

4,4,6,6-Tetrachloro-2,2-(propylene-dioxydi-*o*-phenylenediimino)-2 λ^5 ,4 λ^5 ,6 λ^5 -cyclophosphazene

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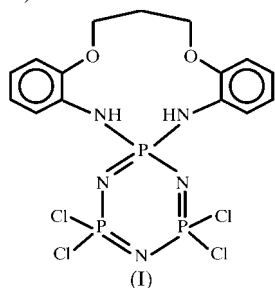
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The title compound, C₁₅H₁₆Cl₄N₅O₂P₃, is a cyclophosphazenic lariat (PNP-pivot) ether with a spiro-cyclic 12-membered macrocyclic ligand containing two ether O and two N atoms; the phosphazene ring is nearly planar. In the macrocyclic ring, there is a four-center (trifurcate) N—H···O/N—H···N hydrogen bond. The relative inner-hole size of the macrocycle is estimated as approximately 0.95 Å.

Comment

N₃P₃Cl₆ is the standard compound for trimeric phosphazene derivatives. It has potential use in the preparation of novel small organocyclophosphazenes and high polymeric phosphazene derivatives with inorganic backbones and various side groups (Allcock *et al.*, 1992; Olshavsky & Allcock, 1995; Hökelek *et al.*, 1996).



The structures of organic, inorganic or organometallic side groups are highly effective in determining the specific physical and chemical properties of phosphazene polymers (Allcock *et al.*, 1987, 1996). Some of the polymeric phosphazene derivatives may be useful as high refractive index glasses (Olshavsky & Allcock, 1995), ferroelectric and non-linear optical polymers (Dembek *et al.*, 1991; Allcock *et al.*, 1995), liquid crystalline materials (Allcock & Kim, 1991) and biomedical materials (Cohen *et al.*, 1990).

The crystal structure of N₃P₃Cl₆ (Bullen, 1971) and of a few of its derivatives with bulky phenoxy groups have been reported.

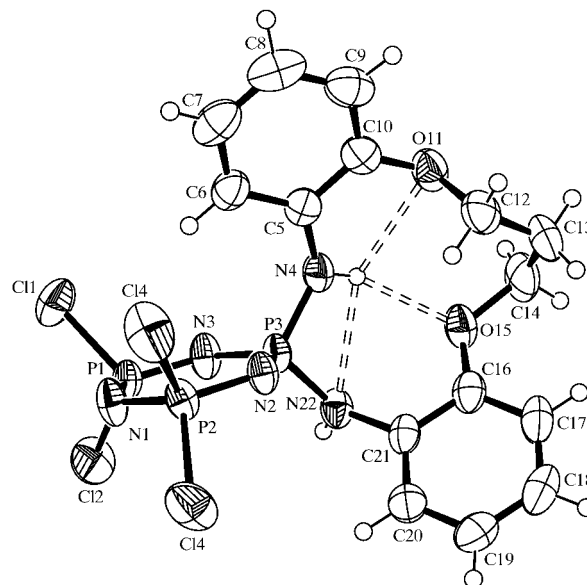


Figure 1

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

In the literature, there are a limited number of reports on the structures of the cyclophosphazenic lariat (PNP-pivot) ethers (Yıldız *et al.*, 1999; Brandt *et al.*, 1999, 2001; Bartsch *et al.*, 2002).

Two kinds of compounds are expected to be formed from the reaction of N₃P₃Cl₆ with propylene glycol bis(2-amino-phenyl ether), namely spiro- and ansa-cyclophosphazenic lariat ethers. However, only the spiro-cyclic 12-membered macrocyclic ligand, (I), has been isolated, which is a new class of macrocyclic multidentate ligand where the macrocycle and the phosphazene rings are linked, forming a novel structure.

The title compound, (I), may be a potential ion-selective reagent for lithium and transition metal cations. The structure determination of (I) was carried out in order to estimate the inner-hole size of the macrocyclic ring and to understand the influence of the highly hindered macrocyclic ring on the structure of the cyclic trimeric phosphazene. The macrocyclic ring (Fig. 1) includes two ether O and two N atoms. The intramolecular distances P3···C13 [5.222 (3) Å], C10···C21 [5.123 (4) Å], N4···O11 [2.730 (4) Å], N4···O15 [2.891 (4) Å], N22···O11 [4.712 (4) Å] and N22···O15 [2.729 (4) Å] may indicate the inner-hole size of the macrocyclic ring. The least-squares plane defined by atoms N4, N22, O11 and O15 has maximum deviations of 0.145 (2), −0.122 (2), −0.080 (2) and 0.070 (2) Å, respectively.

The relative inner-hole size of the macrocyclic ring is estimated as approximately 0.95 Å, taking into account the best least-squares plane defined by atoms N4, N22, O11 and O15, and the trifurcate hydrogen bond in the macrocycle, using the 'modified covalent radii' of Nsp² (0.66 Å) and Osp³ (0.76 Å) atoms (Goodwin *et al.*, 1982; Adam *et al.*, 1983; Drummond *et al.*, 1982). The macrocycle is contracted by a trifurcate N—H···O/N—H···N hydrogen bond, with the central part of the macrocycle being occupied by the trifurcate hydrogen bond.

The phosphazene ring is nearly planar. The P–N bonds are in the range 1.552 (2)–1.604 (2) Å and have a regular variation with the distance from atom P3 in the ring: P3–N3 \simeq P3–N2 > P1–N3 \simeq P2–N2 < P1–N1 \simeq P2–N1. The P–N bonds of the phosphazene ring (Table 1) have double-bond character. On the other hand, the P–N bonds of the macrocycle are near the lower limit of the single-bond-length range. In phosphazene derivatives, the P–N single and double 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 P–N bonds of the macrocycle may be due to electron release from the N atoms of the macrocycle to the phosphazene ring.

In the phosphazene ring, for the angles nearest the macrocycle, *viz.* endocyclic α (N2–P3–N3) of 114.6 (1)° and exocyclic α' (N4–P3–N22) of 103.3 (1)°, α is decreased while α' is increased with increasing electron supply and repulsions of the substituents relative to the N₃P₃Cl₆ standard compound. The β (P2–N2–P3) and β (P1–N3–P3) angles change considerably and seem to increase with increasing electron supply to the N₃P₃ ring (Kılıç *et al.*, 1996). In (I), β (P2–N2–P3) \simeq β (P1–N3–P3) > β (P1–N1–P2); the α angle is significantly smaller and the α' angle a little larger than the corresponding values [118.3 (2) and 101.2 (1)°, respectively] in the N₃P₃Cl₆ standard compound, but the β angles [123.3 (1) and 123.2 (1)°] are larger than the reported value [121.4 (3)°] in the N₃P₃Cl₆ standard compound (Bullen, 1971).

On the other hand, the α angle is larger than the corresponding value of 109.2 (4)° in [N₃P₃Cl₄(NPPH₃)₂] (Fincham *et al.*, 1986), but not significantly different from the values of 114.4 (1) and 114.5 (2)° in [N₃P₃Cl₅(NPPH₃)₃] (Fincham *et al.*, 1986) and [N₃P₃Cl₄Ph(PPh₂)₂] (Allcock *et al.*, 1990), and a little smaller than the α values of 115.8 (1), 115.1 (1) and 115.8 (1)° in N₃P₃Cl₂[(OC₆H₃)(NO₂)CH₂(OC₆H₃)(NO₂)(Ph₂)] (Hökelek *et al.*, 2001), [N₃P₃Cl₅(OC₆H₂-2,6-^tBu₂-4-Me)] (Hökelek *et al.*, 1999) and [N₃P₃Cl₅(OC₆H₂-2,4,6-^tBu₃)] (Kılıç *et al.*, 1996), respectively. In (I), the macrocycle releases electrons to the N₃P₃ ring, as seen for one of the NPPH₃ groups in

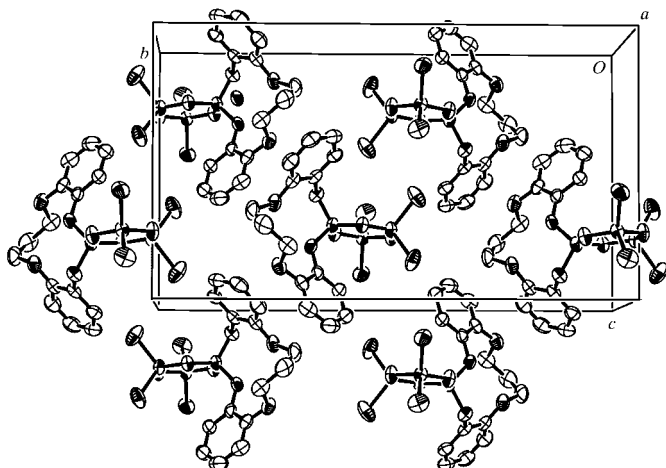


Figure 2
Packing diagram of (I).

[N₃P₃Cl₄(NPPH₃)₂] (Fincham *et al.*, 1986); the NPPH₃ group is known to be a very strong electron-releasing group in phosphazene chemistry.

In the macrocycle, there is a four-center (trifurcate) N–H···O/N–H···N hydrogen bond (Table 2). The Cremer & Pople (1975) total puckering amplitude for the macrocycle is $Q_T = 1.602$ (4) Å and the torsion angles (Table 1) have the sequence $-ap, +ap, +sp, -sc, +ap, -sc, -sc, -sc, +ap, +sp, -ac$ and $+sc$ (*sp* denotes synperiplanar, *sc* synclinal and *ap* antiperiplanar), corresponding to the P3–N4, . . . , N22–P3 bond sequence. The conformation of the macrocyclic ring is conditioned by the three hydrogen bonds (Fig. 1) and the planarity of the two benzo-fused N–C–C–O systems.

As can be seen from the packing diagram (Fig. 2), the macrocyclic rings are elongated approximately parallel to the (0 $\frac{1}{2}$ 1) planes and stacked along the *a* axis. Dipole–dipole and van der Waals interactions are also effective in the molecular packing.

Experimental

A solution of N₃P₃Cl₆ (2.5 g, 7.18 mmol) in acetonitrile (100 ml) was added dropwise to a mixture of propylene glycol bis(2-aminophenyl ether) (1.85 g, 7.20 mmol) and NEt₃ (3.63 g, 35.9 mmol) in acetonitrile (50 ml) at 263 K over a period of 1 h. After the mixture had been allowed to reach ambient temperature, stirring was continued for 26 h with argon being passed over the reaction mixture. The precipitated amine hydrochloride was filtered off and the solvent was evaporated under reduced pressure. The residue was dissolved in benzene (20 ml) and subjected to column chromatography (silica gel 40 g, eluting with benzene) and crystallized from benzene–dichloromethane (2:1) (m.p. 467 K; yield 2.53 g, 66%).

Crystal data

C₁₅H₁₆Cl₄N₅O₂P₃
 $M_r = 533.04$
 Monoclinic, $P2_1/n$
 $a = 7.7094$ (6) Å
 $b = 22.404$ (2) Å
 $c = 12.6960$ (14) Å
 $\beta = 93.751$ (7)°
 $V = 2188.2$ (4) Å³
 $Z = 4$

$D_x = 1.618$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 10$ –15°
 $\mu = 0.78$ mm⁻¹
 $T = 293$ (2) K
 Block, colorless
 0.40 × 0.25 × 0.25 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 Non-profiled ω scans
 4703 measured reflections
 4385 independent reflections
 3132 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.022$

$\theta_{max} = 26.3^\circ$
 $h = 0 \rightarrow 9$
 $k = -27 \rightarrow 0$
 $l = -15 \rightarrow 15$
 3 standard reflections
 frequency: 120 min
 intensity decay: 1%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.110$
 $S = 1.02$
 4385 reflections
 322 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0525P)^2 + 1.1216P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.39$ e Å⁻³
 $\Delta\rho_{min} = -0.38$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

P3—N2	1.603 (2)	P1—N3	1.559 (2)
P3—N3	1.604 (2)	P1—N1	1.583 (2)
P3—N22	1.635 (3)	P2—N2	1.552 (2)
P3—N4	1.636 (3)	P2—N1	1.579 (2)
N2—P3—N3	114.57 (12)	N3—P1—N1	119.53 (12)
N2—P3—N22	112.02 (13)	N2—P2—N1	119.83 (12)
N3—P3—N22	106.58 (13)	P2—N2—P3	123.30 (13)
N2—P3—N4	107.80 (13)	P1—N3—P3	123.22 (14)
N3—P3—N4	112.01 (14)	P2—N1—P1	119.43 (14)
N22—P3—N4	103.33 (13)		
N4—P3—N22—C21	75.1 (3)	C10—O11—C12—C13	169.3 (3)
P3—N22—C21—C16	−87.3 (3)	O11—C12—C13—C14	−52.3 (5)
C12—O11—C10—C5	−89.9 (3)	C16—O15—C14—C13	−70.4 (5)
N4—C5—C10—O11	2.4 (4)	C12—C13—C14—O15	−39.9 (6)
C14—O15—C16—C21	173.5 (3)	C10—C5—N4—P3	151.0 (2)
N22—C21—C16—O15	2.9 (4)	N22—P3—N4—C5	−159.1 (2)

Atom H20 was positioned geometrically at a distance of 0.93 Å from the parent C20 atom; a riding model was used during the refinement process. The remaining H atoms were located in a difference synthesis and were refined isotropically [C—H = 0.87 (4)–0.97 (3) Å, N—H = 0.79 (3)–0.863 (19) Å and CH₂ C—H = 0.88 (5)–0.97 (3) Å].

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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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1648). Services for accessing these data are described at the back of the journal.

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