Structure of 1,*cis*-3,*cis*-5,*trans*-7-Tetrachloro-1,3,5,7-tetrakis(dimethylamino)cyclotetraphosphazene

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Crystals of the title compound, one of the non-geminally substituted tetrakis(dimethylamino)chlorotetraphosphazenes, are monoclinic with $a = 36.473(13)$, $b = 9.360(3)$, $c = 13.684(3)$ Å, $\beta = 105.04(2)°$, space group $C2/c$, $Z = 8$. Atomic positions have been determined by Patterson and Fourier methods from *X*-ray diffractometer data and refined by least squares to *R* 0.11 for 1 489 reflections. One feature of the structure is the inequality of the ring-bond distances at N(6). The structure determination confirms the *cis,cis,cis,trans* orientation of the dimethylamino-groups which leads to a mixed 'crown-saddle' conformation for the P_4N_4 ring.

THE low-temperature reaction between octachlorocyclotetraphosphazene, $P_4N_4Cl_8$, and 8 mol equivalents of dimethylamine gives three of the four possible non-geminally substituted isomers, $P_4N_4Cl_4(NMe_2)_4$ [see formulae (1)—(3)].[1] The crystal structure of the *cis,cis,-trans,trans*-isomer (1) has been determined [2] and, as the electronic effects in this isomer and in 2 and 3 are expected to be broadly similar, structures for the latter two isomers are also of interest. This paper reports the results of an *X*-ray study of the structure of the unsymmetrically substituted *cis,cis,cis,trans*-isomer (2).

In the mixtures obtained from the $P_4N_4Cl_8$–$8NMe_2H$ reaction, g.l.c. analysis using a variety of stationary phases showed only two peaks associated with tetra-substituted species, *i.e.* compounds (1) and (3).[1] These two compounds could be readily obtained pure, but it was shown by a series of fractional crystallizations that the bulk sample of (1) contained a second isomer (2) which had identical g.l.c. behaviour. This more soluble compound was obtained pure in small quantities only and proved difficult to obtain in a suitable form for *X*-ray diffraction studies.

EXPERIMENTAL

The compound [m.p. 130 °C, compound (VII) in ref. 1] was obtained from a reaction between $P_4N_4Cl_8$ and 8 mol equivalents of dimethylamine in diethyl ether at -78 °C. Repeated fractional crystallizations from light petroleum led to its separation from the 1,*cis*-3,*trans*-5,*trans*-7-isomer (1) with which it is formed. Good quality crystals were impossible to obtain even though a variety of solvents was used. The crystal eventually chosen was a thin plate obtained from diethyl ether solution.

Crystal Data.—$C_8H_{24}Cl_4N_8P_4$, $M = 498$, Monoclinic, $a = 36.473(13)$, $b = 9.360(3)$, $c = 13.684(3)$ Å, $\beta = 105.04(2)°$.

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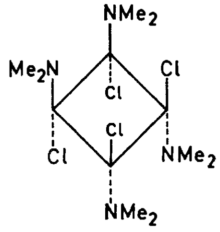
[1] D. Millington and D. B. Sowerby, *J.C.S. Dalton*, 1972, 2035.

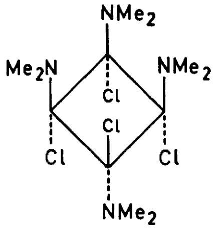
[2] G. J. Bullen and P. A. Tucker, *J.C.S. Dalton*, 1972, 2437.

$U = 4\,511.6$ Å^3, $Z = 8$, $D_c = 1.47$ g cm^{-3}, $F(000) = 2\,048$, Space group $C2/c$ from systematic absences, hkl when $h + k = 2n + 1$, $h0l$ when $l = 2n + 1$ and subsequent refinement, Cu-K_α radiation, $\lambda = 1.5418$ Å, μ(Cu-K_α) = 74.7 cm^{-1}.

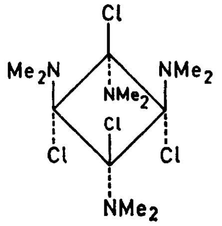
The unit-cell parameters were determined initially from oscillation and Weissenberg photographs and refined on a Hilger and Watts four-circle diffractometer using Cu-K_α radiation. Of the reflections, 1 489 with net counts $I > 3\sigma(I)$ measured using the diffractometer were considered observed and the intensities were corrected for Lorentz and polarization effects, but not for absorption or secondary extinction. Data reduction and subsequent calculations used the '*X*-ray '70' programs;[3] atomic scattering factors were taken from ref. 4. Possible positions of the four phosphorus atoms in the asymmetric unit were deduced from a three-dimensional Patterson map and after two cycles of full-matrix least-squares refinement, a three-dimensional Fourier map revealed the positions of the four chlorine and eight nitrogen atoms. After three cycles of block-diagonal least-squares refinement R was reduced to 0.26 and the positions of the eight carbon atoms were obtained from a difference-Fourier map. Two cycles of block-diagonal least-squares refinement then reduced R to 0.18 and after four further cycles of refinement with anisotropic temperature factors R converged at 0.12. Analysis of the reflection data showed that unit weight should be assigned to those with $F_o \leqslant 60$ but for those with $F_o > 60$ the weighting should be $w = (60/F_o)^2$. Convergence using this weighting scheme occurred after two further cycles of refinement at R 0.11. A final difference Fourier showed a number of peaks close to the heavy atom positions but there were no other peaks >0.5 eÅ^{-3}. The map did show possible positions for some of the 24 hydrogen atoms but it was not possible to locate all of them and this aspect of the structure was not pursued. Attempts to refine the structure further by using full-matrix least-squares methods did not lead to a significant lowering of the R value. The position of the ring nitrogen N(6) was unsymmetrical with respect to P(2) and P(3) and as this is unusual the atom position was reloaded in a more symmetrical position and allowed to refine. After four cycles of block-diagonal refinement both the position of N(6) and R had returned to their original values.



(1)



(2)



(3)

The final atomic co-ordinates are listed in Table 1; the numbering of the atoms, together with the torsion angles of the ring bonds, are shown in Figure 1. Observed and calculated structure factors and the anisotropic thermal parameters are listed in Supplementary Publication No. SUP 21856 (8 pp., 1 microfiche).*

TABLE 1

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

	x/a	y/b	z/c
P(1)	1 071(1)	4 546(4)	2 459(3)
P(2)	707(1)	2 020(4)	1 512(3)
P(3)	1 425(1)	1 018(4)	1 247(2)
P(4)	1 770(1)	3 697(4)	2 016(3)
Cl(1)	716(1)	6 112(5)	1 680(3)
Cl(2)	519(1)	353(5)	2 218(4)
Cl(3)	1 528(2)	−322(5)	2 473(3)
Cl(4)	2 054(2)	3 378(5)	3 514(3)
N(1)	1 178(4)	5 059(11)	3 642(8)
C(11)	910(6)	4 815(20)	4 267(11)
C(12)	1 411(7)	6 351(21)	3 889(14)
N(2)	341(4)	2 559(14)	665(10)
C(21)	226(6)	1 861(22)	−373(13)
C(22)	−1(5)	3 197(25)	949(15)
N(3)	1 512(4)	62(12)	331(9)
C(31)	1 912(6)	−199(21)	316(14)
C(32)	1 227(6)	−1 150(20)	−94(14)
N(4)	2 055(4)	4 621(13)	1 522(10)
C(41)	2 370(6)	3 991(23)	1 234(17)
C(42)	2 133(8)	6 156(23)	1 853(21)
N(5)	828(4)	3 132(13)	2 407(9)
N(6)	1 014(3)	1 359(12)	968(8)
N(7)	1 750(4)	2 203(13)	1 513(9)
N(8)	1 418(3)	4 638(13)	1 995(8)

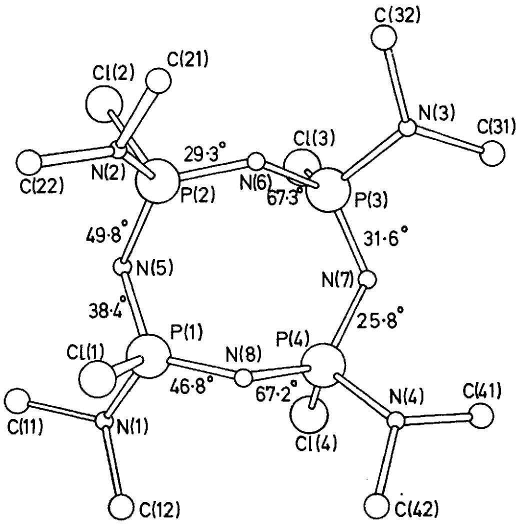


FIGURE 1 The numbering of atoms and torsion angles of the ring bonds

DISCUSSION

Bond lengths and angles for the compound are summarized in Table 2 and there is a further sketch of the molecule showing the ring conformation and the orientation of the exocyclic groups in Figure 2.

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* For details see Notice to Authors No.7 in *J.C.S. Dalton*, 1976, Index issue (items less than 10 pp. are supplied as full-size copies).

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

[4] 'International Tables for *X*-ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1965.

The results of this determination confirm the structure as the *cis,cis,cis,trans*-isomer which was made initially on the basis of ^1H n.m.r. and i.r. data.[1,5] The formation of this isomer in the $P_4N_4Cl_8$–NMe_2H system follows logically from the di- and tri-substituted compounds isolated in earlier stages of the reaction if there is a tendency for the yield of non-geminally substituted isomers with dimethylamino-groups in *trans*-positions to be maximized. This seems to be the case when the degree of substitution does not exceed four but it has recently been shown that in a pentasubstituted compound, $P_4N_4Cl_3(NMe_2)_5$, the three non-geminal amine groups are all *cis* to each other.[6]

TABLE 2

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

P(1)–N(1)	1.64(1)	P(1)–Cl(1)	2.06(1)
P(2)–N(2)	1.60(1)	P(2)–Cl(2)	2.04(1)
P(3)–N(3)	1.64(1)	P(3)–Cl(3)	2.05(1)
P(4)–N(4)	1.63(2)	P(4)–Cl(4)	2.06(1)
P(1)–N(5)	1.58(1)	N(1)–C(11)	1.47(2)
P(1)–N(8)	1.56(1)	N(1)–C(12)	1.47(2)
P(2)–N(5)	1.58(1)	N(2)–C(21)	1.52(2)
P(2)–N(6)	1.62(1)	N(2)–C(22)	1.53(2)
P(3)–N(6)	1.48(1)	N(3)–C(31)	1.49(3)
P(3)–N(7)	1.59(1)	N(3)–C(32)	1.54(2)
P(4)–N(7)	1.55(1)	N(4)–C(41)	1.42(3)
P(4)–N(8)	1.55(1)	N(4)–C(42)	1.52(3)
N(5)–P(1)–N(8)	122.1(7)	P(1)–N(5)–P(2)	128.8(9)
N(5)–P(2)–N(6)	121.2(7)	P(2)–N(6)–P(3)	137.6(8)
N(6)–P(3)–N(7)	123.2(7)	P(3)–N(7)–P(4)	132.7(11)
N(7)–P(4)–N(8)	123.9(7)	P(4)–N(8)–P(1)	135.8(8)
Cl(1)–P(1)–N(5)	107.8(5)	Cl(1)–P(1)–N(8)	102.5(5)
Cl(2)–P(2)–N(5)	101.4(5)	Cl(2)–P(2)–N(6)	111.6(7)
Cl(3)–P(3)–N(6)	107.5(6)	Cl(3)–P(3)–N(7)	105.8(5)
Cl(4)–P(4)–N(7)	105.3(5)	Cl(4)–P(4)–N(8)	107.5(5)
N(1)–P(1)–N(5)	106.1(7)	N(1)–P(1)–N(8)	112.2(7)
N(2)–P(2)–N(5)	111.6(7)	N(2)–P(2)–N(6)	109.3(7)
N(3)–P(3)–N(6)	107.6(7)	N(3)–P(3)–N(7)	106.3(8)
N(4)–P(4)–N(7)	104.9(8)	N(4)–P(4)–N(8)	107.9(7)
Cl(1)–P(1)–N(1)	105.0(5)	C(11)–N(1)–C(12)	115(1)
Cl(2)–P(2)–N(2)	105.5(6)	C(21)–N(2)–C(22)	111(1)
Cl(3)–P(3)–N(3)	105.1(5)	C(31)–N(3)–C(32)	116(1)
Cl(4)–P(4)–N(4)	106.1(5)	C(41)–N(4)–C(42)	112(1)
C(11)–N(1)–P(1)	121(1)	C(31)–N(3)–P(3)	119(1)
C(12)–N(1)–P(1)	116(1)	C(32)–N(3)–P(3)	117(1)
C(21)–N(2)–P(2)	121(1)	C(41)–N(4)–P(4)	123(1)
C(22)–N(2)–P(2)	121(1)	C(42)–N(4)–P(4)	118(1)

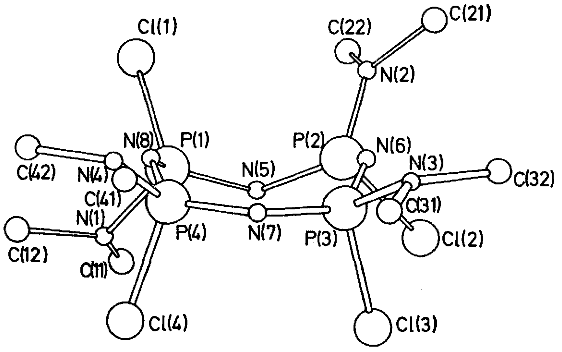

FIGURE 2 Molecular configuration

Ring Bonds and Angles.—An immediately noticeable feature of the structure is the unsymmetrical position of the ring nitrogen atom N(6) with respect to the flanking phosphorus atoms P(2) and P(3). The bond distances, 1.62 and 1.48 Å respectively, are markedly different from the mean ring-bond length of 1.56 Å, which is also the value found previously [2] in the structure of the *cis,cis,-trans,trans*-isomer (1). Although the estimated standard deviations here are relatively large as a result of the initial difficulties in obtaining a well-formed crystal, the bond distances to N(6) are outside the possible range of error and must be considered significant. This is the first time that such large variations in ring-bond lengths have been observed in a cyclophosphazene containing equivalently substituted phosphorus atoms. It is difficult to offer a precise explanation for this observation. Examination of the non-bonded interactions involving N(6) do not reveal significant differences from those associated with, for example, N(7). The only feature distinguishing the immediate environment of N(6) from that of the other ring nitrogen atoms is the Cl(2) ··· Cl(3) contact distance which is 3.67(1) Å. For the equivalent separations in the molecule, the distances are much longer as Cl(1) is *trans* to both Cl(2) and Cl(4) while the Cl(3) ··· Cl(4) distance is >4.0 Å. As the van der Waals diameter for chlorine is *ca.* 3.6 Å, it appears that the molecule is distorted in the P(2)–N(6)–P(3) segment such that the chlorine atoms approach as close as possible, or alternatively that distortion in the molecule forces the chlorine atoms closer and stops at the observed position because the Cl(2) ··· Cl(3) distance reaches a minimum value. As in many similar situations it is difficult to determine which of these factors is the cause and which is the effect.

The endocyclic angles at nitrogen vary from 128.8 at N(5) to 137.6° at the asymmetrically bonded N(6) [mean 133.7°]. The ring angles at phosphorus have a mean value of 122.6°, which is normal for this type of structure.

Exocyclic Groups.—Within experimental error, the P–N(amine) bonds are all equal in length (1.63 Å) as are the P–Cl bonds (2.05 Å). The former are shorter than the accepted single-bond distance, and in agreement with some degree of π bonding to phosphorus the stereochemistry around the nitrogen atoms approaches planarity. This is shown by the angles summing to 352° in each case and an average deviation of 0.24 Å for the nitrogen atoms from the respective PC_2 plane. As found in other systems containing non-geminal dimethylamino-groups, the plane of the NC_2 group is almost normal (mean 84.7°) to the plane through the respective P–N–Cl atoms. In this way steric repulsions are minimized.

Ring Conformation.—The equations for a number of planes associated with the P_4N_4 ring are given in Table 3, which also includes the deviations of various atoms from these planes. From the disposition of the substituents, the maximum possible symmetry for the molecule is a mirror plane passing through P(1) and P(3), but it is clear from the deviations about the mean ring plane that

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[5] D. Millington and D. B. Sowerby, *Spectrochim. Acta*, 1973, **A29**, 765.

[6] T. T. Bamgboye, M. J. Begley, and D. B. Sowerby, *J.C.S. Dalton*, 1975, 2617.

this is not present. The torsion angles of the ring bonds (see Figure 1) also show no particular inter-relationship and as might be predicted from the unsymmetrical substitutent orientation the system is without symmetry.

Table 3

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

Atoms in plane	Equation
P(1)—(4) and N(5)—(8)	$0.094x - 0.443y + 0.892z = 1.276$
[P(1) −0.022, P(2) 0.140, P(3) −0.216, P(4) −0.106, N(5) −0.466, N(6) 0.384, N(7) −0.143, N(8) 0.428]	
P(1)—(4)	$0.019x - 0.428y + 0.903z = 1.103$
[P(1) −0.069, P(2) 0.068, P(3) −0.068, P(4) 0.068, N(5) −0.557, N(6) 0.428, N(7) 0.066, N(8) 0.494]	
N(5)—(8)	$0.177x - 0.452y + 0.875z = 1.491$
[N(5) −0.350, N(6) 0.355, N(7) −0.361, N(8) 0.356, P(1) 0.035, P(2) 0.237, P(3) −0.358, P(4) −0.290]	
P(2)—(4)	$-0.009x - 0.373y + 0.928z = 1.131$
[P(1) −0.270, N(5) −0.708, N(6) 0.448, N(7) 0.094, N(8) 0.343]	
P(1)—P(2)—P(4)	$0.047x - 0.483y + 0.875z = 0.932$
[P(3) −0.273, N(5) −0.538, N(6) 0.268, N(7) −0.100, N(8) 0.509]	

The best plane through the four phosphorus atoms has phosphorus atoms alternatively above and below this plane while the nitrogen atoms show two large positive deviations [N(6) and N(8)], one large negative deviation [N(5)], and finally a small negative deviation for N(7) implying that the segment P(3)–N(7)–P(4) is almost parallel to the mean ring plane. This aspect is clearly shown in Figure 2. A plane drawn through the four ring nitrogen atoms shows that these atoms are also distributed alternately above and below the plane, but there is no apparent relationship with the phosphorus atom arrangement.

There is however a close relationship between the ring conformation here and that found earlier [6] for the penta-substituted dimethylamino-derivative, $P_4N_4Cl_3(NMe_2)_5$, in which the three non-geminal dimethylamino-groups occupy *cis* positions. In many respects this similarity is predictable from the empirical relationship we have previously developed between substituent orientation and observed ring conformation in substituted tetraphosphazenes.[7] The ring conformation here can therefore be described as a mixed 'crown-saddle'. The 'crown' section is that associated with the P(2)–P(4) ring segment in which the three amino-groups are all *cis*, and the nitrogen atoms N(6), N(7), and N(8) all show positive deviations from the plane described by P(2)–P(4) (see Table 3). In passing it should be noted that the deviation of N(7) is very small. The 'saddle' part concerns the P(2)–P(1)–P(4) segment where the amino-substituents have a *cis,trans,cis* arrangement, and here N(5) and N(7) have negative deviations while N(6) and N(8) are above the P(2)–P(1)–P(4) plane.

[6/925 *Received*, 14*th May*, 1976]

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