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# 1-Chloro-1,3,3,5,5-pentaphenoxycyclotriphosphazene: a precursor of functionalized cyclophosphazene derivatives

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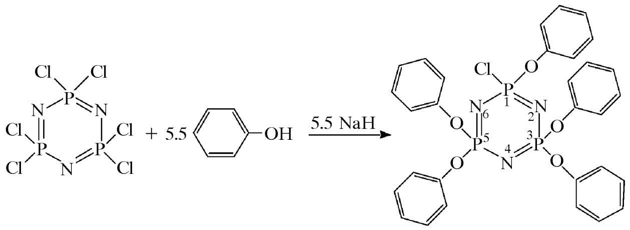
The crystal structure of the title compound, $C_{30}H_{25}ClN_3O_5P_3$, shows that the direct bonding between P and Cl does not modify the structural parameters in the vicinity of this P atom. It also confirms the structural difference between the two P atoms which are each bonded to two phenoxy groups, observed in the $^{31}P$ NMR spectrum. The crystal packing consists principally of complex stacking interactions.

## Comment

The title compound, (I), also known as monochloropentaphenoxycyclotriphosphazene, has already been used to synthesize polymer precursors (Dez & De Jaeger, 1996). More recently, it has been used to synthesize a wide range of cyclotriphosphazene derivatives, such as cyclotriphosphazene hydrazides (Chandrasekhar *et al.*, 2003), cyclotriphosphazene with *N*,*N*,*N*′,*N*′-tetramethylguanidine groups (Bloy & Diefenbach, 2000), and cyclotriphosphazene with 2-, 3- and 4-pyridylmethoxy groups (Diefenbach *et al.*, 1999). Its synthesis and NMR data have been described elsewhere (Reuben, 1987; Selvaraj *et al.*, 1991). To date, however, structural data for (I) are not available in the Cambridge Structural Database (CSD, Version 5.24; Allen, 2002). We thus present here the results of the first X-ray crystal structure analysis of (I).

Fig. 1 shows a view of the asymmetric unit of (I), which consists of one molecule. The phosphazene ring is planar, with the maximum deviation from the mean least-squares plane being 0.093 (1) Å for atom P3. A small asymmetry within the bond angles of the phospazene ring is noted (Table 1), as was also observed in the related cyclic (*p*-halogenophenoxy)-phosphazene structures (Allcock *et al.*, 1994). The mean values of the N—P—N and P—N—P angles are 117.87 and 121.54°, respectively. The P—O, P—N, P—Cl and O—C bond lengths are in agreement with the values observed in analogous structures deposited in the CSD (Table 3). It is interesting to note that the occurrence of a Cl atom directly attached to a P atom (P1) does not modify the structural parameters in the vicinity of this atom.



(I)

The benzene rings lie on both sides of the phospazene ring, three on one side and two on the other, close to which lies the Cl atom. The disposition of the three phenoxy side groups on the side opposite to the Cl atom is such that the plane of phenoxy group *C* (C521–C526) attached to atom O52 (on P5) is approximately perpendicular to the phosphazene ring, with a dihedral angle of 78.59 (9)°. Phenoxy ring *B* (C321–C326) attached to atom O32 (on P3) is more tilted towards the phosphazene ring, with a dihedral angle of about 69.52 (9)°, and the third ring (*A*, C111–C116), attached to atom O11 (on P1), is nearly parallel to the phosphazene ring, with a dihedral angle of 21.6 (2)°. Furthermore, owing to optimization of C—H$\cdots\pi$ stacking interactions, these three benzene rings are oriented so that they are approximately mutually perpendicular. Benzene ring *A* is oriented perpendicular to benzene ring *B*, with a dihedral angle of about 89.6 (1)°, and the distance between atom C116 and the centroid of ring *B*, *CgB*, is about 3.71 Å (Table 4). Benzene ring *B* is perpendicular to

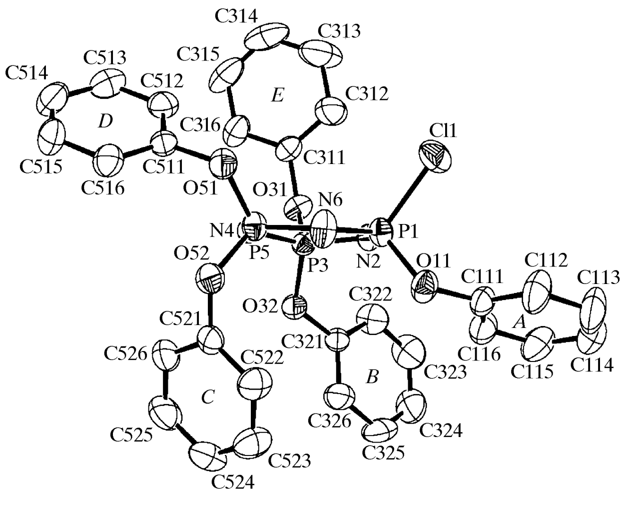


**Figure 1**
A view of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.

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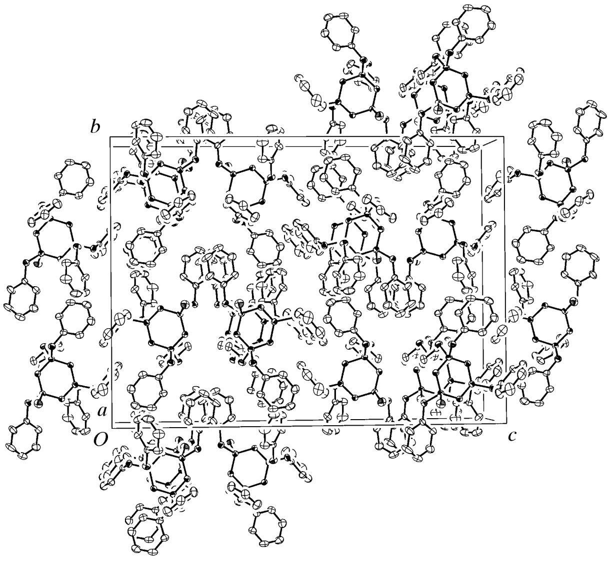

**Figure 2**
A general view of the crystal packing of (I), projected along the *a* axis.

ring *C*, with a dihedral angle of 82.4 (1)°, and the distance between atom C326 and the centroid of ring *C*, *CgC*, is about 4.18 Å (Table 4).

On the same side as the Cl atom, benzene ring *E* (C311–C316) attached to atom O31 is perpendicular to the phosphazene ring, with a dihedral angle of 85.8 (1)°, whereas benzene ring *D* (C511–C516) attached to atom O51 is more tilted towards the phosphazene ring, with a dihedral angle of 45.62 (6)°. The dihedral angle between rings *E* and *D* [52.8 (1)°] indicates that these two rings are not in an optimal perpendicular stacking interaction. However, atom C512 is situated at a distance of 3.99 Å from the centroid of ring *E*, *CgE* (Table 4).

Surprisingly, the $^{31}$P NMR spectrum of (I) shows a doublet of a doublet at 22.33 p.p.m. ($J_{PNP}$ = 81 and 84 Hz), attributed to atoms P3 and P5, and a doublet at 7.03 p.p.m. ($J_{PNP}$ = 83 Hz), attributed to P1, instead of the expected triplet (P3 and P5) and doublet (P1). These results indicate that P3 and P5 are not strictly equivalent. A significant difference between these two P atoms is observed in the crystal structure and concerns the positions of the phenoxy groups. This difference could explain the non-equivalence observed for P3 and P5 in the NMR spectrum.

In the crystal packing of (I), benzene rings from neighbouring molecules complete the intramolecular stacking interactions between the phenoxy units on both sides of the phosphazene ring (Fig. 2). C—H$\cdots\pi$ interactions are observed between rings *E* and *B* and between rings *E* and *D*. These benzene rings make dihedral angles of 58.5 (1) and 70.9 (1)°, respectively. For the former interaction, atom C325 is at a distance of 3.90 Å from *CgE*, and for the latter, atom C314 is at a distance of 3.85 Å from the centroid of ring *D*, *CgD* (Table 4). At the same time, a C—H group from a symmetry-related molecule is situated close to each N atom of the phosphazene ring, at distances ranging from 3.35 to 3.67 Å (Table 2). According to the geometric parameters, the C523—H523$\cdots$N6 interaction is weak, and it may be difficult to assert the occurrence of a real C—H$\cdots$N interaction.

## Experimental

Hexachlorocyclotriphosphazene (1 g, 1 equivalent) in solution in anhydrous tetrahydrofuran (THF) under nitrogen was stirred with NaH (60% dispersion in mineral oil, 0.63 g, 5.5 equivalents) at 268 K. A solution of phenol (1.49 g, 5.5 equivalents) in THF was added dropwise to maintain the temperature at around 268 K. The mixture was then stirred at room temperature for 24 h. The THF was evaporated and the residue dissolved in dichloromethane, washed with water and dried over anhydrous sodium sulfate. After removal of the dichloromethane under reduced pressure, the yield reached 86% for (I), and the $^{31}$P NMR spectrum indicated the presence of hexaphenoxycyclotriphosphazene as a side product. The title compound was crystallized in a desiccator by slow diffusion of pentane into a concentrated solution of (I) in THF. The $^{31}$P NMR spectrum was recorded using a Bruker DRX400 and samples were dissolved in $CDCl_3$ to a concentration of 10% *w*/*v*.

### *Crystal data*

$C_{30}H_{25}ClN_3O_5P_3$
$M_r$ = 635.89
Orthorhombic, *Pbca*
$a$ = 9.8044 (7) Å
$b$ = 21.3628 (13) Å
$c$ = 29.2053 (15) Å
$V$ = 6117.0 (7) Å$^3$
$Z$ = 8
$D_x$ = 1.381 Mg m$^{-3}$
Mo *Kα* radiation
Cell parameters from 25 reflections
$\theta$ = 18–21°
$\mu$ = 0.33 mm$^{-1}$
$T$ = 293 (2) K
Prism, colourless
0.52 × 0.52 × 0.41 mm

### *Data collection*

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: Gaussian (*JANA*98; Petříček & Dušek, 1998)
$T_{min}$ = 0.663, $T_{max}$ = 0.706
17 273 measured reflections
8884 independent reflections
4539 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.077
$\theta_{max}$ = 30.0°
$h = -13 \rightarrow 13$
$k = 0 \rightarrow 30$
$l = 0 \rightarrow 41$
3 standard reflections frequency: 60 min
intensity decay: 7.2%

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.153
$S$ = 1.01
8884 reflections
379 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0617P)^2 + 1.4945P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.007
$\Delta\rho_{max}$ = 0.37 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.27 e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Cl1—P1 | 2.0064 (10) | P3—O31 | 1.5830 (18) |
| P1—N6 | 1.561 (2) | P3—O32 | 1.5866 (17) |
| P1—O11 | 1.5693 (19) | N4—P5 | 1.576 (2) |
| P1—N2 | 1.572 (2) | P5—O51 | 1.5711 (19) |
| N2—P3 | 1.580 (2) | P5—N6 | 1.576 (2) |
| P3—N4 | 1.571 (2) | P5—O52 | 1.5871 (19) |
| | | | |
| N2—P1—Cl1 | 107.68 (9) | P3—N4—P5 | 121.74 (12) |
| P1—N2—P3 | 120.59 (12) | N4—P5—N6 | 117.12 (11) |
| N4—P3—N2 | 117.82 (11) | P1—N6—P5 | 122.30 (14) |

**Table 2**
Hydrogen-bonding geometry (Å, °).

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C523—H523···N6$^{i}$ | 0.93 | 2.69 | 3.352 (4) | 129 |
| C315—H315···N4$^{ii}$ | 0.93 | 2.89 | 3.621 (4) | 136 |
| C515—H515···N2$^{iii}$ | 0.93 | 3.05 | 3.672 (4) | 126 |

Symmetry codes: (i) $\frac{1}{2}+x, y, \frac{1}{2}-z$; (ii) $x-\frac{1}{2}, \frac{1}{2}-y, -z$; (iii) $\frac{1}{2}-x, y-\frac{1}{2}, z$.

**Table 3**
Comparison of mean P—N and P—O distances (Å) and P—N—P and N—P—N angles (°) in (I) and in reported cyclic (*p*-halogenophenoxy)-phosphazene structures.

| Compound | P—N | P—O | P—N—P | N—P—N |
|---|---|---|---|---|
| (I)† | 1.573 | 1.584 | 121.5 | 117.9 |
| (*p*-Bromophenoxy)phosphazene‡ | 1.571 | 1.585 | 121.7 | 116.6 |
| (*p*-Chlorophenoxy)phosphazene‡ | 1.572 | 1.578 | 122.3 | 117.6 |
| (*p*-Fluorophenoxy)phosphazene‡ | 1.578 | 1.581 | 122.0 | 117.4 |
| (*p*-Iodophenoxy)phosphazene‡ | 1.572 | 1.568 | 121.0 | 117.9 |

† This work. ‡ Allcock *et al.* (1994).

**Table 4**
Geometry of selected C—H···π interactions in (I).

*CgB* is the centroid of the C321–C326 ring *B*, *CgC* is the centroid of the C521–C526 ring *C*, *CgD* is the centroid of the C511–C516 ring *D* and *CgE* is the centroid of the C311–C316 ring *E*.

| C—H (ring) | Centroid | Distance (Å) | Dihedral angle (°) |
|---|---|---|---|
| C116—H116 (*A*) | *CgB* | 3.71 | 89.6 (1) |
| C326—H326 (*B*) | *CgC* | 4.18 | 82.4 (1) |
| C512—H512 (*D*) | *CgE* | 3.99 | 52.9 (1) |
| C323—H323 (*B*) | *CgE*$^{i}$ | 3.90 | 58.5 (1) |
| C314—H314 (*E*) | *CgD*$^{ii}$ | 3.85 | 70.9 (1) |

Symmetry codes: (i) $-1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $1+x, y, z$.

H atoms were treated as riding, with C—H distances in the range 0.93–0.96 Å and with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C).

Data collection: *CAD*-4-*PC Software* (Enraf–Nonius, 1996); cell refinement: *CAD*-4-*PC Software*; data reduction: *JANA*98 (Petříček & Dušek, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN1053). Services for accessing these data are described at the back of the journal.

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