Instrumental Achievements

Crystal Structure of 2,4,4,6,6-Pentachloro-2-(2,4,6-trimethylphenoxy)cyclo-2λ^5,4λ^5,6λ^5-triphosphazatriene

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The phenoxy derivatives of 2,2,4,4,6,6-hexachlorocyclo-2λ^5,4λ^5,6λ^5-triphosphazatriene, $N_3P_3Cl_6$, have potential use in the preparation of new small organocyclophosphazenes and high polymeric phosphazene derivatives with inorganic backbones and aryloxy side groups.[1] The structures of the organic, inorganic or organometallic side groups are highly effective in determining the specific physical and chemical properties of phosphazene polymers.

The title compound was prepared from a mixture of 2,4,6-trimethylphenol (5.37 g, 0.012 mol), Na (0.500 g, 0.022 mol) and $N_3P_3Cl_6$ (4.18 g, 0.012 mol) in THF (100 mL) according to the literature.[2] The residue was dissolved in hexane and set aside for crystallization. The results of an X-ray structure determination are given in Tables 1 – 3.

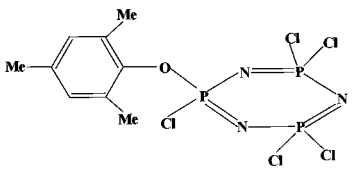

Fig. 1 Chemical structure.

The title molecule (Fig. 2) contains a non-polar cyclic trimeric phosphazene ring with a 2,4,6-trimethylphenoxy group attached to the P2 atom. The three N atoms are displaced on opposite sides (+ and –) with respect to the plane through the P atoms, as follows: N1 –0.193(6), N3 –0.008(5), N5 +0.253(7)Å.

The ranges of the P–N–P and N–P–N bond angles are 120.1(5) – 122.5(5)° and 116.0(4) – 117.8(4)°, respectively. In tetrameric phosphazenes, the P–N–P bond angles range between 133.6(2) and 139.3(2)° as found in 2-(2,6-di-*t*-butyl-4-methylphenoxy)-2,4,4,6,6,8,8-heptachlorocyclo-2λ^5,4λ^5,6λ^5,8λ^5-tetraphosphazatetraene.[3] The interatomic distance, O1···H71= 2.382(7)Å, indicates a possible hydrogen bond.

The P–N bond distances vary between 1.539(8) and 1.602(9)Å. In related compounds,[4-6] the corresponding bond lengths are 1.57(1) – 1.60(1)Å. In trimeric phosphazenes, the P-N bond lengths may be correlated with the orbital

Table 1 Crystal and experimental data

Formula:	$C_9H_{11}N_3OP_3Cl_5$
Formula weight =	447.39
Crystal system:	monoclinic
Space group:	C2/c Z = 8
a =	11.237(1)Å
b =	11.785(2)Å
c =	27.371(1)Å
β =	101.06(1)
V =	3557.4(7)Å
D_x =	1.671 g/cm^3
R = 0.075	wR = 0.071
$(\Delta/\sigma)_{max}$ =	0.01
$(\Delta\rho)_{max}$ =	0.45 eÅ^{-3}
$(\Delta\rho)_{min}$ =	–0.34 eÅ^{-3}
Radiation:	Cu K_α
No. of reflections used =	1402
Measurements:	Enraf-Nonius CAD-4 diffractometer
Program system:	CAD-4-EXPRESS Software
Structure determination:	SHELXS86
Treatment of hydrogen atoms:	geometric calculation
Refinement:	full-matrix least-squares

Table 2 Final atomic coordinates and equivalent isotropic thermal parameters

Atom	x	y	z	B_{eq}/Å
Cl1	0.2907(3)	0.8101(3)	0.2545(1)	6.29(9)
Cl2	0.1437(2)	0.6008(3)	0.2112(1)	5.52(8)
Cl3	0.5899(2)	0.6297(3)	0.3551(1)	5.85(8)
Cl4	0.5196(2)	0.3872(2)	0.3189(1)	4.81(8)
Cl5	0.1165(3)	0.4514(3)	0.3638(1)	5.82(9)
P2	0.2373(2)	0.5758(2)	0.3646(1)	3.41(7)
P4	0.4442(2)	0.5347(2)	0.3279(1)	3.32(7)
P6	0.2580(2)	0.6515(2)	0.2714(1)	3.48(7)
O1	0.2216(5)	0.6416(6)	0.4132(2)	3.91(9)
N1	0.1936(7)	0.6513(7)	0.3188(3)	4.07(9)
N3	0.3685(7)	0.5237(7)	0.3714(3)	3.68(8)
N5	0.3754(7)	0.5802(7)	0.2763(3)	4.09(7)
C1	0.3186(9)	0.6748(9)	0.4505(4)	3.79(7)
C2	0.3745(9)	0.7792(9)	0.4468(4)	3.89(7)
C3	0.4643(10)	0.8108(9)	0.4858(4)	4.47(8)
C4	0.4988(10)	0.7454(10)	0.5279(4)	4.66(8)
C5	0.4418(10)	0.6415(9)	0.5298(4)	4.28(9)
C6	0.3520(9)	0.6043(9)	0.4920(4)	3.81(8)
C7	0.2908(9)	0.4938(9)	0.4953(4)	4.71(7)
C8	0.3361(10)	0.8543(10)	0.4029(5)	5.73(9)
C9	0.6012(12)	0.7847(11)	0.5708(5)	6.25(9)

$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* (\boldsymbol{a}_i \cdot \boldsymbol{a}_j)$.

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Table 3 Bond distances (Å) and angles (°)

Cl1-P6	1.977(4)	P6-N5	1.548(8)
Cl2- P6	1.977(3)	O1-C1	1.399(7)
Cl3- P4	2.005(3)	C1-C2	1.394(7)
Cl4-P4	1.970(3)	C1-C6	1.400(8)
Cl5-P2	1.995(4)	C2-C3	1.372(7)
P2-O1	1.579(7)	C2-C8	1.488(9)
P2-N1	1.539(8)	C3-C4	1.379(8)
P2-N3	1.575(8)	C4-C5	1.387(8)
P4-N3	1.596(9)	C4-C9	1.549(7)
P4-N5	1.569(8)	C5-C6	1.371(8)
P6-N1	1.602(9)	C6-C7	1.483(9)
Cl5-P2-O1	100.6(3)	P2-O1-C1	123.7(6)
Cl5-P2-N3	109.5(3)	P6-N1-P2	122.5(5)
Cl5-P2-N1	107.8(3)	P4-N3-P2	120.1(5)
O1-P2-N3	110.2(4)	P4-N5-P6	121.9(5)
O1-P2-N1	109.4(4)	O1-C1-C6	118.5(9)
N3-P2-N1	117.8(4)	O1-C1-C2	119.5(9)
Cl4-P4-Cl3	101.5(2)	C6-C1-C2	121.9(9)
Cl4-P4-N3	109.0(3)	C1-C2-C3	117.2(8)
Cl4-P4-N5	109.8(3)	C1-C2-C8	121.2(7)
Cl3-P4-N3	106.4(3)	C8-C2-C3	121.5(8)
Cl3-P4-N5	111.7(3)	C4-C3-C2	123.1(8)
N3-P4-N5	117.3(4)	C5-C4-C9	121.1(9)
Cl1-P6-N5	109.9(3)	C5-C4-C3	117.8(9)
Cl1-P6-N1	108.9(3)	C9-C4-C3	121.0(8)
Cl2-P6-N1	110.6(3)	C4-C5-C6	122.1(7)
Cl2-P6-Cl1	102.2(2)	C5-C6-C7	121.1(7)
Cl2-P6-N5	108.3(3)	C1-C6-C5	117.8(9)
N5-P6-N1	116.0(4)	C1-C6-C7	121.0(9)

electronegativities of groups of atoms, as in the tetrameric phosphazenes. The short bonds in the ring have an appreciable double-bond character. The phenoxy group is very effective in determining the shape of the molecule.

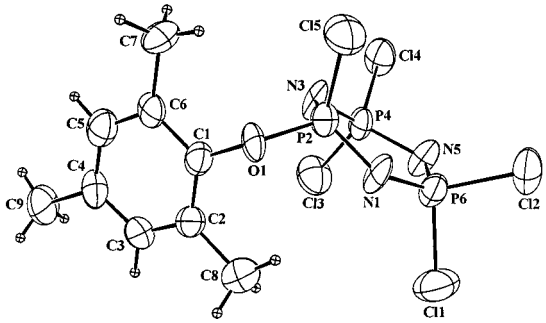

Fig. 2 Molecular structure of the title compound with atom-numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

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