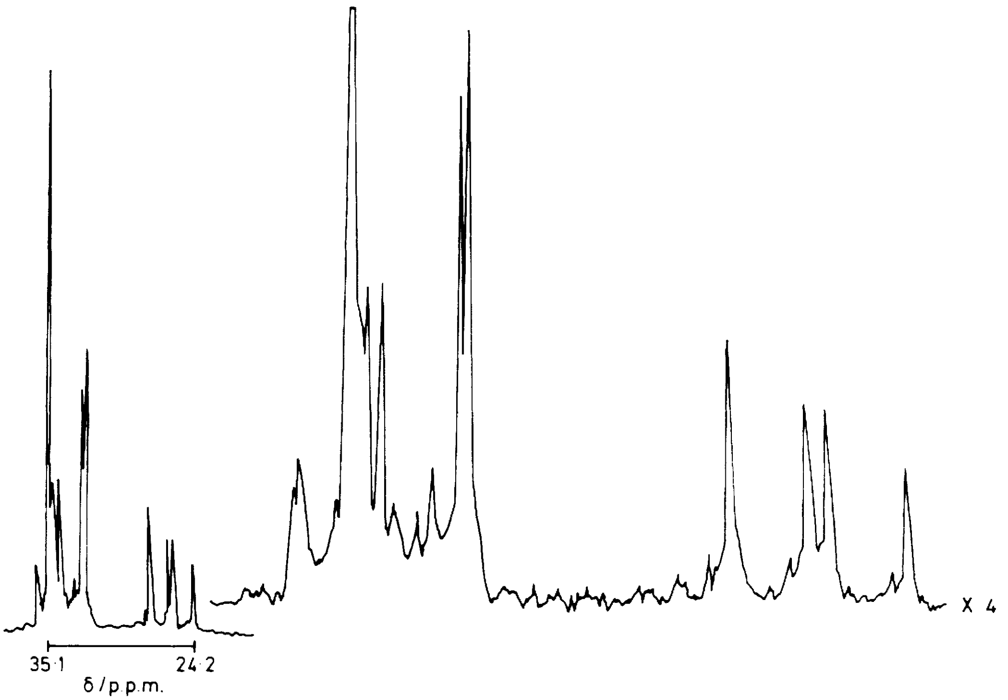


Figure 2. The $^{31}P-\{^1H\}$ n.m.r. spectrum of $N_3P_3(NMeCH_2CH_2O)_3$

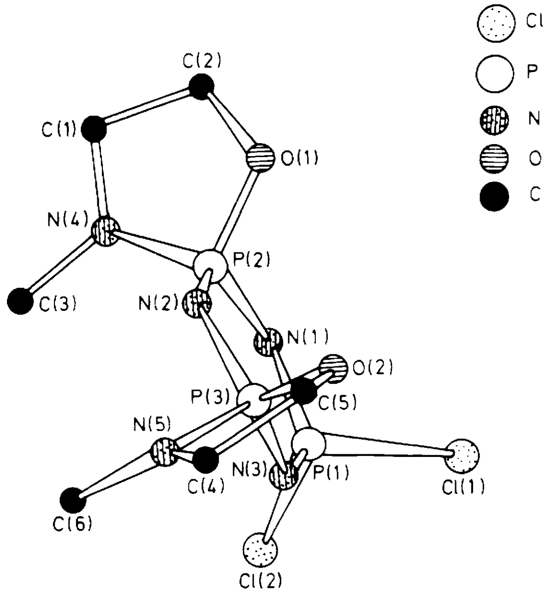


Figure 3. The molecule of $N_3P_3(NMeCH_2CH_2O)_2Cl_2$ (3) viewed down the *a* axis

in compounds containing six and higher membered spiro rings, thus indicating ring strain in the former. All the three rings, *viz.* the phosphazene ring and the two spirocyclic rings are planar for the dispiro compound (3) as is observed for $N_3P_3(O_2C_6H_4)_3$.[13] Whereas the 1,3-diaminopropane derivative, $N_3P_3[NH(CH_2)_3NH]Cl_4$ shows a planar phosphazene ring and a puckered spirocyclic ring,[4] the monospiro derivative, $N_3P_3(NMe_2)_4(NHCH_2CH_2NH)$ shows puckering of both the phosphazene and the spirocyclic rings.[3] One reason for the puckering of the spirocyclic and or the phosphazene ring in these compounds could be the formation of intermolecular hydrogen bonds. Because of the absence of any such interaction, the dispiro molecule (3) prefers a planar conformation. In all the spirocyclic systems, the spirocyclic ring is approximately perpendicular to the phosphazene ring. Such an arrangement is presumably the most favourable one from a steric point of view.

Phosphorus-31 *Chemical Shifts for Spirocyclic Phosphazenes.* —The phosphorus-31 chemical shifts for spirocyclic phosphazenes are compared with those for (primary amino)chlorocyclotriphosphazenes in Table 3. The chemical shift of the phosphorus nuclei incorporated in a five-membered spiro ring occurs at a much lower field than that observed for $\geqslant P(NHR)_2$ in chloro(primary amino)cyclophosphazenes;[10,11,14] in contrast, the chemical shift of $\geqslant P$(spiro) in derivatives containing six- or seven-membered spiro rings is slightly upfield. Similar trends are observed for spirocyclic phosphazenes derived from chlorocyclophosphazenes and aliphatic glycols[15] and also for monocyclic phosphorus compounds.[16] Theoretical calculations have revealed that the phosphorus atom incorporated in a five-membered ring has a greater positive charge than that in an acyclic or a six-membered analogue.[17] The five-membered ring is subject to steric strain (see above) and as a consequence there is a decrease of π-electron release to the phosphorus atom from the exocyclic substituents. The P–N bond distances within the spiro ring also confirm this conclusion. These P–N distances for $N_3P_3(NMeCH_2CH_2O)_2Cl_2$ (3) and $N_3P_3(NMe_2)_4(NHCH_2CH_2NH)$ are 1.63 and 1.67 Å respectively and are longer than that observed (1.618 Å) for the analogous P–N bond in the 1,3-diaminopropane derivative $N_3P_3[NH(CH_2)_3NH]Cl_4$.[4] In the latter, the spiro phosphorus has equal bond distances to all the four nitrogen atoms and such an isotropic arrangement presumably leads to a greater shielding of the phosphorus atom by reducing the contribution of the paramagnetic term to the net shielding.[4] Arguments based on ring strain and consequent changes in π-electron density at the phosphorus nuclei have also been

Table 4. Structural parameters for spirocyclic and related cyclophosphazenes

Compound	Atoms attached to P		Phosphazene ring conformation	Conformation of spirocyclic group	Average ring P–N bond lengths (Å)	Average endocyclic bond angles (°)		X–P–Y/°	Dihedral angle between ring NPN and exocyclic XPY	Ref.
	X	Y				P–N–P	N–P–N			
(3) $N_3P_3(NMeCH_2CH_2O)_2Cl_2$	N	O	Planar	Planar	1.565 1.602 1.579	122.9	116.6	95.9	89.9 89.1	This work
$N_3P_3(NMe_2)_4[NH(CH_2)_2NH]$	N [a]	N [a]	Non-planar	Envelope	1.594	123.6	115.8	95.5	101.3	3
$N_3P_3[NH(CH_2)_3NH]Cl_4$	N	N	Planar	Non-planar	1.613 1.553 1.579	122.8	116.3	101.4	99.0	4
$N_3P_3(O_2C_6H_4)_3$	O	O	Planar	Planar	1.576	122.0	119.0	97.0	107.0	13
$N_3P_3[O_2(C_6H_4)_2]_3$	O	O	Distorted	*b*	1.572	121.0	118.4	102.7	105.6	*c*
$N_3P_3(NHPr^i)_4Cl_2$	N	N	Non-planar		1.56 1.64	121.3	117.3	104.7		*d*
$N_3P_3(NMe_2)_6$	N	N	Non-planar		1.588	123.0	116.7	102.0		*e*

[a] The N atoms belong to the spirocyclic substituent. [b] Two of the $O_2(C_6H_4)_2$ groups are twisted in a ' propeller ' fashion at 43° in one direction while the third is twisted at 52° in the opposite direction. [c] H. R. Allcock, M. T. Stein, and J. A. Stanxo, *J. Am. Chem. Soc.*, 1971, **93**, 3173. [d] W. Polder and A. J. Wagner, *Cryst. Struct. Commun.*, 1976, **5**, 253. [e] S. J. Rettig and J. Trotter, *Can. J. Chem.*, 1973, **52**, 1295.

advanced by Westheimer [18] to explain the rapid hydrolysis of five-membered cyclic phosphorus esters.

Pathways in the Reactions of $N_3P_3Cl_6$ *with Aliphatic Difunctional Reagents.*—The reactions of chlorocyclotriphosphazenes with aliphatic difunctional reagents lead mainly to the formation of spirocyclic derivatives; ' *ansa* ' type compounds have remained elusive.[2] In contrast to the reaction of the hexachloride (1) with ethanolamine where only the monospiro derivative is isolated in moderate yields and the two geometrical isomers of the dispiro derivative are only obtained in traces, *N*-methylethanolamine gives good yields of mono-, di- and tri-spiro compounds. The suggestion [1,19] that it is the P–NH moiety in five-membered rings which is responsible for the resin-forming reactions is thus vindicated. The present investigation also shows that the bis(*N*-methylethanolamino) derivative (3) has a ' *cis* ' disposition of the two exocyclic nitrogen atoms. This compound is the major component in the reaction mixture (see Experimental section). In view of the greater nucleophilicity of amines over alcohols towards phosphorus, it is likely that the initial step is attack at the $\geqslant PCl_2$ centre by the nitrogen end of the difunctional reagent. After the formation of the monospiro compound, a second molecule of *N*-methylethanolamine attacks at an adjacent phosphorus from the less-hindered side of the ring followed by an inversion which would lead to the formation of the ' *cis* ' dispiro compound (3). Further work is needed with many other unsymmetrical difunctional reagents to unravel the factors responsible for the stereochemical course of these reactions.

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