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Phosphorus–Nitrogen Compounds. I. Structure of 2,*cis*-4,*trans*-6,*trans*-8-Tetrachloro-2,4,6,8-tetrakis(diethylamino)cyclotetra(phosphazene)

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Abstract. $C_{16}H_{40}Cl_4N_8P_4$, $M_r = 610{\cdot}252$, monoclinic, $P2_1/c$, $a = 15{\cdot}374$ (5), $b = 9{\cdot}758$ (3), $c = 10{\cdot}117$ (3) Å, $\beta = 97{\cdot}41$ (2)°, $V = 1505{\cdot}03$ (2) Å^3, $Z = 4$, $D_m = 2{\cdot}61$, $D_x = 2{\cdot}694$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 12{\cdot}505$ cm^{-1}, $F(000) = 1280$, $T = 293$ K, $R = 0{\cdot}042$ for 871 observed reflections. The structure consists of four chloro and four diethylamino groups connected to P atoms of the non-planar cyclotetra(phosphazene) ring.

Introduction. The investigation of cyclic phosphazenes has attracted great interest in their synthetic, spectroscopic and unusual structural properties and dramatic advances have been observed in this area during the past decade (Allcock, 1972; Shaw, 1980; Fincham, Hursthouse, Parkes, Shaw & Shaw, 1986; Krishnamurty & Woods, 1987).

Cyclophosphazenes are used in the production of phosphazene polymers for different purposes (Allcock, 1985) and some of them are thought to be useful as cancer chemotherapeutic agents (Chernov, Lytkina, Sergievskaya, Kropacheva, Parshina & Sventsitkaya, 1959; Huizen, 1984). A relationship has been observed between the structures of the cyclophosphazenes and cytostatic activity (van der Huizen, 1984) and for effective tumour growth inhibition, electron-donating groups (*e.g.* aziridine, pyrrolidine, primary and other secondary amines) in the P–N ring skeletons seem to be essential. The aminolyses of octachlorocyclotetra(phosphazene), $N_4P_4Cl_8$, with various primary and secondary alkylamines in different solvents, give partially or fully substituted aminotetra(phosphazenes), according to the reaction conditions (Contractor, Kılıç & Shaw, 1987; Katti & Krishnamurty, 1985).

The reaction in ether between $N_4P_4Cl_8$ and an excess of the diethylamine led to the isolation of tetrachlorotetrakisdiethylaminocyclotetra(phosphazene) which is the only major product (m.p. 409 K). Several types of isomerization, such as *cis-/trans-*, geminal-*cis-/trans-* and geminal-geminal can be expected for the structure of this compound.

The unknown isomer of $N_4P_4Cl_4(NEt_2)_4$ (m.p. 445 K) has been reported previously (Ray, Shaw & Smith, 1963), which is different from the title compound. A structure determination of the title compound was undertaken to permit a comparison of its structure with that of previously reported analogues.

Experimental. 240 mmol of freshly distilled anhydrous diethylamine in 50 cm^3 of anhydrous diethyl ether was cooled to 273 K and added dropwise to a stirred solution of 10 mmol $N_4P_4Cl_8$ in 200 cm^3 anhydrous diethyl ether cooled to 268 K. The reaction mixture was stirred for 3 h and then boiled under reflux for 24 h. After removal of diethylamine hydrochloride and of solvent the residue was subjected to column chromatography using tetrahydrofuran–dichloromethane mixture as eluant on silica gel to remove salt and coloured products. The resulting solid substance was crystallized from

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Table 1. *Experimental data and structure refinement parameters*

Method of measuring D_m	Pycnometer (CCl_4)
Crystal shape and size (mm)	Prismatic, 0·25 × 0·25 × 0·3
Diffractometer used and data-collection technique	Four-circle diffractometer (Enraf–Nonius) CAD-4, ω–2θ scan
Number and θ range of reflections used for measuring lattice parameters	25 reflections with $8 \le 2\theta \le 21°$
Maximum value of $\sin\theta/\lambda$ reached in intensity measurements (Å^{-1})	0·504
Range of h, k and l	$-1 \le h \le 17, -1 \le k \le 11, -11 \le l \le 11$
Standard reflections and their intensity variation throughout experiment (%)	004, $5\bar{2}1$, $\bar{3}3\bar{3}$, variation 0, −1, −1% respectively
Number of reflections measured	2151
Number of unique reflections	1463
Number of unobserved reflections	592
Criterion for recognizing unobserved reflections	$I \le 3\sigma(I)$
Method used to solve structure	Direct methods
Use of F or F^2 magnitudes in least-squares refinement	F
Parameters refined	Coordinates and anisotropic temperature factors of non-H atoms, 144
Values of R, wR	0·042, 0·052, S not calculated
Method used to calculate w	$w = 1$
Final residual electron densities (e Å^{-3}) for max. and min. peaks	+0·68 and −0·68
Max. (Δ/σ)	0·00
Source of atomic scattering factors and f', f'' values	*International Tables for X-ray Crystallography* (1974)
Computer programs used	*SHELXS*86 (Sheldrick, 1986), *CRYSTALS* (Watkin, Carruthers & Betteridge, 1985), *SNOOPI* (Davies, 1983)

hexane. In about two days, colourless prismatic crystals (m.p. 409 K) were obtained from dichloromethane–hexane–benzene mixture.

Experimental data, the method used to solve the structure and other related parameters and procedures are given in Table 1. Non-H atoms were included with anisotropic thermal parameters. Difference Fourier calculations did not show clearly the electron density for H atoms. Therefore, H atoms were geometrically positioned 1·0 Å from C atoms with coordinates and isotropic temperature factor coefficients ($U = 0·07$ Å^2) kept fixed and a riding model was used in the refinement process of H-atom positions.

Table 2. *Atomic coordinates* (× 10^4) *and isotropic or equivalent isotropic thermal parameters* (Å^2 × 10^4) *with e.s.d.'s in parentheses*

$$U_{eq} = (1/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U/U_{eq}(Å^2)
N1	−1480 (3)	−2247 (6)	1295 (5)	415
N2	−413 (3)	−218 (6)	1652 (5)	446
N3	−53 (4)	2145 (6)	2701 (6)	526
N4	835 (4)	1422 (7)	782 (5)	547
P1	325 (1)	876 (2)	1900 (2)	455
P2	−642 (1)	−1528 (2)	780 (2)	410
C1	−1516 (5)	−2392 (9)	2738 (7)	608
C2	−574 (5)	1815 (8)	3797 (8)	592
C3	−2240 (6)	−1596 (11)	3189 (9)	821
C4	919 (8)	3945 (14)	3643 (13)	1299
C5	−1452 (6)	2395 (12)	3568 (13)	1165
C6	−2122 (5)	−3078 (8)	397 (8)	599
C7	−1898 (6)	−4538 (10)	351 (11)	975
C8	254 (6)	3551 (9)	2621 (9)	759
Cl1	391 (1)	−2865 (2)	1187 (3)	782
Cl2	1319 (1)	17 (3)	3224 (2)	778

Table 3. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

N1—P2	1·611 (5)	N4—P1	1·550 (6)
N1—C1	1·474 (9)	N4—P2*B*	1·573 (6)
N1—C6	1·492 (9)	P1—Cl2	2·074 (3)
N2—P1	1·556 (6)	P2—Cl1	2·056 (3)
N2—P2	1·566 (6)	C1—C3	1·48 (1)
N3—P1	1·628 (6)	C2—C5	1·45 (1)
N3—C2	1·484 (9)	C4—C8	1·41 (1)
N3—C8	1·46 (1)	C6—C7	1·47 (1)
C1—N1—P2	119·7 (5)	N4*B*—P2—N2	120·7 (3)
C6—N1—P2	122·3 (4)	C3—C1—N1	112·5 (7)
C6—N1—C1	116·3 (5)	C5—C2—N3	112·0 (8)
P2—N2—P1	139·2 (4)	Cl2—P1—N2	106·7 (2)
C2—N3—P1	118·0 (5)	Cl2—P1—N3	105·5 (3)
C8—N3—P1	123·3 (5)	Cl2—P1—N4	102·1 (3)
C8—N3—C2	117·1 (6)	Cl1—P2—N1	106·8 (2)
N3—P1—N2	107·6 (3)	Cl1—P2—N2	107·1 (2)
N4—P1—N2	123·0 (3)	Cl1—P2—N4*B*	106·5 (3)
N4—P1—N3	110·4 (3)	C7—C6—N1	114·0 (7)
N2—P2—N1	107·7 (3)	C4—C8—N3	115·2 (9)
N4*B*—P2—N1	107·4 (3)	P2—N4*B*—P1*B*	135·1 (4)

Symmetry operation *B*: −x, −y, −z.

Discussion. Final coordinates and isotropic or equivalent isotropic thermal parameters are given in Table 2.* Bond lengths and angles are given in Table 3. The structure of the title compound is shown in Fig. 1. The structure consists of four chloro and four diethylamino groups connected to P atoms of a non-planar cyclotetra(phosphazene) ring.

In such structures, the dependence of P—N distances on the electronegativity of the substituents is very important. In the case of electron-donating groups being present, different P—N distances in the cyclotetra(phosphazene) ring could be expected. But for this structure, in the segments N4*B*—P2—N2 and N2—P1—N4, there is no clear difference in the electronegativities of the atoms attached to P1 and P2 because the two P atoms have the same substituents. Thus the four P—N bonds in the ring are approximately the same, and the mean P—N bond distance in the ring is 1·561 Å. In related compounds the corresponding mean bond lengths are 1·58 Å in $N_4P_4(NMe_2)_8$ (Bullen, 1962) and 1·56–1·57 Å in $N_4P_4Cl_8$ (Hazekamp, Migchelsen & Vos, 1962;

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52806 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Wagner & Vos, 1968*a*). This value for P—N bonds is considerably smaller than a single P—N bond length of 1·77 Å (Cruickshank, 1964; Hobbs, Corbridge & Raistrick, 1953).

The short bond lengths in the ring have appreciable double-bond character and this confirms bond contraction in the skeleton.

The mean exocyclic P—N bond length (1·618 Å) is much shorter than the exocyclic bonds in $N_4P_4(NMe_2)_8$ (1·679 Å) (Bullen, 1962). It has been generally observed that the exocyclic P—N bonds are longer than the endocyclic P—N bonds in the ring (Ahmed & Pollard, 1972). The mean P—Cl bond length (2·065 Å) is as long as in *cis*-$N_4P_4Cl_4Ph_4$ (Bullen & Tucker, 1972*a*) and $N_4P_4Cl_4(NMe_2)_4$ (Bullen & Tucker, 1972*b*).

The endocyclic and exocyclic angles at P1 and P2 have different values. The endocyclic N4*B*—P2—N2 and N2—P1—N4 angles are 120·7 and 123·0° respectively. The exocyclic Cl1—P2—N4*B*, Cl1—P2—N2, N1—P2—N4*B*, N1—P2—N2 and N1—P2—Cl1 angles are 106·5, 107·1, 107·4, 107·7 and 106·8° while the exocyclic Cl2—P1—N2, Cl2—P1—N4, Cl2—P1—N3, N2—P1—N3 and N4—P1—N3 angles are 106·7, 102·1, 105·5, 107·6 and 110·4° respectively. Hence, Cl—P—N(*endo*/*exo*) or N(*exo*)—P—N(*endo*) angles are approximately equal. The distribution of bonds around P1 and P2 indicates a distorted tetrahedral geometry.

The endocyclic P2—N4*B*—P1*B* and P2—N2—P1 angles are 135·1 and 139·2° respectively. A similar spread of the P—N—P angles was found in *cis*-$N_4P_4Cl_4Ph_4$ (Bullen & Tucker, 1972*a*) and it was specified that such large angles appear to be characteristic of molecules containing chlorine and fluorine (George, Mackay & Stobart, 1972).

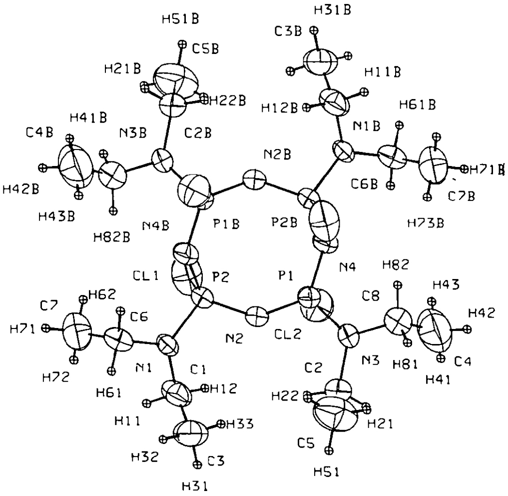

Fig. 1. Structure of the title compound with the atomic labelling scheme.

The mean C—N—C angle in the NEt_2 substituent is only 116·7° whereas the P—N—C angles are nearer to 120°. Other phosphazenes containing dimethylamino groups also show C—N—C angles smaller than the P—N—C angles, *e.g.* $N_6P_6(NMe_2)_{12}$ with mean C—N—C = 112·9° (Wagner & Vos, 1968*b*), $N_4P_4(NMe_2)_8$ with mean C—N—C = 116° (Bullen, 1962).

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