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trans-2,6-Bis(ethylamino)-2,4,4,6,8,8-hexapiperidinocyclo-2λ^5,4λ^5,6λ^5,8λ^5-tetraphosphazatetraene

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Abstract

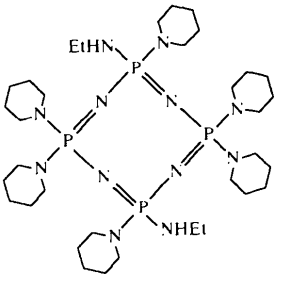
The title compound, $C_{34}H_{72}N_{12}P_4$, consists of a chair-shaped cyclic tetrameric phosphazene ring with six bulky piperidino and two ethylamino side groups. The two ethylamino side groups are in *trans* positions. The bulky substituents are instrumental in determining the eight-membered-ring conformation. The endocyclic N—P—N angles, which have different substituents, are not the same as the P—N—P angles of the macrocyclic ring.

Comment

During the last two decades, the structures and properties of the bulky phenoxy derivatives of hexachlorocyclo-2λ^5,4λ^5,6λ^5-triphosphazene, $N_3P_3Cl_6$, and octachlorocyclo-2λ^5,4λ^5,6λ^5,8λ^5-tetraphosphazene, $N_4P_4Cl_8$, have attracted great interest in the synthesis of new, small-molecule organocyclophosphazenes (Allcock, Dembek *et al.*, 1992) and high polymeric phosphazenes with inorganic backbones (Allcock, 1985; Allcock *et al.*, 1987) and aryloxy side groups which may be useful as high refractive index glasses (Olshavsky & Allcock, 1995), ferroelectric and non-linear optical polymers (Allcock *et al.*, 1991), liquid crystalline materials (Allcock & Kim, 1991) and biomedical materials (Cohen *et al.*, 1990). Some of the phosphazene polymers are thought to be useful as cancer chemotherapeutic agents (Chernov *et al.*, 1959; van der Huizen, 1984). A relationship has been determined 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, and primary and secondary amines) in the P—N ring skeletons seem to be essential. The important physical or chemical properties of phosphazene polymers are imposed by the structure of the organic, inorganic or metal–organic side groups (Allcock, 1985). The organophosphazene derivatives are used in polymer synthesis and the resulting polymers are expected to have unique physical properties (Allcock, 1972; Allcock *et al.*, 1987). Polyphosphazenes with aryloxy, alkoxy and metallocenyl side groups are of special interest (Allcock *et al.*, 1984).

There are two crystal modifications, generally called the *K* and *T* forms, of $N_4P_4Cl_8$, which is a standard compound for tetrameric phosphazenes (Hazekamp *et al.*, 1962; Wagner & Vos, 1968). The crystal structures of some $N_4P_4Cl_8$ derivatives such as $[N_4P_4(NMe_2)_8]$, (1), (Bullen, 1962), $[N_4P_4Cl_4(NEt_2)_4]$, (2), (Hökelek & Kılıç, 1990), $[N_4P_4Cl_7(OC_6H_2$-2,6-$^tBu_2$-4-Me)], (3), (Hökelek *et al.*, 1996) and $[N_4P_4(NC_4H_8O)_6(NHCH_2CH_3)]$, (4), (Hökelek *et al.*, 1998) have been determined.

The main objective of this study was to determine the influences of the relatively hindered side groups, and also of steric and electronic factors, on the macrocyclic tetraphosphazene ring. The title molecule, (I), is shown



(I)

in Fig. 1. Its structure consists of a non-planar cyclic tetrameric phosphazene ring in a chair conformation with two ethylamino (in 2,6-*trans* positions) and six bulky piperidino side groups. The N atoms are displaced

with respect to the plane through the P atoms by N1 +0.396 (2) and N2 +0.579 (2) Å. The conformation of the macrocyclic phosphazene ring can be clarified from the torsion angles of the ring bonds in which the symmetry operation reverses the sign of a torsion angle (Table 1). The total puckering amplitude of the phosphazene ring is 0.719 (2) Å (Cremer & Pople, 1975). As can also be seen from the distribution of the endocyclic torsion angles (Table 1), the asymmetry parameters indicate three local pseudo twofold axes running along P2···P2^{i}, the midpoints of P1—N2 and P1^{i}—N2^{i}, the midpoints of N1—P2 and N1^{i}—P2^{i}, and a pseudo mirror running along P1···P1^{i} (Nardelli, 1983) [symmetry code: (i) $2-x, 1-y, 1-z$].

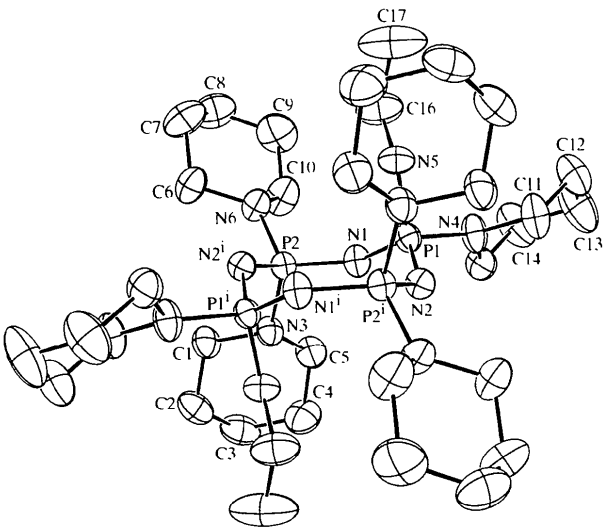


Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of the title molecule with the atom-numbering scheme [symmetry code: (i) $2-x, 1-y, 1-z$]. The displacement ellipsoids are drawn at the 50% probability level.

The P—N—P bond angles are 130.1 (1) and 130.0 (1)°. In compounds (2), (3) and (4), the P—N—P bond angles are in the ranges 135.1 (4)–139.2 (4), 133.6 (2)–139.3 (2) and 127.3 (2)–134.4 (2)°, respectively. It was reported that such large angles appear to be characteristic of molecules containing chlorine or fluorine (George *et al.*, 1972). Although the title compound contains neither chlorine nor fluorine, large P—N—P angles appear to be due to the different substituents on the P atoms. The interesting point is that in the title compound, (I), the P—N—P bond angles in the macroring are unique, but in the similar compound (4), the corresponding bond angles differ by ~7°, although only the piperidino groups are substituted for the morpholino groups. In addition, the N—P—N bond angles range from 117.9 (1) to 122.0 (1)° [average 120.0 (1)°].

In trimeric phosphazenes, it has been observed that endocyclic (N—P—N) angles decrease while exocyclic (*R*—P—*R'*) angles increase (Contractor *et al.*, 1985; Fincham *et al.*, 1986; Kılıç *et al.*, 1996; Hökelek *et al.*, 1994, 1996, 1998). The title compound and other tetrameric phosphazenes containing bulky phenoxy groups (Allcock, Dembek *et al.*, 1992; Allcock, Ngo, *et al.*, 1992; Allcock *et al.*, 1995) are different. The exocyclic angle N3—P2—N6 [109.9 (1)°] is highly affected, while the endocyclic angle N1—P2—N2^{i} [122.0 (1)°] is less affected, by the existence of the two repelling piperidino groups bonded to the P2 atom, compared with $N_4P_4Cl_8$ (Cl—P—Cl 103.1 and N—P—N 120.5°; Wagner & Vos, 1968). On the other hand, the exocyclic angle N4—P1—N5 [104.4 (1)°] increases while the endocyclic N1—P1—N2 [117.9 (1)°] decreases as a result of the piperidino and ethylamino groups bonded to the P1 atom. These interactions show that steric factors are more dominant than the electronic factors with respect to the ring skeleton. The P1—N1—P2 [130.1 (1)] and P1—N2—P2^{i} [130.0 (1)°] angles are narrower than the corresponding angles in $N_4P_4Cl_8$ (133.6 and 137.6°; Wagner & Vos, 1968).

When electron-donating groups are present, different P—N distances in the cyclotetraphosphazene ring could be expected (Bullen & Tucker, 1972), but there is no clear difference in the present structure between the electronegativities of the atoms attached to the P atoms. In the chair-shaped cyclic tetrameric phosphazene ring, the P—N bond distances vary from 1.577 (2) to 1.592 (2) Å. The average ring P—N bond length is 1.585 (2) Å. In related compounds, (2), (3) and (4), the corresponding mean bond lengths are 1.561 (6), 1.558 (3) and 1.583 (4) Å, respectively. The values of P—N bonds are considerably smaller than the single P—N bond length of 1.683 (5) Å (Allen *et al.*, 1987), 1.77 Å (Cruickshank, 1964; Hobbs *et al.*, 1953) and 1.78 (6) Å [*cf.* Table 4.1.4 in *International Tables for X-ray Crystallography* (1968, Vol. III)]. The short bonds in the ring have an appreciable double-bond character; this is generally observed for phosphanitrilic molecules (Wagner & Vos, 1968).

Experimental

In this study, compound (I) was prepared from the reaction of piperidine (21.8 g, 256 mmol) and *trans*-2,6-$N_4P_4Cl_6(NEt)_2$ (3.2 g, 6.4 mmol) in chloroform (80 ml). Triethylamine (10.4 g, 102 mmol) was added to this mixture, which was worked up according to the literature method of Contractor *et al.* (1987). The compound was crystallized from acetonitrile [m.p. 450 K; yield 1.11 g (23%)].

Crystal data

$C_{34}H_{72}N_{12}P_4$ — Mo $K\alpha$ radiation
M_r = 772.93 — λ = 0.71073 Å

Monoclinic
$P2_1/n$
a = 13.088 (1) Å
b = 8.765 (1) Å
c = 18.717 (1) Å
β = 97.77 (1)°
V = 2127.3 (7) Å^3
Z = 2
D_x = 1.207 Mg m^{-3}
D_m not measured

Cell parameters from 25 reflections
θ = 10–18°
μ = 0.21 mm^{-1}
T = 298 K
Block-like
0.30 × 0.20 × 0.15 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans *MolEN* (Fair, 1990)
T_{min} = 0.976, T_{max} = 0.999
4812 measured reflections
4309 independent reflections

2763 reflections with $F > 3\sigma(F)$
R_{int} = 0.017
θ_{max} = 26.3°
$h = -16 \rightarrow 0$
$k = 0 \rightarrow 10$
$l = -23 \rightarrow 23$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F
R = 0.037
wR = 0.053
S = 1.20
2763 reflections
226 parameters
H atoms: see text
$w = 1/[\sigma(F)^2]$

$(\Delta/\sigma)_{max}$ = 0.01
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.09 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

P1—N1	1.586 (2)	P2—N1	1.577 (2)
P1—N4	1.658 (2)	P2—N6	1.673 (2)
P1—N5	1.651 (2)	P2—N2^i	1.581 (2)
P1—N2	1.592 (2)	P2—N3	1.689 (2)
N1—P1—N4	103.2 (1)	N1—P2—N3	103.7 (1)
N1—P1—N5	114.5 (1)	N6—P2—N3	109.9 (1)
N1—P1—N2	117.9 (1)	N1—P2—N2^i	122.0 (1)
N4—P1—N5	104.4 (1)	P1—N1—P2	130.1 (1)
N4—P1—N2	110.0 (1)	P2—N2^i—P1^i	130.0 (1)
N5—P1—N2	106.0 (1)	P1—N2—P2^i	130.0 (1)
N1—P2—N6	107.9 (1)		
N4—P1—N1—P2	−170.4 (2)	N2^i—P2—N1—P1	−17.3 (2)
N5—P1—N1—P2	−58.0 (2)	N1—P2—N2^i—P1^i	−53.1 (1)
N2—P1—N1—P2	68.0 (2)	N6—P2—N2^i—P1^i	−175.3 (1)
N1—P1—N2—P2^i	−88.0 (2)	N3—P2—N2^i—P1^i	67.3 (1)
N4—P1—N2—P2^i	154.1 (2)	P1—N2—P2^i—N1^i	53.1 (2)
N5—P1—N2—P2^i	41.9 (2)	N2^i—P1^i—N1^i—P2^i	−68.0 (1)
N6—P2—N1—P1	103.2 (2)	N1^i—P1^i—N2^i—P2	88.0 (1)
N3—P2—N1—P1	−140.0 (2)	N2—P2—N1^i—P1^i	17.3 (1)

Symmetry code: (i) $2-x, 1-y, 1-z$.

The structure was solved by direct methods. The H5 position was determined from difference synthesis and the other H-atom positions were calculated geometrically and a riding model was used during the refinement process.

Data collection: *MolEN* (Fair, 1990). Cell refinement: *MolEN*. Data reduction: *MolEN*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1406). Services for accessing these data are described at the back of the journal.

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