Table 4. *Hydrogen-bonding parameters*

A–H···B		$A\cdots B$ (Å)	A–H (Å)	H···B (Å)	$\angle A$–H···B (°)
N(16)–H(16)···O(24)	$x, \frac{1}{2}-y, -\frac{1}{2}+z$	2·942 (4)	0·96 (3)	2·01 (3)	163 (3)
N(16)–H(16′)···O(25)	$2-x, -\frac{1}{2}+y, \frac{1}{2}-z$	2·997 (5)	1·02 (4)	1·98 (4)	174 (3)
N(10)–H(10)···N(28)	x, y, z	2·814 (4)	1·04 (4)	1·79 (4)	167 (3)
N(15)–H(15)···O(25)	$1-x, 1-y, 1-z$	2·914 (4)	1·14 (4)	1·85 (4)	153 (3)
N(15)–H(15)···N(26)	$1-x, 1-y, 1-z$	3·478 (4)	1·14 (4)	2·58 (4)	135 (3)]
N(15)–H(15′)···N(16)	$1-x, \frac{1}{2}+y, \frac{1}{2}-z$	3·034 (5)	0·88 (3)	2·20 (3)	159 (3)

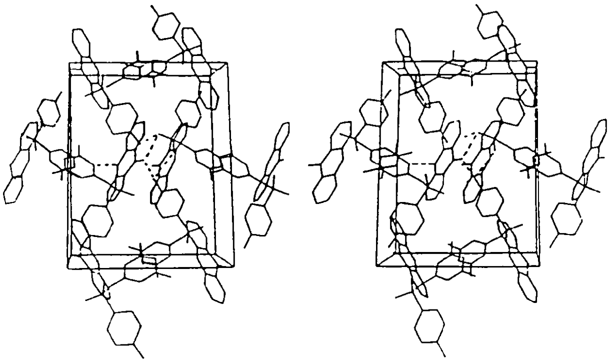

Fig. 2. Packing diagram; view along **a**, **b** horizontal, **c** vertical. One example of each type of hydrogen bond is shown.

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Structure of the First Genuine Ansa Derivative, $N_3P_3Cl_4[HN(CH_2)_2O(CH_2)_2NH]$

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(*Received* 22 *January* 1988; *accepted* 23 *May* 1988)

Dedicated to Professor J.-M. Lehn, Nobel Prize for Chemistry, 1987

Abstract. 2,4,6,6-Tetrachloro-2,4-oxybis(ethyleneimino)cyclotriphosphazatriene, $C_4H_{10}Cl_4N_5OP_3$, $M_r = 378{\cdot}9$, orthorhombic, $Pnma$, $a = 14{\cdot}429\ (3)$, $b = 12{\cdot}258\ (5)$, $c = 8{\cdot}054\ (2)$ Å, $V = 1425\ (1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}767\ (1)$, $D_m = 1{\cdot}75\ (3)$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 1{\cdot}2$ mm^{-1}, $F(000) = 760$, $T = 292$ K, $R = 0{\cdot}039$ for 1265 unique observed reflections and 85 variable parameters. The structure exhibits a spatial

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arrangement of $N_3P_3Cl_4$ with $HN{-}(CH_2)_2{-}O{-}(CH_2)_2{-}NH$ as an arch on two phosphorus atoms of the N_3P_3 ring.

Introduction. The so-called spiro loop *versus* ansa arch controversy related to the structure of products of the reaction of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, with difunctional reagents has been clarified recently. In fact, no genuine ansa derivative from $N_3P_3Cl_6$ itself has ever been observed, whereas many compounds containing one or several difunctional groups grafted in spiro (loop) and/or bino (bridge) configurations are now well documented, their neat synthesis coming under the rules of the BASIC chemical game, a kind of 'Lego box of bricks' on the ångström scale (Labarre, 1985). Until recently, the only mono ansa species within the cyclophosphazenic series was obtained (Harris & Williams, 1984) by reaction of 3-amino-1-propanol with the monomethyl derivative of $N_3P_3Cl_6$, *i.e.* $N_3P_3Cl_5(CH_3)$. The ansa structure was identified both by NMR and X-ray studies (Labarre, 1985; Galy, Enjalbert & Labarre, unpublished results). It must be emphasized that this mono ansa derivative was obtained first by the skilful use of the electron-donor properties of the methyl group for the linkage of the amino group of the 3-amino-1-propanol and then of its OH group (under drastic conditions) to the adjacent P atom of the cyclophosphazenic ring. In other words, no genuine mono ansa derivative from $N_3P_3Cl_6$ itself had ever been synthetized, the mono ansa derivative of Harris & Williams (1984) being most uncommon.

We recently reported a rapid and simple synthesis (a few hours at room temperature) of the first genuine mono ansa derivative from $N_3P_3Cl_6$ (Castera, Faucher, Labarre & Perly, 1987), the difunctional reagent being the simplest Lehn's ligand, $H_2N{-}(CH_2)_2{-}O{-}(CH_2)_2{-}NH_2$. The present paper reports on the X-ray structure of this unique chemical, which incidentally exhibits a very unusual chemical behaviour (Castera, Faucher, Graffeuil & Labarre, 1988).

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters of non-*H *atoms*

$$B_{\rm eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j(\mathbf{a}_i.\mathbf{a}_j)\beta_{ij}.$$

	x	y	z	$B_{\rm eq}$(Å^2)
P(1)	0·2222 (1)	$\frac{1}{4}$	0·2768 (2)	2·44 (2)
P(2)	0·27546 (6)	0·13624 (6)	−0·0046 (1)	1·97 (1)
Cl(1)	0·2839 (2)	$\frac{1}{4}$	0·4972 (2)	5·36 (4)
Cl(2)	0·0889 (1)	$\frac{1}{4}$	0·3475 (2)	4·36 (3)
Cl(3)	0·39363 (7)	0·04887 (8)	−0·0197 (2)	3·71 (2)
N(1)	0·2437 (2)	0·1394 (2)	0·1859 (4)	2·42 (6)
N(2)	0·2983 (3)	$\frac{1}{4}$	−0·0864 (5)	2·18 (8)
N(3)	0·2058 (2)	0·0568 (3)	−0·1048 (4)	2·76 (6)
C(1)	0·1060 (3)	0·0584 (3)	−0·0803 (5)	3·17 (8)
C(2)	0·0587 (3)	0·1536 (4)	−0·1629 (6)	3·57 (8)
O	0·0874 (3)	$\frac{1}{4}$	−0·0795 (5)	2·85 (7)

Table 2. *Interatomic distances* (Å) *and angles* (°)

P(1)–Cl(1)	1·986 (2)	C(1)–C(2)	1·507 (6)
P(1)–Cl(2)	2·006 (2)	C(2)–O	1·421 (4)
P(1)–N(1)	1·572 (2)	P(1)–O	3·467 (4)
P(2)–Cl(3)	2·018 (2)	P(2)–O	3·110 (4)
P(2)–N(1)	1·602 (3)	N(1)–O	3·391 (4)
P(2)–N(2)	1·577 (2)	N(2)–O	3·043 (5)
P(2)–N(3)	1·616 (3)	N(3)–O	2·927 (3)
N(3)–C(1)	1·453 (4)		

Cl(1)–P(1)–Cl(2)	100·1 (1)	N(1)–P(2)–N(3)	108·4 (1)
Cl(1)–P(1)–N(1)	109·1 (2)	N(2)–P(2)–N(3)	117·1 (2)
Cl(2)–P(1)–N(1)	108·7 (1)	P(1)–N(1)–P(2)	121·5 (2)
N(1)–P(1)–N(1′)	119·3 (2)	P(2)–N(2)–P(2′)	124·3 (2)
Cl(3)–P(2)–N(1)	108·3 (2)	P(2)–N(3)–C(1)	122·7 (2)
Cl(3)–P(2)–N(2)	105·5 (1)	N(3)–C(1)–C(2)	113·6 (3)
Cl(3)–P(2)–N(3)	100·1 (2)	C(1)–C(2)–O	107·6 (3)
N(1)–P(2)–N(2)	116·0 (2)	C(2)–O–C(2)	112·6 (4)

Experimental. Colourless block; 0·4 × 0·3 × 0·3 mm; density measured by flotation; preliminary crystallographic study: precession camera, orthorhombic system, space group *Pnma* or $Pn2_1a$; intensity measurements: Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$; take-off angle 4·0°; lattice parameters determined with 25 reflections (θ range: 7–17°); 1991 measured reflections; $\theta_{\rm max} = 28°$; $h\,0{\to}19$, $k\,0{\to}16$, $l\,0{\to}8$; θ–2θ scan technique with $\Delta\theta$ scan = $1{\cdot}0° + 0{\cdot}35°\tan\theta$, prescan speed = 10° min^{-1}; for final scan: $\sigma(I)/I = 0{\cdot}018$, max. time: 80 s; standard reflections: 630, 351, 080; no significant variation of their intensity; Lorentz and polarization factors; no absorption correction (unnecessary). Structure determination: direct methods; 1265 unique observed reflections with $I > 3\sigma(I)$; 85 refined parameters; full-matrix least squares (F); function minimized: $\sum w(\Delta F)^2$; atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). $R = 0{\cdot}039$; $wR = 0{\cdot}040$; $w = 1$; $S = 1{\cdot}4$; $(\Delta/\sigma)_{\rm max} = 0{\cdot}01$; max. height in final synthesis: $0{\cdot}7\ {\rm e\ Å^{-3}}$ situated at 1·1 Å from Cl atoms. Calculations with *SDP* (B. A. Frenz & Associates, 1985) and illustrations with *ORTEP* (Johnson, 1976) using a DEC VAX/11730 computer.

Fractional coordinates and equivalent isotropic thermal parameters of non-hydrogen atoms are listed in Table 1.* H atoms located at 0·97 Å from their associated attached atoms and affected by a 4·5 Å^2 isotropic temperature factor. Interatomic distances and bond angles are given in Table 2.

Discussion. A ball-and-spoke drawing of a perspective view of the title molecule is given in Fig. 1 (the hydrogen numbering is omitted for clarity). The molecule admits a symmetry plane *viz.* the mirror of the

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51067 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Pnma space group; five atoms are settled on the mirror ($y = 1/4$): Cl(1), Cl(2), P(1), N(2) and O. The HN—$(CH_2)_2$—O—$(CH_2)_2$—NH arch is one-side developed with regard to the cyclophosphazenic ring.

Phosphazenic ring. The average plane of the cycle P(1) N(1) P(2) N(2) P(2′) N(1′), *i.e.* 'N_3P_3', is quasi-perpendicular to the mirror [dihedral angle 90·9 (1)°]. The distances of the various atoms to this plane are less than 0·04 Å. Nevertheless, if one considers the plane formed by P(1) N(1) P(2), it is evident that N(2) is moved outside the later plane, in the opposite direction, to a distance of 0·22 Å. A slight deformation of the ring then appears at the level of N(2) correlating with the arch branching. The P—N bond lengths (Table 2) are homogeneous and equivalent to those already encountered in analogous compounds, 1·572 (2), 1·577 (2) and 1·602 (3) Å *versus* 1·553–1·609 and 1·558–1·608 Å, respectively. In this case, the average value, 117·1°, of the angles N—P—N is lower than the average 122·6° encountered in the compounds $N_3P_3az_4Cl_2$ (Enjalbert, Guerch, Sournies, Labarre & Galy, 1983) and $(NPaz_2)_2(NSOaz)$ (Galy, Enjalbert, van der Huizen, van de Grampel & Labarre, 1981).

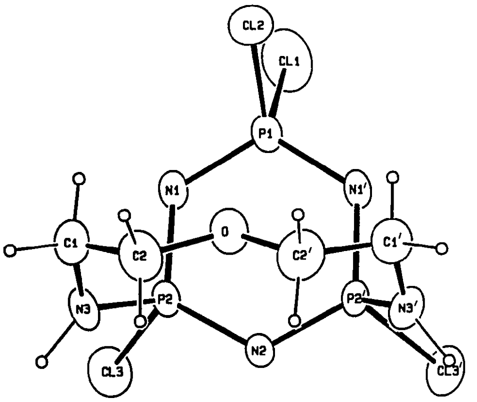

Fig. 1. Molecular structure of ansa molecule with crystallographic numbering scheme.

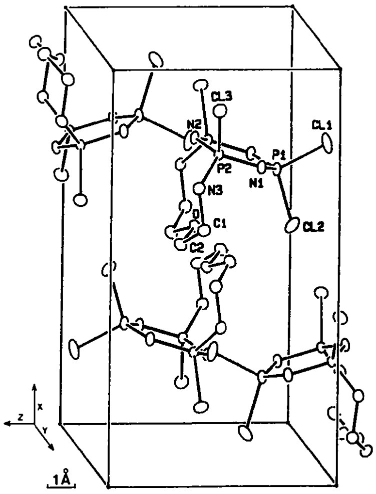

Fig. 2. Perspective view of the contents of a unit cell.

P—Cl *bonds*. These do not exhibit particular features, since they are analogous to those of similar compounds. The small size of the thermal ellipsoids of the Cl atoms can be underlined, indicating a relative densification of the packing.

$HN(CH_2)_2O(CH_2)_2NH$ *arch*. The ligand is grafted onto the cyclophosphazenic ring N_3P_3 *via* two P atoms, like an arch; such a situation is *unique* so far. This geometry finally develops a 'decacycle' of non-hydrogen atoms, *i.e.* N(2) P(2) N(3) C(1) C(2) O C(2′) C(1′) N(3′) P(2′). The average plane of this decacycle is quasi-perpendicular to the mirror of the molecule, 88·7 (1)°. The average plane of the arch and the N_3P_3 plane form a dihedral angle of 80·3 (1)°. The arch has a chair conformation, readily visible on the packing representation of the cell in Fig. 2, with regard to the plane defined by N(3) C(1) C(1′) N(3′). The O atom is in the plane (at +0·03 Å) and P(2) and C(2) atoms are at −0·94 and +0·75 Å, respectively. The C(1) C(2) O C(2′) C(1′) modulus shows a *W* form. The O atom is drawn towards the N_3P_3 ring and one of its lone pairs sits above the ring. It is also surrounded by four H atoms linked to C(2) atoms and located at 1·975 (3) Å (Table 2). The geometry of this *W* modulus is similar to crown-ether structures. Obviously, the molecule seems to be free of drastic constraints and there is no hydrogen-bonding system. The arch is susceptible to be a host for suitable guests and partially protects the cyclophosphazenic ring, mainly *versus* aminolysis (Castera, Faucher, Graffeuil & Labarre, 1988).

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