Acta Crystallographica Section E
**Structure Reports Online**
ISSN 1600-5368

# 4,4,6,6-Tetrachloro-1′,3′-[2,2′-(3-oxapentane-1,5-dioxy)dibenzyl]-$2\lambda^5$,$4\lambda^5$,$6\lambda^5$-cyclotriphosphazene-2-spiro-2′-1,3,2-diazaphospholane benzene hemisolvate

**Barış Tercan,[a] Tuncer Hökelek,[a]* Selen Bilge,[b] Şemsay Demiriz[b] and Zeynel Kılıç[b]**

[a]Hacettepe University, Department of Physics, 06800 Beytepe, Ankara, Turkey, and [b]Ankara University, Department of Chemistry, 06100 Tandoğan, Ankara, Turkey

Correspondence e-mail: merzifon@hacettepe.edu.tr

Received 28 June 2004
Accepted 13 July 2004
Online 24 July 2004

**Key indicators**

Single-crystal X-ray study
$T$ = 293 K
Mean $\sigma$(C–C) = 0.009 Å
$R$ factor = 0.067
$wR$ factor = 0.197
Data-to-parameter ratio = 15.3

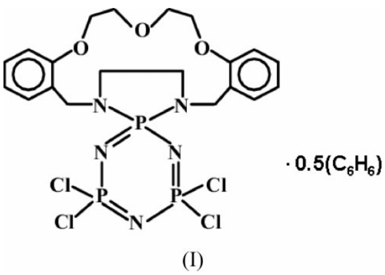
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_{20}H_{24}Cl_4N_5O_3P_3 \cdot 0.5C_6H_6$, is a novel crypta-phosphazene derivative containing three ether O and two N atoms in the macrocycle. The cavity radius of the macrocycle is estimated to be approximately 1.52 Å. The benzene solvent molecule lies on a crystallographic twofold rotation axis.

## Comment

Condensation reactions between hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, and dibenzo-diaza crown ethers have been studied recently (İlter *et al.*, 2004; Bilge, Kılıç, Çaylak & Hökelek, 2004). Chlorophosphazenes have been a useful class of molecules, preparing the way for other substituted phosphazene frameworks. Furthermore, dibenzo-diaza crown ethers are also a very important family of compounds for transition metal ion recognition (Bilge, Kılıç, Hökelek & Erdoğan, 2004).

Cyclophosphazene derivatives are considered to be on the boundary between inorganic and organic chemistry and have been reviewed several times over the years (Shaw, 1980; Allen, 1991; Chandrasekhar & Nagendran, 2001). $N_3P_3Cl_6$ has potential use in the synthesis of small organocyclophosphazenes and polymeric phosphazene derivatives with inorganic backbones and various side groups (Olshavsky & Allcock, 1995). The structures of organic, inorganic or organometallic side groups play an important role in the determination of the physical and chemical properties of phosphazene polymers (Allcock *et al.*, 1996). Some of these phosphazenes may be used in the preparation of high refractive index glasses, ferroelectric and non-linear optical polymers, and liquid crystalline and biomedical materials (Olshavsky & Allcock, 1995; Dembek *et al.*, 1991; Allcock & Kim, 1991; Cohen *et al.*, 1990).



(I)

Two kinds of compounds are expected to be formed from the reaction of $N_3P_3Cl_6$ with dibenzo-diaza crown ethers, *viz*. spiro- and bino-cyclophosphazene derivatives. However, only the title spiro-cyclic 18-membered crypta-phosphazene, (I), has been isolated. This represents a new class of macrocyclic

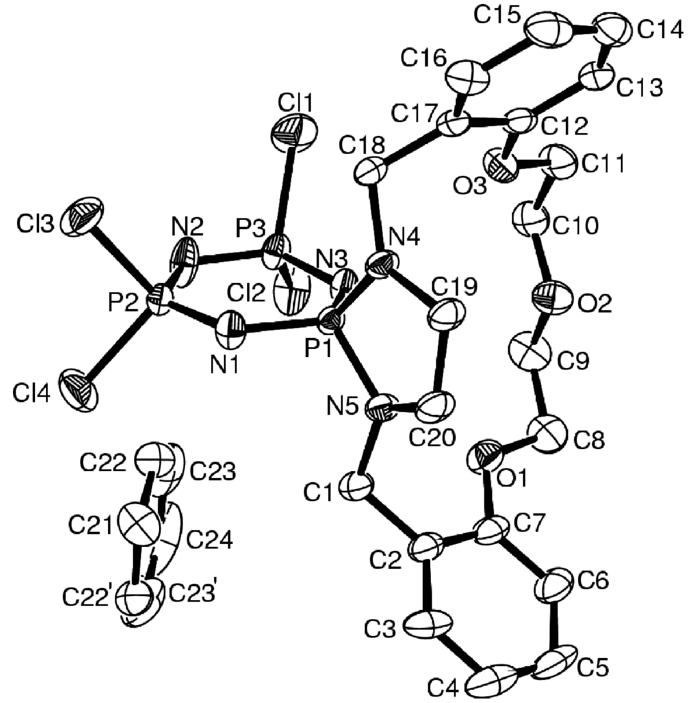
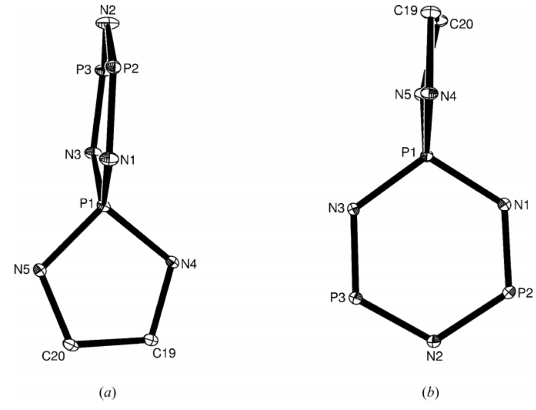


**Figure 1**
A view of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted. Atoms labelled with a prime are related to unprimed atoms by the symmetry operation $(-x, y, \frac{1}{2} - z)$.



(*a*) (*b*)

**Figure 2**
The conformations of (*a*) the phosphazene ring *A* and (*b*) the five-membered ring *B* in (I). Substituents have been omitted for clarity.

multidentate ligand, where the macrocycle and the phosphazene rings are linked, forming a novel structure. The crystal structure determination of (I) was carried out in order to estimate the cavity size of the macrocyclic ring and to understand the influence of the highly hindered macrocyclic ring on the structure of the cyclic trimeric phosphazene.

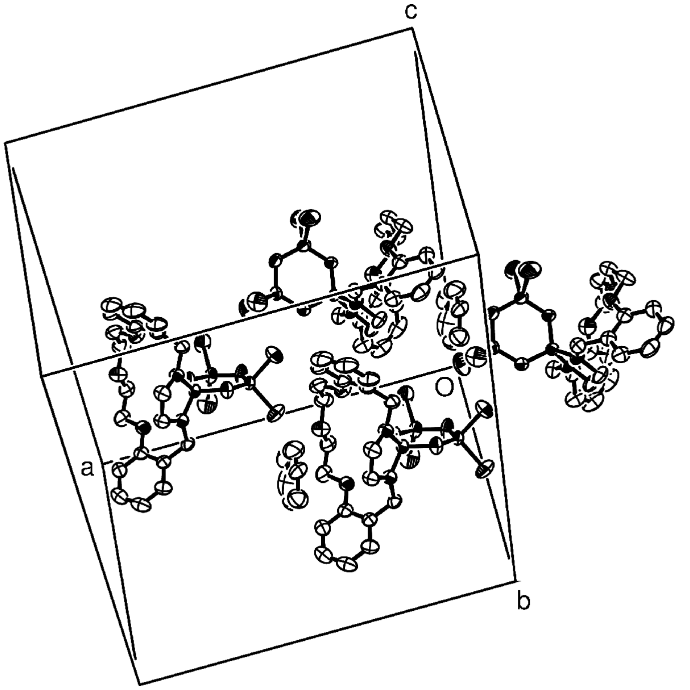


**Figure 3**
A partial packing diagram for (I). H atoms have been omitted.

The macrocyclic ring of (I) (Fig. 1) contains three ether O and two N atoms. The intramolecular distances C7···C17 [7.114 (3)], C2···C12 [6.987 (4)], P1···C9 [4.778 (4)], N4···O1 [4.745 (4)], N4···O2 [4.490 (4)], N5···O2 [4.236 (4)] and N5···O3 [4.386 (3) Å] may be indicative of the cavity size of the macrocyclic ring. The least-squares plane defined by atoms N4, N5, O1 O2 and O3 has a maximum deviation of 0.011 (4) Å for atom O2. Taking this mean plane into account, and using the 'modified covalent radii' of the N$sp^2$ (0.66 Å) and O$sp^3$ (0.76 Å) atoms (Goodwin *et al.*, 1982; Adam *et al.*, 1983; Drummond *et al.*, 1982), the macrocyclic cavity radius of (I) is estimated to be approximately 1.52 Å.

The phosphazene ring *A* is not planar (Fig. 2*a*), with a total puckering amplitude of $Q_T$ = 0.107 (3) Å (Cremer & Pople, 1975). A non-crystallographic mirror plane passes through atoms P2 and N3, as can be deduced from the torsion angles (Table 1). Atoms N1, N2 and N3 are displaced from the plane through the P atoms by 0.023 (4), 0.034 (5) and 0.144 (4) Å, respectively. The five-membered ring *B*, spiro-fused to ring *A*, is not planar (Fig. 2*b*); the maximum deviation from the least-squares plane is 0.145 (6) Å for atom C20.

For the macrocyclic ring, the total puckering amplitude is $Q_T$ = 2.188 (5) Å. The torsion angles of the macrocycle (Table 1) have the sequence +*ap*, −*ap*, +*sc*, −*sp*, +*ap*, +*ap*, −*sc*, −*ap*, −*ap*, +*sc*, −*ap*, +*ap*, +*sp*, −*sc*, +*ap* and +*ap* (*sp* is synperiplanar, *sc* is synclinal and *ap* is antiperiplanar), corresponding to the P1—N4···N5—P1 bond sequence. The conformation of the macrocyclic ring is influenced by the planarity of C2–C7/O1 and C12–C17/O3, and by the nonplanarity of the five-membered ring.

All P···P distances in (I) are in the range 2.700 (3)–2.813 (3) Å. The sums of the bond angles around atoms N4 and N5 [359.9 and 356.1°] indicate trigonal planar geometry. This is in contrast with our observations on a similar cryptaphosphazene compound, where the five-membered ring is replaced by a six-membered ring (İlter *et al.*, 2004). In the phosphazene ring of (I), the P—N bond lengths are in the range 1.553 (4)–1.622 (4) Å, and exhibit a regular variation with distance from atom P1: P1—N1 ≃ P1—N3 > P2—N2 ≃ P3—N2 > P2—N1 ≃ P3—N3.

The endocyclic N1—P1—N3 angle [111.6 (2)°] and the exocyclic N4—P1—N5 angle [95.4 (2)°] of the phosphazene ring are both smaller than in the 'standard' compound, $N_3P_3Cl_6$ (Bullen, 1971). In the latter, the corresponding angles are 118.3 and 118.5, and 101.2 and 101.6°, respectively. The substantial narrowing of the N1—P1—N3 angle may be due to the unexpectedly large electron release from atoms N4 and N5 to the phosphazene ring. The P1—N1—P2 [124.7 (2)] and P1—N3—P3 [124.0 (2)] angles are increased, while P2—N2—P3 [118.0 (2)°] is slightly decreased, with electron donation and withdrawal by the $N_3P_3$ ring (Kılıç *et al.*, 1996). These may be compared with the average value reported for $N_3P_3Cl_6$, *viz.* 121.4 (3)° (Bullen, 1971).

The asymmetric unit of (I) contains one-half of a benzene solvent molecule. A crystallographic twofold rotation axis passes through atoms C21 and C24. As can be seen from the packing diagram (Fig. 3), the benzene molecules fill the spaces between the macrocyclic lariat ether ligands, approximately parallel to [011]. Dipole–dipole and van der Waals interactions are effective in the molecular packing.

## Experimental

A solution of $N_3P_3Cl_6$ (1.95 g, 5.60 mmol) in dry tetrahydrofuran (100 ml) was slowly added to a solution of 3,4,6,7,15,16,17,18,19,20-decahydro-2,5,8-trioxa-16,19-diazatricyclo[19.4.0.0$^{9,14}$]pentacosa-9,11,13,21,23,25(1)-hexaene hemihydrate (2.00 g, 2.70 mmol) and $NEt_3$ (1.80 g, 17.4 mmol) in dry tetrahydrofuran (75 ml). The pure title compound, (I), was obtained according to the published procedure of Bilge *et al.* (2004). The compound was crystallized from *n*-heptane (m.p. 481 K; yield 1.95 g, 56%).

### *Crystal data*

$C_{20}H_{24}Cl_4N_5O_3P_3\cdot 0.5C_6H_6$
$M_r = 656.23$
Monoclinic, $C2/c$
$a = 18.531$ (5) Å
$b = 13.431$ (3) Å
$c = 24.043$ (4) Å
$\beta = 95.23$ (2)°
$V = 5959$ (2) Å$^3$
$Z = 8$
$D_x = 1.463$ Mg m$^{-3}$
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 12$–22°
$\mu = 5.43$ mm$^{-1}$
$T = 293$ (2) K
Prism, colourless
0.40 × 0.25 × 0.25 mm

### *Data collection*

Enraf–Nonius CAD-4 diffractometer
Non-profiled $\omega$ scans
Absorption correction: none
10 505 measured reflections
5913 independent reflections
3612 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.041$
$\theta_{\rm max} = 74.2$°
$h = 0 \rightarrow 23$
$k = 0 \rightarrow 16$
$l = -30 \rightarrow 29$
3 standard reflections
frequency: 120 min
intensity decay: 1%

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.067$
$wR(F^2) = 0.197$
$S = 1.03$
5113 reflections
335 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1326P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.50$ e Å$^{-3}$
$\Delta\rho_{\rm min} = -1.24$ e Å$^{-3}$
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0023 (2)

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

| | | | |
|---|---|---|---|
| P1—N3 | 1.598 (4) | P3—N3 | 1.562 (4) |
| P1—N4 | 1.617 (4) | P3—N2 | 1.570 (4) |
| P1—N1 | 1.622 (4) | P2—N1 | 1.553 (4) |
| P1—N5 | 1.625 (4) | P2—N2 | 1.579 (4) |
| | | | |
| N3—P1—N4 | 113.1 (2) | C18—N4—P1 | 123.3 (3) |
| N3—P1—N1 | 111.60 (19) | C19—N4—P1 | 113.4 (3) |
| N4—P1—N1 | 112.1 (2) | P2—N1—P1 | 124.7 (2) |
| N3—P1—N5 | 112.2 (2) | P3—N3—P1 | 124.0 (2) |
| N4—P1—N5 | 95.43 (18) | C20—N5—C1 | 121.3 (4) |
| N1—P1—N5 | 111.5 (2) | C20—N5—P1 | 112.5 (3) |
| N3—P3—N2 | 120.3 (2) | C1—N5—P1 | 122.3 (3) |
| N1—P2—N2 | 119.9 (2) | P3—N2—P2 | 118.0 (2) |
| C18—N4—C19 | 123.2 (4) | | |
| | | | |
| C9—O2—C10—C11 | −179.2 (5) | C1—C2—C7—O1 | 2.0 (7) |
| O2—C10—C11—O3 | −78.4 (6) | N4—P1—N5—C1 | 170.5 (4) |
| N5—P1—N4—C18 | 174.1 (4) | O3—C12—C17—C18 | −1.1 (6) |
| P1—N4—C18—C17 | −142.9 (4) | N4—C18—C17—C12 | 66.4 (6) |
| C10—C11—O3—C12 | 172.8 (4) | N3—P3—N2—P2 | 9.0 (5) |
| C11—O3—C12—C17 | 176.8 (4) | N1—P2—N2—P3 | −3.8 (5) |
| N2—P2—N1—P1 | 3.5 (5) | C7—O1—C8—C9 | −173.0 (5) |
| N3—P1—N1—P2 | −7.5 (4) | P1—N5—C1—C2 | 157.2 (4) |
| N2—P3—N3—P1 | −14.5 (5) | C7—C2—C1—N5 | −68.5 (6) |
| N1—P1—N3—P3 | 12.9 (4) | C10—O2—C9—C8 | −174.4 (5) |
| C8—O1—C7—C2 | 175.4 (5) | O1—C8—C9—O2 | 76.9 (6) |

The H atoms were positioned geometrically at C—H distances of 0.93 ($Csp^2$—H) and 0.97 Å ($Csp^3$—H), and were refined using a riding model, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$. The deepest residual electron-density hole is 0.08 Å from atom C22. Probably due to the poor crystal quality, most of the reflections were weak. To improve the $R$ factor, 800 reflections for which the difference between observed and calculated structure factors was 20–40% were suppressed in the refinement process.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*-4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The authors acknowledge the purchase of the CAD-4 diffractometer and the financial support of this work under grants DPT/TBAG1 of the Scientific and Technical Research Council of Turkey, and Ankara University, Scientific Research Unit, grant No. BAP-2001-07-05-064.

## References

Adam, K. R., Leong, L. J., Lindoy, L. F., Lip, H. C., Skelton, B. W. & White, A. H. (1983). *J. Am. Chem. Soc.* **105**, 4645–4651.
Allcock, H. R., Al-Shali, S., Ngo, D. C., Visscher, K. B. & Parvez, M. (1996). *J. Chem. Soc. Dalton Trans.* pp. 3521–3532.
Allcock, H. R. & Kim, C. (1991). *Macromolecules*, **24**, 2846–2851.
Allen, C. W. (1991). *Chem. Rev.* **91**, 119–135.
Bilge, S., Kılıç, Z., Çaylak, N. & Hökelek, T. (2004). *J. Mol. Struct.* In the press.
Bilge, S., Kılıç, Z., Hökelek, T. & Erdoğan, B. (2004). *J. Mol. Struct.* **691**, 85–96.
Bullen, G. J. (1971). *J. Chem. Soc. A*, pp. 1450–1453.
Chandrasekhar, V. & Nagendran, S. (2001). *Chem. Soc. Rev.* **30**, 193–203.
Cohen, S., Bano, W. C., Visscher, K. B., Chow, M., Allcock, H. R. & Langer, R. (1990). *J. Am. Chem. Soc.* **112**, 7832–7833.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

**o1372** Barış Tercan *et al.* • $C_{20}H_{24}Cl_4N_5O_3P_3\cdot 0.5C_6H_6$ *Acta Cryst.* (2004). E**60**, o1370–o1373

Dembek, A. A., Kim, C., Allcock, H. R., Devine, R. L. S., Shi, Y., Steiner, W. H. & Spangler, C. W. (1991). *Macromolecules*, **24**, 1000–1010.

Drummond, L. A., Henrick, K., Kanagasundaram, M. J. L., Lindoy, L. F., McPartlin, M. & Tasker, P. A. (1982). *Inorg. Chem.* **21**, 3923–3927.

Enraf–Nonius (1994). *CAD*-4 *EXPRESS*. Enraf–Nonius, Delft, The Netherlands.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Goodwin, H. J., Henrick, K., Lindoy, L., McPartlin, M. & Tasker, P. A. (1982). *Inorg. Chem.* **21**, 3261–3264.

Harms, K. & Wocadlo, S. (1995). *XCAD*4. University of Marburg, Germany.

İlter, E. E., Çaylak, N., Işıklan, M., Asmafiliz, N., Kılıç, Z. & Hökelek, T. (2004). *J. Mol. Struct.* **697**, 119–129.

Kılıç, A., Begeç, S., Çetinkaya, B., Hökelek, T., Kılıç, Z., Gündüz, N. & Yıldız, M. (1996). *Heteroatom Chem.* **7**, 249–256.

Olshavsky, M. A. & Allcock, H. R. (1995). *Macrocycles*, **28**, 6188–6197.

Shaw, R. A. (1980). *Pure Appl. Chem.* **52**, 1063–1097.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.