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trans-2,6-Dichloro-2,4,4,6-tetrakis[methyl(trimethylsilyl)amino]-1,3,5,$2\lambda^5$,$4\lambda^5$,$6\lambda^5$-triazatriphosphorine

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The title tetrasubstituted phosphazene, $C_{16}H_{48}Cl_2N_7P_3Si_4$, is formed by the reaction of $P_3N_3Cl_6$ with heptamethyldisilazane, HpMDSA. The compound is the first *trans* non-geminal tetrasubstituted derivative of this class of compounds to be structurally characterized. The molecule lies on a crystallographic twofold rotation axis.

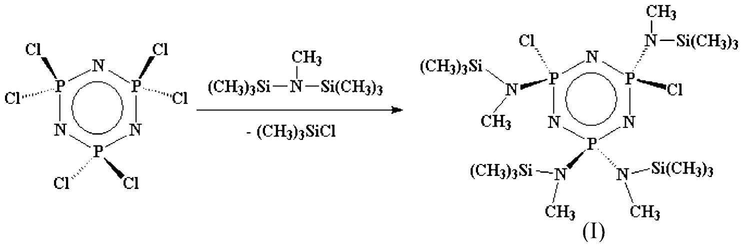
Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(N–C) = 0.003 Å
R factor = 0.038
wR factor = 0.097
Data-to-parameter ratio = 17.2

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

Comment

Phosphazenes date back to the late 20th century (Allcock, 1972; Allen, 1991). Most studies have focused on nucleophilic substitutions of hexahalogeno-*cyclo*-triphosphazene $P_3N_3X_6$ (X = F, Cl, Br) (Allcock, 1987, 1972, 2003; Allen, 1987, 1991; Gleria & De Jaeger, 2002). Little attention has been paid to reactions of cyclic phosphazenes with silylated amines (Mattogno & Tarli, 1964, Mattogno *et al.*, 1965; Fields & Allen, 1974) although Fields & Allen (1974) prepared $P_3N_3Cl_4[NHSi(CH_3)_3]_2$, and its crystal structure was determined by Allen *et al.* (1988).



(I)

Many crystal structures of amido derivatives of chlorophosphazenes have been reported (*e.g.* Polder & Wagner, 1976; Bartlett *et al.*, 2006; Ahmed & Gabe, 1975, Ahmed & Fortier, 1980). Compound (I) is the first *trans* non-geminal tetrasubstituted derivative of this class of compounds to be structurally characterized (Fig. 1). The molecule lies on a crystallographic twofold rotation axis. A comparison of corresponding bond lengths with literature data (Allen *et al.*, 1988; Ahmed & Gabe, 1975, Ahmed & Fortier, 1980) shows that there is no significant difference in the length of either the exocyclic P—Cl bond or the P—N(Me) bond. However, a remarkable deviation was found in the P—N bond distances of the P_3N_3 ring. The P—N lengths in compound (I) are in the range 1.591 (2)–1.6168 (18) Å, compared with literature values of 1.574–1.586 Å (Allen *et al.*, 1988; Ahmed & Gabe, 1975, Ahmed & Fortier, 1980). A significant elongation was also found for N—C bonds [1.484 (3)–1.491 (3) Å in (I) compared to 1.456–1.473 Å in *trans*-$P_3N_3Cl_4[N(CH_3)_2]_2$ (Ahmed & Fortier, 1980)]. The P1—N2—P1^{i} [symmetry code:

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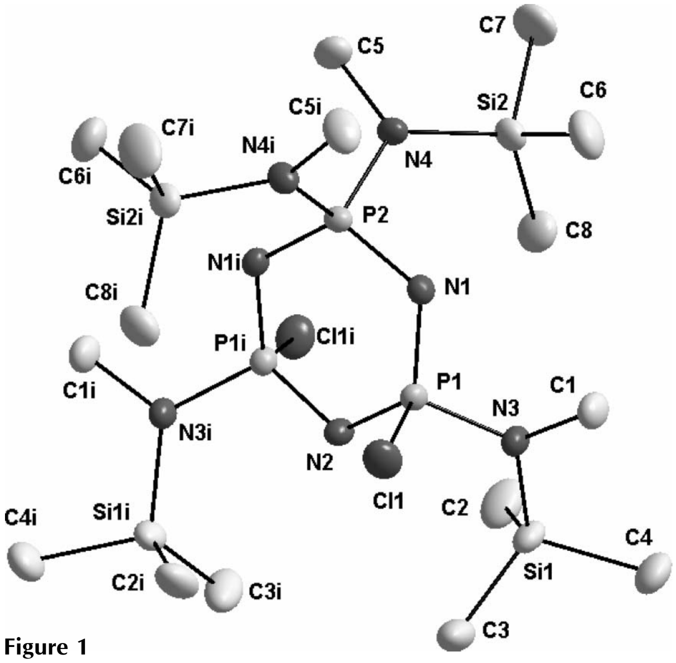

Figure 1
The molecular structure of (I). Displacement ellipsoids represent 50% probability levels. All H atoms have been omitted for clarity. [Symmetry code: (i) $-x, y, -z+\frac{1}{2}$.]

(i) $-x, y, -z+\frac{1}{2}$] and N1—P1—N2 angles of the phosphazene ring are comparable to those of similar phosphazene amidoderivatives (Allen *et al.*, 1988; Ahmed & Gabe, 1975, Ahmed & Fortier, 1980) but there are some differences in the values of N1—P2—N1^i and P1—N1—P2 angles. The former angle increased to 115.28 (14)° (*cf* 111.57°; Allen *et al.*, 1988) while the latter decreased to 121.96 (11)° (124.80°; Allen *et al.*, 1988). The P_3N_3 ring is slightly distorted with atoms N1 and N1^i atoms deviating from the P1,N2,P1^i,P2 plane by 0.2181 (18) Å. The angle between the P1,N2,P1^i,P2 ring and N4,P2,N4^i is 88.12 (4)° (*cf* 87.14°; Allen *et al.*, 1988) while the angle between the ring plane P1,P1^i,P2 and planes formed by atoms Cl1,P1,N3 or Cl1^i,P1^i,N3^i decreased to 81.17 (3)° (85.43–89.60°; Ahmed & Gabe, 1975, Ahmed & Fortier, 1980). This deviation can be attributed to the presence of two bulky $N(CH_3)Si(CH_3)_3$ groups on P2.

No important intermolecular interactions were found in the crystal structure of (I). The molecules of (I) form a system of two coplanar [011] planes. The appropriate description of the structure motif is $[ABAB]_\infty$.

Experimental

Compound (I) was prepared by reaction of $P_3N_3Cl_6$ with heptamethyldisilazane in acetonitrile (see Scheme). $P_3N_3Cl_6$ (0,201 g, 0,6 mmol) dissolved in acetonitrile (5 cm^3) and HpMDSA (0,416 g, 2,4 mmol) were placed into a Schlenk vessel equipped with a screw cap. The reaction mixture was heated on an oil bath at 399–405 K for 48 h. After cooling, the solvent and resulting trimethylchlorosilane were completely evaporated and the remaining solid was again dissolved in acetonitrile. This solution was stored at 248 K for several weeks. Crystals of (I) for suitable X-ray analysis were removed from the solution under a dry nitrogen atmosphere.

Crystal data

$C_{16}H_{48}Cl_2N_7P_3Si_4$
$M_r = 614.78$
Monoclinic, $C2/c$
$a = 17.470$ (3) Å
$b = 11.360$ (2) Å
$c = 17.270$ (3) Å
$\beta = 101.21$ (3)°
$V = 3362.0$ (10) Å^3
$Z = 4$
$D_x = 1.215$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.50$ mm^{-1}
$T = 120$ (2) K
Prism, white
0.25 × 0.20 × 0.20 mm

Data collection

Kuma KM-4 CCD diffractometer
ω scans
Absorption correction: none
13131 measured reflections
2829 independent reflections
2569 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.030$
$\theta_{\rm max} = 25.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.097$
$S = 1.04$
2620 reflections
154 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.049P)^2 + 7.9146P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.54$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.34$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cl1—P1	2.0730 (9)	N3—C1	1.491 (3)
P1—N1	1.591 (2)	P2—N1^i	1.6168 (18)
P1—N2	1.6010 (15)	P2—N4	1.6645 (18)
P1—N3	1.6491 (19)	P2—N4^i	1.6645 (18)
N1—P2	1.6168 (18)	N4—C5	1.484 (3)
N2—P1^i	1.6010 (15)		
N1—P1—N2	118.79 (11)	P1—N2—P1^i	119.36 (17)
N3—P1—Cl1	103.57 (8)	N1—P2—N1^i	115.28 (14)
P1—N1—P2	121.96 (11)	N4—P2—N4^i	107.19 (14)

Symmetry code: (i) $-x, y, -z+\frac{1}{2}$.

H atoms were positioned geometrically (C—H = 0.98Å) and refined as riding with $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm C})$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *KM-4 Software* (Kuma Diffraction, 2006); data reduction: *KM-4 Software*; program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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