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7,11-(Butane-1,4-diyldioxydi-*o*-phenylenedimethylene)-6,6-dichloro-4,4-bis(pyrrolidin-1-yl)-2λ^5,4λ^5,6λ^5-triphosphaza-1,3,5,7,11-pentaazaspiro[5.5]undeca-1,3,5-triene

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Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.003 Å
R factor = 0.034
wR factor = 0.089
Data-to-parameter ratio = 11.4

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

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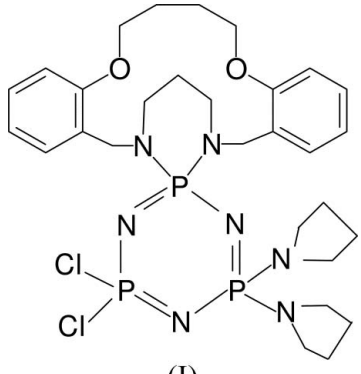
The title compound, $C_{29}H_{42}Cl_2N_7O_2P_3$, is a phosphazene derivative with a bulky substituent attached through a spiro junction with two pyrrolidine rings. The six-membered C_3N_2P ring has a chair conformation, while the phosphazene ring has a slight envelope conformation. The two N atoms in the C_3N_2P ring are likely to be stereogenic.

Comment

During the last two decades, organophosphazene derivatives have attracted considerable interest for a variety of reasons. They are useful starting materials in producing polyorganophosphazene polymers with different side groups (Dez *et al.*, 1999; Mathew *et al.*, 2000). The stereogenic properties of phosphazene derivatives have also attracted much interest (Uslu *et al.*, 2005; Beşli *et al.*, 2003; Coles *et al.*, 2002), as has their use in the design of highly selective anticancer (Baek *et al.*, 2000), antibacterial (Konar *et al.*, 2000) and anti-HIV (Brandt *et al.*, 2001) agents. Moreover, they have found industrial applications in the production of inflammable textile fibers, advanced elastomers (Blonsky *et al.*, 1986), rechargeable lithium batteries (Allcock, Napierala *et al.*, 1996) and biomedical materials (Allcock & Kwon, 1986) including synthetic bones (Greish *et al.*, 2005).



(I)

Hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, is known as the 'standard' compound in the field of phosphazene chemistry. It has been used in the preparation of novel small organocyclophosphazenes and polyphosphazenes with different substituents (Allcock *et al.*, 1992; Olshavsky & Allcock, 1995). These substituents are very effective in determining the specific physical and chemical properties of polyorganophosphazenes (Allcock, Al-Shali *et al.*, 1996; Dembek *et al.*, 1991).

The reactions of $N_3P_3Cl_6$ with bidentate ligands, such as diazacrown ethers, afford novel crypta-phosphazene deriva-

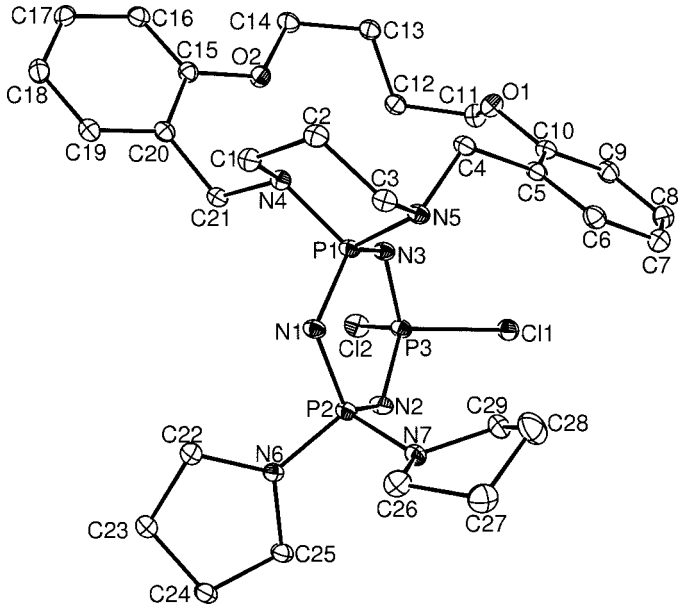


Figure 1
An *ORTEP-3* (Farrugia, 1997) drawing of the title molecule with the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level. H atoms have been omitted.

tives (İlter *et al.*, 2004; Bilge *et al.*, 2004). The crystal structure of $N_3P_3Cl_6$ (Bullen, 1971) and a few of its derivatives with bulky N/O groups have been reported (Tercan, Hökelek, Dal *et al.*, 2004; Tercan, Hökelek, Işıklan *et al.*, 2004). Contrary to expectation, the reaction of 4,4,6,6-tetrachloro[butane-*N*,*N*′-bis(1,4-oxybenzyl]-1,3,5,7,11-pentaaza-2,4,6-triphosphaza(6-P^V)spiro[5.5]undeca-1,3,5-triene with an excess of pyrrolidine led to the formation of a geminal product, instead of non-geminal *cis*/*trans* ones (Lensink *et al.*, 1984).

Fig. 1 shows the molecular structure of (I), with the atomic numbering scheme. The phosphazene ring (*A*) is not completely planar and adopts an envelope conformation with N1 at the flap, with a puckering amplitude, Q_T, of 0.223 (1) Å (Cremer & Pople, 1975). The six-membered P1/N4/C1/C2/C3/N5 ring (*B*) has a total puckering amplitude of 0.603 (2) Å and a chair conformation.

In ring *A*, the P—N bond lengths are in the range 1.559 (2)–1.621 (2) Å. The P—N bonds of the phosphazene ring (Table 1) have double-bond character. The exocyclic P1—N4 [1.670 (2)] and P1—N5 [1.665 (2) Å] bonds have single-bond character. In phosphazene derivatives, P—N single- and double-bond lengths are generally in the ranges 1.628–1.691 and 1.571–1.604 Å, respectively (Allen *et al.*, 1987). The shortness of the exocyclic P—N bonds in (I) indicates that electron release has occurred from the lone pair of electrons of atoms N4 and N5 to the phosphazene ring. On the other hand, ring *A* has a pseudo-mirror plane running through the atoms N1 and P3, as can be deduced from the torsion angles.

The sums of the bond angles around N4 and N5 are 337.3 and 339.8°, respectively, which establish that the nitrogen atoms have pyramidal geometry. Therefore, the N atoms may have stereogenic configurations. In ring *A*, for the angles nearest to the bulky substituent, *viz*. endocyclic α(N1—P1—N3) [116.5 (1)°], exocyclic α'(N4—P1—N5) [103.6 (1)°], endocyclic β(P1—N1—P2) [122.0 (1)°], endocyclic γ(N1—P2—N2) [114.0 (1)°] and exocyclic γ'(N6—P2—N7) [103.3 (2)°], α and γ are decreased, and α', β and γ' are increased with increasing electron supply and repulsions of the substituents relative to the standard compound $N_3P_3Cl_6$ (Bullen, 1971). The bond angles in ring *A* are comparable to the corresponding ones reported for $N_3P_3Cl_6$, *viz*. α [118.3 (2)°], α' [101.2 (1)°] and β [121.4 (3)°].

The macrocyclic ring of (I) (Fig. 1) contains two ether O and two N atoms. The least-squares plane defined by atoms O1, O2, N4 and N5 has a maximum deviation of 0.108 (1) Å for atom N4. For the macrocyclic ring, the total puckering amplitude is Q_T = 2.456 (2) Å. The conformation of the macrocyclic ring is influenced by the planarity of the two benzo-fused C—C—C—O systems.

Experimental

A solution of 4,4,6,6-tetrachloro[butane-*N*,*N*′-bis(1,4-oxybenzyl]-1,3,5,7,11-pentaaza-2,4,6-triphosphaza(6-P^V)spiro[5.5]undeca-1,3,5-triene (3.00 g, 4.38 mmol) in dry tetrahydrofuran (THF, 150 ml) was added slowly to a solution of pyrrolidine (3.74 g, 52.60 mmol) with stirring and refluxing for 25 h under an argon atmosphere. THF was evaporated under reduced pressure and the residue was dissolved in benzene (200 ml), then an excess amount of triethylamine was added to the solution. The solvent was evaporated after refluxing for 3 h and the resulting product was purified by column chromatography [eluent THF/toluene (1:3), silica gel (60 g)], and crystallized from n-heptane (yield 1.8 g, 60%; m.p. 468 K).

Crystal data

$C_{29}H_{42}Cl_2N_7O_2P_3$
M_r = 684.51
Monoclinic, $P2_1/c$
a = 9.2618 (4) Å
b = 23.6323 (8) Å
c = 15.1606 (7) Å
β = 103.023 (4)°
V = 3233.0 (2) Å^3
Z = 4
D_x = 1.406 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 44825 reflections
θ = 1.4–26.1°
μ = 0.39 mm^{-1}
T = 100 K
Prism, colorless
0.46 × 0.39 × 0.32 mm

Data collection

STOE IPDS-II diffractometer
φ scans
Absorption correction: integration (*X-RED*; Stoe & Cie, 2002)
T_{min} = 0.841, T_{max} = 0.886
45677 measured reflections
6351 independent reflections
5232 reflections with $I > 2\sigma(I)$
R_{int} = 0.069
θ_{max} = 26.0°
$h = -11 \rightarrow 11$
$k = -29 \rightarrow 29$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.089
S = 1.04
6351 reflections
556 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.053P)^2 + 0.4055P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.46 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

P1—N1	1.5922 (14)	P2—N2	1.6206 (15)
P1—N3	1.6020 (15)	P2—N6	1.6280 (15)
P1—N5	1.6654 (15)	P2—N7	1.6430 (16)
P1—N4	1.6701 (15)	P3—N2	1.5594 (15)
P2—N1	1.5957 (15)	P3—N3	1.5720 (15)
N1—P1—N3	116.51 (8)	N2—P2—N6	111.95 (8)
N1—P1—N5	109.50 (8)	N1—P2—N7	115.61 (8)
N3—P1—N5	109.05 (8)	N2—P2—N7	105.02 (8)
N1—P1—N4	109.49 (8)	N6—P2—N7	103.26 (8)
N3—P1—N4	107.94 (7)	N2—P3—N3	121.89 (8)
N5—P1—N4	103.56 (7)	P1—N1—P2	122.01 (9)
N1—P2—N2	113.99 (8)	P3—N2—P2	120.89 (9)
N1—P2—N6	106.60 (8)	P3—N3—P1	118.86 (9)
N3—P1—N1—P2	27.80 (14)	C14—O2—C15—C20	179.43 (16)
N1—P1—N3—P3	−15.39 (14)	P1—N4—C21—C20	−169.46 (12)
N5—P1—N4—C21	177.97 (11)	P1—N5—C4—C5	−91.54 (17)
N4—P1—N5—C4	−71.99 (13)	C10—C5—C4—N5	124.03 (18)
N2—P2—N1—P1	−27.19 (14)	C4—C5—C10—O1	1.1 (2)
N1—P2—N2—P3	15.20 (14)	O1—C11—C12—C13	59.39 (19)
N3—P3—N2—P2	−4.93 (16)	C14—C13—C12—C11	−169.53 (16)
N2—P3—N3—P1	4.81 (15)	C12—C13—C14—O2	57.7 (2)
C11—O1—C10—C5	−146.35 (16)	C21—C20—C15—O2	−5.6 (2)
C10—O1—C11—C12	143.66 (15)	C15—C20—C21—N4	75.2 (2)
C15—O2—C14—C13	164.11 (16)		

H atoms were located in a difference synthesis and refined isotropically [C—H = 0.93 (2)–1.11 (3) Å and U_{iso}(H) = 0.021 (5)–0.082 (10) Å^2].

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3* for Windows (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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