Crystal Structure of 2,*trans*-4,*cis*-6,*trans*-8-Tetrachloro-2,4,6,8-tetrakis-(dimethylamino)cyclotetraphosphazene

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Crystals of the title compound $N_4P_4Cl_4(NMe_2)_4$, m.p. 168 °C, are monoclinic with a = 18.76(1), b = 18.86(1), c = 13.67(1) Å, β = 109.17(1)°, space group $P2_1/c$, and Z = 8. Atomic positions have been determined by Patterson and Fourier methods from X-ray diffractometer data and refined by least squares to R 0.066 for 3 300 reflections. The asymmetric unit contains two molecules which have the *cis-trans-cis-trans* arrangement of NMe_2 groups as suggested previously. The overall structure is very similar to that of the corresponding fluoro-derivative, $N_4P_4F_4(NMe_2)_4$. Ring P–N distances vary from 1.528 to 1.580 Å (mean 1.556 Å); mean values for other parameters are P–N(amine) 1.625 and P–Cl 2.053 Å, and N–P–N 120.9 and P–N–P 136.3°. The ring conformation, intermediate between the saddle and tub, is that expected on the basis of the substituent arrangement.

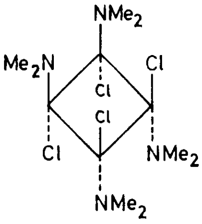
AMONG the products isolated from reactions between the tetrameric dichlorocyclophosphazene $N_4P_4Cl_8$ and anhydrous dimethylamine in diethyl ether solution are four isomeric tetrasubstituted derivatives, $N_4P_4Cl_4(NMe_2)_4$.[1] In one of these compounds the dimethylamino-groups have replaced pairs of chlorine atoms at two of the phosphorus atoms giving a geminal compound; in the other three compounds i.r., n.m.r., and g.l.c. data point to the replacement of one chlorine atom at each phosphorus centre. For two of the compounds, single-crystal X-ray studies have confirmed the non-geminal arrangement of substituents and assigned, respectively, *cis-cis-trans-trans* (1)[2] and *cis-cis-cis-trans* (2)[3] substituent orientations. Possible configurations for the third isomer are then either *cis-cis-cis-cis* (3) or *cis-trans-cis-trans* (4), but chemical and spectroscopic data[1] tend to support the latter. This configuration has so far been substantiated[4] only in a (dimethylamino)-fluorocyclotetraphosphazene, $N_4P_4F_4(NMe_2)_4$.

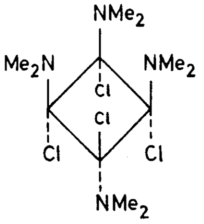
This paper reports the results of a single-crystal X-ray study of the chloro(dimethylamino)-compound $N_4P_4Cl_4(NMe_2)_4$ with a m.p. of 168 °C and was carried out to determine the substituent orientation and the conformation adopted by the N_4P_4 ring.

EXPERIMENTAL

Crystals of the compound (m.p. 168 °C) were obtained by fractional crystallization from light petroleum of the mixture of products obtained from a reaction of $N_4P_4Cl_8$ with anhydrous dimethylamine (8 mol).[1]

Crystal Data.—$C_8H_{24}Cl_4N_8P_4$, M = 498, Monoclinic, a = 18.76(1), b = 18.86(1), c = 13.67(1) Å, β = 109.17(1)°, U = 4 568.9 Å^3, Z = 8, D_c = 1.45 g cm^{-3}, $F(000)$ = 2 048, space group $P2_1/c$ from systematic absences ($h0l$ when $l = 2n + 1$ and $0k0$ when $k = 2n + 1$), Mo-K_α radiation, λ = 0.710 7 Å, μ = 8.04 cm^{-1}.


(1)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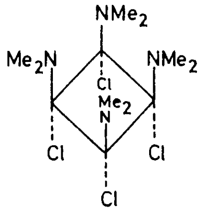
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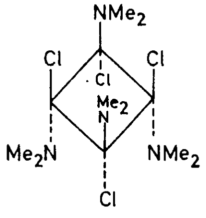
(4)

The unit-cell dimensions originally obtained from oscillation and Weissenberg photographs were refined by a least-squares procedure on the positions of 12 strong reflections, accurately measured on a Hilger and Watts four-circle diffractometer. Intensity data were collected on the diffractometer by use of an ω—2θ scan in the range 0 ⩽

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

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

[3] M. J. Begley, T. J. King, and D. B. Sowerby, *J.C.S. Dalton*, 1977, 149.

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

$2\theta \leqslant 50°$ using Mo-K_{α} radiation. Because of a substantial decrease in the intensity of the standard counts, it was necessary to use two crystals to obtain the complete set of data, which consisted of 3 300 reflections with counts greater than 3.5σ. The intensities were corrected for Lorentz and polarization effects but not for absorption or secondary extinction. Initially, the data reduction and subsequent calculations used the '*X*-RAY '70' package[5] on the University of Nottingham ICL 1906 A computer with 2 080 reflections with net counts >100. Later, the complete data were processed with the '*X*-RAY '70' system on the University of Manchester CDC 7600 computer. Atomic scattering factors were taken from ref. 6.

A three-dimensional Patterson synthesis gave possible positions for the eight phosphorus atoms in the two independent molecules in the asymmetric unit and a Fourier synthesis phased on these atoms revealed the positions of the eight chlorine atoms. After two cycles of full-matrix least-squares refinement a difference-Fourier synthesis showed the positions of the other non-hydrogen atoms. Three cycles of block-diagonal refinement with isotropic thermal parameters led to a reduction of R to 0.160.

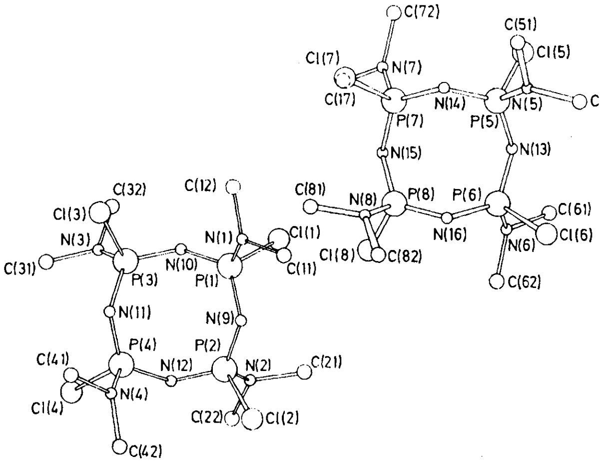

FIGURE 1 Projection of the molecules in the xy plane showing the numbering of the atoms

Block-diagonal refinement was then continued using the full reflection file. Convergence occurred at R 0.143 with isotropic thermal parameters and at R 0.079 with anisotropic thermal parameters after four further cycles of refinement. A difference-Fourier showed the positions of the 48 hydrogen atoms, and two cycles of refinement with isotropic thermal parameters for the hydrogen atoms reduced R to 0.069. A weighting scheme that assigned unit weight to reflections having $F_o \leqslant 46$ but a weight of $(46/F_o)^2$ for $F_o > 46$ was introduced and final convergence occurred at R 0.066.

The final atomic co-ordinates are listed in Table 1, and a diagram showing the numbering of the atoms in the two independent molecules is given in Figure 1. Observed and calculated structure factors, anisotropic thermal parameters for the non-hydrogen atoms, and hydrogen-atom co-ordinates are listed in Supplementary Publication No. SUP 22281 (19 pp.).*

DISCUSSION

Data on the molecular parameters of the two independent molecules are given in Table 2 and a further diagram emphasizing the ring conformation is in Figure 2. These results clearly show that the dimethylamino-groups in this derivative are alternately above and below the ring and thus the *cis-trans-cis-trans* configuration suggested earlier on the basis of spectroscopic and other data is confirmed. The mutual *trans* arrangement of the NMe_2 groups is probably sterically favourable and this isomer might be expected to be formed as a reasonable proportion of the product from tetrasubstitution of $N_4P_4Cl_8$. In the earlier stages of this reaction there is a developed tendency for NMe_2 groups to occupy positions on separate phosphorus atoms which are *trans* to the amine groups already present. The precursors of

TABLE 1

Atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
P(1)	856(1)	1 340(1)	2 663(2)
P(2)	728(1)	−178(1)	2 326(2)
P(3)	−740(1)	1 381(1)	2 379(2)
P(4)	−702(1)	−141(1)	2 693(2)
Cl(1)	1 328(2)	1 740(2)	1 618(2)
Cl(2)	1 390(2)	−896(2)	3 347(3)
Cl(3)	−894(2)	2 093(2)	3 425(2)
Cl(4)	−1 685(2)	−550(2)	1 686(2)
N(1)	1 288(4)	1 733(4)	3 745(6)
C(11)	2 049(7)	1 510(10)	4 347(10)
C(12)	1 154(9)	2 473(8)	3 815(11)
N(2)	849(5)	−329(5)	1 227(7)
C(21)	1 594(9)	−215(9)	1 153(14)
C(22)	414(9)	−889(8)	564(10)
N(3)	−1 410(4)	1 539(4)	1 298(6)
C(31)	−2 187(6)	1 356(8)	1 231(9)
C(32)	−1 347(7)	2 192(7)	749(9)
N(4)	−582(4)	−550(5)	3 788(6)
C(41)	−1 020(7)	−309(8)	4 432(9)
C(42)	−428(9)	−1 321(7)	3 832(11)
N(9)	1 079(5)	542(5)	2 828(7)
N(10)	29(4)	1 566(5)	2 210(6)
N(11)	−854(5)	648(5)	2 862(6)
N(12)	−95(5)	−358(5)	2 185(6)
P(5)	5 946(1)	3 850(1)	7 630(2)
P(6)	5 896(1)	2 329(1)	7 273(2)
P(7)	4 358(1)	3 815(2)	7 344(2)
P(8)	4 439(1)	2 294(2)	7 538(2)
Cl(5)	6 054(2)	4 558(2)	6 541(3)
Cl(6)	6 860(1)	1 889(2)	8 277(2)
Cl(7)	3 887(2)	4 140(2)	8 431(3)
Cl(8)	3 803(2)	1 603(2)	6 438(4)
N(5)	6 639(4)	4 026(5)	8 673(6)
C(51)	6 607(7)	4 687(7)	9 235(11)
C(52)	7 406(5)	3 862(8)	8 748(10)
N(6)	5 776(4)	1 949(4)	6 162(5)
C(61)	6 237(8)	2 179(7)	5 540(10)
C(62)	5 606(7)	1 195(7)	6 056(9)
N(7)	3 935(5)	4 303(5)	6 318(6)
C(71)	3 188(8)	4 082(10)	5 673(11)
C(72)	4 098(9)	5 070(7)	6 358(12)
N(8)	4 248(5)	2 124(6)	8 592(9)
C(81)	3 471(9)	2 240(10)	8 579(15)
C(82)	4 611(8)	1 556(8)	9 266(11)
N(13)	6 067(4)	3 126(5)	7 156(6)
N(14)	5 209(4)	4 013(5)	7 845(7)
N(15)	4 113(4)	3 033(5)	7 047(7)
N(16)	5 267(4)	2 101(4)	7 728(6)

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[5] '*X*-RAY' program system, eds. J. M. Stewart and F. A. Kundell, University of Maryland Technical Report 6758, 1967, revised 1970.

[6] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1965, vol. 3.

compound (4) would therefore be the 2,*trans*-4-disubstituted compound and the 2,*trans*-4,*cis*-6-trisubstitution product, both of which have been identified in products from other $N_4P_4Cl_8$–NMe_2H reactions. Of the other tetrasubstitution products previously investigated by X-ray methods the *cis-cis-trans-trans* isomer (1) would necessarily have the 2,*trans*-6-disubstitution product and the 2,*cis*-4,*trans*-6-trisubstitution product as precursors while the *cis-cis-cis-trans* isomer (2) could result from either of these two routes.

Table 2

Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

P(1)–N(1)	1.614(8)	P(5)–N(5)	1.618(7)
P(2)–N(2)	1.618(11)	P(6)–N(6)	1.626(9)
P(3)–N(3)	1.623(7)	P(7)–N(7)	1.648(9)
P(4)–N(4)	1.632(9)	P(8)–N(8)	1.625(13)
P(1)–Cl(1)	2.055(5)	P(5)–Cl(5)	2.059(5)
P(2)–Cl(2)	2.045(5)	P(6)–Cl(6)	2.052(3)
P(3)–Cl(3)	2.052(5)	P(7)–Cl(7)	2.055(5)
P(4)–Cl(4)	2.054(4)	P(8)–Cl(8)	2.050(5)
P(1)–N(9)	1.559(8)	P(5)–N(13)	1.561(9)
P(1)–N(10)	1.531(8)	P(5)–N(14)	1.535(10)
P(2)–N(9)	1.567(9)	P(6)–N(13)	1.556(9)
P(2)–N(12)	1.528(10)	P(6)–N(16)	1.564(9)
P(3)–N(10)	1.571(9)	P(7)–N(14)	1.561(8)
P(3)–N(11)	1.578(9)	P(7)–N(15)	1.558(10)
P(4)–N(11)	1.546(9)	P(8)–N(15)	1.580(10)
P(4)–N(12)	1.570(11)	P(8)–N(16)	1.536(8)
N(1)–C(11)	1.46(1)	N(5)–C(51)	1.48(2)
N(1)–C(12)	1.43(2)	N(5)–C(52)	1.44(1)
N(2)–C(21)	1.45(2)	N(6)–C(61)	1.46(2)
N(2)–C(22)	1.46(2)	N(6)–C(62)	1.46(2)
N(3)–C(31)	1.47(1)	N(7)–C(71)	1.45(2)
N(3)–C(32)	1.47(1)	N(7)–C(72)	1.48(2)
N(4)–C(41)	1.46(2)	N(8)–C(81)	1.47(2)
N(4)–C(42)	1.48(2)	N(8)–C(82)	1.43(2)
N(9)–P(1)–N(10)	121.0(5)	N(13)–P(5)–N(14)	121.2(5)
N(9)–P(2)–N(12)	120.6(5)	N(13)–P(6)–N(16)	120.9(5)
N(10)–P(3)–N(11)	120.9(5)	N(14)–P(7)–N(15)	120.9(5)
N(11)–P(4)–N(12)	120.8(5)	N(15)–P(8)–N(16)	120.6(5)
P(1)–N(9)–P(2)	136.1(5)	P(5)–N(13)–P(6)	137.7(7)
P(1)–N(10)–P(3)	137.4(6)	P(5)–N(14)–P(7)	136.3(6)
P(3)–N(11)–P(4)	136.4(7)	P(7)–N(15)–P(8)	133.2(5)
P(2)–N(12)–P(4)	137.3(6)	P(6)–N(16)–P(8)	136.3(6)
Cl(1)–P(1)–N(9)	107.5(4)	Cl(5)–P(5)–N(13)	101.8(4)
Cl(1)–P(1)–N(10)	103.1(4)	Cl(5)–P(5)–N(14)	108.5(4)
Cl(2)–P(2)–N(9)	101.6(3)	Cl(6)–P(6)–N(13)	107.1(3)
Cl(2)–P(2)–N(12)	107.5(4)	Cl(6)–P(6)–N(16)	103.7(3)
Cl(3)–P(3)–N(10)	107.7(4)	Cl(7)–P(7)–N(14)	103.4(4)
Cl(3)–P(3)–N(11)	102.3(4)	Cl(7)–P(7)–N(15)	108.1(4)
Cl(4)–P(4)–N(11)	107.0(3)	Cl(8)–P(8)–N(15)	101.5(4)
Cl(4)–P(4)–N(12)	103.1(3)	Cl(8)–P(8)–N(16)	106.6(4)
N(1)–P(1)–N(9)	106.3(5)	N(5)–P(5)–N(13)	111.2(4)
N(1)–P(1)–N(10)	112.4(5)	N(5)–P(5)–N(14)	107.7(5)
N(2)–P(2)–N(9)	113.1(6)	N(6)–P(6)–N(13)	107.4(5)
N(2)–P(2)–N(12)	106.8(5)	N(6)–P(6)–N(16)	111.1(5)
N(3)–P(3)–N(10)	107.4(5)	N(7)–P(7)–N(14)	112.1(5)
N(3)–P(3)–N(11)	111.8(4)	N(7)–P(7)–N(15)	106.8(5)
N(4)–P(4)–N(11)	107.1(5)	N(8)–P(8)–N(15)	112.7(6)
N(4)–P(4)–N(12)	112.4(5)	N(8)–P(8)–N(16)	107.9(5)
Cl(1)–P(1)–N(1)	105.5(4)	Cl(5)–P(5)–N(5)	105.2(4)
Cl(2)–P(2)–N(2)	106.2(4)	Cl(6)–P(6)–N(6)	105.5(3)
Cl(3)–P(3)–N(3)	105.7(4)	Cl(7)–P(7)–N(7)	104.3(4)
Cl(4)–P(4)–N(4)	105.2(4)	Cl(8)–P(8)–N(8)	106.4(4)
C(11)–N(1)–C(12)	114.0(10)	C(51)–N(5)–C(52)	110.8(9)
C(21)–N(2)–C(22)	114.9(12)	C(61)–N(6)–C(62)	112.5(10)
C(31)–N(3)–C(32)	114.2(8)	C(71)–N(7)–C(72)	116.9(11)
C(41)–N(4)–C(42)	114.9(11)	C(81)–N(8)–C(82)	112.4(13)
P(1)–N(1)–C(11)	119.3(9)	P(5)–N(5)–C(51)	118.3(7)
P(1)–N(1)–C(12)	117.6(7)	P(5)–N(5)–C(52)	120.9(8)
P(2)–N(2)–C(21)	118.2(9)	P(6)–N(6)–C(61)	119.0(7)
P(2)–N(2)–C(22)	119.0(10)	P(6)–N(6)–C(62)	118.9(8)
P(3)–N(3)–C(31)	117.9(7)	P(7)–N(7)–C(71)	117.1(10)
P(3)–N(3)–C(32)	116.9(6)	P(7)–N(7)–C(72)	118.7(8)
P(4)–N(4)–C(41)	118.1(8)	P(8)–N(8)–C(81)	117.7(10)
P(4)–N(4)–C(42)	117.9(9)	P(8)–N(8)–C(82)	121.5(10)

The two independent molecules are nearly parallel (see Figure 1), the angle between the mean ring planes being 2.7°. In most other respects the two molecules are also very similar and overall mean values for the major parameters are P–N(ring) 1.556, P–N(amine) 1.625, P–Cl 2.053, and N–C 1.46 Å, N–P–N(ring) 120.9, P–N(ring)–P 136.3, Cl–P–N(amine) 105.5, P–N–C 118.6, Cl–P–N(ring) 107.5 and 102.6, N(amine)–P–N(ring) 112.1 and 107.1, and C–N–C 113.8°.

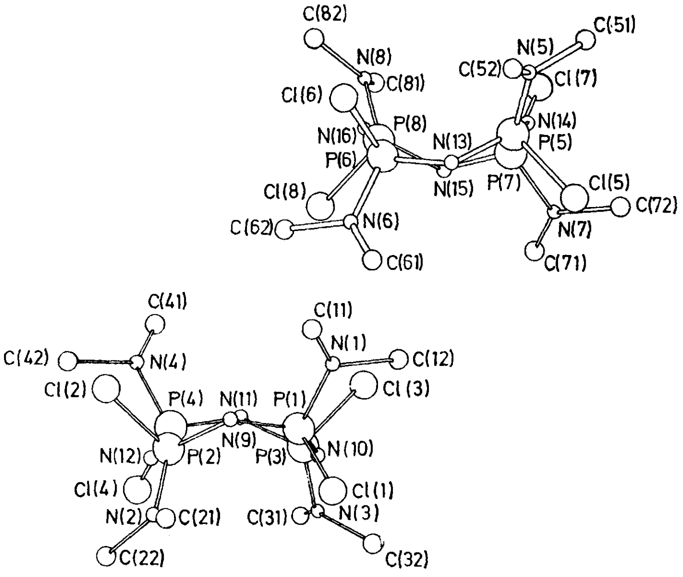

Figure 2 Projection of the molecules in the *yz* plane showing ring conformation

The mean ring P–N distance is the same as that in the *cis-cis-trans-trans* isomer[2] and perhaps more surprising the value is also that found for the analogous *cis-trans-cis-trans* tetrafluoride (1.557 Å).[4] The spread of values however [1.528—1.578 Å for the P(1)—P(4) molecule and 1.535—1.580 Å for the P(5)—P(8) molecule] is much greater than found in the fluoride structure. There is some alternation in ring bond lengths but it is not regular and there is no suggestion that this should be identified with alternate single- and double-bond character. Indeed, the electronic environment of each phosphorus is identical and steric factors should also be closely similar leading to a regular ring system. It is noticeable however that the two shortest bonds in the P(1)—P(4) molecule (1.528 and 1.531 Å) are three bonds apart while in the second molecule the corresponding short bonds (1.535 and 1.536 Å) are four bonds apart. The endocyclic angles at phosphorus vary little, with the mean (120.9°) being that generally observed in comparable tetrameric systems, and with one exception [N(15) 133.2°] the ring-nitrogen angles also show little variation. The mean value (136.3°) should be compared with values of 136.8, 133.7, and 134.7° found for compounds (1),[2] (2),[3] and the fluorine analogue of (4)[4] respectively.

TABLE 3

Equations of mean planes and distances (Å) of relevant atoms from the plane

Plane (*i*): P(1)—P(4) and N(9)—N(12)

$$0.017x - 0.007y + 1.000z = 3.228$$

[P(1) 0.199, P(2) −0.215, P(3) −0.220, P(4) 0.207, N(9) 0.432, N(10) −0.400, N(11) 0.412, N(12) −0.415]

Plane (*ii*): P(5)—P(8) and N(13)—N(16)

$$-0.018x - 0.038y + 0.999z = 9.272$$

[P(5) 0.160, P(6) −0.198, P(7) −0.161, P(8) 0.199, N(13) −0.403, N(14) 0.440, N(15) −0.474, N(16) 0.436]

Plane (*iii*): P(1)—P(4)

$$0.018x - 0.005y + 1.000z = 3.222$$

[P(1) 0.210, P(2) −0.210, P(3) −0.210, P(4) 0.210, N(9) 0.441, N(10) −0.389, N(11) 0.418, N(12) −0.413]

Plane (*iv*): P(5)—P(8)

$$-0.005x - 0.038y + 0.999z = 9.355$$

[P(5) 0.178, P(6) −0.179, P(7) −0.180, P(8) 0.181, N(13) −0.379, N(14) 0.439, N(15) −0.498, N(16) 0.438]

Details for a number of planes through the two molecules are summarized in Table 3, while the torsion angles of the ring bonds are listed in Table 4. The ring systems in both molecules are extensively puckered with the phosphorus atoms being *ca.* 0.20 Å alternately above and below the mean ring plane. The nitrogen atoms are similarly disposed but the mean deviation is *ca.* 0.43 Å. From these data, both molecules adopt a ring conformation which is intermediate between the ideal saddle and tub conformations. In the former the N_4P_4 ring, with D_{2d} symmetry, has coplanar phosphorus atoms with the nitrogens displaced alternately above and below this plane. In the tub conformation (S_4 symmetry) the phosphorus and nitrogen atoms are displaced by equal amounts in pairs alternately above and below the mean ring plane.

TABLE 4

Torsion angles (°) of ring bonds

P(1)–N(9)	26.9	P(5)–N(13)	39.7
P(1)–N(10)	45.3	P(5)–N(14)	31.7
P(2)–N(9)	50.4	P(6)–N(13)	19.8
P(2)–N(12)	23.1	P(6)–N(16)	50.4
P(3)–N(10)	22.3	P(7)–N(14)	46.6
P(3)–N(11)	47.7	P(7)–N(15)	34.2
P(4)–N(11)	23.1	P(8)–N(15)	54.7
P(4)–N(12)	48.1	P(8)–N(16)	24.8

The intermediate conformation is shown in the first instance by the torsion angles (see Table 4) which for perfect D_{2d} symmetry would be equal. There is a considerable spread in the values for each molecule [22.3—50.4 and 19.8—50.4° respectively for the P(1)—P(4) and P(5)—P(8) molecules] and the mean angles (35.8 and 37.7°) suggest a small difference in conformation for the two molecules. Confirmation of this difference comes when the mean deviations of the phosphorus and nitrogen atoms from the best plane through the eight ring atoms are examined for the individual molecules. For the P(1)—P(4) molecule $\Delta P/\Delta N$ is 0.210/0.415, *i.e.* 0.51, while for the second molecule it is 0.180/0.438, *i.e.* 0.41. Thus, although both molecules have the intermediate conformation, the second is closer to the saddle conformation for which $\Delta P/\Delta N$ tends to zero. In the fluorine analogue of this compound $\Delta P/\Delta N$ is 0.31 and the ring conformation is even closer to the ideal saddle.

The shortening of the P–N(amine) bond to 1.625 Å from the accepted single-bond distance is expected in these systems and results from π donation from the amine nitrogen lone pair. A consequence of this is the flattening of the PNC_2 system which is shown by (*a*) the sum of the angles at each nitrogen approaching 360° (a mean value of 351.1° is observed) and (*b*) the deviation of the nitrogen atom from the plane through the phosphorus atom and the two carbons of the amine group (here the average is 0.27 Å). In the corresponding fluoride there appears to be more effective flattening of the NMe_2 group since the average for the sum of the angles at nitrogen is 354.8°, and the nitrogen is displaced from the relevant PCC plane by an average of 0.20 Å.

As can be seen qualitatively from Figure 1, the NMe_2 groups are orientated so that steric interaction with the chlorine atom attached to the same phosphorus atom is minimized. This leads to two sets of angles describing the positions of the chlorine and amine nitrogen atoms with respect to the two flanking ring-nitrogen atoms, and to the NC_2 plane of a given amine group being almost normal (mean 84.6°) to the plane containing the relevant P–N–Cl atoms.

The small difference in molecular structure of $N_4P_4Cl_4(NMe_2)_4$ (4) and its fluorine analogue is on the surface a little surprising. In the octahalogenotetraphosphazenes substitution of fluorine for chlorine leads to both a shortening of the P–N ring bonds from 1.57 (ref. 7) to 1.51 Å (ref. 8) and an opening of the ring angles at nitrogen from 131.3 to 147.4°. (The values quoted for the chloride refer to the K form.) In the tetrakis-(dimethylamino)-compounds, beyond a slightly greater flattening of the PNC_2 systems and a ring conformation somewhat closer to the saddle, the change from chlorine to fluorine substituents has only minor consequences.

The ring conformation for compound (4) provides an example where there is a direct relationship between the symmetry of the substituent orientation and the symmetry of the adopted ring conformation. This relationship, which has been discussed earlier,[4] is probably the result of the interaction of a number of factors. In a general case the adopted conformation will be that leading to maximum bond strength and minimum intra- and inter-molecular steric repulsions. In the present case intramolecular effects are in fact minimized by the more bulky NMe_2 groups occupying a mutually *trans*

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arrangement (substituent symmetry, D_{2d}) and the ring is then able to adopt a conformation close to the saddle (ideal symmetry, D_{2d}) where ring π bonding is thought to be strong. In comparison with the fluoride, the ring system in compound (4) is distorted further from the ideal saddle, in agreement with the greater steric requirements of the larger chlorine atoms.

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