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trans-2,4,4,6,8,8-Hexamorpholino-2,6-bis(*n*-propylamino)cyclo-2λ^5,4λ^5,6λ^5,8λ^5-tetraphosphazatetraene

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The title compound, $C_{30}H_{64}N_{12}O_6P_4$, consists of a centrosymmetric chair-shaped cyclic tetrameric phosphazene ring with six bulky morpholino and two *n*-propylamino side groups. The two *n*-propylamino side groups are in *trans* positions. The bulky substituents mainly determine the eight-membered-ring conformation. The endocyclic N—P—N angles around the P atoms having different substituents are not the same as the P—N—P angles of the macrocyclic ring.

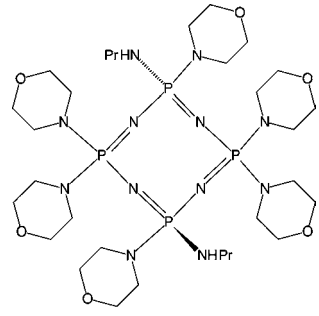
Comment

Cyclophosphazenes have attracted much interest as a result of their potential use in the synthesis of new small-molecule organocyclophosphazenes (Allcock *et al.*, 1992) and high polymeric phosphazenes with inorganic backbones, which have many different uses (Allcock *et al.*, 1987; Hökelek *et al.*, 1996), 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).

On the other hand, some of the aminophosphazenes 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, morpholine, and primary and secondary amines) in the P–N ring skeletons seem to be essential.

The crystal structures of some $N_4P_4Cl_8$ derivatives, such as $[N_4P_4(NMe_2)_8]$, (II) (Bullen, 1962), β-*trans*-$N_4P_4(NHMe)_4Ph_4$, (III) (Bullen & Mallinson, 1972), $[N_4P_4Cl_4(NEt_2)_4]$, (IV) (Hökelek & Kılıç, 1990), $[N_4P_4Cl_7(OC_6H_2$-2,6-^{t}Bu$_2$-4-Me)], (V) (Hökelek *et al.*, 1996), $[N_4P_4(NC_4H_8O)_6(NHCH_2CH_3)$, (VI) (Hökelek *et al.*, 1998), and $[N_4P_4(NC_5H_{10})_6(NHEt)_2]$, (VII) (Hökelek *et al.*, 1999), have been determined.

A structure analysis of the title compound, (I), was undertaken to determine the influences of the relatively hindered side groups, and also of the steric and electronic factors, on the macrocyclic tetraphosphazene ring. The title compound is illustrated in Fig. 1. The structure consists of a centrosymmetric non-planar cyclic tetrameric phosphazene ring in a chair conformation, with two *n*-propylamino (in 2,6-*trans* positions) and six bulky morpholino side groups. The four P atoms are coplanar and the four N atoms are displaced above (+) and below (−) their plane by equal amounts [N1 −0.513 (4) Å and N6 −0.317 (4) Å]. The conformation of the macrocyclic phosphazene ring is indicated by the torsion angles of the ring bonds in which the symmetry operation reverses the sign of a torsion angle (Fig. 2).



(I)

As can be seen from the distribution of the endocyclic torsion angles, it appears that in the central ring there are two local pseudo-mirrors, one running along the midpoints of the N6—P2′ and N6′—P2 bonds, the other along the midpoints of the P1—N1 and P1′—N1′ bonds. The P—N—P bond angles are 130.4 (2) and 136.9 (2)° (average 133.7°). The P—N—P bond angles are in the ranges 135.1 (4)–139.2 (4), 133.6 (2)–139.3 (2), 127.3 (2)–134.4 (2) and 130.0 (1)–130.1 (1)° in compounds (IV), (V), (VI) and (VII), 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 endocyclic N—P—N angles vary in the range 117.5 (2)–122.5 (2)° (average 120.0°).

In trimeric phosphazenes, it has been observed that the endocyclic (N—P—N) angles about P decrease, while the exocyclic (*R*—P—*R*′) angles increase (Kılıç *et al.*, 1996; Hökelek *et al.*, 1996, 1998, 1999). The title compound and other tetrameric phosphazenes containing bulky phenoxy groups (Allcock *et al.*, 1995) are different. The exocyclic N2—P2—N3 angle [110.1 (2)°] is highly affected, while the endocyclic N1—P2—N6′ angle [122.5 (2)°] is less affected, by the existence of the two repelling morpholino groups bonded to the P2 atom, compared with the parent compound $N_4P_4Cl_8$ (Cl—P—Cl 103.1° and N—P—N 120.5°; Wagner & Vos, 1968). On the other hand, the exocyclic N4—P1—N5 angle [103.1 (2)°] remains unchanged, while the endocyclic N1—P1—N6 angle [117.5 (2)°] decreases as a result of the morpholino and *n*-propylamino groups bonded to the P1 atom. These interactions show that steric factors are more

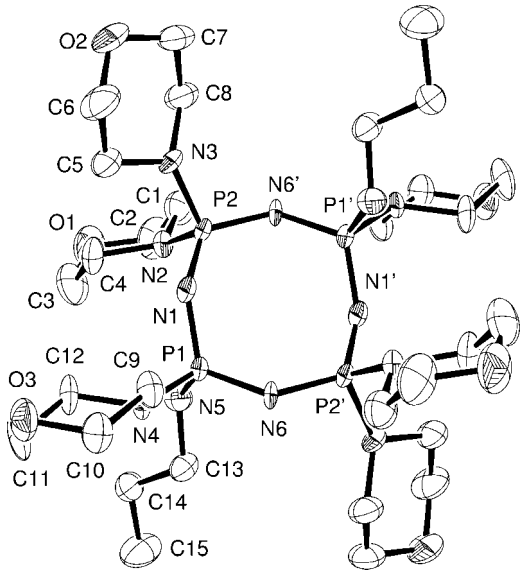


Figure 1
An *ORTEP*-3 (Farrugia, 1997) drawing of the title molecule with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Primed atoms are related to their unprimed equivalents by the transformation $(1-x, 1-y, 1-z)$.

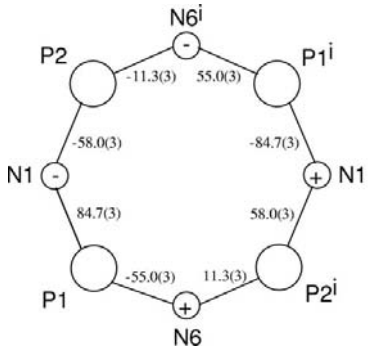


Figure 2
The shape of the phosphazene ring in (I) with torsion angles (°) given. [Symmetry code: (i) $1-x, 1-y, 1-z$.]

dominant than electronic factors, with respect to the ring skeleton. The P1—N1—P2 angle is 136.9 (2)°, but the P1—N6—P2′ angle [130.4 (2)°] is narrowed compared with the corresponding angles in $N_4P_4Cl_8$ (133.6 and 137.6°; Wagner & Vos, 1968).

In tetrameric phosphazenes, the P—N bond lengths have been correlated with the electronegativities of the substituents (Bullen & Tucker, 1972). In the present structure, the bulky morpholino and *n*-propylamino groups are electron donating. In the chair-shaped cyclic tetrameric phosphazene ring, the P—N bond distances vary from 1.573 (3) to 1.587 (4) Å. The average ring P—N bond length is 1.581 (5) Å. In related compounds, the mean bond lengths are 1.561 Å in (IV), 1.558 Å in (V), 1.583 Å in (VI) and 1.585 Å in (VII). The P—N bond lengths are considerably shorter than the P—N single-bond length of 1.683 (5) Å (Allen *et al.*, 1987). The short bonds in the ring have an appreciable double-bond character; this is generally observed for phosphanitrilic molecules (Wagner & Vos, 1968).

The mean exocyclic bond length [1.668 (16) Å] is nearly the same as that in (II) (1.679 Å). 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).

Experimental

In this study, compound (I) was prepared from the reaction of morpholine (5.23 g, 6.00 mmol) and 2-*trans*-6-$N_4P_4Cl_6(N^nPr)_2$ (2.04 g, 4.00 mmol) in acetonitrile (150 ml). Triethylamine (6.07 g, 6.00 mmol) was added to this mixture at 253 K, which was then worked up according to the literature method of Contractor *et al.* (1987). The compound was crystallized from acetonitrile [m.p. 483 K (decomposition); yield: 2.37 g (73%)].

Crystal data

$C_{30}H_{64}N_{12}O_6P_4$
$M_r = 812.81$
Triclinic, $P\overline{1}$
$a = 8.502$ (8) Å
$b = 10.939$ (14) Å
$c = 11.814$ (7) Å
$\alpha = 66.39$ (9)°
$\beta = 81.63$ (7)°
$\gamma = 81.74$ (10)°
$V = 991.7$ (17) Å^3
$Z = 1$
$D_x = 1.361$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10$–11°
$\mu = 0.25$ mm^{-1}
$T = 293$ (2) K
Rod, colourless
0.30 × 0.25 × 0.20 mm

Data collection

Enraf–Nonius TurboCAD-4 diffractometer
Non-profiled ω scans
Absorption correction: refined from ΔF (*SHELX*97; Sheldrick, 1998)
$T_{min} = 0.928$, $T_{max} = 0.952$
4298 measured reflections
4016 independent reflections
2115 reflections with $I > 2\sigma(I)$
$R_{int} = 0.053$
$\theta_{max} = 26.3°$
$h = 0 \rightarrow 10$
$k = -13 \rightarrow 13$
$l = -14 \rightarrow 14$
3 standard reflections
frequency: 120 min
intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.069$
$wR(F^2) = 0.183$
$S = 0.89$
3578 reflections
239 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1149P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.43$ e Å^{-3}
$\Delta\rho_{min} = -0.33$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

P1—N1	1.584 (4)	P2—N1	1.587 (4)
P1—N4	1.672 (3)	P2—N2	1.684 (4)
P1—N5	1.642 (4)	P2—N3	1.675 (4)
P1—N6	1.573 (3)	P2—N6^i	1.578 (3)
N1—P1—N4	107.90 (18)	N1—P2—N3	103.06 (19)
N1—P1—N5	108.8 (2)	N1—P2—N6^i	122.53 (17)
N1—P1—N6	117.50 (17)	N2—P2—N3	110.07 (18)
N4—P1—N5	103.09 (17)	N2—P2—N6^i	104.83 (18)
N4—P1—N6	103.34 (19)	N3—P2—N6^i	107.50 (17)
N5—P1—N6	114.88 (19)	P1—N1—P2	136.9 (2)
N1—P2—N2	108.59 (17)	P1—N6—P2^i	130.4 (2)
N1—P1—N6—P2^i	−55.0 (3)	N6—P1—N1—P2	84.7 (3)
N4—P1—N1—P2	−159.1 (3)	N2—P2—N1—P1	64.3 (3)
N4—P1—N6—P2^i	−173.7 (2)	N3—P2—N1—P1	−179.0 (3)
N5—P1—N1—P2	−48.0 (3)	N6^i—P2—N1—P1	−58.0 (3)
N5—P1—N6—P2^i	74.8 (3)		

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

The position of the H atom (H5) bonded to N5 was obtained from the difference syntheses and refined isotropically. The remaining H atoms were calculated geometrically at distances of 0.96 (CH_3) and 0.97 Å (CH_2) from their attached atoms and a riding model was used during the refinement process. It was not easy to obtain suitable high quality single crystals of the title compound in different solvents. Thus, the reason of the poor quality of the reported data and the high s.u.'s of the lattice constants may be due to the poor quality of the crystal used.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1085). Services for accessing these data are described at the back of the journal.

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