très proche de celle de l'épicorazine A: la différence ne porte que sur une isomérie *cis–trans* et encore sur une moitié de molécule seulement. Ceci explique que ces métabolites ne puissent être séparés que par chromatographie sur couche mince.

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# Conformational Studies of the Triphenylphosphazenyl Side Chain in Cyclophosphazenes. II.* Crystal and Molecular Structure of 2,4,4,6,6,8,8-Heptachloro-2-triphenylphosphazenylcyclotetra(phosphazene), $N_4P_4Cl_7(NPPh_3)$

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## Abstract

$C_{18}H_{15}Cl_7N_5P_5$ crystallizes in the triclinic space group $P\bar{1}$ with $a = 8{\cdot}987\,(2)$, $b = 9{\cdot}795\,(3)$, $c = 16{\cdot}459\,(5)$ Å, $\alpha = 100{\cdot}77\,(2)$, $\beta = 91{\cdot}13\,(2)$, $\gamma = 101{\cdot}04\,(2)°$, $Z = 2$. The structure was refined to $R = 0{\cdot}043$ for 3301 counter reflections. The cyclophosphazene ring exhibits a hybrid crown–saddle conformation. The exocyclic $NPPh_3$ group exhibits a type III conformation. This is the first example of a type III conformation for an $NPPh_3$ group in cyclophosphazenes.

## Introduction

Basicity studies of cyclophosphazenes with a triphenylphosphazenyl substituent have shown two types of behaviour, which have been related to endocyclic and exocyclic protonation (Biddlestone, Nabi & Shaw, 1975). The significance of these conformations, designated as type I and type II respectively, has been discussed (Shaw, 1975, 1976). Subsequently, a type III conformation, intermediate between types I and II, has been proposed for geminal groupings (Shaw, 1976). We have taken up the crystallographic studies of triphenylphosphazenylcyclophosphazenes to study the conformational aspects of the exocyclic $NPPh_3$ group. In part I the structure of $N_3P_3Cl_5(NPPh_3)$ was presented and it was shown that the $NPPh_3$ group exhibits type I conformation. We now report the structure of $N_4P_4Cl_7$-$(NPPh_3)$ which is the first cyclotetra(phosphazene) with a triphenylphosphazenyl group to be investigated by X-ray crystallography. A preliminary communication has been published (Sudhakara Babu, Manohar, Cameron & Shaw, 1978).

## Experimental

### *Crystal data*

$N_4P_4Cl_7(NPPh_3)$, triclinic, $a = 8{\cdot}987\,(2)$, $b = 9{\cdot}795\,(3)$, $c = 16{\cdot}459\,(5)$ Å, $\alpha = 100{\cdot}77\,(2)$, $\beta = 91{\cdot}13\,(2)$, $\gamma = 101{\cdot}04\,(2)°$, $V = 1395$ Å$^3$, $Z = 2$, $D_c = 1{\cdot}67$ Mg m$^{-3}$, $M_r = 704{\cdot}35$, m.p. 359·5 K, space group $P\bar{1}$, $\mu$(Mo $K\alpha$) = 1·010 mm$^{-1}$.

The title compound is obtained from the reaction of $N_4P_4Cl_8$ with two mole equivalents of triphenylphosphazene. Crystals were grown from light petroleum (Biddlestone & Shaw, 1973). A crystal 0·5 × 0·3 × 0·3 mm was used for data collection on a CAD-4 diffractometer by the $\omega$–$2\theta$ scan technique (scan width ~1°) with monochromated Mo $K\alpha$ radiation. Three control reflections were measured every 50 reflections. The fluctuation in their intensities was below 3%. Of the 4119 reflections measured up to $2\theta = 45°$, 3301 were found to be above the threshold $[I > 3\sigma(I)]$.

Intensities were corrected for Lorentz and polarization effects, but not for absorption. The struc-

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* Part I: Sudhakara Babu, Manohar & Cameron (1979).

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ture was solved with *MULTAN* (Main, Woolfson & Germain, 1971). Sixteen atoms corresponding to the phosphazene ring could be identified from the *E* map calculated with the set of phases having the lowest Karle *R* value of 28·6%. Two cycles of refinement, followed by a Fourier synthesis, enabled the remaining atoms to be identified. The structure was refined by block-diagonal least squares with anisotropic thermal parameters. H atoms were included in calculated positions. The structure converged to an *R* of 0·043. In the final cycle most parameter shifts were $<0{\cdot}2\sigma$, though a few were in the range $0{\cdot}3$–$0{\cdot}5\sigma$. The weighting scheme used was that of Cruickshank, Bujosa, Lovell & Truter (1961), $w = 1/[6{\cdot}93 - 0{\cdot}0416|F| + 0{\cdot}0027|F|^2]$. Scattering factors were from Cromer & Waber (1965). The final atomic coordinates of the non-hydrogen atoms are given in Table 1.*

## Discussion

### *Bond distances and angles*

A view of the molecule down **a** is shown in Fig. 1. Bond distances and angles are given in Table 2.* The dependence of P—N distances on the electronegativity of the substituents is well known (Ahmed, Singh & Barnes, 1969). In view of the presence of the electron-donating $NPPh_3$ group we expect four different P—N distances in the ring. In the segments P(2)—N(1)—P(1) and P(2)—N(2)—P(3), the greater electronegativity of Cl atoms attached to P(1) and P(3), compared to the substituents at P(2), causes electrons to be drawn into P(1)—N(1) and P(3)—N(2) $\pi$ bonds. Thus, these two are expected to be the shortest P—N bonds in the ring. Correspondingly, P(2)—N(1) and P(2)—N(2) should be the longest. P(1)—N(4) and P(3)—N(3), adjacent to the short P—N bonds, are expected to be long as the donation of $\pi$ electrons from N(4) and N(3) is less favoured because of the availability of electrons from N(1) and N(2). This causes N(3) and N(4) to be in a more favourable position to donate electrons into

Table 1. *Final fractional atomic coordinates* ($\times 10^4$) *with e.s.d.'s in parentheses*

| | *x* | *y* | *z* |
|---|---|---|---|
| Cl(1) | 3981 (3) | 1421 (2) | 277 (1) |
| Cl(2) | 2672 (3) | 4034 (3) | 1068 (2) |
| Cl(3) | 6097 (3) | 494 (2) | 1967 (2) |
| Cl(4) | 9257 (3) | 3238 (3) | 2713 (2) |
| Cl(5) | 8309 (3) | 5162 (3) | 4267 (2) |
| Cl(6) | 8954 (2) | 5388 (3) | 1149 (2) |
| Cl(7) | 6401 (3) | 7030 (3) | 1634 (2) |
| P(1) | 4326 (2) | 3004 (2) | 1264 (1) |
| P(2) | 4909 (2) | 1806 (2) | 2692 (1) |
| P(3) | 7487 (2) | 4084 (2) | 3151 (1) |
| P(4) | 6983 (2) | 5197 (2) | 1702 (1) |
| P(5) | 2525 (2) | −441 (2) | 3000 (1) |
| N(1) | 3995 (7) | 2453 (7) | 2071 (4) |
| N(2) | 6151 (8) | 2923 (7) | 3299 (4) |
| N(3) | 7272 (8) | 5241 (7) | 2643 (4) |
| N(4) | 5900 (8) | 3942 (7) | 1130 (4) |
| N(5) | 3843 (8) | 925 (8) | 3229 (4) |
| C(11) | 3096 (8) | −1891 (8) | 3371 (5) |
| C(12) | 4169 (9) | −1551 (10) | 4034 (5) |
| C(13) | 4583 (10) | −2618 (12) | 4382 (6) |
| C(14) | 3990 (11) | −4004 (12) | 4062 (7) |
| C(15) | 2933 (12) | −4361 (11) | 3398 (7) |
| C(16) | 2471 (10) | −3305 (10) | 3066 (6) |
| C(21) | 1892 (8) | −1028 (8) | 1924 (5) |
| C(22) | 2661 (8) | −1896 (9) | 1394 (5) |
| C(23) | 2203 (10) | −2292 (10) | 560 (5) |
| C(24) | 985 (11) | −1834 (11) | 263 (5) |
| C(25) | 224 (10) | −982 (11) | 776 (6) |
| C(26) | 674 (9) | −562 (9) | 1609 (5) |
| C(31) | 882 (9) | −91 (8) | 3533 (5) |
| C(32) | −436 (10) | −1154 (10) | 3414 (6) |
| C(33) | −1750 (11) | −881 (12) | 3777 (7) |
| C(34) | −1742 (12) | 408 (13) | 4266 (6) |
| C(35) | −469 (12) | 1444 (11) | 4402 (6) |
| C(36) | 870 (11) | 1197 (10) | 4034 (6) |

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

| | | | |
|---|---|---|---|
| P(1)—Cl(1) | 1·999 (3) | Cl(1)—P(1)—Cl(2) | 101·4 (1) |
| P(1)—Cl(2) | 2·003 (3) | Cl(1)—P(1)—N(1) | 111·5 (3) |
| P(2)—Cl(3) | 2·054 (3) | Cl(1)—P(1)—N(4) | 104·1 (3) |
| P(3)—Cl(4) | 2·016 (3) | Cl(2)—P(1)—N(1) | 106·5 (3) |
| P(3)—Cl(5) | 1·989 (4) | Cl(2)—P(1)—N(4) | 108·8 (3) |
| P(4)—Cl(6) | 2·000 (3) | N(1)—P(1)—N(4) | 122·5 (4) |
| P(4)—Cl(7) | 1·986 (3) | Cl(3)—P(2)—N(1) | 106·1 (3) |
| P(1)—N(1) | 1·537 (7) | Cl(3)—P(2)—N(2) | 105·4 (3) |
| P(1)—N(4) | 1·576 (7) | Cl(3)—P(2)—N(5) | 109·0 (3) |
| P(2)—N(1) | 1·591 (7) | N(1)—P(2)—N(2) | 115·4 (4) |
| P(2)—N(2) | 1·587 (7) | N(1)—P(2)—N(5) | 112·6 (4) |
| P(2)—N(5) | 1·563 (7) | N(2)—P(2)—N(5) | 108·0 (4) |
| P(3)—N(2) | 1·545 (7) | Cl(4)—P(3)—Cl(5) | 102·2 (2) |
| P(3)—N(3) | 1·566 (7) | Cl(4)—P(3)—N(2) | 111·2 (3) |
| P(4)—N(3) | 1·556 (8) | Cl(4)—P(3)—N(3) | 107·9 (3) |
| P(4)—N(4) | 1·555 (7) | Cl(5)—P(3)—N(2) | 106·1 (3) |
| P(5)—N(5) | 1·588 (8) | Cl(5)—P(3)—N(3) | 105·0 (3) |
| P(5)—C(11) | 1·801 (8) | N(2)—P(3)—N(3) | 122·3 (4) |
| P(5)—C(21) | 1·802 (8) | Cl(6)—P(4)—Cl(7) | 101·2 (1) |
| P(5)—C(31) | 1·789 (8) | Cl(6)—P(4)—N(3) | 109·9 (3) |
| Cl(6)—P(4)—N(4) | 105·0 (3) | Cl(7)—P(4)—N(3) | 105·3 (3) |
| Cl(7)—P(4)—N(4) | 110·9 (3) | N(3)—P(4)—N(4) | 122·4 (4) |
| N(5)—P(5)—C(11) | 109·2 (4) | N(5)—P(5)—C(21) | 117·1 (4) |
| N(5)—P(5)—C(31) | 108·7 (4) | C(11)—P(5)—C(21) | 108·6 (4) |
| C(11)—P(5)—C(31) | 107·0 (4) | C(21)—P(5)—C(31) | 105·7 (4) |
| P(1)—N(1)—P(2) | 135·6 (5) | P(2)—N(2)—P(3) | 132·7 (5) |
| P(3)—N(3)—P(4) | 133·0 (5) | P(1)—N(4)—P(4) | 132·7 (5) |
| P(2)—N(5)—P(5) | 132·9 (5) | P(5)—C(11)—C(12) | 117·2 (6) |
| P(5)—C(11)—C(16) | 123·9 (7) | P(5)—C(21)—C(22) | 120·3 (6) |
| P(5)—C(21)—C(26) | 120·2 (6) | P(5)—C(31)—C(32) | 118·6 (6) |
| P(5)—C(31)—C(36) | 121·7 (7) | | |

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* Lists of structure factors, anisotropic thermal parameters and the dimensions of the phenyl rings have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34500 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* The values for cell parameters and bond lengths are slightly different from values reported in the earlier communication since the structure was refined further.

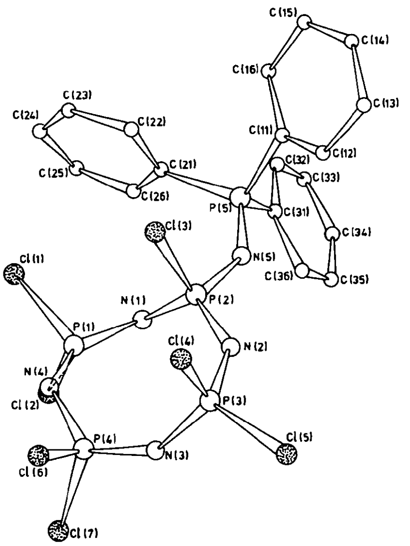

Fig. 1. View of the molecule down a.

P(4)–N(3) and P(4)–N(4) and thus these bonds should be short. The mean distances of equivalent bonds, in the order mentioned above, are 1·541, 1·589, 1·571 and 1·555 Å and they indicate the above trend. The non-geminal P–Cl bond is longer than the geminal P–Cl bonds, as expected.

The exocyclic P–N distances in the $NPPh_3$ substituent are not equal. P(2)–N(5), which is adjacent to the phosphazene ring, is significantly shorter than P(5)–N(5). This is in contrast to $N_3P_3Cl_4Ph(NPPh_3)$ where the two exocyclic P–N distances are equal (Biddlestone, Bullen, Dann & Shaw, 1974). Thus the replacement of the phenyl group by an electron-withdrawing Cl atom appears to have affected the exocyclic P–N bond distances also, in the present structure. It has been generally observed that the exocyclic P–N bonds are longer than the ring P–N bonds (Ahmed & Pollard, 1972). However, in the present structure the exocyclic P(2)–N(5) is shorter than the adjacent endocyclic P(2)–N(1) and P(2)–N(2). This unusual feature is also observed in $N_3P_3Cl_4Ph(NPPh_3)$. This short bond indicates considerable multiple-bond character for the exocyclic P(2)–N(5) compared to the endocyclic P(2)–N(1) and P(2)–N(2).

The endocyclic and exocyclic angles at P(1), P(3) and P(4) are similar to those observed in both the *T* and *K* forms of $N_4P_4Cl_8$ (Hazekamp, Migchelsen & Vos, 1962; Wagner & Vos, 1968). However, at P(2) the endocyclic N–P–N angle is 115·4°. This is one of the smallest angles observed in eight-membered phosphazene rings, and is similar to the endocyclic angle at the triphenylphosphazenyl-substituted P atom in $N_3P_3Cl_5(NPPh_3)$ (113·7°) (Sudhakara Babu, Manohar & Cameron, 1979) and $N_3P_3Cl_4Ph(NPPh_3)$ (111·7°). This reduction in the endocyclic angle from its normal value indicates the approach of bonds around P(2) towards tetrahedral geometry. This is also supported by the increase in the corresponding exocyclic angle (108·9°). The endocyclic angles at N atoms are approximately equal and are in the range 132·7–135·6°.

### *Conformation of the phosphazene ring*

Eight-membered phosphazene rings exhibit a wide variety of conformations because of their flexibility. The four main conformations exhibited are crown, saddle, chair and boat. Bullen & Tucker (1972) describe the first three conformations in terms of a plane through the P atoms with the N atoms above and below this plane. The boat conformation is described in terms of a plane formed by two P and two N atoms. In the present structure the four P atoms are coplanar and the N atoms are displaced above and below this plane. N(1), N(2) and N(3) are on one side at distances of 0·48, 0·28 and 0·49 Å respectively, whereas N(4) is on the other at a distance of 0·50 Å. Thus, in Bullen's notation, the ring has a hybrid conformation intermediate between crown and saddle or crown and chair. A similar conformation was observed in a non-geminally substituted dimethylamino derivative, $N_4P_4Cl_4(NMe_2)_4$ (Bullen & Tucker, 1972).

### *Conformation of the triphenylphosphazenyl group*

The most interesting feature in this structure is the conformation of the $NPPh_3$ group. In the corresponding trimer, $N_3P_3Cl_5(NPPh_3)$, the N–P bond of the substituent is nearly perpendicular (type I conformation) to the adjacent P–Cl bond. On the other hand, in the other trimeric compound, $N_3P_3Cl_4Ph(NPPh_3)$, the N–P bond is coplanar (type II) with the

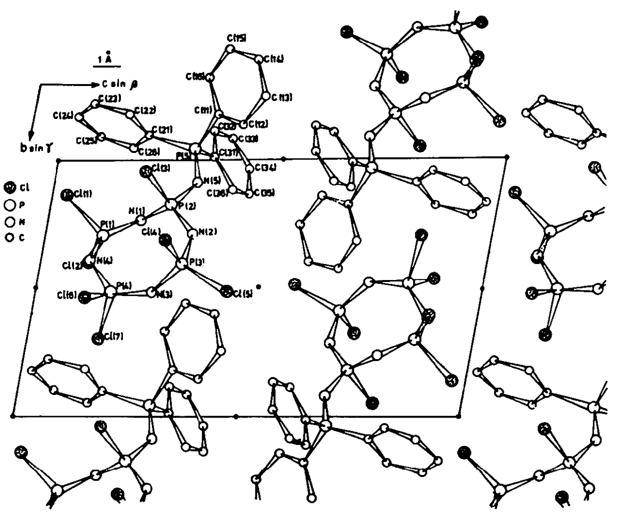

Fig. 2. Contents of the unit cell viewed down a.

Table 3. *Intermolecular contacts* <3·9 Å

E.s.d.'s are ~0·004 Å for Cl–Cl and ~0·01 Å for the rest.

| | |
|---|---|
| C(12)–C(34)$^{\mathrm{I}}$ | 3·73 Å |
| C(24)–C(25)$^{\mathrm{I}}$ | 3·82 |
| C(25)–C(25)$^{\mathrm{I}}$ | 3·54 |
| C(31)–C(34)$^{\mathrm{I}}$ | 3·77 |
| C(31)–C(35)$^{\mathrm{I}}$ | 3·87 |
| C(32)–C(35)$^{\mathrm{I}}$ | 3·74 |
| C(33)–C(35)$^{\mathrm{I}}$ | 3·75 |
| C(33)–C(36)$^{\mathrm{I}}$ | 3·76 |
| C(34)–C(35)$^{\mathrm{I}}$ | 3·84 |
| C(34)–C(36)$^{\mathrm{I}}$ | 3·60 |
| N(4)–C(23)$^{\mathrm{I}}$ | 3·58 |
| Cl(1)–C(24)$^{\mathrm{I}}$ | 3·73 |
| Cl(5)–C(14)$^{\mathrm{I}}$ | 3·69 |
| Cl(5)–C(35)$^{\mathrm{I}}$ | 3·78 |
| Cl(6)–C(23)$^{\mathrm{I}}$ | 3·70 |
| Cl(6)–C(24)$^{\mathrm{I}}$ | 3·82 |
| Cl(1)–Cl(1)$^{\mathrm{I}}$ | 3·606 |
| Cl(1)–Cl(3)$^{\mathrm{I}}$ | 3·810 |
| Cl(1)–Cl(7)$^{\mathrm{I}}$ | 3·775 |
| C(12)–C(33)$^{\mathrm{II}}$ | 3·65 Å |
| C(12)–C(34)$^{\mathrm{II}}$ | 3·78 |
| C(13)–C(33)$^{\mathrm{II}}$ | 3·66 |
| Cl(4)–C(35)$^{\mathrm{II}}$ | 3·59 |
| Cl(4)–C(36)$^{\mathrm{II}}$ | 3·67 |
| Cl(2)–Cl(6)$^{\mathrm{II}}$ | 3·820 |
| N(1)–C(15)$^{\mathrm{III}}$ | 3·76 |
| Cl(2)–C(15)$^{\mathrm{III}}$ | 3·85 |
| Cl(2)–C(16)$^{\mathrm{III}}$ | 3·83 |
| Cl(3)–Cl(7)$^{\mathrm{III}}$ | 3·400 |
| N(3)–C(32)$^{\mathrm{IV}}$ | 3·71 |
| Cl(4)–C(15)$^{\mathrm{IV}}$ | 3·69 |
| Cl(6)–C(22)$^{\mathrm{IV}}$ | 3·80 |
| Cl(6)–C(23)$^{\mathrm{IV}}$ | 3·61 |
| Cl(6)–C(24)$^{\mathrm{IV}}$ | 3·54 |
| Cl(6)–C(25)$^{\mathrm{IV}}$ | 3·69 |
| Cl(7)–C(22)$^{\mathrm{IV}}$ | 3·74 |

Symmetry code

| | | | |
|---|---|---|---|
| (I) | $\bar{x},\bar{y},\bar{z}$ | (III) | $x, 1+y, z$ |
| (II) | $1+x, y, z$ | (IV) | $1+x, 1+y, z$ |

adjacent P—Ph bond. On considerations discussed previously (Shaw, 1976) one would expect type I conformation for the $NPPh_3$ group in the present structure also. This is, however, not the case, the values for the torsion angles N(1)—P(2)—N(5)—P(5), N(2)—P(2)—N(5)—P(5) and Cl(3)—P(2)—N(5)—P(5) being 59, −172 and −58° respectively (e.s.d.'s are of the order of 1°). The deviation from type I towards type III conformation appears to be due to steric factors. The contact distances P(5)—N(1) and P(5)—Cl(3) are 3·52 and 3·71 Å respectively, the corresponding distances in $N_3P_3Cl_5(NPPh_3)$ being 3·49 and 3·97 Å respectively. If the $NPPh_3$ group in the present structure were to assume an exact type I conformation [Cl(3)—P(2)—N(5)—P(5) ~90°], the contact distance P(5)—N(1) would have been too short. This is the first instance of a type III conformation for the $NPPh_3$ group in cyclophosphazenes.

## *Packing*

The packing of the molecules in the unit cell is shown in Fig. 2. The molecules are arranged in sheets parallel to (100). All the short intermolecular contacts that determine the packing are given in Table 3. The orientation of the phenyl rings is influenced by the short intermolecular contacts which they make with the atoms of the phosphazene ring and with the C atoms of symmetrically related phenyl rings.

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