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Instrumental Achievements

Crystal Structure of *trans*-2,6-Bis(*n*-propylamino)-2,4,4,6,8,8-hexapyrrolidinocyclo-2λ^5, 4λ^5, 6λ^5, 8λ^5-tetraphosphazatetraene

Tuncer HÖKELEK,*† Levent ÖZTÜRK,* Muhammet IŞIKLAN, and Zeynel KILIÇ****

**Hacettepe University, Department of Physics, 06532 Beytepe-Ankara, Turkey*
***Ankara University, Department of Chemistry, 06100 Tandoğan-Ankara, Turkey*

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Hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, and octachlorocyclotetraphosphazene, $N_4P_4Cl_8$, have attracted great interest in the synthesis of new, small-molecule organocyclophosphazenes and phosphazene polymers with inorganic backbones.[1] Some of the aminophosphazene derivatives are thought to be useful as cancer chemotherapeutic agents.

A relationship has been observed between the structures of the aminocyclophosphazenes and cytostatic activity and for effective tumor growth inhibition, electron-donating groups (*e.g.* aziridine, and pyrrolidine) in the P-N ring skeletons appear to be essential.[2] The crystal structures of some $N_4P_4Cl_8$ derivatives, such as $[N_4P_4Cl_4(Net_2)_4]$[3], $[N_4P_4Cl_7(OC_6H_2\text{-}2,6\text{-}^tBu_2\text{-}4\text{-}Me)]$[4], $[N_4P_4(NC_4H_8O)_6(NHEt)_2]$[5], $[N_4P_4(NC_5H_{10})_6(NHEt)_2]$[6], have been determined.

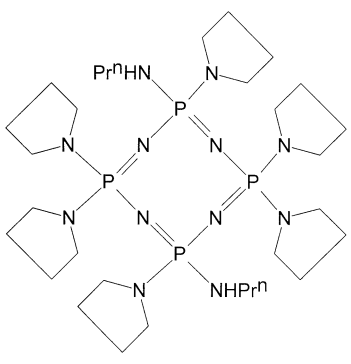
The title compound, $[N_4P_4(NC_4H_8)_6(NHPr^n)_2]$ (Pr^n: *n*-propylamino), was prepared from the reaction of *trans*-2,6-$N_4P_4Cl_6(NHEt)_2$ (3.20 g, 6.40 mmol), triethylamine (10.4 g, 102 mmol) and pyrrolidine (18.2 g, 256 mmol) in acetonitrile (100 ml).

The compound was recrystallized from acetonitrile; m.p., 379 K. The results of an X-ray structure determination are given in Tables 1 – 3.

The title molecule (Fig. 2) consists of a chair-shaped cyclic tetrameric phosphazene ring with two *n*-propylamino (in 2,6-*trans* positions) and six pyrrolidino side groups. The four P atoms are coplanar and the four N atoms are displaced above (+) and below (–) their plane by equal amounts [N1 –0.570(4) and N6 –0.311(5)Å].[4] The conformation of the macrocyclic ring is indicated by the torsion angles of the ring bonds in which the symmetry operation reverses the sign of a torsion angle (illustrated in Fig. 3). From the distribution of the endocyclic torsion angles, it seems that in the central ring there are two local pseudo-mirrors, one running along the midpoints of the N1–P1 and $N1^i$–$P1^i$ bonds, the other along the midpoints of the P2–$N6^i$ and $P2^i$–N6 bonds [*i*: 1–*x*, –*y*, –*z*].

Table 1 Crystal and experimental data

Formula: $C_{30}H_{64}N_{12}P_4$
Formula weight = 716.82
Crystal system: triclinic
Space group: $P\bar{1}$ $Z = 1$
a = 9.102(2)Å
b = 10.664(1)Å
c = 10.926(3)Å
α = 72.70(2)°
β = 85.30(2)°
γ = 79.50(1)°
V = 995.2(4)Å^3
D_x = 1.196 g/cm^3
μ(Mo K$_\alpha$) = 0.227 mm^{-1}
T = 293 K
Colorless
Crystal size: 0.15 × 0.20 × 0.30 mm
λ(Mo K$_\alpha$) = 0.71073 Å
R_{int} = 0.036
R = 0.1811 wR = 0.1490 [for all reflections]
R = 0.0568 wR = 0.1108 [for $I > 2\sigma(I)$]
No. of reflections measured = 3244
No. of reflections used = 1209
[$I > 2\sigma(I)$]
No. of parameters = 240
Goodness-of-fit = 0.844
$(\Delta/\sigma)_{max}$ = 0.000
$(\Delta\rho)_{max}$ = 0.137
$(\Delta\rho)_{min}$ = –0.172
$2\theta_{max}$ = 51.3°
Measurements: Enraf-Nonius CAD-4 diffractometer
Program system: CAD-4 EXPRESS Software
Structure determination: MolEN
Treatment of hydrogen atoms: geometrical calculation
Refinement: full matrix least-squares



Prn: n-propylamino

Fig. 1 Chemical diagram.

† To whom correspondence should be addressed.

Table 2 Final atomic coordinates with isotropic and anisotropic thermal parameters

Atom	*x*	*y*	*z*	U_{iso}/Å^2
C1	0.3207(6)	0.3001(7)	0.6806(6)	0.1117(18)
C2	0.2810(10)	0.3248(10)	0.8076(7)	0.145(2)
C3	0.3788(11)	0.2378(11)	0.9060(9)	0.171(3)
C4	0.4998(8)	0.1734(7)	0.8352(5)	0.1146(19)
C5	0.8487(7)	0.1041(7)	0.6198(8)	0.124(2)
C6	0.9516(9)	0.2061(10)	0.5882(11)	0.170(3)
C7	0.8784(10)	0.3277(9)	0.5095(10)	0.180(3)
C8	0.7160(8)	0.3222(5)	0.5278(7)	0.1170(19)
C9	0.2128(6)	0.2813(6)	0.2226(6)	0.1094(17)
C10	0.1488(11)	0.4249(7)	0.1534(10)	0.168(3)
C11	0.2512(13)	0.5012(8)	0.1760(11)	0.275(7)
C12	0.3875(9)	0.4171(5)	0.2305(8)	0.127(2)
C14	0.6988(8)	0.1366(10)	0.1795(8)	0.139(2)
C15	0.8450(14)	0.174(2)	0.1461(13)	0.250(7)
C16	0.9162(18)	0.1536(18)	0.0444(14)	0.253(7)
N1	0.4445(4)	0.1741(3)	0.4837(3)	0.0751(10)
N2	0.4521(4)	0.1970(4)	0.7063(3)	0.0828(11)
N3	0.7086(4)	0.1777(4)	0.5744(3)	0.0843(11)
N4	0.3657(4)	0.2811(3)	0.2422(3)	0.0818(11)
N5	0.6371(5)	0.1645(4)	0.2968(5)	0.1054(14)
N6	0.4089(4)	0.0291(3)	0.3245(3)	0.0735(10)
P1	0.46451(13)	0.15429(10)	0.34442(11)	0.0684(4)
P2	0.54625(13)	0.12391(10)	0.60436(11)	0.0691(4)

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
C1	0.098(4)	0.109(5)	0.135(5)	-0.064(5)	-0.009(4)	0.016(4)
C2	0.140(7)	0.163(7)	0.149(6)	-0.093(5)	0.017(5)	0.004(5)
C3	0.183(7)	0.203(8)	0.129(6)	-0.097(7)	-0.032(6)	0.060(7)
C4	0.157(6)	0.110(5)	0.087(4)	-0.043(4)	-0.028(4)	-0.012(4)
C5	0.098(5)	0.106(4)	0.177(7)	-0.036(5)	-0.037(4)	-0.037(4)
C6	0.086(6)	0.172(9)	0.278(10)	-0.080(9)	-0.011(6)	-0.057(5)
C7	0.132(7)	0.111(6)	0.314(11)	-0.059(7)	-0.010(7)	-0.068(5)
C8	0.165(6)	0.068(3)	0.139(5)	-0.037(4)	-0.012(4)	-0.056(4)
C9	0.110(5)	0.092(4)	0.110(4)	-0.011(4)	-0.018(4)	0.001(3)
C10	0.166(7)	0.094(5)	0.233(9)	-0.046(5)	-0.093(6)	0.045(5)
C11	0.389(15)	0.069(5)	0.375(14)	-0.059(7)	-0.285(13)	0.060(7)
C12	0.157(6)	0.066(4)	0.162(6)	-0.029(4)	-0.038(5)	-0.020(4)
C14	0.098(5)	0.185(8)	0.167(7)	-0.086(6)	0.036(5)	-0.065(5)
C15	0.168(11)	0.44(2)	0.160(10)	-0.146(10)	0.090(9)	-0.036(11)
C16	0.203(12)	0.236(15)	0.274(17)	0.024(12)	-0.048(11)	-0.061(11)
N1	0.078(2)	0.0497(19)	0.101(3)	-0.0260(18)	-0.0186(19)	-0.0045(17)
N2	0.087(3)	0.078(2)	0.091(3)	-0.045(2)	-0.020(2)	0.009(2)
N3	0.071(3)	0.063(2)	0.129(3)	-0.036(2)	-0.008(2)	-0.0201(19)
N4	0.093(3)	0.048(2)	0.104(3)	-0.0198(18)	-0.037(2)	0.0019(19)
N5	0.086(3)	0.123(4)	0.132(4)	-0.062(3)	-0.003(3)	-0.039(3)
N6	0.077(2)	0.0443(18)	0.104(2)	-0.0219(17)	-0.0322(19)	-0.0092(16)
P1	0.0758(9)	0.0491(6)	0.0869(9)	-0.0226(6)	-0.0183(6)	-0.0149(6)
P2	0.0783(9)	0.0491(6)	0.0890(8)	-0.0293(6)	-0.0205(6)	-0.0100(6)

Table 3 Bond distances (Å) and angles (°)

P1-N6	1.589(3)	P2-N1	1.575(3)
P1-N1	1.589(3)	P2-N6^{i}	1.577(3)
P1-N5	1.626(4)	P2-N2	1.643(4)
P1-N4	1.646(3)	P2-N3	1.655(4)
N1-P1-N6	117.7(2)	N1-P2-N2	103.2(2)
N1-P1-N5	107.5(2)	N6^{i}-P2-N2	108.5(2)
N6-P1-N5	113.4(2)	N1-P2-N3	112.4(2)
N1-P1-N4	109.8(2)	N6^{i}-P2-N3	103.5(2)
N6-P1-N4	103.1(2)	N2-P2-N3	106.9(2)
N5-P1-N4	104.4(2)	P2-N1-P1	133.2(2)
N1-P2-N6^{I}	121.6(2)	P2-N6-P1	130.0(2)

Symmetry code: (i) 1–*x*, –*y*, 1–*z*.

The ranges of the endocyclic P–N–P and N–P–N bond angles are 130.0(2) – 133.2(2)° and 117.7(2) - 121.6(2)°, respectively, which can be compared with the corresponding ones.[3-6] Although the average value of the macrocyclic ring P–N bond distances is 1.584(3)Å, the average value of the other P–N bond lengths is 1.643(4)Å.

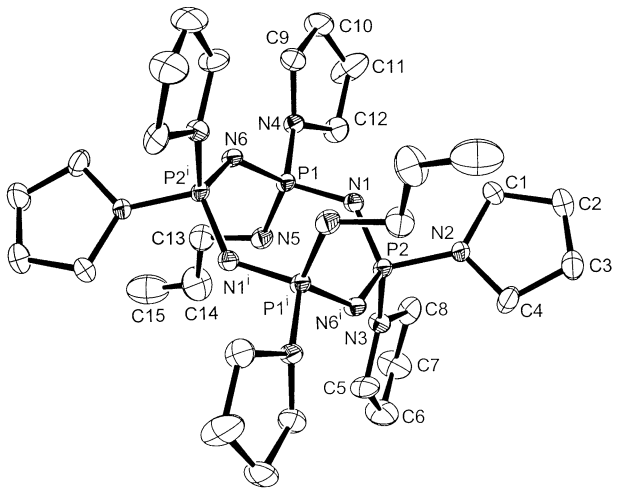


Fig. 2 Molecular structure of the title compound along with the atom-numbering scheme [symmetry code: (i) 1–*x*, –*y*, –*z*]. The thermal ellipsoids are drawn at the 30% probability level.

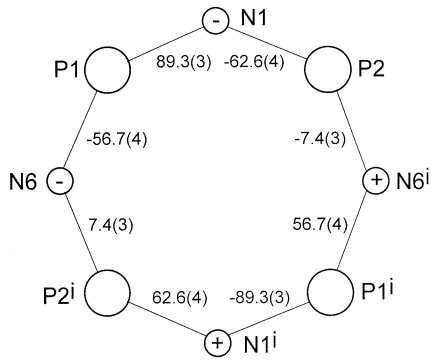


Fig. 3 Shape of the phosphazene ring along with the torsion angles (°). Symmetry code: (i) 1–*x*, –*y*, –*z*.

In tetrameric phosphazenes, the P–N bond lengths may be correlated with the orbital electronegativities of groups of atoms. The short bonds in the ring have an appreciable double-bond character. The bulky pyrrolidino groups may be highly effective in determining the shape of the molecule.

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