

# 4,4,6,6-Tetrachloro-4a',8'-dihydrodinaphtho-[2,1-c';2,1-g']-2 $\lambda$ <sup>5</sup>,4 $\lambda$ <sup>5</sup>,6 $\lambda$ <sup>5</sup>-cyclotriphosphazene-1-spiro-1'-[2,5,8a,1]dioxazaphosphanaphthalene

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## Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean  $\sigma(\text{C}-\text{C}) = 0.007\text{ \AA}$

$R$  factor = 0.050

w $R$  factor = 0.148

Data-to-parameter ratio = 13.7

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound,  $\text{C}_{22}\text{H}_{15}\text{Cl}_4\text{N}_4\text{O}_2\text{P}_3$ , is a spiro phosphazene derivative with two bulky naphthalene rings. The phosphazene and the two six-membered N/O rings are not planar. The aliphatic C atom (in ArCH-OAr) and the N atom (in ArCH<sub>2</sub>-N), which has a pyramidal geometry, are capable of representing stereogenic centres.

## Comment

Cyclophosphazene derivatives are on the borderline between inorganic and organic chemistry and have been reviewed over the years (Shaw, 1980; Allen, 1991; Chandrasekhar & Nagendran, 2001).

Hexachlorocyclotriphosphazene,  $\text{N}_3\text{P}_3\text{Cl}_6$ , generally known as trimeric phosphazene, can be considered as the 'standard' compound in the field of phosphazene chemistry (Bullen, 1971).

In the reactions of  $\text{N}_3\text{P}_3\text{Cl}_6$  with bidentate ligands, *e.g.* diols and diamines, four possible routes have been observed: (i) replacement of two geminal Cl atoms to afford a spiro architecture, (ii) replacement of two non-geminal Cl atoms to give ansa derivatives, (iii) intermolecular reactions between Cl atoms of phosphazene rings to yield bino compounds, or (iv) intermolecular condensation reactions to afford cycloliner or cyclomatrix polymers (Dez *et al.*, 1999; Mathew *et al.*, 2000).

To the best of our knowledge, until now, the reaction of  $\text{N}_3\text{P}_3\text{Cl}_6$  with {1-[*N*-(1-(2-hydroxynaphthylmethyl)amino-methylidene)]-2(1*H*)-naphthalenone} has only been investigated by our group (İlter *et al.*, 2004). In contrast to our expectations, the resulting reaction gave only the novel spiro phosphazene derivative, (I), instead of ansa or bino phosphazene architectures.

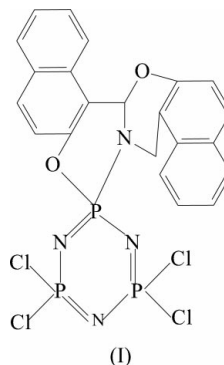
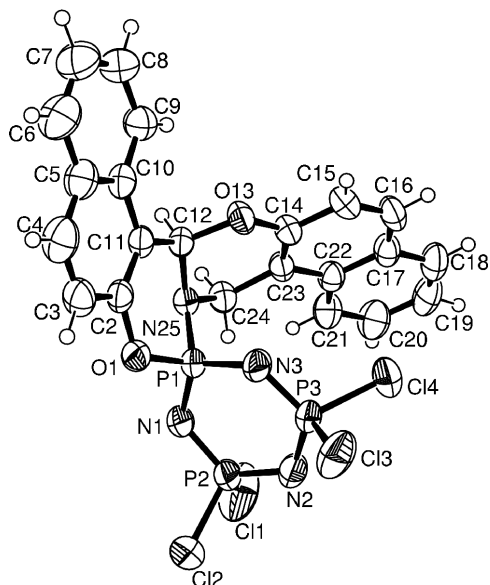


Fig. 1 shows the molecular structure of (I) with the atomic numbering scheme. The phosphazene ring (*A*) is not planar, with a total puckering amplitude of  $Q_T = 0.127(3)\text{ \AA}$  (Cremer & Pople, 1975). Atoms N1, N2 and N3 are displaced from the

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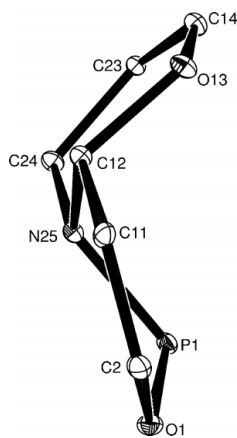
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**Figure 1**

An ORTEP-3 (Farrugia, 1997) drawing of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

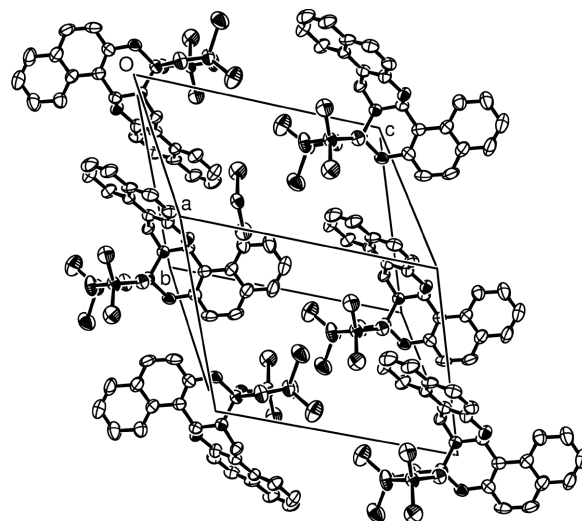


**Figure 2**

The conformation of the bicyclic system in (I). The substituents have been omitted for clarity.

plane through the P atoms by  $-0.007$  (4),  $-0.114$  (4) and  $0.136$  (4) Å, respectively. As expected, the naphthalene rings are planar. Ring B (P1/O1/C2/C11/C12/N25) and ring C (C12/O13/C14/C23/C24/N25) are not planar, with total puckering amplitudes of  $0.455$  (3) and  $0.468$  (3) Å, respectively. The bicyclic system made up of rings B and C has a highly irregular conformation (Fig. 2), probably because of the bulky naphthalene rings surrounding rings B and C on both sides.

In the bicyclic system, the maximum separations are P1...O13 [ $3.293$  (4) Å] and O1...C14 [ $4.601$  (4) Å]. All P...P distances are in the range  $2.715$  (2)– $2.779$  (2) Å. The sum of the bond angles around atom N25 ( $346.7^\circ$ ) shows a change in the hybridization of atom N25 from trigonal planar towards pyramidal. Hence, atom N25 may represent a stereogenic centre. The pyramidal configuration of N25 may depend strongly on the conformation of the bicyclic system (Fig. 2). Furthermore, atom C12 has four different attachments and thus it is also a stereogenic centre of the molecule.



**Figure 3**

A packing diagram of (I). H atoms have been omitted.

In the phosphazene ring, the P–N bond lengths are in the range  $1.554$  (3)– $1.607$  (3) Å, exhibiting an irregular variation and showing (Table 1) double-bond character. However, the exocyclic P1–N25 bond [ $1.650$  (3) Å] is at the lower limit of the single-bond length. In phosphazene compounds, the P–N and P=N bonds are generally in the ranges  $1.628$ – $1.691$  and  $1.571$ – $1.604$  Å, respectively (Allen *et al.*, 1987). The shortening in the P1–N25 [ $1.650$  (3) Å] bond is probably due to electron transfer from atom N25 to the phosphazene ring.

In the phosphazene ring, the endocyclic N1–P1–N3 angle [ $115.0$  (2) $^\circ$ ] is decreased and the exocyclic O1–P1–N25 angle [ $101.0$  (1) $^\circ$ ] is not changed, with electron donation and withdrawal by the substituents, relative to the 'standard' compound N<sub>3</sub>P<sub>3</sub>Cl<sub>6</sub> (Bullen, 1971). In the latter compound, the corresponding angles are  $118.3$ ,  $118.5$ ,  $101.2$  and  $101.6^\circ$ , respectively.

The P1–N3–P3, P3–N2–P2 and P2–N1–P1 angles are  $123.1$  (2),  $119.2$  (2) and  $121.9$  (2) $^\circ$ , respectively; P1–N3–P3 is increased while P3–N2–P2 is decreased, with electron donation and withdrawal by the N<sub>3</sub>P<sub>3</sub> ring (Kılıç *et al.*, 1996). They can be compared with the average value reported for N<sub>3</sub>P<sub>3</sub>Cl<sub>6</sub>, *viz.*  $121.4$  (3) $^\circ$ .

As can be seen from the packing diagram (Fig. 3), the molecules are elongated parallel to the (110) plane and stacked along the *b* axis. Dipole–dipole and van der Waals interactions are also effective in the molecular packing.

## Experimental

[1-*N*-(1-(2-Hydroxynaphthylmethyl)aminomethylidene)]-2(1*H*)-naphthalenone (1.65 g, 5.00 mmol) in dry tetrahydrofuran (THF, 100 ml) was added slowly to K<sub>2</sub>CO<sub>3</sub> (0.69 g, 5.00 mmol), with stirring and refluxing, and with argon passing over the reaction mixture, at 253 K. After 0.5 h, the mixture was allowed to reach ambient temperature and N<sub>3</sub>P<sub>3</sub>Cl<sub>6</sub> (1.74 g, 5.00 mmol) in dry THF (50 ml) was added with stirring. The mixture was refluxed for 2 h, the precipitated salts were filtered off and the solution was evaporated under reduced pressure. The oily residue was crystallized from *n*-heptane (m.p. 491 K; yield 1.39 g, 46%).

## Crystal data

$C_{22}H_{15}Cl_4N_4O_2P_3$   
 $M_r = 602.09$   
 Triclinic,  $P\bar{1}$   
 $a = 9.6154$  (7) Å  
 $b = 11.5957$  (10) Å  
 $c = 13.1996$  (15) Å  
 $\alpha = 66.198$  (8)°  
 $\beta = 74.053$  (8)°  
 $\gamma = 67.858$  (6)°  
 $V = 1234.1$  (2) Å<sup>3</sup>

$Z = 2$   
 $D_x = 1.620$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 25 reflections  
 $\theta = 11\text{--}23^\circ$   
 $\mu = 0.71$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Block, colourless  
 $0.40 \times 0.20 \times 0.10$  mm

## Data collection

Enraf–Nonius CAD-4 diffractometer  
 Non-profiled  $\omega$  scans  
 Absorption correction: none  
 5079 measured reflections  
 4751 independent reflections  
 2645 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.024$

$\theta_{max} = 26.3^\circ$   
 $h = -11 \rightarrow 11$   
 $k = 0 \rightarrow 14$   
 $l = -15 \rightarrow 16$   
 3 standard reflections  
 frequency: 120 min  
 intensity decay: 1%

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.050$   
 $wR(F^2) = 0.148$   
 $S = 0.99$   
 4151 reflections  
 304 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0915P)^2 + 0.0022P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.94$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.37$  e Å<sup>-3</sup>

Table 1

Selected geometric parameters (Å, °).

N25–P1	1.650 (3)	P3–N3	1.554 (3)
Cl2–P2	2.0124 (17)	P3–N2	1.566 (4)
Cl1–P2	1.9441 (19)	P3–Cl4	1.9809 (14)
P1–O1	1.572 (3)	P3–Cl3	2.0037 (17)
P1–N1	1.592 (3)	P2–N1	1.563 (3)
P1–N3	1.607 (3)	P2–N2	1.582 (3)
O1–P1–N1	107.21 (17)	Cl4–P3–Cl3	101.02 (7)
O1–P1–N3	108.41 (16)	N1–P2–N2	120.23 (17)
N1–P1–N3	115.03 (17)	N1–P2–Cl1	110.53 (17)
O1–P1–N25	101.03 (14)	N2–P2–Cl1	107.87 (16)
N1–P1–N25	110.00 (19)	N1–P2–Cl2	107.74 (14)
N3–P1–N25	113.99 (16)	N2–P2–Cl2	107.75 (17)
N3–P3–N2	119.38 (17)	Cl1–P2–Cl2	100.98 (9)
N3–P3–Cl4	110.46 (13)	C2–O1–P1	120.8 (2)
N2–P3–Cl4	108.02 (15)	P2–N1–P1	121.88 (19)
N3–P3–Cl3	108.08 (14)	P3–N3–P1	123.1 (2)
N2–P3–Cl3	108.30 (18)	P3–N2–P2	119.19 (19)

The large difference between the numbers of independent and refined reflections is probably due to the fact that most of the reflections were weak, as a result of the crystal quality. H atoms were positioned geometrically at distances of 0.93 ( $Csp^2-H$ ) and 0.97 Å ( $Csp^3-H$ ) from the carrier atoms; a riding model was used during the refinement process. The  $U_{iso}(H)$  values were constrained to be  $1.2U_{eq}$  of the carrier atom.

Data collection: CAD-4 EXPRESS (Enraf–Nonius, 1994); cell refinement: CAD-4 EXPRESS; data reduction: XCAD4 (Harms & Wocadlo, 1995); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

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