Molecular Structures of Non-geminally Substituted Phosphazenes. Part II.[1] Crystal Structure of 2,*cis*-4,*cis*-6,*cis*-8-Tetrachloro-2,4,6,8-tetraphenylcyclotetraphosphazatetraene

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Crystals of the title compound (α-modification, m.p. 190 °C) are triclinic, a = 14·07, b = 11·67, c = 9·00 Å, α = 99·7, β = 88·5, γ = 102·1°, space group $P\bar{1}$, Z = 2. The structure was solved by direct methods; atomic positions were determined by least-squares refinement from X-ray diffractometer intensity data, the final R being 0·056 for 4519 reflections. The eight-membered phosphazene ring has an irregular crown conformation with P–N–P angles ranging from 133·1 to 142·0°. Mean bond lengths are: P–N 1·570, P–Cl 2·041, P–C 1·783, and C–C 1·39 Å. The bond lengths are discussed in terms of the electronegativity of the exocyclic groups and the ring conformation is discussed in terms of steric factors.

IN this series of papers the crystal structures of a number of non-geminally substituted phosphazenes (I) are being studied in order to examine differences in configuration and conformation of the phosphazene ring in closely related or isomeric compounds. In Part I β-*trans*-$N_4P_4(NHMe)_4Ph_4$ † (II; R = NHMe) was shown to possess a chair-shaped ring with the approximate symmetry $2/m$ and centrosymmetrically arranged substituents.[1] $N_4P_4Cl_4Ph_4$ (I; X = Cl, Y = Ph) is known as three geometric isomers [2] which have been assigned *cis*- or *trans*-structures from ^{1}H n.m.r. studies and dielectric constant measurements.[3] The molecule of the β-*trans*-isomer (II; R = Cl) has been shown by crystal-structure analysis [4] to be similar in shape to that of β-*trans*-$N_4P_4(NHMe)_4Ph_4$ with a ring having the chair conformation. The structure of *cis*-$N_4P_4Cl_4Ph_4$ † (III),

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† The following abbreviations will be used throughout this paper: β-*trans* = 2,*cis*-4,*trans*-6,*trans*-8-, and *cis* = 2,*cis*-4,*cis*-6,*cis*-8-; the full *cis–trans* nomenclature is taken from R. A. Shaw, B. W. Fitzsimmons, and B. C. Smith, *Chem. Rev.*, 1962, **62**, 250.

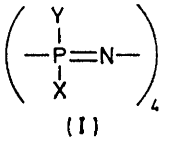
[1] Part I, G. J. Bullen and P. R. Mallinson, *J.C.S. Dalton*, 1972, 1412.

[2] R. A. Shaw and C. Stratton, *J. Chem. Soc.*, 1962, 5004.

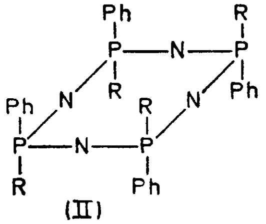
[3] B. Grushkin, A. J. Berlin, J. M. McClanahan, and R. G. Rice, *Inorg. Chem.*, 1966, **5**, 172.

[4] G. J. Bullen, P. R. Mallinson, and A. H. Burr, *Chem. Comm.*, 1969, 691.

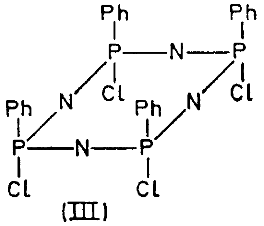
described here, was examined for comparison with the β-*trans*-isomer. *cis*-$N_4P_4Cl_4Ph_4$ exists in two crystalline modifications which possess different melting points and *X*-ray powder patterns, and which we shall designate α (m.p. 190 °C) and β (m.p. 226 °C). The conditions for the preparation of the α form and its conversion to β have been reported.[5] Once formed, the β-modification remains unchanged even at room temperature (for at least a week and possibly longer) but reverts to α when recrystallised from solution at room temperature. The crystal structure described here is that of the α-modification.



(I)



(II)



(III)

EXPERIMENTAL

Crystal Data.—$C_{24}H_{20}Cl_4N_4P_4$, $M = 629{\cdot}7$, Triclinic, $a = 14{\cdot}07 \pm 0{\cdot}02$, $b = 11{\cdot}67 \pm 0{\cdot}02$, $c = 9{\cdot}00 \pm 0{\cdot}01$ Å, $\alpha = 99{\cdot}7 \pm 0{\cdot}3°$, $\beta = 88{\cdot}5 \pm 0{\cdot}3°$, $\gamma = 102{\cdot}1 \pm 0{\cdot}2°$, $U = 1423$ Å^3, $D_m = 1{\cdot}45$ (by flotation), $Z = 2$, $D_c = 1{\cdot}47$, $F(000) = 640$. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) $= 6{\cdot}6$ cm^{-1}. Space group $P\bar{1}$ (C_i^1, No. 2).

Suitable crystals of the α-modification were grown from benzene–light petroleum (b.p. 40—60 °C) solutions at room temperature. The forms commonly developed are the pinacoids {001}, {010}, and {1$\bar{1}$0}. The crystals are roughly equidimensional in cross-section but slightly elongated along *c*. The unit-cell dimensions quoted were used in preference to those of the reduced cell ($a = 14{\cdot}07$, $b = 13{\cdot}48$, $c = 9{\cdot}00$ Å, $\alpha = 121{\cdot}4°$, $\beta = 91{\cdot}5°$, $\gamma = 99{\cdot}4°$) in order to avoid the large α angle of the latter.

X-Ray intensity data comprising the 13 layers of reflections *hk*0—12 were measured on a Philips PAILRED diffractometer by use of monochromatised Mo-K_α radiation. 4519 reflections having $I > 2\sigma(I)$ were obtained by measuring all reflections with $\sin\theta/\lambda \leqslant 0{\cdot}70$ Å^{-1}, from a crystal of dimensions *ca*. 0·2 × 0·3 × 0·5 mm. These intensities were corrected for Lorentz and polarisation effects, but no absorption correction was applied as the linear absorption coefficient is small.

The least-squares refinement was carried out at the Atlas Computer Laboratory, Chilton, using the '*X*-ray '63' programme package (J. M. Stewart, University of Maryland Technical Report, TR 64 6). Atomic scattering factors were taken from ref. 6.

Structure Determination.—The intensities were adjusted to an absolute scale by Wilson's method[7] and normalised structure factor amplitudes, $|E|$, were calculated. Statistics for these are given in Table 1. A comparison of the experimental with the theoretical values for crystals with randomly distributed atoms indicates that the space group is centrosymmetric and is therefore $P\bar{1}$. The phases of the reflections were determined directly by computer application of the sign relationship $s(E_h) = s(E_{h'} \cdot E_{h-h'})$ (*s* means 'sign of') to the **342** reflections with $|E| > 2{\cdot}0$. The reflections used to specify the origin are given in Table 2 together with three other reflections with large $|E|$ whose signs were represented by the symbols *a*, *b*, and *c*. 316 Phases were determined in terms of these starting signs and symbols. A number of relationships suggested that *b* and *ac* were positive. Since to have all signs positive is not a likely solution, *a* and *c* negative was chosen and an *E*-map calculated. This showed clearly the positions of the four phosphorus and four chlorine atoms in the asymmetric unit. The carbon and nitrogen atoms were located from subsequent Fourier syntheses phased on the heavier atoms.

TABLE 1

Normalised structure-factor statistics

		Calc.	
	Found	$P\bar{1}$	$P1$
Mean E^2	0·991	1·000	1·000
Mean $\|E\|$	0·782	0·798	0·896
$\|E\| > 1$ (%)	30·6	32·0	36·9
$\|E\| > 2$ (%)	4·8	4·6	1·8
$\|E\| > 3$ (%)	0·2	0·3	0·01

TABLE 2

Assigned phases

Phase	*h*	*k*	*l*	$\|E\|$
+	0	3	3	2·61
+	−5	6	2	2·26
+	−6	3	4	2·95
a	−8	−1	1	2·59
b	2	5	1	2·21
c	6	−7	4	2·88

Three cycles of isotropic full-matrix least-squares refinement, including refinement of individual layer scale factors, reduced *R* to 0·11. After the second cycle hydrogen atoms were included as a fixed contribution to the structure factors, their positions being estimated from the molecular geometry assuming C–H 1·08 Å. They were given a temperature factor with *B* 5·0 Å^2. In subsequent cycles of refinement anisotropic temperature factors were introduced and a weighting scheme $w = (0{\cdot}727 + 0{\cdot}015|F_o| + 0{\cdot}00019|F_o|^2)^{-1}$ was used. This weighting scheme gave similar average values of $w\Delta^2$ for ranges of increasing $|F_o|$ and $\sin\theta/\lambda$. Before proceeding with the refinement all layers were put on the same scale as the layers with low *l*. Limitations on computer store prevented all parameters from being refined simultaneously. They were therefore divided into three blocks: one block each for the parameters of the twelve carbon atoms in two phenyl rings and a third block containing parameters associated with the chlorine, phosphorus, and nitrogen atoms. Each block was refined for two cycles, eight reflections having $w^{\frac{1}{2}}\Delta > 10$ (on absolute scale) being excluded from the second cycle. One cycle for refinement of individual

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[5] G. J. Bullen and P. A. Tucker, *Chem. Comm.*, 1970, 1185.

[6] 'International Tables for *X*-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962, pp. 202, 203.

[7] A. J. C. Wilson, *Nature*, 1942, **150**, 152.

layer scale-factors and three cycles of block-diagonal (3×3 normal matrices) refinement of the hydrogen atom co-ordinates reduced R to its final value of 0·056 for 4519 reflections.

RESULTS

The shape of the molecule and the numbering of the atoms are shown in Figure 1. The final atomic co-ordinates and thermal parameters with estimated standard deviations are listed in Tables 3 and 4. Observed and calculated structure factors are given in Supplementary Publication No. 20405 (23 pp., 1 microfiche).* Bond lengths are listed in Table 5 and bond angles in Table 6. Their estimated standard deviations were calculated from the formulae of Jeffrey and Cruickshank,[8] the maximum of $\sigma(x)$, $\sigma(y)$, and $\sigma(z)$ being taken as the standard deviation $\sigma(r)$ of the atomic position. The orientation and magnitudes of the principal axes of the vibration ellipsoids for phosphorus, chlorine, and nitrogen atoms are given in Table 7. The anisotropic thermal parameters of the phenyl carbon atoms were used in an analysis of the vibrations of the atoms in terms of a rigid-body motion for each phenyl group. The translational and librational tensors (Table 8) were calculated by the least-squares procedure of Cruickshank [9] with the origin of the libration axes at the phosphorus atom to which the phenyl group is bonded (see Figure 2).

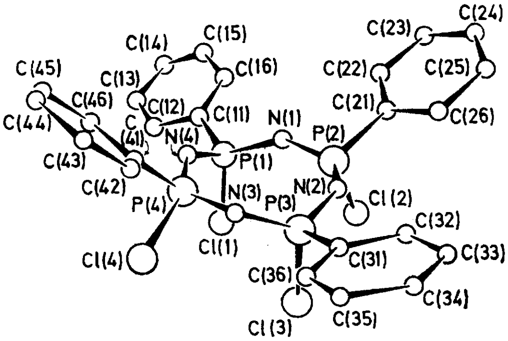

FIGURE 1 Molecular shape and numbering of the atoms

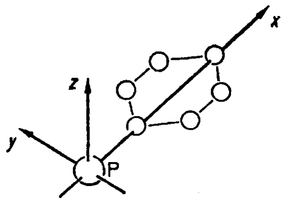

FIGURE 2 Axial system used for analysis of the librational motion of the phenyl groups. The y axis is parallel to the phenyl ring

DISCUSSION

Ring Shape.—All the chlorine atoms in the molecule lie on the same side of the ring so that the compound is the *cis*-isomer as suggested by Grushkin *et al.*[3] The ring shape is different from that of any of the tetrameric phosphazenes hitherto examined. The four nitrogen atoms are nearly coplanar (Table 9). The phosphorus atoms lie at different distances from the mean plane of the nitrogen atoms but all on the same side of it. The ring shape is thus best described as an irregular crown which is rather flat at P(2) and P(4) (Figure 3), probably owing to steric repulsion between chlorine atoms. A

TABLE 3

Atomic co-ordinates (as fractions of unit-cell edges) with estimated standard deviations in parentheses

	x/a	y/b	z/c
Cl(1)	0·21180(13)	0·19757(15)	0·43562(19)
Cl(2)	0·46318(13)	0·19983(18)	0·53811(21)
Cl(3)	0·27502(14)	−0·03142(15)	0·69122(20)
Cl(4)	0·02118(13)	0·06802(17)	0·68074(21)
P(1)	0·23124(10)	0·33406(13)	0·61300(17)
P(2)	0·41210(10)	0·29274(13)	0·72539(17)
P(3)	0·28776(10)	0·10772(13)	0·86601(17)
P(4)	0·11245(9)	0·20001(12)	0·81828(16)
N(1)	0·3397(4)	0·3621(5)	0·6689(6)
N(2)	0·3793(4)	0·2026(4)	0·8387(6)
N(3)	0·1860(4)	0·1408(5)	0·8908(6)
N(4)	0·1469(4)	0·3063(4)	0·7288(6)
C(11)	0·2124(4)	0·4572(6)	0·5320(7)
C(12)	0·1257(7)	0·4482(8)	0·4575(12)
C(13)	0·1098(8)	0·5434(11)	0·3923(15)
C(14)	0·1814(7)	0·6444(9)	0·4023(13)
C(15)	0·2668(6)	0·6548(7)	0·4750(11)
C(16)	0·2832(5)	0·5596(6)	0·5423(9)
C(21)	0·5181(4)	0·3971(6)	0·7978(8)
C(22)	0·5414(5)	0·5060(7)	0·7472(10)
C(23)	0·6277(7)	0·5860(8)	0·8031(13)
C(24)	0·6858(6)	0·5568(11)	0·9027(14)
C(25)	0·6617(6)	0·4481(13)	0·9552(14)
C(26)	0·5766(5)	0·3668(9)	0·9022(10)
C(31)	0·3117(4)	0·0440(5)	1·0248(7)
C(32)	0·4058(5)	0·0622(7)	1·0794(8)
C(33)	0·4229(6)	0·0081(8)	1·2037(8)
C(34)	0·3457(7)	−0·0601(8)	1·2689(10)
C(35)	0·2513(7)	−0·0728(8)	1·2189(11)
C(36)	0·2338(6)	−0·0222(7)	1·0926(10)
C(41)	0·0325(4)	0·2454(5)	0·9625(6)
C(42)	0·0202(5)	0·1922(6)	1·0927(8)
C(43)	−0·0458(6)	0·2247(7)	1·1998(9)
C(44)	−0·0997(6)	0·3089(8)	1·1786(11)
C(45)	−0·0857(6)	0·3618(8)	1·0520(12)
C(46)	−0·0200(5)	0·3306(7)	0·9420(8)
H(12)	0·070(6)	0·364(7)	0·463(9)
H(13)	0·045(6)	0·530(7)	0·354(9)
H(14)	0·163(6)	0·710(7)	0·366(9)
H(15)	0·316(5)	0·723(6)	0·489(8)
H(16)	0·335(6)	0·574(7)	0·613(9)
H(22)	0·500(6)	0·521(7)	0·673(9)
H(23)	0·650(6)	0·682(7)	0·752(9)
H(24)	0·740(6)	0·607(7)	0·935(9)
H(25)	0·706(6)	0·432(7)	1·030(9)
H(26)	0·561(6)	0·282(7)	0·924(9)
H(32)	0·461(5)	0·113(6)	1·033(8)
H(33)	0·492(5)	0·014(6)	1·249(8)
H(34)	0·365(6)	−0·081(7)	1·372(9)
H(35)	0·184(6)	−0·120(7)	1·273(9)
H(36)	0·163(5)	−0·037(6)	1·059(8)
H(42)	0·064(5)	0·134(7)	1·114(8)
H(43)	−0·062(6)	0·183(7)	1·293(9)
H(44)	−0·153(6)	0·331(7)	1·257(9)
H(45)	−0·125(6)	0·434(7)	1·023(9)
H(46)	−0·005(6)	0·372(7)	0·837(9)

The carbon atoms are numbered with two digits, the first being that of the phenyl group to which the atom belongs, *e.g.* atoms C(11)—(16) belong to phenyl group (1); hydrogen atoms are numbered according to the carbon atom to which they are attached.

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[8] G. A. Jeffrey and D. W. J. Cruickshank, *Quart. Rev.*, 1953, **7**, 335.

[9] D. W. J. Cruickshank, *Acta Cryst.*, 1956, **9**, 754.

TABLE 4

Anisotropic thermal parameters ($\times 10^4$) with estimated standard deviations in parentheses *

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Cl(1)	68·4(11)	76·8(14)	132·7(23)	5·8(10)	0·1(12)	1·5(14)
Cl(2)	51·5(9)	120·1(19)	152·6(26)	16·2(11)	17·9(13)	−30·4(18)
Cl(3)	76·1(12)	74·6(14)	140·2(24)	11·4(10)	8·8(13)	−9·5(15)
Cl(4)	55·2(9)	98·5(16)	148·6(25)	−15·9(10)	−10·5(12)	−2·7(16)
P(1)	38·3(7)	58·7(11)	102·9(19)	7·3(7)	3·2(9)	27·6(12)
P(2)	28·5(6)	63·9(12)	114·3(20)	6·6(7)	4·5(9)	6·6(12)
P(3)	36·1(7)	55·5(11)	113·4(19)	16·3(7)	0·7(9)	16·4(12)
P(4)	28·6(6)	56·1(11)	99·8(18)	4·4(6)	−0·8(8)	24·5(11)
N(1)	42(3)	69(4)	146(8)	8(3)	−3(4)	29(5)
N(2)	41(3)	65(4)	147(8)	7(3)	−6(4)	26(5)
N(3)	40(3)	81(5)	154(8)	25(3)	9(4)	45(5)
N(4)	46(3)	70(4)	129(7)	11(3)	10(4)	41(5)
C(11)	43(3)	75(5)	115(8)	11(3)	11(4)	35(5)
C(12)	76(6)	123(9)	301(19)	3(6)	−58(9)	108(11)
C(13)	86(6)	188(14)	393(27)	12(8)	−50(11)	190(16)
C(14)	88(7)	131(10)	298(20)	31(7)	29(9)	136(12)
C(15)	74(5)	82(7)	238(15)	75(5)	34(7)	56(8)
C(16)	51(4)	67(5)	195(12)	15(4)	30(5)	37(6)
C(21)	35(3)	74(5)	146(9)	4(3)	20(4)	−13(6)
C(22)	55(4)	85(6)	202(13)	−13(4)	35(6)	5(7)
C(23)	67(6)	108(9)	266(18)	−26(6)	55(9)	−45(10)
C(24)	48(5)	188(14)	267(20)	−24(7)	30(8)	−127(14)
C(25)	45(5)	194(14)	290(21)	0(7)	−24(7)	−45(14)
C(26)	37(3)	167(10)	175(12)	16(5)	−18(5)	−6(9)
C(31)	45(3)	59(5)	133(9)	23(3)	1(4)	15(5)
C(32)	57(4)	124(8)	137(10)	41(4)	1(5)	17(7)
C(33)	77(5)	150(9)	121(10)	60(6)	−8(6)	23(8)
C(34)	102(7)	113(8)	174(13)	52(6)	4(7)	49(8)
C(35)	93(6)	104(8)	223(15)	13(6)	−2(8)	82(9)
C(36)	67(5)	95(7)	232(14)	5(5)	−18(7)	86(8)
C(41)	27(3)	77(5)	99(7)	10(3)	5(3)	16(5)
C(42)	51(4)	94(6)	143(10)	10(4)	23(5)	38(6)
C(43)	72(5)	113(8)	151(11)	10(5)	33(6)	23(7)
C(44)	61(5)	111(8)	250(17)	14(5)	46(7)	5(9)
C(45)	68(5)	124(9)	291(19)	48(6)	59(8)	56(10)
C(46)	55(4)	101(7)	168(11)	33(4)	18(5)	50(7)

* The temperature factor is in the form: $\exp(-b_{11}h^2 - b_{22}k^2 - b_{33}l^2 - 2b_{12}hk - 2b_{13}hl - 2b_{23}kl)$.

TABLE 5

Bond lengths (Å) with estimated standard deviations in parentheses *

P(1)–N(1)	1·569(6)	C(11)–C(12)	1·38(1)
P(2)–N(1)	1·570(6)	C(12)–C(13)	1·40(2)
P(2)–N(2)	1·579(6)	C(13)–C(14)	1·37(2)
P(3)–N(2)	1·556(6)	C(14)–C(15)	1·36(2)
P(3)–N(3)	1·560(6)	C(15)–C(16)	1·41(1)
P(4)–N(3)	1·569(6)	C(16)–C(11)	1·38(1)
P(4)–N(4)	1·577(5)	C(21)–C(22)	1·39(1)
P(1)–N(4)	1·577(5)	C(22)–C(23)	1·41(1)
Mean	1·570	C(23)–C(24)	1·36(2)
		C(24)–C(25)	1·40(2)
P(1)–Cl(1)	2·036(2)	C(25)–C(26)	1·40(2)
P(2)–Cl(2)	2·045(2)	C(26)–C(21)	1·40(1)
P(3)–Cl(3)	2·043(2)	C(31)–C(32)	1·39(1)
P(4)–Cl(4)	2·041(2)	C(32)–C(33)	1·42(1)
Mean	2·041	C(33)–C(34)	1·39(1)
		C(34)–C(35)	1·38(1)
P(1)–C(11)	1·785(6)	C(35)–C(36)	1·42(1)
P(2)–C(21)	1·776(7)	C(36)–C(31)	1·39(1)
P(3)–C(31)	1·788(6)	C(41)–C(42)	1·41(1)
P(4)–C(41)	1·782(6)	C(42)–C(43)	1·38(1)
Mean	1·783	C(43)–C(44)	1·40(1)
		C(44)–C(45)	1·38(1)
		C(45)–C(46)	1·39(1)
		C(46)–C(41)	1·40(1)
		Mean	1·39

* The C–H bond lengths lie in the range 0·88—1·26 Å, mean 1·04 Å.

TABLE 6

Bond angles (deg.) with estimated standard deviations in parentheses

N(4)–P(1)–N(1)	119·3(3)	P(1)–C(11)–C(12)	119·1(6)
N(1)–P(2)–N(2)	121·5(3)	P(1)–C(11)–C(16)	120·7(5)
N(2)–P(3)–N(3)	121·0(3)	P(2)–C(21)–C(22)	119·0(6)
N(3)–P(4)–N(4)	122·3(3)	P(2)–C(21)–C(26)	119·0(6)
		P(3)–C(31)–C(32)	120·1(5)
P(1)–N(1)–P(2)	137·3(4)	P(3)–C(31)–C(36)	118·5(5)
P(2)–N(2)–P(3)	137·6(4)	P(4)–C(41)–C(42)	119·9(4)
P(3)–N(3)–P(4)	142·0(4)	P(4)–C(41)–C(46)	119·3(5)
P(4)–N(4)–P(1)	133·1(4)		
		C(16)–C(11)–C(12)	120·2(7)
Cl(1)–P(1)–C(11)	103·5(2)	C(11)–C(12)–C(13)	119·9(10)
Cl(2)–P(2)–C(21)	102·4(2)	C(12)–C(13)–C(14)	119·2(11)
Cl(3)–P(3)–C(31)	103·3(2)	C(13)–C(14)–C(15)	121·7(11)
Cl(4)–P(4)–C(41)	102·0(2)	C(14)–C(15)–C(16)	119·6(9)
		C(15)–C(16)–C(11)	119·4(7)
Cl(1)–P(1)–N(1)	109·3(2)	C(26)–C(21)–C(22)	122·0(7)
Cl(1)–P(1)–N(4)	108·2(2)	C(21)–C(22)–C(23)	117·9(8)
Cl(2)–P(2)–N(2)	106·8(2)	C(22)–C(23)–C(24)	120·7(10)
Cl(2)–P(2)–N(1)	106·9(2)	C(23)–C(24)–C(25)	121·4(11)
Cl(3)–P(3)–N(3)	108·1(2)	C(24)–C(25)–C(26)	119·3(10)
Cl(3)–P(3)–N(2)	107·8(2)	C(25)–C(26)–C(21)	118·7(8)
Cl(4)–P(4)–N(4)	107·8(2)	C(36)–C(31)–C(32)	121·3(6)
Cl(4)–P(4)–N(3)	107·4(2)	C(31)–C(32)–C(33)	118·9(6)
		C(32)–C(33)–C(34)	119·8(7)
C(11)–P(1)–N(1)	107·8(3)	C(33)–C(34)–C(35)	121·0(8)
C(11)–P(1)–N(4)	107·6(3)	C(34)–C(35)–C(36)	119·5(8)
C(21)–P(2)–N(2)	109·2(3)	C(35)–C(36)–C(31)	119·3(8)
C(21)–P(2)–N(1)	108·4(3)	C(46)–C(41)–C(42)	120·8(6)
C(31)–P(3)–N(3)	107·0(3)	C(41)–C(42)–C(43)	119·0(7)
C(31)–P(3)–N(2)	108·2(3)	C(42)–C(43)–C(44)	120·5(7)
C(41)–P(4)–N(4)	107·7(3)	C(43)–C(44)–C(45)	120·0(9)
C(41)–P(4)–N(3)	107·8(3)	C(44)–C(45)–C(46)	120·8(9)
		C(45)–C(46)–C(41)	118·9(6)

symmetrical and highly puckered crown conformation is extremely unfavourable owing to the steric repulsions between the four axial exocyclic groups.[10] The flatten-

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[10] N. L. Paddock, *Quart. Rev.*, 1964, **18**, 168.

ing at P(2) and P(4) relieves this by moving Cl(2) and Cl(4) outwards so that the Cl · · · Cl distances (3·67—4·05 Å, Figures 1 and 4), exceed the van der Waals diameter of a chlorine atom. As shown by the torsion angles the symmetry of the ring approximates to *m*, the mirror plane passing through P(1) and P(3).

TABLE 7

Amplitudes of thermal vibration (Å) along the principal axes of the vibration ellipsoids. Each principal axis is specified by its direction cosines *l*, *m*, and *n* referred to orthogonal axes *a′*, *b′*, and *c*, where *b′* lies in the *bc* plane

		l	*m*	*n*
Cl(1)	0·268	0·809	−0·507	0·299
	0·241	−0·499	−0·322	0·805
	0·209	0·312	0·800	0·513
Cl(2)	0·327	−0·102	0·723	−0·683
	0·236	0·803	0·465	0·374
	0·190	−0·588	0·511	0·627
Cl(3)	0·284	0·753	−0·399	0·524
	0·251	−0·655	−0·377	0·655
	0·199	0·064	0·836	0·545
Cl(4)	0·304	−0·481	0·823	−0·301
	0·252	−0·426	0·080	0·901
	0·185	0·766	0·562	0·313
P(1)	0·214	0·009	0·702	0·712
	0·194	0·916	−0·291	0·276
	0·174	0·401	0·650	−0·646
P(2)	0·223	0·115	−0·474	0·873
	0·198	0·062	0·880	0·470
	0·164	0·992	0·000	−0·130
P(3)	0·212	0·079	0·267	0·961
	0·198	0·761	0·607	−0·231
	0·167	−0·644	0·749	−0·155
P(4)	0·210	−0·107	0·705	0·701
	0·177	−0·320	0·643	−0·696
	0·163	0·942	0·298	−0·157
N(1)	0·246	−0·116	0·465	0·878
	0·203	−0·324	0·818	−0·476
	0·196	0·939	0·340	−0·056
N(2)	0·249	−0·181	0·369	0·912
	0·200	−0·401	0·819	−0·411
	0·193	0·898	0·440	0·000
N(3)	0·267	0·293	0·611	0·735
	0·208	0·616	0·467	−0·634
	0·170	0·731	−0·639	0·240
N(4)	0·245	0·269	0·627	0·731
	0·210	0·876	−0·475	0·085
	0·177	0·401	0·617	−0·677

TABLE 8

T_{ij} (Å^2) and ω_{ij} (deg.^{2}) for the phenyl rings, with estimated standard deviations in parentheses

	Ring (1)	Ring (2)	Ring (3)	Ring (4)
T_{11}	0·070(4)	0·041(2)	0·065(3)	0·053(3)
T_{22}	0·041(7)	0·059(4)	0·042(6)	0·043(5)
T_{33}	0·034(10)	0·036(6)	0·039(8)	0·030(7)
T_{12}	−0·009(4)	−0·001(2)	0·000(3)	0·003(3)
T_{13}	−0·003(4)	0·009(2)	0·002(3)	0·009(3)
T_{23}	−0·003(7)	0·006(4)	0·011(6)	−0·007(5)
ω_{11}	75(19)	49(11)	54(15)	41(14)
ω_{22}	14(2)	6(1)	5(2)	6(2)
ω_{33}	8(2)	21(1)	9(1)	11(1)
ω_{12}	16(2)	−2(1)	−4(2)	4(2)
ω_{13}	2(4)	−2(2)	10(3)	−2(3)
ω_{23}	−3(2)	1(1)	2(2)	−4(1)

TABLE 9

Parameters of mean planes through sets of atoms and in square brackets distances (Å) of atoms from the planes. The equation of a plane is $lx + my + nz = p$ with co-ordinates and distances (Å) referred to the orthogonal axes *a′*, *b′*, and *c*, where *b′* lies in the *bc* plane

	l	*m*	*n*	*p*
Plane (1): N(1)—(4)	0·119	0·690	0·714	6·644
[N(1) −0·022, N(2) 0·022, N(3) −0·022, N(4) 0·022, P(1) −0·551, P(2) −0·122, P(3) −0·411, P(4) −0·093]				
Plane (2): C(11)—(16)	−0·395	0·469	0·790	4·159
[C(11) −0·002, C(12) −0·002, C(13) 0·004, C(14) −0·003, C(15) −0·002, C(16) 0·004, P(1) −0·022]				
Plane (3): C(21)—(26)	−0·511	0·526	0·680	2·452
[C(21) −0·007, C(22) 0·003, C(23) 0·004, C(24) −0·007, C(25) 0·003, C(26) 0·004, P(2) −0·059]				
Plane (4): C(31)—(36)	−0·118	0·866	0·485	3·647
[C(31) −0·014, C(32) 0·015, C(33) 0·002, C(34) −0·021, C(35) 0·022, C(36) −0·005, P(3) −0·038]				
Plane (5): C(41)—(46)	0·721	0·586	0·369	4·950
[C(41) −0·006, C(42) 0·004, C(43) 0·004, C(44) −0·009, C(45) 0·007, C(46) 0·001, P(4) −0·091]				

In the β-*trans*-isomer of $N_4P_4Cl_4Ph_4$ the molecule is centrosymmetric and the ring has a chair conformation.[4] There have been attempts to correlate differences of ring shape with electronic factors [10] but here we have different ring shapes in two isomers whose only other difference is one of the *cis–trans* type. The difference in shape therefore seems more likely to arise from steric factors. In both isomers the more bulky phenyl groups occupy the equatorial positions where they point outwards and away from each other. If the conformations were other than those actually found it would not be possible to place all the phenyl groups in equatorial positions. We therefore suggest that the two conformations are uniquely suited to the respective geometric isomers.

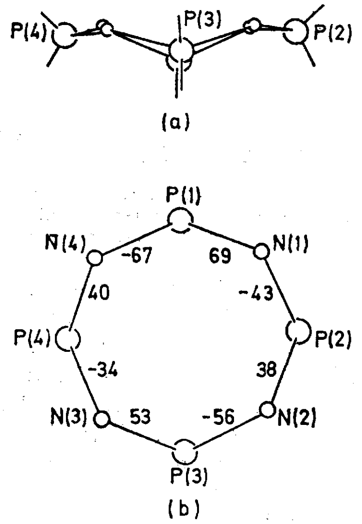

FIGURE 3 (a) Shape of the phosphazene ring; (b) torsion angles (deg.) in the ring

Bond Lengths and Angles.—The P–N bond lengths are equal within experimental error and fall within the range of lengths found for tetrameric phosphazenes. Ansell and Bullen have correlated the bond length with the mean electronegativity of the exocyclic ligand atoms.[11] Wagner has improved on this by use of the orbital electronegativities of groups of atoms[12] but regards $N_4P_4F_8$ as a special case which does not fit the correlation. In Figure 5 we have added to the seven points plotted by Wagner [in Figure 1(b) of ref. 12] a further five points for the non-geminal derivatives studied in our laboratory and the geminal phosphazenes $N_4P_4F_6Me_2$ and $N_4P_4F_4Me_4$. We suggest, on the basis of this larger body of data, that the correlation can include $N_4P_4F_8$ but, because of the limited accuracy of the bond lengths, it is difficult to define by a curve. We prefer instead just to indicate the general trend by a broken line.

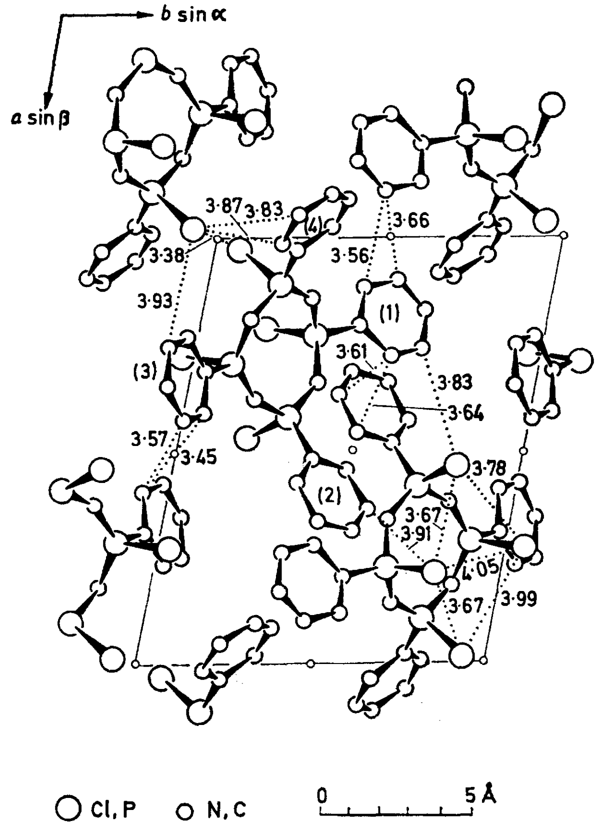

FIGURE 4 Projection of the structure down the *c* axis, showing intramolecular Cl · · · Cl and intermolecular distances (Å). The phenyl group numbers are given in parentheses

Bond lengths and angles for the *cis*- and β-*trans*-isomers of $N_4P_4Cl_4Ph_4$ are compared in Table 10. The data for the β-*trans*-isomer are taken from a preliminary report[4] and their limits of error are rather large. Nevertheless, mean bond lengths and angles in the two isomers appear to be equal despite the difference in conformation. The mean P–Cl length in *cis*-$N_4P_4Cl_4Ph_4$ (2·041 Å) is significantly longer than in the compounds $[NPCl_2]_n$ (n = 3,[13] 4,[14,15] and 5[16]) and is, indeed, longer than the Schomaker–Stevenson estimate for a P–Cl single bond (2·01 Å). The mean P–C bond length (1·783 Å) is on the other hand shorter than in β-*trans*-$N_4P_4(NHMe)_4Ph_4$ (1·808 Å)[1] or the trimeric derivatives $N_3P_3Ph_6$ (1·804 Å),[17] *gem*-$N_3P_3Cl_2Ph_4$ (1·792 Å),[18] and *gem*-$N_3P_3Cl_4Ph_2$ (1·788 Å)[19] in which pairs of phenyl groups are attached to phosphorus. These observations may be rationalised by consideration of the phosphorus environment shown in (IV). If the group R^1 is capable of electron donation (*e.g.* R^1 = NMe_2 or Ph) and the group R^2 of electron withdrawal (*e.g.* R^2 = Cl) resonance structures of the type (V) will be important

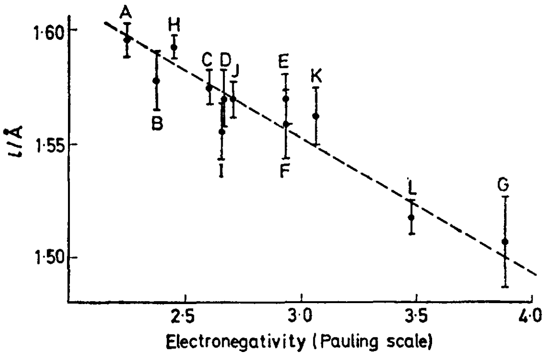

FIGURE 5 Variation of the mean cyclic P–N bond length (l) in tetrameric phosphazenes with the mean orbital electronegativity of the exocyclic groups. Possible error is represented as ±2·5σ. Exocyclic groups in $N_4P_4X_8$ or $N_4P_4X_4Y_4$: A, Me_8 (M. W. Dougill, *J. Chem. Soc.*, 1961, 5471); B, $(NMe_2)_8$ (G. J. Bullen, *J. Chem. Soc.*, 1962, 3193); C, Br_8 (H. Zoer and A. J. Wagner, *Acta Cryst.*, 1972, **B28**, 252); D, $(OMe)_8$ (ref. 11); E, Cl_8 (K form) (ref. 14); F, Cl_8 (T form) (ref. 15); G, F_8 (ref. 21); H, $(NHMe)_4Ph_4$ (ref. 1); I, $Cl_4(NMe_2)_4$ (G. J. Bullen and P. A. Tucker, unpublished work); J, Cl_4Ph_4 (this work); K, F_4Me_4 [W. C. Marsh and J. Trotter, *J. Chem. Soc.* (*A*), 1971, 569]; L, $N_4P_4F_6Me_2$ (ref. 20)

TABLE 10

Comparison of bond lengths (Å) and angles (deg.) in the *cis*- and β-*trans*-isomers of $N_4P_4Cl_4Ph_4$

	cis [a]	β-*trans* [b]
P–N	1·556—1·579	1·55—1·60
P–C	1·776—1·788	1·77, 1·80
P–Cl	2·036—2·045	2·03, 2·04
N–P–N	119·3—122·3	119·5, 121·3
P–N–P	133·1—142·0	132·4, 138·6
Cl–P–C	102·0—103·5	102·2, 105·1

[a] This work. [b] Ref. 4.

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[11] G. B. Ansell and G. J. Bullen, *J. Chem. Soc.* (*A*), 1971, 2498.

[12] A. J. Wagner, *J. Inorg. Nuclear Chem.*, 1971, **33**, 3988.

[13] G. J. Bullen, *J. Chem. Soc.* (*A*), 1971, 1450.

[14] R. Hazekamp, T. Migchelsen, and A. Vos, *Acta Cryst.*, 1962, **15**, 539.

[15] A. J. Wagner and A. Vos, *Acta Cryst.*, 1968, **B24**, 707.

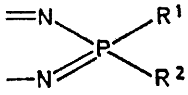
[16] A. W. Schlueter and R. A. Jacobson, *J. Chem. Soc.* (*A*), 1968, 2317.

[17] F. R. Ahmed, P. Singh, and W. H. Barnes, *Acta Cryst.*, 1969, **B25**, 316.

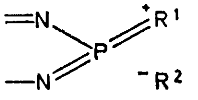
[18] F. R. Ahmed, W. H. Barnes, and N. V. Mani, *Acta Cryst.*, 1967, **21**, 375.

[19] F. R. Ahmed, W. H. Barnes, and N. V. Mani, *Acta Cryst.*, 1965, **19**, 693.

in the overall bonding scheme, leading to shortened P–R^1 and lengthened P–R^2 bonds. The increasing lengths of the P–Cl and P–C bonds in the series $N_3P_3Cl_6$, *gem*-$N_3P_3Cl_4Ph_2$, *gem*-$N_3P_3Cl_2Ph_4$, $N_3P_3Ph_6$ [17] can be accounted for similarly, the effects being transmitted through the nitrogen atoms in the phosphazene ring. With *cis*-$N_4P_4Cl_4Ph_4$ the effects are more pronounced because the electron-donating phenyl and -withdrawing chloro-groups are both attached to the same phosphorus atom. Consequently the P–Cl bonds are longer and the P–C bonds shorter than in these other compounds.



(IV)



(V)

The bond angles are in general similar to those in other phosphazenes. The main interest attaches to the P–N–P angles, whose individual values differ from each other by amounts far greater than their experimental error. Several tetrameric phosphazenes contain P–N–P angles in the range 131—134°. Larger angles, as here, appear characteristic of molecules containing chlorine or fluorine: *T*-$N_4P_4Cl_8$ 138°,[15] β-*trans*-$N_4P_4Cl_4Ph_4$ 139°,[4] $N_4P_4F_6Me_2$ 143·3, 146·7°,[20] $N_4P_4F_8$ 147·2°,[21] and are clearly connected with the approach to planarity in the phosphazene ring.

Orientation of Phenyl Groups.—At phosphorus atoms P(2), P(3), and P(4) the phenyl groups are orientated symmetrically, *i.e.* with their planes perpendicular to the adjoining Cl–P–C plane (Figure 6a). Each chlorine atom is then almost equidistant from the two sides of the neighbouring benzene ring, *e.g.* Cl(2) · · · C(22) 3·70, and Cl(2) · · · C(26) 3·73 Å. These distances are only slightly greater than that expected for a van der Waals separation of chlorine and carbon and it therefore seems reasonable to suggest that the symmetrical placing of the phenyl groups results from equalisation of chlorine–carbon repulsions, particularly as this symmetrical orientation is also found in β-*trans*-$N_4P_4Cl_4$-Ph_4 [22] but not in β-*trans*-$N_4P_4(NHMe)_4Ph_4$. In the latter all the phenyl groups are orientated asymmetrically so that they are eclipsed with one of the nitrogen atoms of the ring (Figure 6b).[1] This difference between the chloro- and methylamino-derivatives could be attributed to the difference in spatial requirements between a chlorine atom and the more asymmetric methylamino-group.

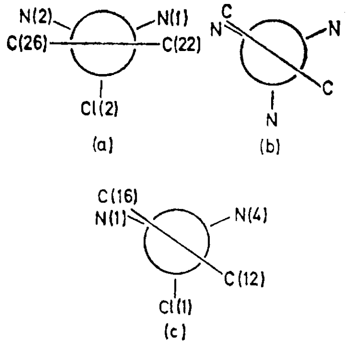


FIGURE 6 Newman projections down carbon–phosphorus bonds: (a) *cis*-$N_4P_4Cl_4Ph_4$ at P(2), (b) β-*trans*-$N_4P_4(NHMe)_4Ph_4$, and (c) *cis*-$N_4P_4Cl_4Ph_4$ at P(1)

The symmetrical placing of phenyl groups in *cis*-$N_4P_4Cl_4Ph_4$ also means that the π system of the group makes the maximum overlap with the phosphorus $3d_{z^2}$ orbital whose axis lies in the Cl–P–C plane (Craig and Paddock co-ordinate system [23]). Although suitable combinations of $3d$ orbitals for overlap can be found whatever the orientation of the phenyl π system, the use of $3d_{z^2}$ for the exocyclic groups is perhaps particularly advantageous because this is the only $3d$ orbital of phosphorus not already involved in π bonding in the phosphazene ring.[23] Since, however, the symmetric orientation is also sterically favoured one cannot say whether π-bonding requirements exert any significant influence on the orientation. The occurrence of asymmetric orientations in β-*trans*-$N_4P_4(NHMe)_4Ph_4$ suggests that they do not, though one must remember that here the presence of an exocyclic nitrogen atom will lessen π interaction between the phenyl group and the phosphorus. A decision between the steric and electronic arguments could more likely be made from a knowledge of the molecular structure of a non-geminal $N_4P_4F_4Ph_4$, since here the electronegative fluorine atoms are also small.

At P(1) the phenyl group is not orientated symmetrically, the Cl–P–C–C torsion angle being 57° (Figure 6c) and the chlorine–carbon contacts unequal: Cl(1) · · · C(12) 3·37, and Cl(1) · · · C(16) 4·08 Å. In this case it seems that intermolecular repulsions affect the situation (see later).

Intermolecular Distances.—Interatomic contacts likely to determine the molecular packing are marked on the projection of the crystal structure shown in Figure 4. The C · · · C and Cl · · · C distances are unexceptional. The Cl . . . Cl distance across a centre of symmetry (3·38 Å), though short, is similar to the shortest intermolecular contacts in solid chlorine (3·34 ± 0·04 Å).[24] Phenyl rings (1) and (2) are very approximately coplanar (see Table 9), so that near the middle of the unit cell van der Waals contact between neighbouring molecules is between pairs of rings [ring (1) in one molecule and ring (2) in the other] which are almost parallel. It seems likely that the twist of phenyl ring (1) about the P–C bond mentioned earlier is forced by the packing together of these rings. It may be that in the high-melting polymorph a rearrangement of the molecules allows a more symmetrical phenyl group orientation at

[20] W. C. Marsh and J. Trotter, *J. Chem. Soc.* (*A*), 1971, 573.

[21] H. McD. McGeachin and F. R. Tromans, *J. Chem. Soc.*, 1961, 4777.

[22] A. H. Burr, personal communication.

[23] D. P. Craig and N. L. Paddock, *J. Chem. Soc.*, 1962, 4118.

[24] R. L. Collin, *Acta Cryst.*, 1952, **5**, 431.

P(1) and possibly also a more symmetrical phosphazene ring (with symmetry closer to *mm*2).

Molecular Oscillations.—The thermal vibrations of the chlorine atoms show considerable anisotropy with the minor axes of the thermal ellipsoids lying approximately along the P–Cl bonds (Table 7). An attempt to rationalise the phosphorus and chlorine atom vibrations in terms of a rigid-body oscillation was not successful. On the other hand such an analysis of the individual phenyl groups did give sensible results although some of the tensor components have large estimated standard deviations (Table 8). The standard deviations were found to be least when the origin of the librational axes was put at or near the phosphorus atom but some may be large because of the difficulty of guaranteeing that the librational axes intersect at the phosphorus atom. As very few of the off-diagonal elements of the tensors are significantly different from zero, the translations and librations can be described satisfactorily in terms of the natural axes of the groups shown in Figure 2.

For the phenyl groups (2), (3), and (4) the order of magnitude $\omega_{11} > \omega_{33} > \omega_{22}$ may be rationalised in terms of the effect of atomic displacements on the bonding. Rotation about axis (1) reduces only the (weak) π overlap between carbon and phosphorus, while rotation about axis (3) reduces σ overlap and rotation about axis (2) reduces both. The larger ω_{11} for phenyl group (1) may reflect a weaker carbon–phosphorus π overlap connected with the twist of the phenyl ring about the P–C bond.

The calculation of the $\boldsymbol{\omega}$ tensors for the phenyl rings allows correction of the bond lengths in the P–Ph groups for librational effects. However as the corrections to the atomic co-ordinates prove to be comparable to or less than the estimated standard deviations of the co-ordinates, they have been disregarded.

In conclusion we suggest that the cyclic and exocyclic bond lengths in tetrameric phosphazenes are considerably influenced by the extent of electron withdrawal from or donation to phosphorus by the exocyclic groups, that in certain instances the orientation of one exocyclic group is determined largely by the nature of the second group attached to the same phosphorus atom, and that with bulky exocyclic groups the conformation of the phosphazene ring is determined primarily by intramolecular steric factors but in a crystal intermolecular forces may sometimes be the over-riding factor.

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