Crystal Structure of 8,8-dichloro-1,2,10,11,13,14-hexahydro-6 λ^5 ,8 λ^5 , 10 λ^5 -6,10-nitrilo[1,3,5,7,2,4,6]tetraazatriphosphonino-bis[1,3,2]oxazaphosphorine

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The title compound, C₆H₁₂N₅O₂P₃Cl₂, a cyclotriphosphazene, has a *spiro-ansa-spiro* architecture in which the bicyclic system is in the *sofa* conformation. The asymmetric unit contains one half a molecule. Two P and two N atoms are capable of representing stereogenic centres (*meso* form). It belongs to the space group *Pnma* with cell parameters *a* = 11.6949(2), *b* = 13.6816(3), *c* = 8.576(2) Å.

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Hexachlorocyclotriphosphazene, N₃P₃Cl₆, is known as a “standard” compound in the field of phosphazene chemistry, which has potential use in the syntheses of many small organo-cyclophosphazene derivatives.¹ In the reactions of N₃P₃Cl₆ with N₂O₂-donor type tetradentate ligands, two kinds of products, *e.g.* *spiro-ansa-spiro* and *spiro-bino-spiro*, are expected to be formed. However, only the *spiro-ansa-spiro* architecture has been isolated.

The title molecule was prepared from the reaction of *N,N'*-bis(2-hydroxyethyl)ethylenediamine (5.00 g, 33.8 mmol), N₃P₃Cl₆ (5.88 g, 16.9 mmol) and K₂CO₃ (18.65 g, 135.1 mmol) in dry THF (250 ml) by vigorous stirring; argon was passed over the reaction mixture for 2 days. The solvent was evaporated and the residue was chromatographed [eluent CH₃CN–benzene (2:1), silica-gel (100 g)] and then crystallized from a CH₃CN–benzene (2:1) mixture (yield 2.48 g, 47%, m.p. 528 K).

The X-ray analysis results are given in Tables 1–3. The H atoms were located in a difference synthesis and refined isotropically.

The title molecule is on a crystallographic mirror plane that passes through N2, P1, C11, and C12; therefore, only half of this molecule is independent. The C3 atom was disordered. The occupancies of the disordered C3A and C3B atoms were fixed at 0.5. The title molecule was also analysed to resolve the disorder in lower symmetry space group *Pna2*₁ by removing the

mirror symmetry in the molecule, but was not successful.

In the title molecule (Fig. 2) the rings, A(P1/N1/P2/N2/P2ⁱ/N1ⁱ) and B(N2/P2/N3/C3a/C3bⁱ/N3ⁱ/P2ⁱ), are not planar with total puckering amplitudes² of *Q*_T = 0.431(4) and 0.839(4) Å, respectively [symmetry code (i): *x*, 1.5 – *y*, *z*]. The five-membered ring C(P2/O1/C1/C2/N3) has a twisted conformation with $\phi_2 = -80.8(5)^\circ$. The bicyclic system is made up of rings A and B in a *sofa* conformation (Fig. 3a). Each ring is V-shaped. Regarding the disordered structure of the N–C–C–N chain, the sums of the bond angles around the N3 atom [335.4(4) and 356.0(3)°] show a change in the hybridization of atom N3 from

Fig. 1 Chemical diagram.

Table 1 Crystal and experimental data

Formula:	C ₆ H ₁₂ N ₅ O ₂ P ₃ Cl ₂
Formula weight:	350.02
Crystal system:	orthorhombic
Space group:	<i>Pnma</i>
<i>Z</i> :	4
<i>a</i> :	11.6949(2) Å
<i>b</i> :	13.6816(3) Å
<i>c</i> :	8.576(2) Å
<i>V</i> :	1372.3(5) Å ³
<i>D</i> _x :	1.694 g/cm ³
μ (Cu <i>K</i> α):	0.762 cm ⁻¹
<i>T</i> :	293 K
Crystal color:	colorless
Crystal size:	0.30 × 0.20 × 0.15 mm
λ (Cu <i>K</i> α):	1.54184 Å
<i>R</i> :	0.0459
<i>wR</i> :	0.1120
No. of reflections measured:	1228
No. of reflections used:	1004 [<i>I</i> > 2 σ (<i>I</i>)]
No. of parameters:	128
Goodness-of-fit:	1.049
($\Delta\sigma$) _{max} :	0.000
($\Delta\rho$) _{max} :	0.533 e Å ⁻³
($\Delta\rho$) _{min} :	-0.332 e Å ⁻³
2 θ _{max} :	148.36°
Measurements:	Enraf-Nonius CAD-4 diffractometer
Program system:	CAD-4 EXPRESS Software
Structure determination:	SHELXS-97
Refinement:	full matrix

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Table 2 Final atomic coordinates and equivalent isotropic thermal parameters

Atom	x	y	z	$U_{eq}(\text{\AA}^2)$
Cl1	0.44307(10)	0.7500	-0.33833(15)	0.0624(4)
Cl2	0.69696(11)	0.7500	-0.42616(13)	0.0680(5)
P1	0.59774(10)	0.7500	-0.23415(12)	0.0436(3)
P2	0.64628(7)	0.65251(6)	0.03614(9)	0.0432(3)
O1	0.7199(2)	0.5600(2)	0.0768(4)	0.0694(8)
N1	0.6137(3)	0.6498(2)	-0.1453(3)	0.0537(7)
N2	0.7081(3)	0.7500	0.0901(4)	0.0447(9)
N3	0.5342(3)	0.6272(2)	0.1458(3)	0.0575(8)
C1	0.5655(5)	0.5513(4)	0.2545(5)	0.0753(14)
C2	0.6542(5)	0.4920(4)	0.1734(7)	0.0848(15)
C3a	0.4773(7)	0.7044(7)	0.2411(9)	0.062(2)
C3b	0.4434(6)	0.7049(7)	0.1514(9)	0.058(2)

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

Table 3 Bond distances ($\text{\AA}$) and angles with selected torsion angles ($^\circ$)

P1	N1	1.579(3)	P2	O1	1.570(3)
P1	Cl1	2.0175(16)	C1	C2	1.490(8)
P1	Cl2	2.0145(16)	C1	N3	1.443(5)
P2	N1	1.602(3)	C2	O1	1.463(5)
P2	N2	1.586(2)	C3a	N3	1.492(9)
P2	N3	1.650(3)	C3b ⁱ	N3 ⁱ	1.504(8)
C3a	C3b ⁱ	1.513(11)			
N1-P1-N1 ⁱ		120.4(2)	N2-P2-N3		111.85(19)
N1-P1-Cl1		108.63(12)	P1-N1-P2		118.49(19)
N1-P1-Cl2		109.07(12)	P2-N2-P2 ⁱ		114.5(2)
Cl1-P1-Cl2		98.89(7)	C1-N3-C3a		105.6(4)
O1-P2-N1		109.14(17)	C1-N3-P2		108.6(3)
O1-P2-N2		111.31(16)	C3a-N3-P2		121.2(4)
O1-P2-N3		98.01(17)	N3-C3a-C3b ⁱ		114.8(5)
N1-P2-N2		114.27(19)	N3 ⁱ -C3b ⁱ -C3a		114.3(5)
N1-P2-N3		111.07(16)	C2-O1-P2		110.5(3)
P2-N1-P1-N1 ⁱ		-0.1(4)	O1-P2-N3-C1		14.9(3)
N1-P2-N2-P2 ⁱ		49.1(3)	P2-O1-C2-C1		-24.6(5)
N2-P2-N1-P1		-24.1(3)	P2-N3-C1-C2		-30.1(4)
N3-P2-O1-C2		6.2(3)	N3-C1-C2-O1		34.0(5)

Symmetry code: (i) x, 1.5 - y, z

trigonal planar towards pyramidal. Thus, atoms N3 and N3ⁱ may represent stereogenic centres. The pyramidity of N3 and N3ⁱ may especially depend on the conformation of ring B (Fig. 3b). On the other hand, atoms P2 and P2ⁱ have four different attachments, and therefore both of them are also expected to be stereogenic centres (meso form). In ring A, the P-N bond lengths are in the range 1.579(3)–1.602(3) $\text{\AA}$, and exhibit a regular variation with the distance from P2: P2-N1 > P2-N2 > P1-N1.

In ring A, the endocyclic N1-P2-N2 [114.3(2) $^\circ$], P2-N2-P2ⁱ [114.5(2) $^\circ$] and the exocyclic O1-P2-N3 [98.0(2) $^\circ$] angles are decreased in contrast to our observations,^{3,4} with increased electron donation and withdrawal by the substituents relative to the "standard" compound,⁵ N₃P₃Cl₆. In the latter compound, the corresponding angles are 118.3, 118.5 and 101.2, 101.6 $^\circ$, respectively.

Fig. 2 Molecular structure of the title compound with atom-numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

Fig. 3 Conformations of (a) the bicyclic system and (b) ring B. The substituents are omitted for clarity.

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