Acta Cryst. (1986). B42, 462-472

Structural Investigations of Phosphorus–Nitrogen Compounds. 2.* The Structures of $N_3P_3(NH_2)_2Cl_4$, $N_3P_3(NPPh_3)(NH_2)Cl_4$ and $N_3P_3(NPPh_3)Cl_5$ and a Comparison with Other Phosphazenylphosphazenes. The Relationship of Conformation in the Solid State to Conformation in Solution†

By John K. Fincham,‡ Michael B. Hursthouse,§ Harold G. Parkes,‡
Leylâ S. Shaw (née Gözen)‡§ and Robert A. Shaw‡||

*Department of Chemistry, Birkbeck College (University of London), Malet Street,
London WC1E 7HX and Department of Chemistry, Queen Mary College (University of London),
Mile End Road, London E1 4NS, England*

(*Received* 15 *November* 1985; *accepted* 21 *February* 1986)

Abstract

The crystal structures of 2,2-diamino-4,4,6,6-tetrachlorocyclotriphosphazatriene, $N_3P_3(NH_2)_2Cl_4$ (1), and of 2-amino-2-triphenylphosphazenyl-4,4,6,6-tetrachlorocyclotriphosphazatriene, $N_3P_3(NPPh_3)(NH_2)Cl_4$ (2), have been determined and that of 2-triphenylphosphazenyl-2,4,4,6,6-pentachlorocyclotriphosphazatriene, $N_3P_3(NPPh_3)Cl_5$ (3), has been redetermined by X-ray analysis. [Crystal data: (1): monoclinic, $P2_1/c$, $a=8{\cdot}328$ (1), $b=23{\cdot}001$ (3), $c=11{\cdot}405$ (1) Å, $\beta=104{\cdot}71$ (1)°, $V=2113{\cdot}1$ (5) Å^3, $Z=8$; (2): monoclinic, $P2_1/n$, $a=13{\cdot}879$ (4), $b=13{\cdot}671$ (3), $c=13{\cdot}623$ (3) Å, $\beta=103{\cdot}93$ (2)°, $V=2508{\cdot}8$ (1·1) Å^3, $Z=4$; (3): monoclinic, $P2_1/n$, $a=19{\cdot}602$ (2), $b=8{\cdot}769$ (1), $c=14{\cdot}627$ (1) A, $\beta=98{\cdot}57$ (1)°, $V=2486{\cdot}2$ (4) Å^3, $Z=4$.] Full-matrix least-squares refinements led to R values of 3·6% for (1) and 3·9% for (2) and (3) using 2899, 3029 and 3238 unique reflections, respectively [$F_o > 3\sigma(F_o)$]. For compound (1) the presence of geminal NH_2 groups is established. Compound (2) is the first triphenylphosphazenyl derivative with a type III conformation, and compound (3) has a type I conformation. Structures are compared with those of related compounds. The relationship between conformation in the solid state as determined by dihedreal angles of the phosphazenyl substituent relative to the ring and the preferred conformations in solution as measured by $^4J(PP)$ spin-spin coupling constants is discussed.

Introduction

We report here the structures of the geminal bisamino derivative (1), and of two triphenylphosphazenyl derivatives (2) and (3) of cyclotriphosphazatriene.

A preliminary report has been made at the 4th International Symposium on Inorganic Ring Systems (Fincham, Hursthouse, Keat, Parkes, Rycroft, Shaw & Shaw, 1985).

Their preparation [(1) (Feistel & Moeller, 1973), (2) and (3) (Keat, Miller & Shaw, 1967)], their basicity in nitrobenzene solution (Nabi, Biddlestone & Shaw, 1975) and some of their NMR spectroscopic properties (Biddlestone, Keat, Rose, Rycroft & Shaw, 1976; Biddlestone, Keat, Parkes, Rose, Rycroft & Shaw, 1985; Fincham, Hursthouse, Keat, Parkes, Rycroft, Shaw & Shaw, 1985) have been reported elsewhere.

Our basicity studies (Nabi, Biddlestone & Shaw, 1975) led us to postulate two different sites of protonation for phosphazenylcyclophosphazenes, the conventional one on a ring nitrogen (Fig. 1*a*) ($X=Cl$) and a novel one on the nitrogen atom (Fig. 1*b*) ($X=NR_2$, Ph, $NPPh_3$) of the phosphazenyl substituent. We linked this different protonation behaviour to the conformation of the N-P part of the phosphazenyl substituent relative to the local NPN segment of the phosphazene ring, to which it was attached. Examination of the crystal structures of numerous phosphazenes carrying NMe_2, Ph, $NPPh_3$ and related substituents, in all of which the linking atom, C or N, is sp^2-hybridized or nearly so, led us to postulate conformational types I, II and III, classified by the relative orientation of the p_z orbital to the reference plane (Shaw, 1975, 1976, 1979) (Fig. 2). In type I these are parallel, in type II at right angles and in type III intermediate between these two.

Experimental

Crystals were grown as follows: (1) from toluene/methylene chloride (3:1), m.p. 435-436 K;

---

* Part 1: Contractor, Hursthouse, Shaw, Shaw & Yılmaz (1985).

† Presented in part at the 4th International Symposium on Inorganic Ring Systems, Université Paris-Sud, France, September 1985. [The chemical nomenclature used throughout this paper conforms to that established by Shaw, Fitzsimmons & Smith (1962) and differs from current IUPAC recommendations.]

‡ Birkbeck College.

§ Queen Mary College.

|| Author for correspondence.

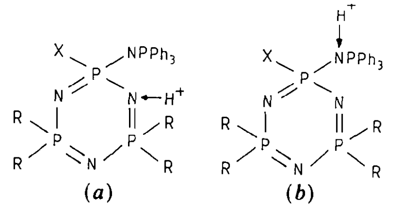
0108-7681/86/050462-11$01.50

Table 1. *Additional crystal data and experimental information*

	(1)	(2)	(3)
M_r	308·80	569·08	588·51
D_m (g cm^{-3})	1·937	1·504	1·576
D_x (g cm^{-3})	1·941	1·506	1·572
μ(Mo $K\alpha$) (cm^{-1})	14·16	6·73	7·79
Crystal size (mm)	0·40 × 0·40 × 0·30	0·37 × 0·37 × 0·13	0·40 × 0·35 × 0·125
Total unique data	3687	4398	4375
Observed [$F_o > 3\sigma(F_o)$]	2899	3029	3238
Max. Δ/σ in final least-squares cycle	0·09	0·06	0·02
Least-squares parameters	249	348	340
$(\Delta\rho)_{\max}$ (e Å^{-3})	≤0·8	≤0·5	≤0·8
Max. h, k, l	±6, 18, 9	16, 16, ±16	±23, 10, 17

(2) from benzene/methylene chloride (2:1), m.p. 445–447 K; (3) from benzene/chloroform (1:1), m.p. 486 K. All the crystals were colourless and rod-like. Densities were measured by the flotation method. Unit-cell parameters were determined by least-squares refinement of the setting angles for 25 reflections [16° < θ(Mo $K\alpha$) < 17°] automatically centred on an Enraf–Nonius CAD-4 diffractometer. Intensity data were recorded on the same instrument at 275 (2) K for (1) (sealed in a thin-walled capillary tube) and at 295 (2) K for (2) and (3), using Mo $K\alpha$ radiation ($\lambda = 0·71069$ Å; graphite-monochromatized), in the $\omega/2\theta$ scan mode, in a manner previously described in detail (Hursthouse, Jones, Malik & Wilkinson, 1979), with a θ range of 1·5 to 25°, and the scan width $(0·8 + 0·35 \tan\theta)°$. Data for all the compounds were corrected for Lorentz and polarization effects. The weight used for the three compounds is $[\sigma^2(F_o) + 0·005F_o^2]^{-1}$. An empirical absorption correction (North, Phillips & Mathews, 1968) was applied to (1); calculated transmission coefficients from 0·82 to 0·99. Additional crystal data and experimental information are given in Table 1.

^{31}P NMR spectra were recorded on a Bruker WH-400 NMR spectrometer operating at 162 MHz. The solvent in each case was acetone-d_6. Chemical shifts were referenced to external 85% H_3PO_4.



(a) (b)

Fig. 1. (a) *Endo* and (b) *exo* protonation of triphenylphosphazenylcyclotriphosphazatrienes.

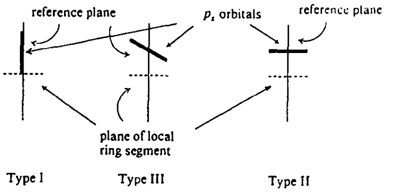


Fig. 2. Conformational types I, II and III. Orientations of p_z orbital and reference plane.

Table 2. *Fractional atomic coordinates* (×10^4) *and equivalent isotropic thermal parameters* (Å^2 × 10^3) *for compound* (1)

$$U_{eq} = \tfrac{1}{3}\sum_i U_{ii}.$$

	x	y	z	U_{eq}
Cl(141)	−1985 (1)	7004 (1)	2070 (1)	47
Cl(142)	−666 (1)	7951 (1)	3980 (1)	50
Cl(161)	5001 (1)	7446 (1)	3742 (1)	53
Cl(162)	3521 (2)	6612 (1)	1630 (1)	62
P(12)	1913 (1)	6363 (1)	4943 (1)	26
P(14)	21 (1)	7192 (1)	3404 (1)	30
P(16)	3077 (1)	6911 (1)	3156 (1)	32
N(11)	3130 (4)	6390 (1)	4049 (3)	34
N(13)	231 (4)	6738 (1)	4435 (3)	36
N(15)	1489 (4)	7311 (2)	2797 (3)	44
N(121)	1598 (4)	5671 (1)	5106 (3)	33
N(122)	2719 (6)	6597 (2)	6291 (4)	45
Cl(241)	4046 (1)	3921 (1)	522 (1)	45
Cl(242)	5083 (1)	5115 (1)	1703 (1)	48
Cl(262)	−1551 (1)	4283 (1)	1202 (1)	45
Cl(261)	−461 (1)	5541 (1)	1932 (1)	43
P(22)	2733 (1)	4177 (1)	3899 (1)	27
P(24)	3501 (1)	4470 (1)	1731 (1)	30
P(26)	459 (1)	4736 (1)	2006 (1)	29
N(21)	1079 (4)	4564 (1)	3384 (3)	32
N(23)	3939 (4)	4170 (2)	2999 (3)	39
N(25)	1688 (4)	4702 (2)	1174 (3)	43
N(221)	3528 (5)	4435 (2)	5238 (3)	48
N(222)	2411 (5)	3500 (2)	4141 (4)	40
H(121)	1356 (56)	5511 (20)	4415 (47)	49 (14)
H(122)	1081 48)	5632 (17)	5615 (39)	32 (11)
H(123)	2293 (56)	6821 (20)	6497 (41)	35 (14)
H(124)	3614 (57)	6441 (20)	6638 (39)	41 (13)
H(221)	4327 (54)	4287 (19)	5622 (39)	37 (13)
H(222)	3482 (52)	4756 (21)	5404 (40)	38 (14)
H(223)	2416 (60)	3294 (22)	3623 (48)	54 (17)
H(224)	1899 (51)	3401 (18)	4640 (40)	35 (12)

Structure determination and refinement

The structures of (1) and (2) were solved by direct methods using *SHELX*84 (Sheldrick, 1984).

(1) 20 non-hydrogen atoms out of 24 of the asymmetric unit (two independent molecules) were located from the best E map. Several cycles of refinement followed by a difference synthesis revealed the remaining non-hydrogen atoms. The refinement converged to $R = 4·1\%$. H atoms were located from Fourier difference maps and refined freely, giving a final R value of 3·6% and $wR = 3·8\%$ (H atoms isotropic, others anisotropic). The positional and equivalent isotropic thermal parameters and bond lengths and angles are listed in Tables 2 and 3, and Fig. 3 shows the averaged bond lengths and angles.*

---

* Throughout this paper the mean values and their standard errors have been calculated using the formulae given by Domenicano, Vaciago & Coulson (1975).

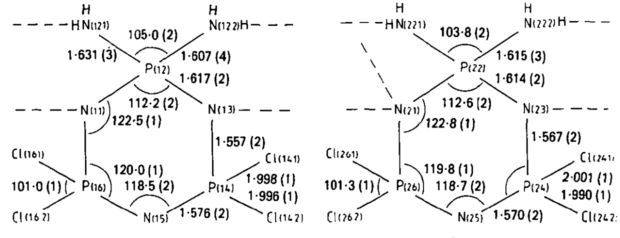


Fig. 3. Averaged molecular dimensions (Å, °) of (1).

Table 3. *Bond lengths* (Å) *and angles* (°) *for compound* (1)

P(14)–Cl(142)	1·999 (1)	P(14)–Cl(141)	2·000 (1)
P(16)–Cl(161)	1·996 (1)	P(16)–Cl(162)	1·992 (2)
N(11)–P(12)	1·611 (3)	N(13)–P(12)	1·622 (3)
N(121)–P(12)	1·631 (3)	N(122)–P(12)	1·607 (4)
N(13)–P(14)	1·550 (3)	N(15)–P(14)	1·574 (3)
N(11)–P(16)	1·565 (3)	N(15)–P(16)	1·578 (3)
P(24)–Cl(241)	2.005 (1)	P(24)–Cl(242)	1·991 (1)
P(26)–Cl(262)	1·988 (1)	P(26)–Cl(261)	1·997 (1)
N(21)–P(22)	1·620 (3)	N(23)–P(22)	1·608 (3)
N(221)–P(22)	1·616 (4)	N(222)–P(22)	1·614 (4)
N(23)–P(24)	1·559 (3)	N(25)–P(24)	1·575 (3)
N(21)–P(26)	1·574 (3)	N(25)–P(26)	1·565 (3)
H(121)–N(121)	0·847 (51)	H(122)–N(121)	0·810 (41)
H(123)–N(122)	0·698 (45)	H(124)–N(122)	0·832 (46)
H(221)–N(221)	0·776 (44)	H(222)–N(221)	0·765 (46)
H(223)–N(222)	0·758 (53)	H(224)–N(222)	0·826 (45)
N(13)–P(12)–N(11)	112·2 (2)	N(121)–P(12)–N(11)	104·8 (2)
N(121)–P(12)–N(13)	114·2 (2)	N(122)–P(12)–N(11)	114·5 (2)
N(122)–P(12)–N(13)	106·0 (2)	N(122)–P(12)–N(121)	105·0 (2)
Cl(141)–P(14)–Cl(142)	100·7 (1)	N(13)–P(14)–Cl(142)	109·0 (1)
N(13)–P(14)–Cl(141)	110·0 (1)	N(15)–P(14)–Cl(142)	108·2 (1)
N(15)–P(14)–Cl(141)	107·2 (1)	N(15)–P(14)–N(13)	120·1 (2)
Cl(162)–P(16)–Cl(161)	101·2 (1)	N(11)–P(16)–Cl(161)	111·5 (1)
N(11)–P(16)–Cl(162)	108·9 (1)	N(15)–P(16)–Cl(161)	106·0 (1)
N(15)–P(16)–Cl(162)	107·7 (1)	N(15)–P(16)–N(11)	119·9 (2)
P(16)–N(11)–P(12)	121·6 (2)	P(14)–N(13)–P(12)	123·4 (2)
P(16)–N(15)–P(14)	118·5 (2)		
N(23)–P(22)–N(21)	112·6 (2)	N(221)–P(22)–N(21)	104·3 (2)
N(221)–P(22)–N(23)	115·7 (2)	N(222)–P(22)–N(21)	115·4 (2)
N(222)–P(22)–N(23)	105·0 (2)	N(222)–P(22)–N(221)	103·8 (2)
Cl(242)–P(24)–Cl(241)	101·1 (1)	N(23)–P(24)–Cl(241)	108·6 (1)
N(23)–P(24)–Cl(242)	110·1 (1)	N(25)–P(24)–Cl(241)	107·3 (1)
N(25)–P(24)–Cl(242)	108·1 (2)	N(25)–P(24)–N(23)	119·9 (2)
Cl(261)–P(26)–Cl(262)	101·4 (1)	N(21)–P(26)–Cl(262)	110·7 (1)
N(21)–P(26)–Cl(261)	107·5 (1)	N(25)–P(26)–Cl(262)	107·3 (2)
N(25)–P(26)–Cl(261)	108·9 (2)	N(25)–P(26)–N(21)	119·6 (2)
P(26)–N(21)–P(22)	122·2 (2)	P(24)–N(23)–P(22)	123·4 (2)
P(26)–N(25)–P(24)	118·7 (2)		
H(121)–N(121)–P(12)	108·9 (32)	H(122)–N(121)–P(12)	108·6 (29)
H(122)–N(121)–H(121)	125·1 (41)	H(123)–N(122)–P(12)	116·4 (38)
H(124)–N(122)–P(12)	114·5 (30)	H(124)–N(122)–H(123)	129·0 (50)
H(221)–N(221)–P(22)	117·4 (32)	H(222)–N(221)–P(22)	123·7 (34)
H(222)–N(221)–H(221)	111·9 (46)	H(223)–N(222)–P(22)	115·9 (40)
H(224)–N(222)–P(22)	121·5 (30)	H(224)–N(222)–H(223)	118·0 (50)

(2) 11 non-hydrogen atoms out of 31 of the asymmetric unit were located from the best E map. Several cycles of refinement followed by a difference synthesis revealed all 20 remaining non-hydrogen atoms. The refinement converged to $R = 6{\cdot}0\%$. H-atoms were located from Fourier difference maps and refined freely giving a final R value of 3·9% and $wR = 4{\cdot}0\%$ (H atoms isotropic, others anisotropic). The positional and equivalent isotropic thermal parameters and bond lengths and angles are listed in Tables 4 and 5, and Fig. 4 shows the bond lengths and angles.

Table 4. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\text{Å}^2 \times 10^3$) *for compound* (2)

$$U_{eq} = \tfrac{1}{3}\sum_i U_{ii}.$$

	x	y	z	U_{eq}
Cl(41)	5186 (1)	1388 (1)	4586 (1)	87
Cl(42)	3630 (1)	2396 (1)	2922 (1)	100
Cl(61)	4073 (1)	−1801 (1)	2767 (1)	78
Cl(62)	2662 (1)	−583 (1)	1157 (1)	74
P(2)	5517 (1)	628 (1)	1625 (1)	41
P(4)	4557 (1)	1247 (1)	3113 (1)	51
P(6)	3996 (1)	−462 (1)	2148 (1)	48
N(1)	4828 (2)	−347 (2)	1578 (2)	52
N(3)	5339 (2)	1383 (2)	2484 (2)	52
N(5)	3897 (2)	293 (2)	2984 (2)	71
P(21)	7403 (1)	−497 (1)	2095 (1)	46
N(22)	5221 (3)	1243 (3)	573 (3)	55
N(21)	6641 (2)	352 (2)	1761 (2)	52
C(11)	8567 (3)	−59 (3)	1893 (3)	55
C(12)	9448 (4)	−552 (4)	2218 (5)	107
C(13)	10314 (4)	−158 (5)	2061 (7)	134
C(14)	10303 (4)	673 (4)	1524 (6)	117
C(15)	9434 (4)	1163 (4)	1173 (4)	84
C(16)	8570 (3)	807 (3)	1374 (3)	59
C(21)	7092 (3)	−1615 (3)	1378 (3)	51
C(22)	7447 (4)	−1793 (4)	527 (3)	75
C(23)	7106 (5)	−2627 (5)	−52 (4)	98
C(24)	6433 (5)	−3234 (4)	193 (5)	94
C(25)	6090 (4)	−3062 (3)	1038 (5)	81
C(26)	6418 (3)	−2259 (3)	1622 (4)	63
C(31)	7587 (3)	−839 (3)	3401 (3)	48
C(32)	7201 (3)	−236 (3)	4035 (3)	56
C(33)	7332 (3)	−471 (4)	5048 (3)	71
C(34)	7866 (4)	−1295 (4)	5425 (4)	75
C(35)	8239 (4)	−1899 (4)	4810 (3)	74
C(36)	8103 (3)	−1678 (3)	3800 (3)	63
H(221)	4682 (34)	1573 (32)	506 (32)	78 (14)
H(222)	5335 (30)	1007 (31)	113 (30)	67 (14)
H(12)	9477 (32)	−1083 (32)	2578 (31)	77 (14)
H(13)	10826 (40)	−488 (37)	2331 (39)	106 (19)
H(14)	10907 (41)	889 (39)	1387 (41)	122 (18)
H(15)	9345 (40)	1685 (39)	766 (41)	115 (20)
H(16)	7998 (30)	1145 (28)	1151 (28)	63 (12)
H(22)	7916 (30)	−1318 (29)	328 (29)	70 (13)
H(23)	7345 (36)	−2651 (37)	−603 (38)	97 (17)
H(24)	6235 (36)	−3880 (43)	−165 (37)	113 (17)
H(25)	5612 (33)	−3518 (33)	1163 (33)	90 (16)
H(26)	6221 (26)	−2176 (27)	2134 (26)	51 (11)
H(32)	6869 (25)	348 (23)	3775 (24)	43 (9)
H(33)	7058 (28)	−52 (29)	5484 (31)	72 (12)
H(34)	7998 (35)	−1412 (33)	6037 (35)	87 (15)
H(35)	8615 (31)	−2447 (32)	5076 (31)	81 (14)
H(36)	8334 (28)	−2096 (27)	3354 (29)	69 (12)

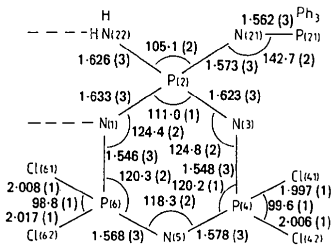


Fig. 4. Molecular dimensions (Å, °) of (2).

(3) The coordinates of all the non-hydrogen atoms were taken from Babu, Manohar & Cameron (1979). Several cycles of least-squares calculation (all non-hydrogen atoms anisotropic) gave an R value of 5·0%. All 15 H atoms were located from a difference map and refined (isotropic) freely giving a final R value of 3·9% and $wR = 3{\cdot}9\%$. The positional and equivalent isotropic thermal parameters and bond lengths and angles are listed in Tables 6 and 7, and Fig. 5 shows the averaged molecular dimensions.

The calculations were performed on a DEC VAX11/750 computer using the *SHELX*76 (Sheldrick, 1976) and *SHELX*84 program systems. Neutral-atom scattering factors were taken from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965) for the non-H and H atoms respectively.*

---

* Lists of anisotropic thermal parameters and structure factors, and data related to least-squares-plane and dihedral-angle calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42804 (118 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 5. *Bond lengths* (Å) *and angles* (°) *for compound* (2)

N(1)–P(2)	1·633 (3)	N(3)–P(2)	1·623 (3)
N(22)–P(2)	1·626 (3)	N(21)–P(2)	1·573 (3)
Cl(41)–P(4)	1·997 (1)	Cl(42)–P(4)	2·006 (1)
N(3)–P(4)	1·548 (3)	N(5)–P(4)	1·578 (3)
Cl(61)–P(6)	2·008 (1)	Cl(62)–P(6)	2·017 (1)
N(1)–P(6)	1·546 (3)	N(5)–P(6)	1·568 (3)
N(21)–P(21)	1·562 (3)	C(11)–P(21)	1·805 (3)
C(21)–P(21)	1·809 (4)	C(31)–P(21)	1·798 (3)
H(221)–N(22)	0·860 (45)	H(222)–N(22)	0·754 (41)
H(12)–C(12)	0·873 (41)	H(13)–C(13)	0·847 (51)
H(14)–C(14)	0·949 (54)	H(15)–C(15)	0·895 (51)
H(16)–C(16)	0·905 (39)	H(22)–C(22)	1·002 (40)
H(23)–C(23)	0·891 (48)	H(24)–C(24)	1·013 (56)
H(25)–C(25)	0·956 (44)	H(26)–C(26)	0·816 (33)
H(32)–C(32)	0·947 (32)	H(33)–C(33)	0·966 (40)
H(34)–C(34)	0·825 (45)	H(35)–C(35)	0·935 (43)
H(36)–C(36)	0·945 (39)		
N(3)–P(2)–N(1)	111·0 (1)	N(22)–P(2)–N(1)	111·5 (2)
N(22)–P(2)–N(3)	104·9 (2)	N(21)–P(2)–N(1)	111·3 (1)
N(21)–P(2)–N(3)	112·7 (2)	N(21)–P(2)–N(22)	105·1 (2)
Cl(42)–P(4)–Cl(41)	99·6 (1)	N(3)–P(4)–Cl(41)	110·4 (1)
N(3)–P(4)–Cl(42)	110·3 (1)	N(5)–P(4)–Cl(41)	107·1 (1)
N(5)–P(4)–Cl(42)	107·2 (1)	N(5)–P(4)–N(3)	120·2 (1)
Cl(62)–P(6)–Cl(61)	98·8 (1)	N(1)–P(6)–Cl(61)	109·4 (1)
N(1)–P(6)–Cl(62)	110·4 (1)	N(5)–P(6)–Cl(61)	107·5 (1)
N(5)–P(6)–Cl(62)	108·3 (1)	N(5)–P(6)–N(1)	120·3 (2)
P(6)–N(1)–P(2)	124·4 (2)	P(4)–N(3)–P(2)	124·8 (2)
P(6)–N(5)–P(4)	118·3 (2)	P(21)–N(21)–P(2)	142·7 (2)
C(11)–P(21)–N(21)	106·1 (2)	C(21)–P(21)–N(21)	114·5 (2)
C(21)–P(21)–C(11)	107·7 (2)	C(31)–P(21)–N(21)	114·0 (2)
C(31)–P(21)–C(11)	108·5 (2)	C(31)–P(21)–C(21)	105·9 (2)
C(12)–C(11)–P(21)	123·3 (3)	C(26)–C(21)–P(21)	119·7 (3)
C(16)–C(11)–P(21)	118·5 (3)	C(22)–C(21)–P(21)	120·9 (3)
C(32)–C(31)–P(21)	118·5 (3)	C(36)–C(31)–P(21)	122·5 (3)
H(221)–N(22)–P(2)	113·2 (28)	H(222)–N(22)–P(2)	116·9 (32)
H(222)–N(22)–H(221)	119·1 (43)	H(12)–C(12)–C(11)	120·5 (30)

Discussion of structures

Generally, in a given cyclophosphazene structure, *e.g.* $N_3P_3R_6$, $N_4P_4R_8$, *etc.*, the ring P–N bonds are of equal length provided all the substitutuents, *R*, are the same, whilst if the substituents have different electron-withdrawing power the ring P–N bonds may show significant variations in bond lengths (*cf.* Contractor, Hursthouse, Shaw, Shaw & Yılmaz, 1985).

The $NPPh_3$ substituent is a strong electron-releasing group relative to Cl (our standard in phosphazene chemistry). This is demonstrated by basicity studies (Nabi, Biddlestone & Shaw, 1975) and chemically by the alcoholysis of the PCl_2 groups (undoubtedly an S_N2 type of reaction), which is retarded in the series (1) < (2) < (4) as we replace NH_2 groups by $NPPh_3$ groups (Fincham, Hursthouse, Parkes, Shaw & Shaw, 1985*b*).

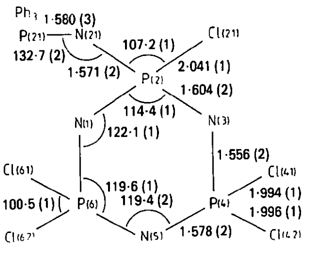


Fig. 5. Averaged molecular dimensions (Å, °) of (3).

Table 6. *Fractional atomic coordinates* ($\times10^4$) *and equivalent isotropic thermal parameters* ($Å^2\times10^3$) *for compound* (3)

$$U_{eq}=\tfrac{1}{3}\sum_i U_{ii}.$$

	x	y	z	U_{eq}
Cl(21)	−1015 (1)	413 (1)	1565 (1)	68
Cl(41)	−1197 (1)	282 (1)	4616 (1)	72
Cl(42)	−107 (1)	2757 (2)	5183 (1)	75
Cl(61)	−2373 (1)	4093 (1)	2304 (1)	70
Cl(62)	−1240 (1)	6362 (1)	3061 (1)	62
P(2)	−450 (1)	2092 (1)	2288 (1)	34
P(4)	−747 (1)	2040 (1)	4080 (1)	39
P(6)	−1379 (1)	4123 (1)	2855 (1)	39
N(1)	−914 (1)	3599 (3)	2139 (2)	46
N(3)	−310 (1)	1493 (3)	3338 (2)	41
N(5)	−1316 (2)	3303 (4)	3824 (2)	56
N(21)	223 (1)	2314 (3)	1838 (2)	40
P(21)	932 (1)	1428 (1)	1946 (1)	37
C(11)	1467 (2)	1825 (4)	3031 (2)	47
C(12)	1311 (2)	3075 (5)	3549 (3)	60
C(13)	1721 (3)	3463 (7)	4358 (4)	87
C(14)	2295 (4)	2617 (10)	4665 (4)	106
C(15)	2459 (3)	1378 (10)	4168 (5)	96
C(16)	2042 (2)	957 (6)	3350 (4)	72
C(21)	1375 (2)	2075 (3)	1024 (2)	42
C(22)	2063 (2)	1753 (5)	1021 (4)	75
C(23)	2376 (3)	2157 (6)	259 (4)	87
C(24)	2006 (2)	2899 (5)	−471 (3)	68
C(25)	1328 (2)	3256 (5)	−471 (3)	62
C(26)	1015 (2)	2823 (4)	285 (2)	47
C(31)	855 (2)	−605 (3)	1838 (2)	42
C(32)	872 (2)	−1307 (4)	983 (3)	53
C(33)	765 (2)	−2865 (4)	894 (3)	62
C(34)	618 (2)	−3698 (5)	1630 (4)	72
C(35)	585 (3)	−3020 (5)	2456 (4)	77
C(36)	705 (2)	−1469 (4)	2573 (3)	62
H(12)	936 (17)	3657 (39)	3303 (22)	39 (9)
H(13)	1638 (35)	4372 (82)	4803 (48)	155 (26)
H(14)	2610 (34)	2771 (77)	5176 (43)	141 (25)
H(15)	2817 (28)	848 (61)	4352 (37)	96 (18)
H(16)	2147 (23)	66 (51)	2956 (31)	75 (14)
H(22)	2347 (22)	1275 (54)	1547 (31)	86 (14)
H(23)	2788 (23)	1939 (55)	241 (31)	83 (15)
H(24)	2225 (23)	3219 (55)	−984 (32)	90 (14)
H(25)	1027 (24)	3886 (55)	−1003 (33)	93 (15)
H(26)	594 (18)	2914 (41)	230 (24)	48 (11)
H(32)	963 (19)	−697 (43)	529 (26)	54 (10)
H(33)	832 (19)	−3294 (45)	315 (26)	59 (11)
H(34)	466 (24)	−4809 (55)	1543 (31)	86 (14)
H(35)	504 (20)	−3584 (51)	2955 (29)	71 (12)
H(36)	697 (20)	−1007 (46)	3186 (29)	68 (12)

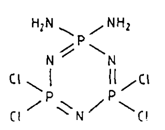
This is further borne out by ^{35}Cl NQR spectroscopy, compound (3) having a very low mean frequency for the chlorine nuclei of the PCl_2 groups (27·60 MHz) (Dalgleish, Keat, Porte, Tong, Hasan & Shaw, 1975).

Some uncertainty remained about the structure of $N_3P_3(NH_2)_2Cl_4$ (1), as some workers had assigned to it a non-geminal structure (Becke-Goehring, John & Fluck, 1959), others a geminal one (Ford, Dickson & Bezman, 1964; Keat & Shaw, 1966; McBee, Okuhara & Morton, 1966; Lehr, 1967; Feistel & Moeller, 1967, 1973). Whilst the bulk of the evidence favoured the geminal arrangement of the amino groups, the reported rearrangement of this compound, (1), to give both geminal, as well as non-geminal alcoholysis products, $N_3P_3(NH_2)_2(OR)_4$ (Fincham, Hursthouse, Parkes, Shaw & Shaw, 1985*a*, *b*) made a structure determination desirable. As basicity studies (Feakins, Nabi, Shaw & Watson, 1969) have indicated a similar electron-releasing power for NH_2 and $NHBu^t$ groups, we include also

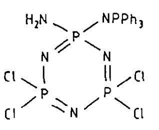
Table 7. *Bond lengths* (Å) *and angles* (°) *for compound* (3)

N(1)–P(2)	1·600 (3)	N(3)–P(2)	1·607 (3)
Cl(21)–P(2)	2·041 (1)	N(21)–P(2)	1·571 (2)
N(3)–P(4)	1·555 (3)	N(5)–P(4)	1·578 (3)
Cl(41)–P(4)	1·994 (1)	Cl(42)–P(4)	1·992 (1)
N(1)–P(6)	1·557 (3)	N(5)–P(6)	1·578 (3)
Cl(61)–P(6)	1·994 (1)	Cl(62)–P(6)	1·999 (1)
P(21)–N(21)	1·580 (3)	C(11)–P(21)	1·801 (4)
C(21)–P(21)	1·801 (3)	C(31)–P(21)	1·794 (3)
H(12)–C(12)	0·923 (33)	H(13)–C(13)	1·057 (73)
H(14)–C(14)	0·905 (62)	H(15)–C(15)	0·852 (54)
H(16)–C(16)	1·010 (44)	H(22)–C(22)	0·975 (45)
H(23)–C(23)	0·834 (43)	H(24)–C(24)	0·960 (46)
H(25)–C(25)	1·060 (48)	H(26)–C(26)	0·821 (33)
H(32)–C(32)	0·891 (39)	H(33)–C(33)	0·954 (38)
H(34)–C(34)	1·021 (47)	H(35)–C(35)	0·915 (43)
H(36)–C(36)	0·985 (41)		
N(3)–P(2)–N(1)	114·4 (1)	Cl(21)–P(2)–N(1)	105·7 (1)
Cl(21)–P(2)–N(3)	105·1 (1)	N(21)–P(2)–N(1)	109·6 (1)
N(21)–P(2)–N(3)	114·0 (1)	N(21)–P(2)–Cl(21)	107·2 (1)
N(5)–P(4)–N(3)	119·6 (1)	Cl(41)–P(4)–N(3)	111·0 (1)
Cl(41)–P(4)–N(5)	107·2 (1)	Cl(42)–P(4)–N(3)	108·5 (1)
Cl(42)–P(4)–N(5)	108·0 (1)	Cl(42)–P(4)–Cl(41)	100·8 (1)
N(5)–P(6)–N(1)	119·6 (1)	Cl(61)–P(6)–N(1)	111·0 (1)
Cl(61)–P(6)–N(5)	107·3 (1)	Cl(62)–P(6)–N(1)	108·1 (1)
Cl(62)–P(6)–N(5)	108·8 (1)	Cl(62)–P(6)–Cl(61)	100·2 (1)
P(6)–N(1)–P(2)	122·0 (2)	P(4)–N(3)–P(2)	122·2 (2)
P(6)–N(5)–P(4)	119·4 (2)	P(21)–N(21)–P(2)	132·7 (2)
C(11)–P(21)–N(21)	112·4 (2)	C(21)–P(21)–N(21)	106·6 (1)
C(21)–P(21)–C(11)	108·5 (2)	C(31)–P(21)–N(21)	114·7 (1)
C(31)–P(21)–C(11)	107·5 (2)	C(31)–P(21)–C(21)	106·9 (1)
C(22)–C(21)–P(21)	121·2 (3)	C(26)–C(21)–P(21)	119·6 (2)
C(32)–C(31)–P(21)	120·2 (2)	C(36)–C(31)–P(21)	120·1 (3)
C(12)–C(11)–P(21)	119·0 (3)	C(16)–C(11)–P(21)	122·0 (3)

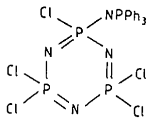
geminal $N_3P_3(NHBu^t)_2Cl_4$ (6) (Begley, Sowerby & Bamgboye, 1979) in our analysis and compare the molecular dimensions of (1) and (6) with those of $N_3P_3(NPPh_3)(NH_2)Cl_4$ (2) (Fig. 4) and $N_3P_3(NPPh_3)_2Cl_4$ (4).



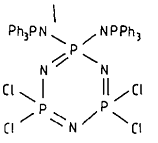
(1)



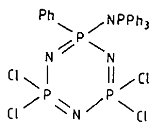
(2)



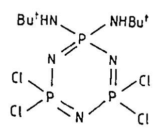
(3)



(4)



(5)



(6)

Compound (1) is involved in a complex hydrogen-bonding pattern, which differs somewhat for the two independent molecules (see below). Both molecules are somewhat nonplanar; in molecule (1) P(12) is 0·13 Å above and N(11) 0.14 Å below the plane of the N_3P_3 ring; whilst in molecule (2), P(22) and N(23) are 0·10 and 0·14 Å respectively above the plane of the N_3P_3 ring. The bond length P(12)–N(122) is significantly shorter at 1·607 (4) Å than P(12)–N(121) at 1·631 (3) Å. The bond lengths P(22)–N(222) and P(22)–N(221) are of equal length at 1·614 (4) and 1·616 (4) Å respectively. All the exocyclic P–N bonds are on the short side (see below) for geminal diamino substituents. The exocyclic bond angle N(121)–P(12)–N(122) at 105·0 (2)° is just significantly larger than the corresponding angle N(221)–P(22)–N(222) at 103·8 (2)°, probably because the N atoms of the former participate more in hydrogen bonding. The average of the ring P–N bonds adjacent to the two amino substituents is 1·615 (2) Å, whilst that of their bonding partners in the same P–N–P segments is 1·562 (2) Å, *i.e.* Δ(P–N) = 0·053 (3) Å. This type of bond variation was first observed by Mani, Ahmed & Barnes (1965) and has been previously discussed (Contractor, Hursthouse, Shaw, Shaw & Yılmaz, 1985). The mean P–Cl bond length is 1·996 (1) Å. The mean endocyclic bond angle at P(2), 112·4 (1)°, is small and indicates the electron-releasing power of the two NH_2 groups, whilst the angle at N(3), 123·4 (1)°, is correspondingly large. The angle at N(1), 121·9 (1)°, is smaller than the one at N(3) because N(1) deviates from the plane of the N_3P_3 ring.

Fig. 6 shows the molecular dimensions (averaged over the two molecules) of $N_3P_3(NHBu^t)_2Cl_4$ (6) (renumbered to conform to our scheme). The ring P–N bonds adjacent to the two $NHBu^t$ substituents P(2)–N(1) and P(2)–N(3) are longer than their partners N(1)–P(6) and N(3)–P(4) in their respective P–N–P segments. The exocyclic P–N bonds are slightly different, with the one which acts as a proton donor in the hydrogen bond being shorter than the other.

In (2), the N_3P_3 ring is approximately planar [maximum deviation from the plane 0·054 (3) Å]. The bonds P(2)–N(1) and P(2)–N(3) are very much longer than their partners N(1)–P(6) and N(3)–P(4) in their respective P–N–P segments. The bond P(2)–N(1) is slightly longer than P(2)–N(3), and this may be related to the fact that N(1) is involved in an intermolecular hydrogen bond, N(22)–H(222)···N(1) (see below). The remaining P–N ring bonds, P(6)–N(5) and P(4)–N(5), are unremarkable.

The exocyclic P–N bonds P(21)–N(21) and N(21)–P(2) of the $NPPh_3$ substituent are short and have typical phosphazene character. The former is marginally shorter than the latter (see below). The remaining P–N bond, P(2)–N(22), is longer than the corresponding bond N(21)–P(2) from the $NPPh_3$ substituent. In general, when there is a geminal pair of

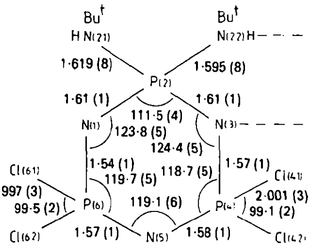


Fig. 6. Molecular dimensions (Å, °) (averaged over the two molecules) of (6).

nitrogenous substituents, exocyclic P–N bonds (with the exception of phosphazenyl substituents) tend to have phosphazane character (1·63–1·65 Å). Thus the mean exocyclic P–N bond lengths in $N_3P_3(NMe_2)_6$ (Rettig & Trotter, 1973), geminal $N_3P_3(NHPr^i)_4Cl_2$ (Polder & Wagner, 1976), and geminal $N_3P_3(NMe_2)_3Cl_3$ (Ahmed & Pollard, 1972*a*) are 1·652 (4), 1·642 (2) and 1·641 (3) Å respectively. By contrast, the mean exocyclic P–N bond lengths in PCl(N*RR*′) moieties are shorter. In *cis*-$N_3P_3(NMe_2)_2Cl_4$, *trans*-$N_3P_3(NMe_2)_3Cl_3$ (Ahmed & Fortier, 1980), geminal $N_3P_3(NMe_2)_3Cl_3$ (Ahmed & Pollard, 1972*a*), *cis*-$N_3P_3(NMe_2)_3Cl_3$ (Ahmed & Pollard, 1972*b*), and *trans*-$N_3P_3(NMe_2)_2Cl_4$ (Ahmed & Gabe, 1975), they are 1·617 (4), 1·615 (4), 1·628 (4), 1·610 (4) and 1·623 (2) Å respectively. However, in geminal $N_3P_3(NH_2)_2F_4$ (Pohl & Krebs, 1976) (effect of F substituents) and geminal $N_3P_3(NHPr^i)_4Cl_2.HCl$ (Mani & Wagner, 1971) (effect of protonation) the mean exocyclic P–N bond lengths are only 1·602 (4) and 1·609 (3) Å respectively. The exocyclic bond N(22)–P(2) in (2) at 1·626 (3) Å is rather on the short side, in view of the adjacent $NPPh_3$. Thus the shortening is very probably due to the hydrogen bonding of H(222). In geminal $N_3P_3(NHBu^t)_2Cl_4$ (6) (Begley, Sowerby & Bamgboye, 1979) only one $NHBu^t$ substituent is involved in hydrogen bonding, mean bond length 1·597 (9) Å, whilst the other has a mean bond length of 1·620 (8) Å.

The endocyclic bond angles in (2) show the expected variations (Shaw, 1985) for strongly electron-releasing substituents at P(2). Thus the angle N(1)–P(2)–N(3) at 111·0 (1)° is small, and the adjacent ones, P(6)–N(1)–P(2) and P(4)–N(3)–P(2), are large, 124·4 (2) and 124·8 (2)° respectively. The related exocyclic angle, P(2)–N(21)–P(21), at 142·7 (2)° is large, indeed larger than the corresponding angles in most of the related structures (131·7–137·6°) (Babu, Manohar & Shaw, 1981; Krishnaiah, Ramamurthy, Ramabrahmam & Manohar, 1981; Manohar, 1985). N(22) is slightly pyramidal, being 0.18 (3) Å out of the plane of the three atoms to which it is bonded.* N(22) is bent 3.3 (3)° out of the plane which bisects the angle N(1)–P(2)–N(3) [N(22)–P(2)–N(3) = 104·9 (2)°, N(22)–P(2)–N(1) = 111·5 (2)°], possibly due to hydrogen bonding.

The P–Cl bonds within each PCl_2 group are significantly different from each other; the mean P–Cl bond length at P(4) is shorter [2·002 (1) Å] than that at P(6) [2·013 (1) Å], and the Cl–P–Cl bond angle at P(4) is correspondingly larger [99·6 (1)°] than the one at P(6)[98·8 (1)°]. The plane Cl(41)–P(4)–Cl(42) does not exactly bisect the angle N(3)–P(4)–N(5), but is bent by 3·3 (1)° away from N(3) and towards N(5), undoubtedly reflecting the shorter N(3)–P(4) bond length and the higher electron content of this bond. The corresponding bending of the Cl(61)–P(6)–Cl(62) plane away from N(1) is only 2·0 (1)°, possibly reflecting some siphoning off of electron density from N(1) by the hydrogen bond to H(222).

Fig. 7 gives the averaged molecular dimensions of $N_3P_3(NPPh_3)_2Cl_4$ (4) (renumbered to conform to our scheme).

The following points are worth noting. The electron release by the two $NPPh_3$ substituents in (4) is somewhat greater than that by $NPPh_3$ and NH_2 in (2) and much greater than that in (1) (two NH_2 groups) and (6) (two $NHBu^t$ groups). This is confirmed by the somewhat longer P–N ring bonds from P(2) and the smaller N(1)–P(2)–N(3) bond angle in (4) than in (1), (2) and (6). The adjacent angles, P(6)–N(1)–P(2) and P(4)–N(3)–P(2), in (4) are anomalously small (119·0°) owing to the bending of P(2) by 0·53 Å out of the plane of P(6)–N(1)–N(3)–P(4). If we compare the difference, Δ(P–N) (Contractor, Hursthouse, Shaw, Shaw & Yılmaz, 1985) between *RR*′P–N [$R = R' = NH_2$ (1), $NHBu^t$ (6); $R = NH_2$, $R' = NPPh_3$ (2); $R = R' = NPPh_3$ (4)] and N–PCl_2 of the same P–N–P segment, we note an increase in the Δ(P–N) values in the non-hydrogen-bonded segments, 0·07 (1) Å (6), 0·075 (4) Å (2) and 0·094 (7) Å (4), and in the hydrogen-bonded segments, 0·04 (1) Å (6), 0·053 (3) Å (1), 0·087 (4) Å (2), in line with the increasing electron release from the substituents *R* and *R*′. The mean P–Cl bond lengths (attached to the non-hydrogen-bonded segments) increase in the same order 1·997 (3) < 2·002 (1) < 2·021 (2) Å for compounds (6), (2) and (4) respectively, again demonstrating the increasing electron release. We would expect the mean ^{35}Cl NQR frequency to increase in this order (Keat, Porte, Tong & Shaw, 1972; Dalgleish, Keat, Porte, Tong, Hasan & Shaw, 1975; Dalgleish, Keat, Porte & Shaw, 1977; Hursthouse, Porte, Shaw & Shaw, 1985).

The exocyclic P–N bonds adjacent to the ring [P(2)–N(22), P(2)–N(21), mean 1·600 (5) Å] in compound (4) are significantly longer than the other [N(22)–P(22), N(21)–P(21), mean 1·557 (5) Å], a trend also noticed for compound (2), thus demonstrating the weakness of the conventional valence-bond picture P–N$=$$PPh_3$. The mean exocyclic P–N–P

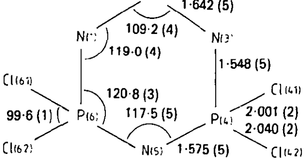


Fig. 7. Averaged molecular dimensions (Å, °) of (4).

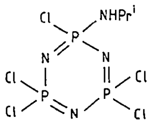
---

* Errors are calculated throughout the text using the formula given by Mosteller, Rourke & Thomas (1970).

bond angle in (4) at 134·3° is considerably smaller than that in (2) [142·7 (2)°].

We now discuss the structure of $N_3P_3(NPPh_3)Cl_5$ (3). This was previously determined by a photographic technique (Babu, Manohar & Cameron, 1979). Trends were observed in the endocyclic P–N bond lengths, but as the authors pointed out, the high e.s.d.'s did not permit firm conclusions. We have therefore redetermined the structure of (3). The averaged molecular dimensions are given in Fig. 5.

Whilst we can compare the bond-length and bond-angle data of (3) with those of (2) and (4), we must take cognizance of the fact that in (3) we have a strong electron donor, $NPPh_3$, as well as a strong electron acceptor, Cl, attached to the same P atom. Hence part of the electron density of the $NPPh_3$ substituent will be transferred to the N_3P_3 ring and part to the P–Cl bond. It is therefore instructive to compare (3) also with $N_3P_3(NHPr^i)Cl_5$ (7) (Bullen, 1982), *i.e.* to observe the changes accompanying the replacement of an NH*R* by an $NPPh_3$ substituent, as in the series (1), (6), (2) and (4).



(7)

In compound (3) the N_3P_3 ring has a slight twist-boat conformation; P(2) and N(5) lie 0·22 (3) and 0·07 (3) Å respectively below the mean plane of the other four ring atoms. As suggested above, a good deal of the electron supply of the $NPPh_3$ substituent has been transferred to the adjacent P–Cl bond, P(2)–Cl(21), which at 2·041 (1) Å is on the long side. In keeping with this, the ^{35}Cl NQR frequency is low (25·12 MHz) (Biddlestone & Shaw, 1973). The remaining P–Cl bonds, arising from PCl_2 units, are much shorter [mean 1·995 (1) Å] than the non-geminal P–Cl bond above, and have correspondingly higher ^{35}Cl NQR frequencies (mean 27·63 MHz).

These geminal P–Cl bonds are markedly shorter than the corresponding bonds in (2) and (4) (see above). As much electron supply has been diverted into the P(2)–Cl(21) bond, not surprisingly the effect of the $NPPh_3$ substituent on the ring is less marked for (3) than for (2) and (4). Even so the ring P–N bonds adjacent to the substituent are long [mean 1·604 (2) Å], and the neighbouring ones short [mean 1·556 (2) Å]. The endocyclic bond angle N(1)–P(2)–N(3) [114·4 (1)°] is smaller and the adjacent one [mean 122·2 (2)°] is larger than corresponding ones in (2) and (4), documenting the lesser electron supply to the N_3P_3 ring. The exocyclic P–N bonds are short and approximately equivalent, with possibly a slight trend in the opposite direction to that in (2). The exocyclic angle P(2)–N(21)–P(21) at 132·7 (2)° is considerably smaller than the corresponding angle in (2) 142·7 (2)°, but similar to those in (4). The Cl–P–Cl bond angles are larger in (3) than in either (2) or (4) in keeping with the shorter P–Cl bond lengths in the first mentioned. Whilst Cl(62) and Cl(42) bisect the angles N(1)–P(6)–N(5) and N(5)–P(4)–N(3) respectively, both Cl(61) and Cl(41) are displaced towards N(5). Cl(21) bisects the angle N(1)–P(2)–N(3), but N(21) is nearer to N(1) [N(21)–P(2)–N(1) 109·6 (1)°, N(21)–P(2)–N(3) 114·0 (1)°].

The structure of $N_3P_3(NHPr^i)Cl_5$ (7) has been reported by Bullen (1982), who has given bond-length data from the least-squares refinement, as well as corrected for molecular oscillations. We have taken the former set of values for comparison, as none of the other crystals discussed in this paper have had their data corrected for molecular oscillations. The data for compound (7) (renumbered to conform to our scheme) are given in Fig. 8.

The picture which emerges is similar to that for (3). Some of the electron density of the nitrogen substituent is transferred to the N_3P_3 ring, some of it to the adjacent P–Cl bond. In both cases the degree of transfer is less for (7) than for (3). Thus the P–Cl bond adjacent to the substituent is 2·041 (1) Å in (3) and only 2·010 (4) Å in (7). The mean of the ring P–N bonds adjacent the $NPPh_3$ substituent in (3) is 1·604 (2) Å, whilst for (7), on the non-hydrogen-bonded side, it is only 1·585 (6) Å. Δ(P–N) is 0·048 (3) Å for (3), whilst for (7) it is only 0·041 (8) Å on the non-hydrogen bonded side, and 0·030 (8) Å on the side involved in hydrogen bonding.

The mean P–Cl bond length of the PCl_2 groups for (3) is 1·995 (1) Å, whilst for (7) the means are 1·975 (3) and 1·992 (2) Å on the non-hydrogen-bonded and hydrogen-bonded sides respectively. The ^{35}Cl NQR spectrum of compound (7) shows higher frequencies for the chlorine nucleus of the non-geminal P–Cl bond (25·85 MHz) and for the nuclei of the geminal PCl_2 groups (mean 28·22 MHz) than the corresponding frequencies for (3).

Thus crystallographic and ^{35}Cl NQR spectroscopic data both demonstrate the greater electron release of the $NPPh_3$ substituent compound to that of an NH*R* (*R* = alkyl) substituent, in line with the observations on compounds (1), (6), (2) and (4) and in keeping

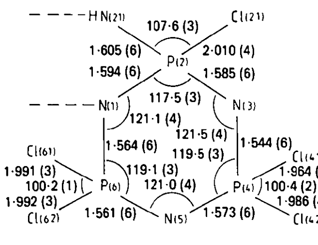


Fig. 8. Molecular dimensions (Å, °) of (7).

Table 8. *Selected structural data illustrating the electron-releasing capacities of the nitrogenous substituent(s) in* (1)–(4), (6) *and* (7)

	(4)	(2)		(1)	(6)		(3)	(7)	
Hydrogen bonded	−	−	+	+	−	+	−	−	+
P(2)–N(1, 3) (Å)	1·642 (5)	1·623 (3)	1·633 (3)	1·615 (2)	1·61 (1)	1·61 (1)	1·604 (2)	1·585 (6)	1·594 (6)
P(4, 6)–N(1, 3) (Å)	1·548 (5)	1·548 (3)	1·546 (3)	1·562 (2)	1·54 (1)	1·57 (1)	1·556 (2)	1·544 (6)	1·564 (6)
Δ(P–N) (Å)	0·094 (7)	0·075 (4)	0·087 (4)	0·053 (3)	0·07 (1)	0·04 (1)	0·048 (3)	0·041 (8)	0·030 (8)
N(1)–P(2)–N(3) (°)	109·2 (4)	111·0 (1)		112·4 (1)	111·5 (4)		114·4 (1)	117·5 (3)	
P–Cl [mean of PCl_2 group(s)] (Å)	2·021 (2)	2·002 (1)	2·013 (1)	1·996 (1)	1·997 (3)	2·001 (3)	1·995 (1)	1·975 (3)	1·992 (2)

with basicity measurements in non-aqueous media (Nabi, Biddlestone & Shaw, 1975).

Needless to say, the effects are greater when a pair of nitrogenous substituents reside on the same phosphorus. The relevant structural data indicating electron transfer are summarized in Table 8 for the six compounds discussed.

It can be seen from Table 8 that the electron transfer to the N_3P_3 ring, both in the non-hydrogen-bonded and in the hydrogen-bonded segments, decreases in the order (4) > (2) > (1) ≃ (6) > (3) > (7).

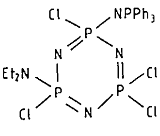
Conformation

Conformation types I, II and III have been described above in terms of the orientations of the p_z orbital to the reference plane. This relates to the possible pathways for the transfer of electrons, but is not accurately defined crystallographically. We therefore define these types for NPR_3 substituents in terms of the dihedral angles P–N–P–*X* (Fig. 9).

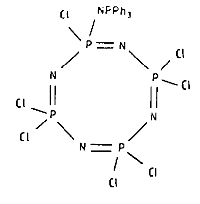
Thus type I corresponds to dihedral angles of ±90°, type II to 0 or 180° and type III to ±45 or ±135°.

Compound (3) with a dihedral angle of −81·6° (e.s.d.'s ~3° for all) is a good approximation to type I, $N_3P_3(NPPh_3)PhCl_4$ (5) (Biddlestone, Bullen, Dann & Shaw, 1974) with an angle of −178·0° to type II, and compound (2) with an angle of −139·2° to type III. Compound (4), also type II, has dihedral angles of 6·9 and −176·8°.

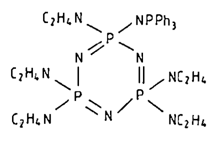
For more precise definition of the conformations of phosphazenyl cyclophosphazenes, we need to introduce the concept of *syn* and *anti* structures, depending on whether the P atom of the phosphazenyl substituent is in a *syn* or *anti* relationship to a specified group or groups. This is best shown by reference to Fig. 10, which shows simplified diagrams (Davies, 1983) of all crystallographically examined $NPPh_3$ derivatives of cyclophosphazenes; for clarity we have omitted all H atoms, as well as the C atoms of the phenyl groups [except for C(21) in compound (5)] and we have renumbered the atoms of the compounds to fit our general scheme. Thus $N_3P_3(NPPh_3)Cl_5$ (3) (dihedral angle −81·6°) has conformation type I *syn* to Cl(42). Non-geminal *trans*-$N_3P_3(NPPh_3)(NEt_2)Cl_4$ (8) (Chandrasekhar, Ramabrahmam & Manohar, 1985) (dihedral angle 64·7°) is type I/III *syn* to Cl(61) and thus pointing towards the $PCl(NEt_2)$ rather than the PCl_2 moiety. $N_4P_4(NPPh_3)Cl_7$ (9) (Babu & Manohar, 1979) (dihedral angle −57·9°) is type I/III *anti* to Cl(81) [or alternatively type I/III *syn* to Cl(21)]. $N_3P_3(NPPh_3)PhCl_4$ (5) (dihedral angle −178·0°) is type II with P(21) *syn* to Cl(42)/Cl(62), whilst $N_3P_3(NPPh_3)(NC_2H_4)_5$ (10) (Kumara Swamy, Poojary, Krishnamurthy & Manohar, 1984) (dihedral angle 15·6°) is type II *anti* to N(61)/N(41). $N_3P_3(NPPh_3)_2Cl_4$ (4) has both type II *syn* and *anti* conformations. The $NPPh_3$ substituent P(22) (dihedral angle 6·9°) is *anti* to Cl(62)/Cl(42) whilst the other $NPPh_3$ group, P(21) (dihedral angle −176·8°) is syn to Cl(61)/Cl(41). $N_3P_3(NPPh_3)(NH_2)Cl_4$ (2) (dihedral angle −139·2°) is type III *syn* to Cl(61). Finally, geminal $N_3P_3(NPPh_3)(NEt_2)Cl_4$ (11) (Babu, Manohar & Shaw, 1981) (dihedral angle 153·8°) is type II/III *syn* to Cl(62).



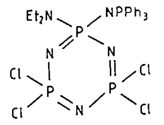
(8)



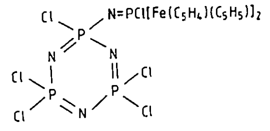
(9)



(10)



(11)



(12)

$^4J(PP)$ spin–spin coupling constants in solution

Concomitant with our basicity, NQR spectroscopic and X-ray crystallographic studies on triphenylphosphazenylcyclophosphazenes, we have carried out ^{31}P NMR spectroscopic studies in solution (Biddlestone,

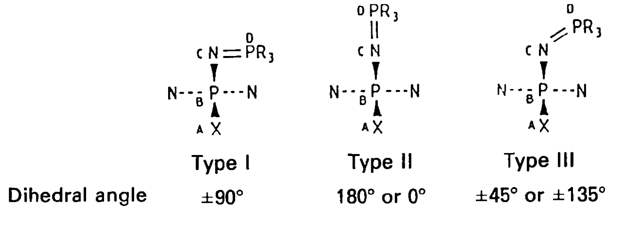


Fig. 9. Conformational types I, II and III and their dihedral angles.

Keat, Rose, Rycroft & Shaw, 1976; Biddlestone, Keat, Parkes, Rose, Rycroft & Shaw, 1985). We noted that, whenever a molecule had a $PCl(NPPh_3)$ grouping, the $^4J(PP)$ spin-spin coupling constants were in the range 3·3–5·7 Hz. We related this to type I conformation (or close to it). On the other hand, compounds containing moieties $PX(NPPh_3)$ ($X = NMe_2$, NH_2, NEt_2, NC_5H_{10}, Ph, $NPPh_3$) had zero or small negative $^4J(PP)$ values [*e.g.* −0·4 Hz for compound (5)], which were associated with types II and III conformations. Confidence in the validity of this relationship was increased by predictions of conformational types from $^4J(PP)$ values (Biddlestone, Keat, Rose, Rycroft & Shaw, 1976), which were confirmed by subsequent X-ray crystallographic investigations (Babu, Manohar & Shaw, 1981; Chandrasekhar, Ramabrahmam & Manohar, 1985).

A recent study (Allcock, Lavin, Riding & Whittle, 1984) demonstrates the utility of this relationship. These authors prepared and studied crystallographically the phosphazenyl derivative, $N_3P_3\{NPCl[Fe(C_5H_4)(C_5H_5)]_2\}Cl_5$ (12), where the usual $NPPh_3$ group is replaced by a more complex substituent, $NPCl[Fe(C_5H_4)(C_5H_5)]_2$. The authors did not comment on its conformation, but their ^{31}P NMR data showed a $^4J(PP)$ value of 4 Hz. This suggested a type I conformation. Calculation of the dihedral angle revealed this to be −97·1°, in excellent agreement with this prediction (Shaw, 1985). It is worth noting that the substituents $NPPh_3$ and $NPCl[Fe(C_5H_4)(C_5H_5)]_2$ appear to have similar electron-releasing powers. In compound (3) the adjacent P–Cl bond is 2·041 (1) Å, in compound (12) it is 2·038 (2) Å. The adjacent mean ring P–N bond lengths are 1·607 (3) Å for both compounds (3) and (12). The angles N(1)–P(2)–N(3) (where the substituents reside) are 114·4 (1) and 114·2 (2)° for (3) and (12) respectively, again a measure of a similar electron supply (Shaw, 1985).

Solution conformations

The $^{31}P\{^1H\}$ NMR spectra at 162 MHz of the triphenylphosphazenyl derivatives, (2), (3) and (5), at room temperature in acetone solution are shown in Figs. 11(*a*), 11(*b*) and 11(*d*).

The four-bond coupling can be clearly seen for the phosphorus nucleus of the $N\underline{P}Ph_3$ substituent in compound (3). Attempts to freeze out different conformations by lowering the temperature to 190 K failed to show hindered rotation, but sharpened the $\underline{P}Cl_2$ signals of (3) sufficiently to allow the observation of $^4J(PP)$ coupling constants for the signals of these nuclei as well (Fig. 11*c*). This sharpening of the $\underline{P}Cl_2$

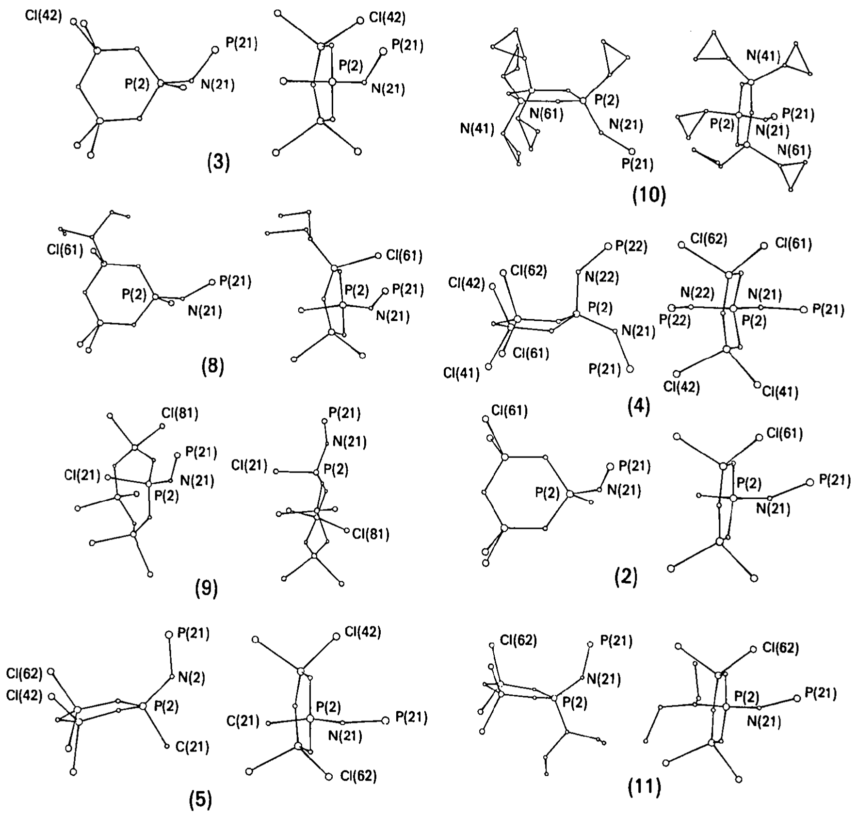


Fig. 10. Simplified molecular diagrams of triphenylphosphazenylcyclophosphazenes emphasizing conformation of $NPPh_3$ group(s). For clarity, all H atoms have been omitted, as have all C atoms of the phenyl groups except C(21) of (5).

signals on lowering the temperature seems to be a general phenomenon (Keat, Shaw & Woods, 1976; Parkes & Shaw, 1985). We can therefore be reasonably confident that the conformational types observed in the solid state are also the preferred conformations in solution.

Hydrogen bonding

We have noted above some effects of hydrogen bonding on bond lengths and angles. We now look in more detail at the aggregates thus formed.

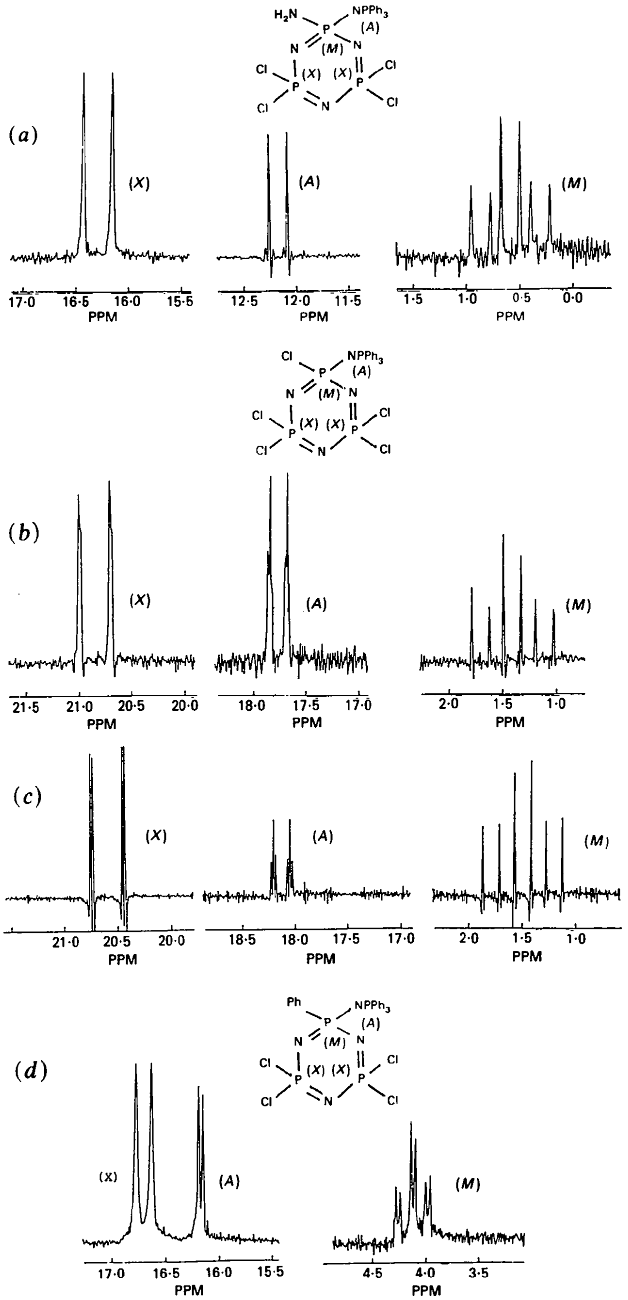


Fig. 11. ^{31}P{^{1}H} NMR spectra in acetone-d_6 at 162 MHz at room temperature of (*a*) (2), (*b*) (3), (*d*) (5) and at 190 K of (*c*) (3).

Compound (1) has two independent molecules. Each of them uses one hydrogen from each amino group for a weak interaction with the *ortho* ring-nitrogen atom of another molecule forming eight-membered hydrogen-bonded rings. Additionally, one further hydrogen of one molecule forms a second weak hydrogen bond to an *ortho* ring-nitrogen atom of the second molecule, the whole giving rise to a macromolecular structure (Fig. 12).

In contrast to the complex hydrogen-bonding behaviour of (1), its fluoro analogue, $N_3P_3(NH_2)_2F_4$ (13), has been reported to exhibit no hydrogen bonding in its crystal (Pohl & Krebs, 1976). The corresponding monoamino derivative, $N_3P_3(NH_2)F_5$ (14), shows, however, a behaviour not unlike (1), with hydrogen bridges forming eight-membered rings (N···N distances 3·16, 3·17 Å), the whole giving rise to a macromolecular structure (Pohl & Krebs, 1975).

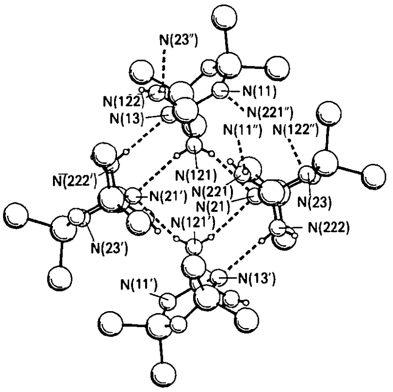


Fig. 12. Hydrogen bonding of (1): N(21)···N(121) 3·178, N(21)···H(121) 2·459 Å, $\angle$N(21)···H(121)–N(121) 143·3°; N(11)···N(221'') 3·296, N(11)···H(221'') 2·579 Å, $\angle$N(11)···H(221'')–N(221'') 154·4°; N(13)···N(222') 3·097, N(13)···(H224') 2·304 Å, $\angle$N(13)···H(224')–N(222') 161·2°; N(21)···N(121') 3·190, N(21)···H(122') 2·406 Å, $\angle$N(21)···H(122')–N(121') 163·0°; N(23)···N(122'') 3·221, N(23)···H(124'') 2·423 Å, $\angle$N(23)···H(124'')–N(122'') 161·0°. Primed and double-primed atoms are related to unprimed atoms by symmetry operations $-x, 1-y, 1-z$ and $1-x, 1-y, 1-z$ respectively.

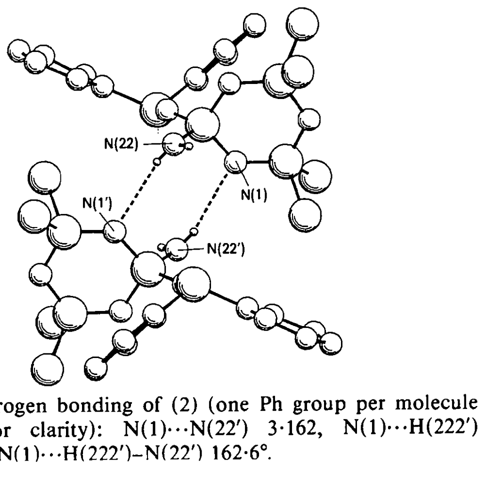
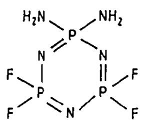
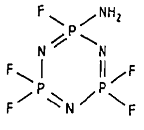


Fig. 13. Hydrogen bonding of (2) (one Ph group per molecule omitted for clarity): N(1)···N(22') 3·162, N(1)···H(222') 2·434 Å, $\angle$N(1)···H(222')–N(22') 162·6°.



(13)



(14)

Compound (2) exhibits a simpler hydrogen-bonding behaviour than (1). It forms dimeric units with H bonds from one of the N–H bonds of the substituent to the ring-nitrogen atom *ortho* to this substituent in the second molecule (N···N 3·162 Å). The result is an eight-membered hydrogen-bonded ring (Fig. 13).

Eight-membered-ring dimeric units analogous to (2) are formed by compounds (6) and (7) and the mean N···N distances in these compounds are 3·15 and 3·20 Å respectively.

JKF is indebted to the ILEA for some day release. MBH and LSS thank the SERC for the provision of crystallographic equipment. RAS is grateful to the Shin Nisso Kako Co. Ltd for gifts of $N_3P_3Cl_6$, and to the University of London Intercollegiate Research Service for some NMR measurements.

References

AHMED, F. R. & FORTIER, S. (1980). *Acta Cryst.* **B36**, 1456-1460.

AHMED, F. R. & GABE, E. J. (1975). *Acta Cryst.* **B31**, 1028-1032.

AHMED, F. R. & POLLARD, D. R. (1972*a*). *Acta Cryst.* **B28**, 513-519.

AHMED, F. R. & POLLARD, D. R. (1972*b*). *Acta Cryst.* **B28**, 3530-3537.

ALLCOCK, H. R., LAVIN, K. D., RIDING, G. H. & WHITTLE, R. R. (1984). *Organometallics*, **3**, 663-669.

BABU, Y. S & MANOHAR, H. (1979). *Acta Cryst.* **B35**, 2363-2366.

BABU, Y. S., MANOHAR, H. & CAMERON, T. S. (1979). *Acta Cryst.* **B35**, 1410-1413.

BABU, Y. S., MANOHAR, H. & SHAW, R. A. (1981). *J. Chem. Soc. Dalton Trans.* pp. 599-603.

BECKE-GOEHRING, M., JOHN, K. & FLUCK, E. (1959). *Z. Anorg. Allg. Chem.* **302**, 103-120.

BEGLEY, M. J., SOWERBY, D. B. & BAMGBOYE, T. T. (1979). *J. Chem. Soc. Dalton Trans.* pp. 1401-1404.

BIDDLESTONE, M., BULLEN, G. J., DANN, P. E. & SHAW, R. A. (1974). *J. Chem. Soc. Chem. Commun.* pp. 56-57.

BIDDLESTONE, M., KEAT, R., PARKES, H. G., ROSE, H., RYCROFT, D. S. & SHAW, R. A. (1985). *Phosphorus Sulfur*, **25**, 25-31.

BIDDLESTONE, M., KEAT, R., ROSE, H., RYCROFT, D. S. & SHAW, R. A. (1976). *Z. Naturforsch. Teil B*, **31**, 1001-1002.

BIDDLESTONE, M. & SHAW, R. A. (1973). *J. Chem. Soc. Dalton Trans.* pp. 2740-2747.

BULLEN, G. J. (1982). *J. Crystallogr. Spectrosc. Res.* **12**, 11-23.

CHANDRASEKHAR, V., RAMABRAHMAM, P. & MANOHAR, H. (1985). Personal communication.

CONTRACTOR, S. R., HURSTHOUSE, M. B., SHAW (NÉE GÖZEN), L. S., SHAW, R. A. & YILMAZ, H. (1985). *Acta Cryst.* **B41**, 122-131.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321-324.

DALGLEISH, W. H., KEAT, R., PORTE, A. L. & SHAW, R. A. (1977). *J. Chem. Soc. Dalton Trans.* pp. 1505-1508.

DALGLEISH, W. H., KEAT, R., PORTE, A. L., TONG, D. A., HASAN, M. & SHAW, R. A. (1975). *J. Chem. Soc. Dalton Trans.* pp. 309-311.

DAVIES, K. (1983). *CHEMGRAPH* Suite. Univ. of Oxford.

DOMENICANO, A., VACIAGO, A. & COULSON, C. A. (1975). *Acta Cryst.* **B31**, 221-234.

FEAKINS, D., NABI, S. N., SHAW, R. A. & WATSON, P. (1969). *J. Chem. Soc. A*, pp. 2468-2475.

FEISTEL, G. R. & MOELLER, T. (1967). *J. Inorg. Nucl. Chem.* **29**, 2731-2737.

FEISTEL, G. R. & MOELLER, T. (1973). *Inorg. Synth.* **14**, 24-27.

FINCHAM, J. K., HURSTHOUSE, M. B., KEAT, R., PARKES, H. G., RYCROFT, D. S., SHAW (NÉE GÖZEN), L. S. & SHAW, R. A. (1985). 4th International Symposium on Inorganic Ring Systems, Univ. Paris-Sud, France. Scientific Abstracts p. 28.

FINCHAM, J. K., HURSTHOUSE, M. B., PARKES, H. G., SHAW (NÉE GÖZEN), L. S. & SHAW, R. A. (1985*a*). *J. Chem. Soc. Chem. Commun.* pp. 252-254.

FINCHAM, J. K., HURSTHOUSE, M. B., PARKES, H. G., SHAW (NÉE GÖZEN), L. S. & SHAW, R. A. (1985*b*). 4th International Symposium on Inorganic Ring Systems, Univ. Paris-Sud, France. Scientific Abstracts p. 31*b*.

FORD, C. T., DICKSON, F. & BEZMAN, I. (1964). *Inorg. Chem.* **3**, 177-182.

HURSTHOUSE, M. B., JONES, R. A., MALIK, K. M. A. & WILKINSON, G. (1979). *J. Am. Chem. Soc.* **101**, 4128-4139.

HURSTHOUSE, M. B., PORTE, A. L., SHAW (NÉE GÖZEN), L. S. & SHAW, R. A. (1985). 4th International Symposium on Inorganic Ring Systems, Univ. Paris-Sud, France. Scientific Abstracts p. 25.

KEAT, R., MILLER, M. C. & SHAW, R. A. (1967). *J. Chem. Soc. A*, pp. 1404-1408.

KEAT, R., PORTE, A. L., TONG, D. A. & SHAW, R. A. (1972). *J. Chem. Soc. Dalton Trans.* pp. 1648-1651.

KEAT, R. & SHAW, R. A. (1966). *J. Chem. Soc. A*, pp. 908-913.

KEAT, R., SHAW, R. A. & WOODS, M. (1976). *J. Chem. Soc. Dalton Trans.* pp. 1582-1589.

KRISHNAIAH, M., RAMAMURTHY, L., RAMABRAHMAM, P. & MANOHAR, H. (1981). *Z. Naturforsch. Teil B*, **36**, 765-767.

KUMARA SWAMY, K. C., POOJARY, D. M., KRISHNAMURTHY, S. S. & MANOHAR, H. (1984). *Z. Naturforsch. Teil B*, **39**, 615-617.

LEHR, W. (1967). *Z. Anorg. Allg. Chem.* **350**, 18-26.

MCBEE, E. T., OKUHARA, K. & MORTON, C. J. (1966). *Inorg. Chem.* **5**, 450-457.

MANI, N. V., AHMED, F. R. & BARNES, W. H. (1965). *Acta Cryst.* **19**, 693-698.

MANI, N. V. & WAGNER, A. J. (1971). *Acta Cryst.* **B27**, 51-58.

MANOHAR, H. (1985). Personal communication.

MOSTELLER, F., ROURKE, R. E. K. & THOMAS, J. B. JR (1970). *Probability with Statistical Applications*, p. 343. Reading, Massachusetts: Addison-Wesley.

NABI, S. N., BIDDLESTONE, M. & SHAW, R. A. (1975). *J. Chem. Soc. Dalton Trans.* pp. 2634-2638.

NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* **A24**, 351-359.

PARKES, H. G. & SHAW, R. A. (1985). Unpublished results.

POHL, S. & KREBS, B. (1975). *Chem. Ber.* **108**, 2934-2940.

POHL, S. & KREBS, B. (1976). *Chem. Ber.* **109**, 2622-2627.

POLDER, W. & WAGNER, A. J. (1976). *Cryst. Struct. Commun.* **5**, 253-257.

RETTIG, S. J. & TROTTER, J. (1973). *Can. J. Chem.* **51**, 1295-1302.

SHAW, R. A. (1975). *Pure Appl. Chem.* **44**, 317-341.

SHAW, R. A. (1976). *Z. Naturforsch. Teil B*, **31**, 641-667.

SHAW, R. A. (1979). *Phosphorus Sulfur*, **5**, 363-369.

SHAW, R. A. (1985). 4th International Symposium on Inorganic Ring Systems, Univ. Paris-Sud, France. Scientific Abstracts p. 11.

SHAW, R. A., FITZSIMMONS, B. W. & SMITH, B. C. (1962).*Chem. Rev.* **62**, 247-281.

SHELDRICK, G. M. (1976). *SHELX*76. A program for automatic solution of crystal structures. Univ. of Cambridge.

SHELDRICK, G. M. (1984). *SHELX*84. Personal communication.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175-3187.