Crystal Structure of 1, *cis*-3, *cis*-5-Trichloro-1,3,5,7,7-pentakis(dimethylamino)cyclotetraphosphazene

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Crystals of the title compound are orthorhombic with $a = 32.484(8)$, $b = 12.816(3)$, and $c = 11.783(3)$ Å, space group *Pbca*, $Z = 8$. The atomic positions have been determined by Patterson and Fourier methods from *X*-ray data and refined by least squares to *R* 0.038 (3 363 reflexions). The ring bond lengths vary in pairs, 1.586, 1.545, 1.570, and 1.564 Å, in a manner explicable in terms of different degrees of ring π bonding involving the nitrogen lone pairs. Exocyclic P–N bond lengths are all equal (1.633 Å) and continue the trend established in similar systems. The irregular ring conformation is best described as a mixed crown–saddle, the former being associated with the three non-geminally substituted atoms [P(1)—(3)] while the latter contains the P(1), P(3), P(4) segment. Details of the ring conformation can be related to substituent orientation.

CRYSTAL structure determinations reported for a number of cyclotetraphosphazenes, carrying two different types of substituent, have been carried out in order to assess the influence of substituent type and orientation on the lengths of the phosphorus–nitrogen ring bonds and on the conformation adopted by the eight-membered P–N ring system. From data for some non-geminally tetrasubstituted compounds, it has been possible to suggest [1] that there is a strong interrelationship between the orientation of the substituents (*i.e.* whether they occupy relative *cis*- or *trans*-positions), and the observed ring conformation. From this point of view the most extensively examined system is that where the substituents are chlorine atoms and dimethylamino-groups. Data are available for the 1, *trans*-5-bis(dimethylamino)-compound, $P_4N_4Cl_6(NMe_2)_2$,[2] the 1,1,3,5,5,7-hexakis(dimethylamino)-compound, $P_4N_4Cl_2(NMe_2)_6$,[3] and the isomeric 1, *cis*-3, *trans*-5, *trans*-7-[4] and 1, *trans*-3,

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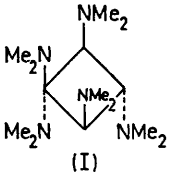
[1] M. J. Begley, D. Millington, T. J. King, and D. B. Sowerby, *J.C.S. Dalton*, 1974, 1162.

[2] G. J. Bullen and P. E. Dann, *J.C.S. Dalton*, 1973, 1453.

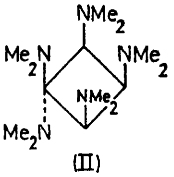
[3] G. J. Bullen, P. E. Dann, V. B. Desai, R. A. Shaw, B. C. Smith, and M. Woods. *Phosphorus*, 1973, **3**, 67.

[4] G. J. Bullen and P. A. Tucker, *J.C.S. Dalton*, 1972, 2437.

cis-5, *trans*-7-tetrachlorotetrakis(dimethylamino)-derivatives.[5] Information on the members of this series is now extended by the results reported here for a penta-substituted compound $P_4N_4Cl_3(NMe_2)_5$ [(IX) in ref. 6]. N.m.r. data (220 MHz) showed the presence of one geminal $P(NMe_2)_2$ grouping, and the positions of the other two doublets were interpreted as indicating structure (I) rather than (II). As this was a tentative assignment, a more rigorous method for assigning the structure was desirable. Further, since the compound is unsymmetrically substituted and represents a new type of substituent arrangement, it was of interest to investigate the ring conformation by *X*-ray methods.



(I)



(II)

EXPERIMENTAL

The compound (m.p. 155°) was prepared as described previously from $P_4N_4Cl_8$ and anydrous dimethylamine in ether solution.[6] Suitable crystals were grown from light petroleum.

Crystal Data.—$C_{10}H_{30}Cl_3N_9P_4$, $M = 506.4$, Orthorhombic, $a = 32.484(8)$, $b = 12.816(3)$, $c = 11.783(3)$ Å, $U = 4\,905.4$ Å^3, $Z = 8$, $D_c = 1.37$ g ml^{-1}, $F(000) = 2\,112$. Space group *Pbca* from systematic absences: $0kl$ when $k = 2n + 1$, $hk0$ when $h = 2n + 1$, and $h0l$ when $l = 2n + 1$. Mo-K_α radiation, $\lambda = 0.710\,7$ Å; μ(Mo-K_α) = 4.2 cm^{-1}.

Unit cell parameters and space group were determined initially from oscillation and Weissenberg photographs and later refined on a Hilger and Watts four-circle diffractometer by use of Mo-K_α radiation. Of 4 313 reflexions measured in the range of $0° < \theta < 25°$, 3 363 having net counts $>3\sigma$ were considered observed. Intensities were corrected for Lorentz and polarization effects but not for absorption or secondary extinction. Data reduction and crystallographic calculations were by use of the '*X*-Ray '70' programs;[7a] atomic scattering factors were taken from ref. 7*b*. The structure was solved initially by use of a file containing 2 177 reflexions with net counts >230 on the University of Nottingham ICL 1906 A computer. Subsequent calculations with the complete data used the University of Manchester CDC 7 600.

A three-dimensional Patterson synthesis gave possible positions for the four phosphorus atoms from the positions of four vectors within 3—5 Å of the origin. A Fourier synthesis phased on these atoms then revealed the positions of the three chlorine atoms and after two cycles of least-squares refinement a second Fourier gave positions for all the other non-hydrogen atoms. Four cycles of block-diagonal least-squares refinement with isotropic temperature factors reduced R to 0.095 and two cycles with anisotropic temperature factors gave R 0.051. All the hydrogen atoms were located from a difference Fourier map. Refinement was then continued by use of the complete file of observed reflexions. A weighting scheme of the type: $w = 1/[1 + \{(F_o - 25)/20\}^2]$ was introduced and after three cycles of refinement, including all the hydrogen atoms with isotropic temperature factors, final convergence was achieved at R 0.038.

Observed and calculated structure factors and anisotropic thermal parameters for non-hydrogen atoms are listed in Supplementary Publication No. SUP 21530 (10 pp. 1 microfiche).* Atomic co-ordinates for non-

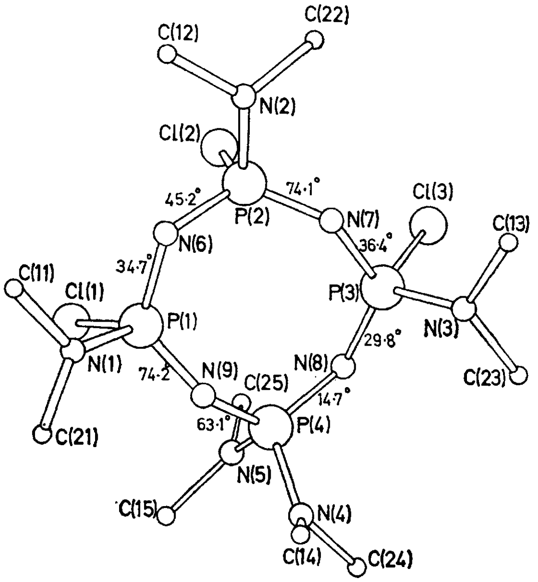


FIGURE 1 The numbering of atoms and dihedral angles of the ring bonds

TABLE 1

Atomic co-ordinates (× 10^5) with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
P(1)	18 287(2)	9 076(5)	20 786(6)
P(2)	13 435(2)	−5 089(5)	33 790(6)
P(3)	6 313(2)	−513(5)	19 728(6)
P(4)	11 612(2)	11 082(5)	4 204(6)
Cl(1)	21 795(3)	−608(6)	10 348(8)
Cl(2)	14 692(3)	−18 921(6)	25 415(8)
Cl(3)	4 122(2)	−15 292(6)	15 854(8)
N(1)	21 561(7)	17 880(18)	25 082(22)
N(2)	13 532(7)	−8 032(19)	47 237(19)
N(3)	2 163(7)	5 970(20)	23 337(20)
N(4)	9 869(8)	22 204(19)	−491(22)
N(5)	13 448(8)	5 412(21)	−7 190(21)
N(6)	17 178(6)	2 298(18)	31 482(19)
N(7)	8 940(6)	−1 737(17)	30 833(18)
N(8)	8 088(7)	3 497(19)	8 376(19)
N(9)	14 961(6)	14 354(17)	13 378(19)
C(11)	24 673(11)	15 077(35)	33 558(37)
C(21)	22 982(10)	25 721(28)	16 920(35)
C(12)	17 452(11)	−9 938(39)	52 860(32)
C(22)	10 144(11)	−14 184(32)	51 950(29)
C(13)	124(11)	3 571(36)	34 022(33)
C(23)	−644(11)	948(32)	14 223(34)
C(14)	9 814(17)	31 547(29)	6 291(41)
C(24)	6 977(14)	22 275(32)	−9 990(38)
C(15)	16 605(13)	10 783(35)	−13 895(33)
C(25)	13 039(13)	−5 699(32)	−9 540(39)

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

[5] M. J. Begley, T. J. King, and D. B. Sowerby, unpublished results.

[6] D. Millington and D. B. Sowerby, *J.C.S. Dalton*, 1972, 2035.

[7] (*a*) '*X*-Ray' program system, ed. J. M. Stewart and F. A. Kurdell, University of Maryland Technical Report 6758, 1967, revised 1970; (*b*) 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1965.

hydrogen atoms are listed in Table 1 and for hydrogen atoms in Table 2. Figure 1 shows one view of the molecule and includes the numbering of the atoms and the dihedral angles of the ring bonds.

TABLE 2

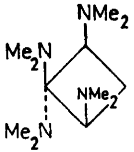
Atomic co-ordinates ($\times 10^3$) and isotropic thermal parameters ($\times 10^3$), with standard deviation in parentheses for hydrogen atoms

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*
H(11)	272(1)	107(4)	294(4)	105(16)
H(12)	235(1)	118(4)	402(4)	83(17)
H(13)	254(3)	217(7)	379(7)	149(35)
H(14)	208(1)	289(2)	114(3)	59(10)
H(15)	249(1)	219(4)	120(4)	76(14)
H(16)	244(1)	316(3)	204(4)	98(15)
H(21)	329(1)	83(3)	110(4)	61(14)
H(22)	302(1)	57(3)	0(3)	99(12)
H(23)	317(2)	170(6)	18(6)	128(34)
H(24)	400(1)	131(3)	103(3)	57(11)
H(25)	427(1)	123(3)	−16(3)	63(13)
H(26)	390(1)	214(3)	14(4)	9(14)
H(31)	23(1)	18(4)	406(4)	74(14)
H(32)	13(1)	456(3)	172(4)	70(16)
H(33)	479(1)	115(4)	141(4)	99(18)
H(34)	11(1)	114(3)	70(3)	62(14)
H(35)	474(1)	150(3)	315(3)	69(10)
H(36)	468(1)	52(3)	361(4)	104(16)
H(41)	121(1)	327(3)	117(4)	113(17)
H(42)	67(2)	345(5)	97(6)	158(25)
H(43)	105(1)	132(3)	525(3)	78(11)
H(44)	37(2)	282(4)	439(5)	66(15)
H(45)	73(2)	361(4)	355(4)	112(20)
H(46)	72(1)	213(4)	355(4)	145(22)
H(51)	161(1)	321(3)	378(4)	71(14)
H(52)	198(1)	424(3)	373(4)	88(11)
H(53)	158(2)	401(4)	279(4)	105(16)
H(54)	396(1)	94(3)	494(4)	73(15)
H(55)	370(1)	72(3)	311(4)	110(15)
H(56)	343(1)	94(3)	409(4)	52(13)

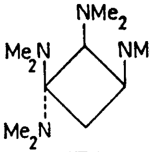
DISCUSSION

It is clear from the results of this structure determination that the arrangement of the three non-geminal amine groups is not that suggested earlier.[6] All three are on the same side of the mean ring plane and the compound is thus the *cis-cis-cis*-isomer (II) rather than the *cis-trans-cis*-isomer (I). This revised structure is still compatible with the ^1H n.m.r. data used to make the original assignment but then it was thought that by the operation of the *cis*-effect[8] (an empirical relationship between the positions of ^1H n.m.r. signals and the detailed environment of the dimethylamino-group under consideration) the signals due to the non-geminal PCl(NMe$_2$) groups would be closer than is observed. This is obviously not the case. The all-*cis* arrangement certainly correlates with the long retention time observed on a silicone gum rubber g.l.c. column but it raises problems concerning its immediate precursor during preparation.

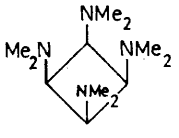
In the $P_4N_4Cl_8$–Me_2NH system the type of product depends on a number of factors which have already been discussed,[6] but when the stoicheiometric amount of dimethylamine is added very slowly at low temperatures there is a general tendency to maximize the yield of non-geminally substituted products with *trans*-arrangements of the amine groups. The four possible tetrasubstituted precursors of (II) are structures (III)—(VI). Two of these, (III) and (IV), contain both geminally and non-geminally substituted phosphorus atoms and as there was no evidence for such species in products from reactions between $P_4N_4Cl_8$ and 8 mol of dimethylamine they are not considered as likely intermediates. Similarly the all-*cis* isomer (V) was never isolated and its absence may be rationalized on steric grounds following the tendency of dimethylamine groups to be substituted in *trans*-positions to groups already present. The unsymmetrical isomer (VI) is then the most likely immediate precursor as this is a product from reactions between $P_4N_4Cl_8$ and dimethylamine. The yield of compound (VI) was uncertain as in all g.l.c. separations attempted[6] it was eluted with a second non-geminal isomer and small samples for analysis could be obtained only by a long series of fractional crystallizations.



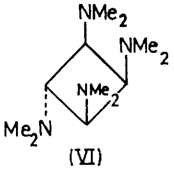
(III)



(IV)



(V)



(VI)

Description of the Structure.—Intramolecular distances and angles are listed in Table 3 and data for a number of planes associated with the molecule are collected in Table 4. Figure 2 shows an alternative view of the molecule, indicating the ring conformation and showing the *cis-cis-cis*-structure.

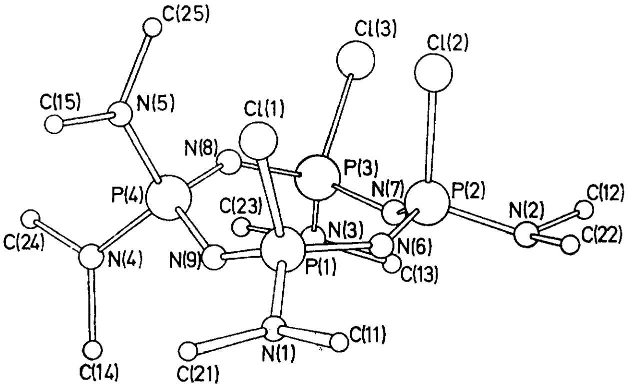


FIGURE 2 Molecular configuration

Ring Bonds and Angles.—The P–N bonds in the ring are all short, as expected, and are equal in pairs about P(4) [see (VII)]. The longest bonds are those from P(4), which carries the two amine substituents, and the general variation in the lengths is similar to that for *gem*-$P_4N_4F_6Me_2$ [see (VIII)].[9] Any rationalization of the

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[8] R. Keat and R. A. Shaw, *J.Chem.Soc.*(*A*), 1966, 908.

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

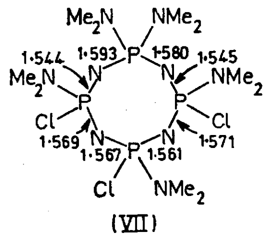
order must be closely similar in the two cases. For the penta-amino-compound, electron donation from the two amine groups at P(4) effectively reduces the π_s component in the P(4)–N(8) and P(4)–N(9) bonds by restricting the involvement of the nitrogen lone pairs on both N(8) and N(9). This electron density is thus available for strengthening the π_s component in the next-nearest bonds which are the shortest. Competition between P(1) and P(3) on the one hand and P(2) on the other for the lone-pair electron density at N(6) and N(7) will then lead to the observed bond distances, the argument being simplified as the three phosphorus atoms carry equivalent substituents in equivalent orientations.

TABLE 3

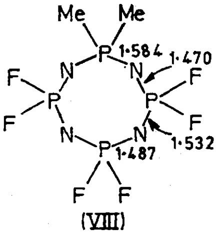
Intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Distances *			
P(1)–Cl(1)	2.086(1)	P(2)–Cl(2)	2.069(1)
P(1)–N(1)	1.631(2)	P(2)–N(2)	1.629(2)
P(1)–N(6)	1.569(2)	P(2)–N(6)	1.567(2)
P(1)–N(9)	1.544(2)	P(2)–N(7)	1.561(2)
P(3)–Cl(3)	2.075(1)	P(4)–N(4)	1.628(2)
P(3)–N(3)	1.639(2)	P(4)–N(5)	1.636(3)
P(3)–N(7)	1.571(2)	P(4)–N(8)	1.580(2)
P(3)–N(8)	1.545(2)	P(4)–N(9)	1.593(2)
N(1)–C(11)	1.456(5)	N(4)–C(14)	1.448(5)
N(2)–C(21)	1.467(5)	N(4)–C(24)	1.463(5)
N(2)–C(12)	1.456(4)	N(5)–C(15)	1.458(5)
N(2)–C(22)	1.459(4)	N(5)–C(25)	1.456(5)
N(3)–C(13)	1.440(5)		
N(3)–C(23)	1.470(4)		
(*b*) Angles			
N(1)–P(1)–Cl(1)	103.8(1)	N(2)–P(2)–Cl(2)	105.1(1)
N(1)–P(1)–N(6)	106.4(1)	N(2)–P(2)–N(6)	107.2(2)
N(1)–P(1)–N(9)	109.2(1)	N(2)–P(2)–N(7)	107.4(1)
Cl(1)–P(1)–N(6)	105.6(1)	Cl(2)–P(2)–N(6)	106.4(1)
Cl(1)–P(1)–N(9)	108.2(1)	Cl(2)–P(2)–N(7)	108.2(1)
N(6)–P(1)–N(9)	122.2(1)	N(6)–P(2)–N(7)	121.4(1)
N(3)–P(3)–Cl(3)	103.8(1)	N(4)–P(4)–N(5)	103.6(1)
N(3)–P(3)–N(7)	106.3(1)	N(4)–P(4)–N(8)	113.2(1)
N(3)–P(3)–N(8)	111.3(1)	N(4)–P(4)–N(9)	103.7(1)
Cl(3)–P(3)–N(7)	106.1(1)	N(5)–P(4)–N(8)	104.3(1)
Cl(3)–P(3)–N(8)	104.0(1)	N(5)–P(4)–N(9)	115.2(1)
N(7)–P(3)–N(8)	123.5(1)	N(8)–P(4)–N(9)	116.4(1)
P(1)–N(1)–C(11)	119.7(2)	P(2)–N(2)–C(12)	119.8(2)
P(1)–N(1)–C(21)	118.5(2)	P(2)–N(2)–C(22)	118.6(2)
C(11)–N(1)–C(21)	113.4(3)	C(12)–N(2)–C(22)	113.4(3)
P(3)–N(3)–C(13)	119.9(2)	P(4)–N(4)–C(14)	123.1(3)
P(3)–N(3)–C(23)	118.7(2)	P(4)–N(4)–C(24)	118.9(2)
C(13)–N(3)–C(23)	113.1(3)	C(14)–N(4)–C(24)	114.7(3)
		C(4)–N(5)–C(15)	119.2(2)
		P(4)–N(5)–C(25)	123.6(2)
		P(15)–N(5)–C(25)	115.0(3)
P(1)–N(6)–P(2)	130.8(2)		
P(2)–N(7)–P(3)	136.2(2)		
P(3)–N(8)–P(4)	138.1(2)		
P(4)–N(9)–P(1)	138.2(2)		

* C–H distances vary between 0.96 and 1.20 Å, mean 1.04 Å.



(VII)



(VIII)

TABLE 4

Equations of mean planes and, in square brackets, distances (Å) of relevant atoms from the plane

Plane (1): P(1)—(4), N(6)—(9)

$$0.322x - 0.811y - 0.489z = -0.308$$

[P(1) 0.079, P(2) 0.295, P(3) −0.115, P(4) 0.128, N(6) 0.051, N(7) −0.352, N(8) 0.308, N(9) −0.394]

Plane (2): P(1)—(4)

$$-0.271x + 0.807y + 0.525z = 0.496$$

[P(1) 0.116, P(2) −0.117, P(3) 0.114, P(4) −0.113, N(6) 0.175, N(7) 0.442, N(8) −0.330, N(9) 0.501]

Plane (3): N(6)—(9)

$$0.375x - 0.809y - 0.453z = -0.100$$

[N(6) 0.276, N(7) −0.274, N(8) 0.278, N(9) −0.280, P(1) 0.281, P(2) 0.463, P(3) −0.130, P(4) 0.143]

Plane (4): P(1)—(3)

$$-0.255x + 0.743y + 0.619z = 0.867$$

[P(4) −0.466, N(6) 0.226, N(7) 0.475, N(8) −0.593, N(9) 0.242]

Plane (5): P(1), P(3), P(4)

$$-0.285x + 0.858y + 0.429z = 0.356$$

[P(2) −0.451, N(6) −0.101, N(7) 0.182, N(8) −0.298, N(9) 0.517]

In general agreement with this explanation is the variation in angles at the ring nitrogen atoms which also broadly mirror the extent of π_s delocalization of the nitrogen lone-pairs. At N(8) and N(9), the values are both close to 138° while the mean at N(6) and N(7) is smaller, as expected (133.5°). The situation is however less clear if the N(6) and N(7) angles are considered separately [130.8 and 136.2°]. Such a difference might be expected to be reflected in the bond lengths involving these two atoms but this is not the case. One consequence of the small angle at N(6) is the smaller deviation of this atom (0.18 Å) from the best plane through the four phosphorus atoms; corresponding deviations for N(7)—(9) are 0.44, −0.33, and 0.50 Å. Measured contact distances involving N(6) are very similar to those for N(7) and it is probable that minor crystal-packing effects are responsible for the observed differences.

The endocyclic phosphorus angles, while close to the usual 120°, vary according to the substituents carried. That at P(4) is the smallest (116.4°), as generally found for an atom carrying two dimethylamino-groups, but here the closing up of the angle is much greater than in other structures with geminal groups.[10,11]

Exocyclic Groups.—The P–Cl and P–N(amine) distances are in the expected ranges, but the bonds to the amine groups are all equal. In general, it is found that P–N bond lengths at geminally substituted atoms are longer than those involving non-geminal amine groups. However Bullen and Dann [11] have pointed out that

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[10] G. J. Bullen, *J.Chem.Soc.*, 1962, 3193.

[11] G. J. Bullen and P. E. Dann, *J.C.S. Dalton*, 1974, 705.

increasing amination leads to P–N bond lengthening and with the present compound the operation of the two effects leads to equal geminal and non-geminal distances. The P–Cl bond distances in the pentakis compound fall into the trend already established of increasing bond distance with degree of amination.[11]

There are small differences in the bond angles associated with the three non-geminal $PCl(NMe_2)$ groups. The exocyclic Cl–P–N (amine) angle at P(2) is larger than that for P(1) and P(3) reflecting the more highly symmetrical environment and this is probably also the reason for the equality of the N(2)–P(2)–N (ring) angles; the analogous angles involving P(1) and P(3) on the other hand differ by some 3°.

The sum of the angles at the amine nitrogen atoms of the non-geminal groups is 351.7° in each case, while the corresponding values at N(4) and N(5) are 356.7 and 357.8°. This difference is mirrored by mean deviation of 0.26 Å for the nitrogen from the local PCC plane in the non-geminal groups and of 0.15 Å for the geminal groups. The greater planarity of the latter should be reflected in increased exocyclic π-bonding leading to shorter bonds to P(4). As noted earlier however, there is no difference in any of the exocyclic bonds to amine groups. This is all the more surprising as the orientation of the geminal and non-geminal amine groups with respect to the local NPN ring segments are different and this should lead to different degrees of π overlap between the amine lone-pair and suitable phosphorus acceptor orbitals. The relevant angles are 76.3 and 69.3° respectively for $N(4)C_2$ and $N(5)C_2$ with the N(8), P(4), N(9) plane and 23.0, 25.3, and 20.0° for the amine groups at P(1)—(3) respectively.

Non-bonded interactions between exocyclic groups are minimized by the non-geminal NC_2 groups being orientated at an angle of 88.5° to the respective ClPN(amine) plane, while at P(4) the angle between the planes of the two NC_2 groups is 88.9°.

Ring Conformation.—It is perhaps not surprising that the pattern of substituents in (II) should lead to an irregularly puckered ring system. This is well illustrated by the deviations of the individual ring atoms from the mean ring plane which show no particular inter-relationships and by the dihedral angles of the ring bonds (see Figure 1). The mean planes through the phosphorus atoms on the one hand and the nitrogens on the other both indicate that the phosphorus atoms are alternately above and below the plane while three nitrogens [N(6), (7), and (9)] are above and one [N(8)] is below. Although the phosphorus atoms are symmetrically displaced, the nitrogen deviations vary markedly. The deviation of the geminally substituted phosphorus P(4) is no greater than those of P(1)—(3).

We have previously pointed to the possibility of relating the ring conformation in substituted tetraphosphazenes with the orientation of the substituents and shown that, with one exception, the approach is valid for non-geminally tetrasubstituted species.[1] One way of approaching the ring conformation of the present molecule is to consider it in two parts, *i.e.* the segment of the ring containing P(1)—(3) which will have some character of an all *cis*-tetrasubstituted compound (crown conformation) and that from P(1), P(3), and P(4) which will have characteristics of a *cis-trans-cis-trans* compound (saddle conformation). In each comparison there will be distortions from the idealized symmetry due to the effect of the phosphorus atom omitted, but in the second comparison the geminal substitution at P(4) will have a more direct influence, as this atom is now included directly. Planes have been calculated on the two segments of the ring (see Table 4) and the deviations of adjacent nitrogen atoms point to a distorted crown type conformation for the P(1)—(3) segment and a distorted saddle for the second segment.

The saddle–crown conformation has been observed previously in the non-geminal *cis-cis-trans-trans*-$P_4N_4Cl_4(NMe_2)_4$ isomer.[4] Here the more highly symmetrical chair conformation would have been more appropriate as is indeed found with the analogous fluoride.[12] In the present case, this less highly symmetrical ring conformation is exactly that which would be predicted on the basis of substituent orientation.

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[12] D. Millington, T. J. King, and D. B. Sowerby, *J.C.S. Dalton*, 1973, 396.