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6-Propylamino-2,6-propylepimino-2,4,4,8,8-pentakis(pyrrolidin-1-yl)-1,3,5,7,2λ^5,4λ^5,6λ^5,8λ^5-tetraazatetraphosphorocine

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The title compound, $C_{26}H_{55}N_{11}P_4$, consists of a bicyclic phosphazene ring with five bulky pyrrolidino and one propylamino group, together with a second propylamino group bridging the two P atoms. The asymmetric unit contains two molecules with very similar conformations. The bulky substituents are instrumental in determining the bicyclic P_4N_5 ring conformation. Each of the fused six-membered N_3P_3 rings is in a sofa conformation. The P—N distances in the bridge are non-equivalent and one of them is the longest P—N bond in the molecule. The hybridization of the bridging N atom is pyramidal. The single and double P—N bonds cannot easily be distinguished, since they retain their phosphazenic character in the phosphazene macro-rings.

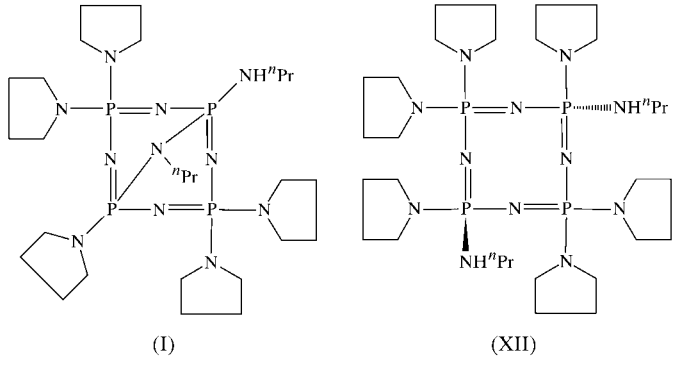
Comment

The structures of tri- and tetraphosphazene derivatives with different substituents have been the subject of much interest in our laboratory. Examples include 2,*cis*-4,*trans*-6,*trans*-8-tetrachloro-2,4,6,8-tetrakis(diethylamino)cyclotetra(phosphazene), (II) (Hökelek & Kılıç, 1990), 2-(2,6-di-*tert*-butylphenoxy)-2′,4,4,4′,4′,6,6,6′,6′-nonachloro-2,2′-bi(cyclotri-λ^5-phosphazene), (III) (Hökelek *et al.*, 1994), $N_3P_3Cl_5$-[$OC_6H_2(^tBu)_3$-2,4,6], (IV) (Kılıç *et al.*, 1996), 2-(2,6-di-*tert*-butyl-4-methylphenoxy)-2,4,4,6,6,8,8-heptachlorocyclo-2λ^5,-4λ^5,6λ^5,8λ^5-tetraphosphazatetraene, (V) (Hökelek *et al.*, 1996), *trans*-2,6-bis(ethylamino)-2,4,4,6,8,8-hexamorpholinocyclo-2λ^5,4λ^5,6λ^5,8λ^5-tetraphosphazatetraene, (VI) (Hökelek *et al.*, 1998), 2,4,4,6,6-pentachloro-2-(2,6-di-*tert*-butyl-4-methylphenoxy)cyclo-2λ^5,4λ^5,6λ^5-triphosphazatriene, (VII) (Hökelek, Kılıç, Begeç & Kılıç, 1999), *trans*-2,6-bis(ethylamino)-2,4,4,6,8,8-hexapiperidinocyclo-2λ^5,4λ^5,6λ^5,8λ^5-tetraphosphazatetraene, (VIII) (Hökelek, Kılıç & Kılıç 1999), 2,2′-[triethyleneglycolbis(pentylether-2-amino)-2,2′,4,4,4′,4′,6,6,6′,6′-decachlorobicyclo-2λ^5,2′λ^5,4λ^5,4′λ^5,6λ^5,6′λ^5-triphosphazatriene, (IX) (Yıldız *et al.*, 1999), 2,4-[2,2′-methylenebis(4-nitrophenoxy)]-2,4,6,6-tetrachlorocyclo-2λ^5,4λ^5,6λ^5-triphosphazatriene (ansa), (X) (Hökelek, Akduran, Yıldız *et al.*, 2000), and 2,4,4,6,6-pentachloro-2-(2,4,6-trimethylphenoxy)cyclo-2λ^5,4λ^5,6λ^5-triphosphazatriene, (XI) (Hökelek, Akduran, Kılıç *et al.*, 2000).

The bicyclic P_4N_5 ring system, based on cyclotetraphosphazatetraene, was discovered by Sau in 1975 (Cameron *et al.*, 1975; Sau, 1976). Since then, several studies devoted to the formation of this class of compounds have been published (Contractor *et al.*, 1987; Krishnamurthy, 1989; Narayanaswamy *et al.*, 1985; Krishnamurthy *et al.*, 1979). These involved the reactions of 2,*trans*-6-bis(primary alkylamino)hexachloro derivatives, *viz* dimethylamine, diethylamine, dibenzylamine, pyrrolidine, *tert*-butylamine, piperidine and morpholine (Krishnamurthy, 1989).

Some of the aminophosphazene derivatives are thought to be useful as chemotherapeutic agents for the treatment of cancer (Chernov *et al.*, 1959; van der Huizen, 1984). A relationship has been observed between the structures of the cyclophosphazenes and cytostatic activity (van der Huizen, 1984). For effective inhibition of tumour growth, electron-donating groups (*e.g.* aziridine and pyrrolidine) in the P–N ring skeletons seem to be essential.

The crystal structures of some bicyclic phosphazene derivatives, such as $N_4P_4(NMe_2)_5(NHR)(NR)$ and $N_4P_4(NHR)_6(NR)$ (*R* is Me or Et), have been reported in the literature (Deutsch *et al.*, 1987; Cameron & Mannan, 1977; Cameron *et al.*, 1979, 1986; Krishnamurthy *et al.*, 1982). We have investigated the reactions of *trans*-2,6-bis(propylamino)-2,4,4,6,8,8-hexachlorocyclo-2λ^5,4λ^5,6λ^5,8λ^5-tetraphosphazatetraene and pyrrolidine in $CHCl_3$. The reaction yielded two different products, *viz*. bicyclic (I) and monocyclic (XII), both fully substituted tetraphosphazene derivatives. The title compound, (I), was separated as a major product from the reaction mixture by column chromatography, and it is the first example of N^{n}Pr-bridged bicyclic phosphazenes. The main objective of this study was to determine the influences of the highly hindered bridged N^{n}Pr chain and the pyrrolidine and NH^{n}Pr side groups on the structure of the bicyclic phosphazene ring.



(I) (XII)

The title compound, (I), is shown in Fig. 1. The asymmetric unit contains two molecules, almost related by a non-crystallographic inversion centre at approximately ($\frac{1}{4}$,$\frac{3}{4}$,$\frac{7}{8}$). The phos-

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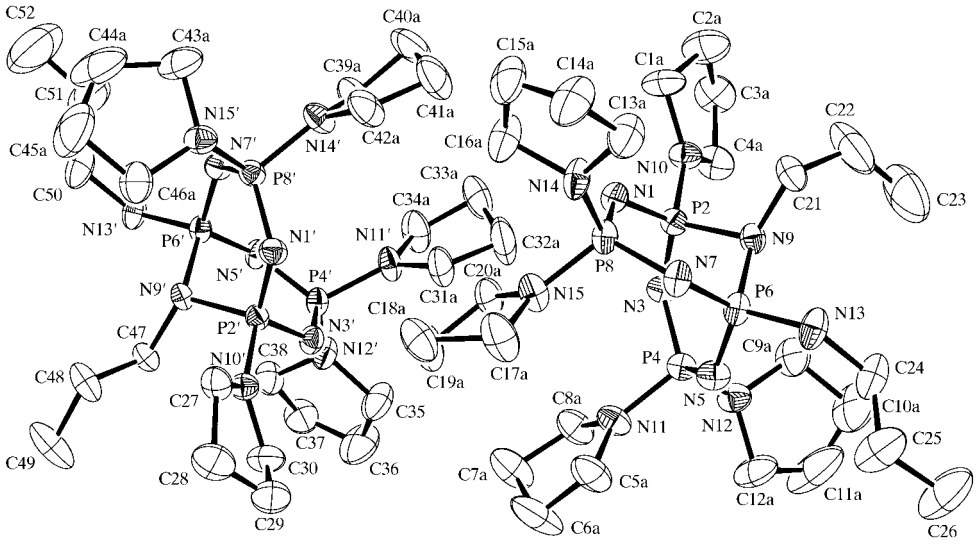

Figure 1
A view of the two independent molecules of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

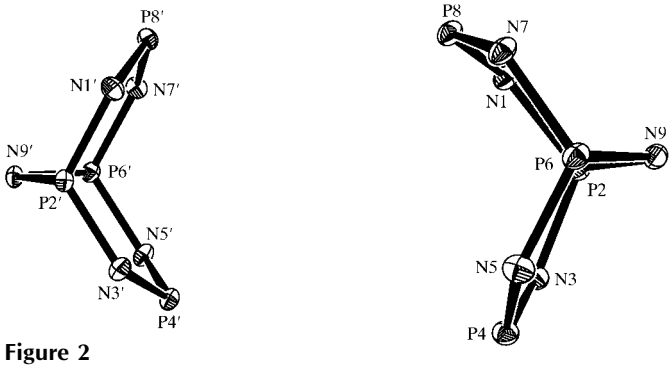

Figure 2
The conformations of the bicyclic macro-rings in (I). The substituents have been omitted for clarity.

phazene consists of an eight-membered ring, $(PN)_4$, with the second and sixth P atoms in the ring being bridged by a propylamino group. One of the bridged P atoms has a second propylamino group attached, while the other is substituted by a pyrrolidino group. The other P atoms have pyrrolidino groups attached. The bicyclic molecule is made up of two N_3P_3 rings fused by a common PNP fragment. The six-membered rings are in sofa conformations (Fig. 2). Each ring is V-shaped, with each of the two halves (P2/N3/P4/N5/P6, P2/N1/P8/N7/P6, P2′/N3′/P4′/N5′/P6′ and P2′/N1′/P8′/N7′/P6′) being essentially planar. In the two molecules, the two halves are inclined at angles of 62.2 (2) and 62.3 (2)°. The halves make angles of 62.5 (2) and 55.4 (2), and 56.3 (2) and 61.4 (2)° with the planes defined by the propylamino bridges, *i.e.* P2/N9/P6 and P2′/N9′/P6′.

The maximum separations between the two non-bridged P atoms in each molecule are P4···P8 4.013 (4) Å and P4′···P8′ 4.108 (4) Å. All other P···P distances in the two molecules are in the ranges 2.751 (2)–2.809 (2) and 2.773 (2)–2.804 (3) Å, with means of 2.778 (2) and 2.787 (2) Å, respectively. The N atoms are displaced above (+) and below (−) the least-squares planes through the P atoms by the following distances: N1 −0.608 (4), N3 −0.447 (4), N5 0.446 (4), N7 0.073 (3) and N9 1.596 (4), and N1′ 0.329 (3), N3′ 0.525 (4), N5′ −0.011 (3), N7′ −0.218 (3) and N9′ −1.616 (3) Å.

The conformations of the bicyclic phosphazenes resemble the 'adamantane' structure. The dihedral angles of the bicyclic rings in (I) (Fig. 2) reflect the structural aspects. The sums of the bond angles around atoms N9 and N9′ [338.9 (2) and 339.7 (2)°] show a change in the hybridization of the N atoms from trigonal planar towards pyramidal.

In the P_4N_4 tetraphosphazene ring systems, the endocyclic P—N and P′—N′ bond distances vary from 1.584 (2) to 1.611 (2) Å [average 1.592 (2) Å] and from 1.582 (2) to 1.606 (2) Å [average 1.591 (2) Å] in the two molecules. The longest P—N bonds in the present bicyclic molecules are those involving the bridging groups. The P—N bonds of the bridging propylamine groups [N9—P2 1.715 (2) and N9—P6 1.724 (2) Å; N9′—P2′ 1.724 (2) and N9′—P6′ 1.707 (2) Å] have different values in both molecules. The corresponding values reported in the literature are 1.73 (1) and 1.76 (1) Å in $N_4P_4(NMe_2)_5(NHEt)(NEt)$ (Cameron & Mannan, 1977), 1.709 (6) and 1.723 (6) Å in $N_4P_4(NHMe)_6(NMe)$ (Cameron *et al.*, 1979), and 1.706 (4) and 1.725 (4) Å in $N_4P_4(NMe_2)_5(NHMe)(NMe)$ (Cameron *et al.*, 1986). The exocyclic P—N and P′—N′ bond distances vary from 1.610 (2) to 1.655 (2) Å [average 1.636 (2) Å] and from 1.611 (3) to 1.652 (2) Å [average 1.636 (2) Å] for the two molecules. Structure determinations carried out in our laboratory of the trimeric and tetrameric phosphazenes, compounds (II)–(XI), have shown that the P—N bond-length ranges are 1.55–1.61 and 1.63–1.66 Å for endo- and exocyclic values, respectively.

In bicyclic phosphazenes, three types of P—N bonds are observed: the peripheral bonds (1.57–1.61 Å) retain their phosphazenic character, the exocyclic P—N bonds (1.63–1.66 Å) are slightly longer and the P—N bonds at the bridgehead (1.71–1.76 Å) are close to the value associated with a P—N single bond (1.77–1.80 Å; Krishnamurthy, 1994). In (I), the single- and double-bond character of the endo- and exocyclic P—N bonds cannot be easily distinguished (Table 1), since they retain their phosphazenic character in the phosphazene macro-rings. On the other hand, the bridgehead P—N bonds are outside the limits of the usual P—N single-bond range.

The packing of the molecules in the unit cell is due to van der Waals and dipole–dipole interactions (Fig. 3). The mol-

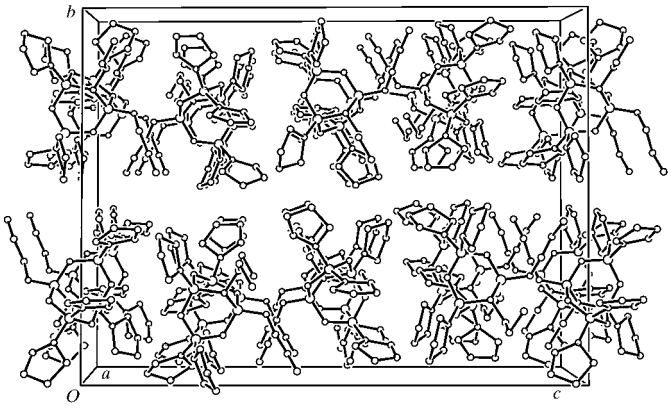

Figure 3
The packing diagram for (I).

ecules are aligned parallel to the *bc* plane, while, in the *a* direction, the molecules are packed in staggered layers.

In conclusion, the substituents bonded to P atoms play a very important role in the conformations of bicyclic phosphazene rings.

Experimental

Compound (I) was prepared from the reaction of 2,*trans*-6-bis-(propylamino)cyclotetraphosphazatetraene (2.16 g, 4.00 mmol), pyrrolidine (4.27 g, 60.0 mmol) and triethylamine (6.07 g, 60.0 mmol) in chloroform (200 ml). The mixture was stirred at 258 K for 2 h and then immediately refluxed for 12 h. The solvent was evaporated and benzene (150 ml) with triethylamine (10.1 g, 100 mmol) was added to the residue. The resulting mixture was refluxed for 3 h and then filtered to remove triethylamine hydrochloride. The solvent was removed by rotary evaporation and the residue chromatographed on silica gel. Compound (I) was purified by fractional crystallization in light petroleum (m.p. 430 K; yield 2.27 g, 83%).

Crystal data

$C_{26}H_{55}N_{11}P_4$
M_r = 645.69
Monoclinic, $P2_1/c$
a = 11.405 (11) Å
b = 21.545 (5) Å
c = 28.893 (16) Å
β = 97.73 (6)°
V = 7035 (8) Å^3
Z = 8
D_x = 1.219 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 10–18°
μ = 0.25 mm^{-1}
T = 293 (2) K
Rod, colourless
0.30 × 0.20 × 0.15 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
14 219 measured reflections
13 799 independent reflections
7479 reflections with $I > 2\sigma(I)$
R_{int} = 0.056
θ_{max} = 26.3°
$h = -14 \rightarrow 14$
$k = -26 \rightarrow 2$
$l = -21 \rightarrow 36$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.121
S = 1.03
13 799 reflections
803 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.055P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.004
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—P8	1.587 (2)	N1′—P2′	1.582 (2)
N1—P2	1.594 (2)	N1′—P8′	1.590 (2)
P2—N3	1.589 (2)	P2′—N3′	1.588 (2)
P2—N9	1.715 (2)	P2′—N9′	1.724 (2)
N3—P4	1.588 (2)	N3′—P4′	1.588 (2)
P4—N5	1.584 (2)	P4′—N5′	1.602 (2)
N5—P6	1.584 (2)	N5′—P6′	1.606 (2)
P6—N7	1.611 (2)	P6′—N7′	1.588 (2)
P6—N9	1.724 (2)	P6′—N9′	1.707 (2)
N7—P8	1.602 (2)	N7′—P8′	1.583 (2)
P8—N1—P2	122.07 (14)	P2′—N1′—P8′	122.93 (13)
N3—P2—N1	120.53 (12)	N1′—P2′—N3′	120.14 (12)
N3—P2—N9	105.18 (11)	N1′—P2′—N9′	105.48 (10)
N1—P2—N9	106.95 (11)	N3′—P2′—N9′	106.64 (11)
P4—N3—P2	121.15 (13)	P4′—N3′—P2′	122.48 (14)
N5—P4—N3	116.48 (11)	N3′—P4′—N5′	116.93 (12)
P6—N5—P4	124.88 (14)	P4′—N5′—P6′	120.77 (13)
N5—P6—N7	118.27 (12)	N7′—P6′—N5′	118.24 (12)
N5—P6—N9	105.16 (11)	N7′—P6′—N9′	105.06 (11)
N7—P6—N9	107.01 (12)	N5′—P6′—N9′	107.83 (12)
P8—N7—P6	117.81 (12)	P8′—N7′—P6′	124.29 (13)
N1—P8—N7	116.79 (12)	N7′—P8′—N1′	115.73 (11)
P2—N9—P6	107.86 (12)	P6′—N9′—P2′	107.84 (11)

The positions of atoms H13 and H13′ were obtained from a difference synthesis and refined isotropically, while the remaining H atoms were positioned geometrically at distances of 0.96 and 0.97 Å for CH_3 and CH_2 bonds, respectively, and allowed to ride on their attached atoms. The N13—H13 and N13′—H13′ bond lengths are 0.81 (4) and 0.68 (4) Å, respectively. The N13′—H13′ bond distance is shorter than the conventional N—H value but was not further restrained. For eight of the pyrrolidino groups, the C atoms in the 3- and 4-positions were disordered. The occupancies of each disordered group were allowed to refine while applying a restraint that the geometries be similar.

Data collection: *MolEN* (Fair, 1990); cell refinement: *MolEN*; data reduction: *MolEN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); 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: DA1202). Services for accessing these data are described at the back of the journal.

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