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4,4,6,6-Tetrachloro-2,2-(ethylenedioxydi-*o*-phenylenediimino)-2λ^5,4λ^5,6λ^5-cyclotriphosphazene

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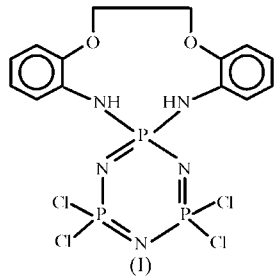
The title ligand, $C_{14}H_{14}Cl_4N_5O_2P_3$, is a cyclophosphazene lariat (PNP pivot) ether with a spiro-cyclic 11-membered macrocyclic ring containing two ether O and two N atoms; the phosphazene ring is nearly planar. The macrocyclic ring contains a four-centred (trifurcate) N—H···O/N—H···N hydrogen bond, and the relative inner-hole size of the macrocycle is ∼1.14 Å in radius. The molecules are linked about inversion centres by N—H···N hydrogen bonds into centrosymmetric dimers.

Comment

Chlorocyclophosphazenes are a useful class of molecules that have prepared the ground for other substituted phosphazene frameworks. The reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, with amines (Contractor *et al.*, 1987), diamines (Parwolik-Czomperlik *et al.*, 2002; Beşli *et al.*, 2003), polyamines (Kılıç *et al.*, 1991; Coles *et al.*, 2002), aryloxides (Kılıç *et al.*, 1996; Chandrasekhar *et al.*, 2002) and oligoethylene glycols (Shaw & Ture, 1991; Al-Madfa *et al.*, 1990) under different conditions have been investigated over the last three decades. Cyclophosphazene (PNP pivot) lariat ethers and other phosphazene derivatives have been synthesized with the aim of designing highly ion-selective macrocyclic multidentate ligands (Yıldız *et al.*, 1999; Allcock *et al.*, 1991; Kruszynski *et al.*, 2001; Bartsch *et al.*, 2002; Brandt, Seliger *et al.*, 2001), and anticancer (Song *et al.*, 2003), antibacterial (Konar *et al.*, 2000) and anti-HIV (Brandt, Bartczak *et al.*, 2001) agents, and of investigating the stereogenic properties of cyclophosphazene derivatives (Davies *et al.*, 2000; Coles *et al.*, 2002).

The title ligand, (I), a spiro-cyclic 11-membered macrocyclic ligand, belongs to a new class of lariat ether ligand in which the macrocyclic and phosphazene rings are linked together, forming a novel structure. Compound (I) is a potential ion-selective reagent for lithium and transition-metal cations. A structure determination of (I) was carried out in order to ascertain 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.



(I)

The macrocyclic ring of (I) contains two ether O and two N atoms (Fig. 1 and Table 1), and a trifurcate N—H···O/N—H···N hydrogen bond (Table 2). Atoms N4, N5, O1 and O2 deviate from the least-squares plane defined by these atoms by 0.103 (4), −0.084 (4), −0.066 (4) and 0.108 (5) Å, respectively. The intramolecular C6···C14 [5.346 (3) Å], P1···C7 [4.435 (4) Å], N4···O1 [2.659 (4) Å], N4···O2 [2.788 (4) Å], N5···O1 [4.609 (4) Å] and N5···O2 [2.782 (4) Å] distances may indicate the inner-hole size of the macrocyclic ring. The relative macrocyclic inner-hole size is ∼1.14 Å in radius, taking into account the mean plane defined by atoms N4, N5, O1 and O2, and using the 'modified covalent radii' of Nsp^2 (0.66 Å) and Osp^3 (0.76 Å) atoms (Goodwin *et al.*, 1982; Adam *et al.*, 1983; Drummond *et al.*, 1982).

The phosphazene ring is nearly planar, with P—N bond lengths in the range 1.554 (3)–1.610 (3) Å. The P—N bonds lengths have a regular dependence on the distance from atom P1 in the ring, such that P1—N1 ≃ P1—N3 > P2—N1 ≃ P3—N3 < P2—N2 ≃ P3—N2. The phosphazene ring P—N bonds have double-bond character, while the P—N bond lengths in

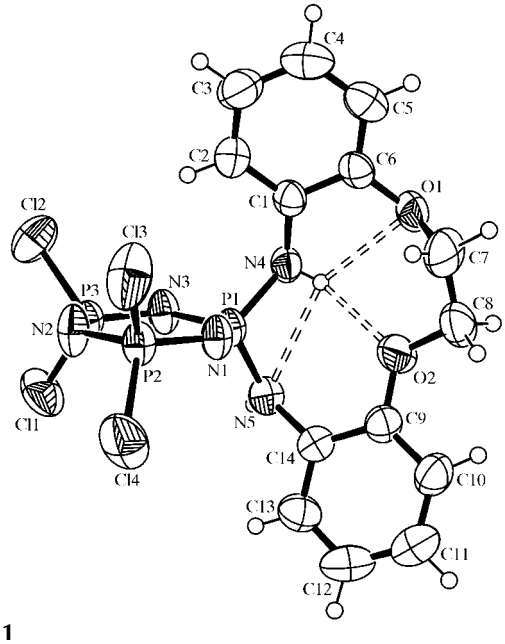


Figure 1
An *ORTEP*-3 (Farrugia, 1997) drawing of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and broken lines indicate hydrogen bonds.

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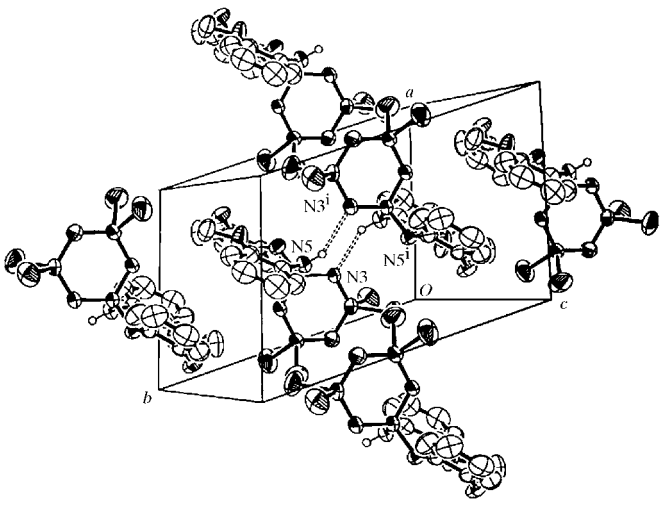

Figure 2
A packing diagram of (I). Broken lines indicate hydrogen bonds. [Symmetry code: (i) $1-x, 1-y, 1-z$.]

the macrocycle correspond to the lower limit of the typical single-bond length; 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 of the macrocycle P—N bonds in (I) is probably due to electron release from the N atoms of the macrocycle to the phosphazene skeleton.

In the phosphazene ring in (I), for the angles nearest to the macrocycle, *viz*. the endocyclic α(N1—P1—N3) and exocyclic α'(N4—P1—N5) angles, α decreases while α' increases with increasing electron supply and repulsion of the substituents relative to the standard compound $N_3P_3Cl_6$. The β(P1—N1—P2 and P1—N3—P3) values in (I) differ considerably from those in $N_3P_3Cl_6$ and seem to increase with increasing electron supply to the N_3P_3 ring (Kılıç *et al.*, 1996). In (I), β(P1—N1—P2) $\simeq$ β(P1—N3—P3) > (P2—N2—P3); α [114.2 (2)°] is significantly smaller and α' [105.8 (2)°] is slightly larger than the corresponding values in $N_3P_3Cl_6$ [118.3 (2) and 101.2 (1)°, respectively], but the β angles in (I) [122.9 (2) and 122.9 (2)°] are larger than the value [121.4 (3)°] reported for $N_3P_3Cl_6$ (Bullen, 1971). The α and β angles in (I) are nearly identical to those reported for 4,4,6,6-tetrachloro-2,2-(propylenedioxy-di-*o*-phenylenediimino)-2λ^5,4λ^5,6λ^5-cyclotriphosphazene, (II) (Tercan *et al.*, 2004), but α' in (I) [105.8 (2)°] is larger than the corresponding value in (II) [103.3 (1)°].

For the phosphazene and macrocyclic rings, the Cremer & Pople (1975) total puckering amplitudes, Q_T, are 0.096 (3) and 0.916 (4) Å, respectively. The torsion angles of the macrocycle (Table 1) have the sequence *−ap*, *+ap*, *−sp*, *−sc*, *+ap*, *−sc*, *−ap*, *+ap*, *+sp*, *−ac*, *+sc* (*sp* is synperiplanar, *sc* is synclinal, *ac* is anticlinal and *ap* is antiperiplanar), corresponding to the P1—N4, ..., N5—P1 bond sequence. The conformation of the macrocyclic ring is conditioned by the three hydrogen bonds and the planarity of the two benzo-fused N—C—C—O systems. As can be seen from the packing diagram (Fig. 2), intermolecular N—H···N hydrogen bonds lead to the formation of centrosymmetric dimers.

Experimental

A solution of $N_3P_3Cl_6$ (1.77 g, 5 mmol) in acetonitrile (100 ml) was added dropwise to a mixture of ethylene glycol bis(2-aminophenyl) ether (1.22 g, 5 mmol) and NEt_3 (2.52 g, 25 mmol) in acetonitrile (50 ml) at 263 K over a period of 1 h. After the mixture had been allowed to reach ambient temperature, it was stirred for 24 h under argon. The precipitated amine hydrochloride was filtered off and the solvent was evaporated under reduced pressure. The residue was dissolved in benzene and subjected to column chromatography (silica gel 35 g, benzene eluant) and crystallized from *n*-heptane (m.p. 486 K; yield 1.35 g, 52%).

Crystal data

$C_{14}H_{14}Cl_4N_5O_2P_3$
M_r = 519.01
Triclinic, $P\overline{1}$
a = 9.045 (2) Å
b = 11.647 (3) Å
c = 12.225 (2) Å
α = 103.663 (17)°
β = 107.458 (19)°
γ = 109.78 (2)°
V = 1071.1 (5) Å^3
Z = 2
D_x = 1.609 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 10–15°
μ = 0.80 mm^{-1}
T = 293 (2) K
Plate, colourless
0.40 × 0.25 × 0.20 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Non-profiled ω scans
4615 measured reflections
4329 independent reflections
3011 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
θ_{max} = 26.3°
$h = 0 \rightarrow 11$
$k = -14 \rightarrow 13$
$l = -15 \rightarrow 14$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.172
S = 1.03
4329 reflections
257 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0935P)^2 + 0.849P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.89 e Å^{-3}
$\Delta\rho_{min}$ = −0.44 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

P1—N1	1.603 (3)	P3—N3	1.560 (3)
P1—N3	1.610 (3)	P3—N2	1.578 (4)
P1—N5	1.635 (3)	P2—N1	1.554 (3)
P1—N4	1.644 (3)	P2—N2	1.580 (3)
N1—P1—N3	114.17 (17)	N3—P3—N2	119.45 (17)
N1—P1—N5	110.85 (18)	N1—P2—N2	120.11 (18)
N3—P1—N5	107.03 (18)	P2—N1—P1	122.89 (19)
N1—P1—N4	110.94 (18)	P3—N2—P2	119.1 (2)
N3—P1—N4	107.67 (19)	P3—N3—P1	122.9 (2)
N5—P1—N4	105.75 (18)		
C9—C14—N5—P1	−62.0 (5)	C8—O2—C9—C14	168.0 (5)
N4—P1—N5—C14	84.9 (4)	N5—C14—C9—O2	6.9 (6)
N5—P1—N4—C1	−162.6 (3)	C6—O1—C7—C8	136.2 (4)
C7—O1—C6—C1	−95.2 (5)	C9—O2—C8—C7	−148.5 (5)
P1—N4—C1—C6	142.2 (3)	O1—C7—C8—O2	−54.9 (6)
O1—C6—C1—N4	−0.1 (5)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4···O1	0.78 (4)	2.29 (5)	2.659 (5)	110 (4)
N4—H4···O2	0.78 (4)	2.12 (5)	2.788 (5)	144 (6)
N4—H4···N5	0.78 (4)	2.47 (6)	2.614 (6)	92 (4)
N5—H5···N3^{i}	0.86	2.25	3.026 (5)	151

Symmetry code: (i) $1-x, 1-y, 1-z$.

Atom H4 was located in a difference synthesis and refined isotropically [N4—H4 = 0.78 (4) Å]. All other H atoms were positioned geometrically at distances of 0.93 (Csp^2—H) and 0.97 Å (Csp^3—H) from their parent 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: *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).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1177). Services for accessing these data are described at the back of the journal.

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