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2,4,4,6,6-Pentachloro-2-(2,6-di-*tert*-butyl-4-methylphenoxy)cyclo-2λ^5,4λ^5,6λ^5-triphosphazatriene

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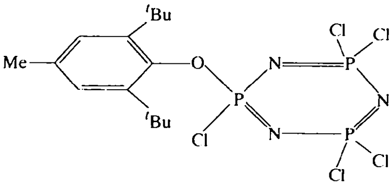
Abstract

The title compound, $C_{15}H_{23}Cl_5N_3OP_3$, consists of a non-planar trimeric phosphazene ring and a bulky 2,6-di-*tert*-butyl-4-methylphenoxy side group in which the phenyl ring shows a small but significant distortion from planarity. The bulky group predominantly determines the molecular shape. The endocyclic angle about the P atom bonded to the substituent is decreased, while the exocyclic angle is increased. The situation is not similar to that of tetrameric phosphazene derivatives.

Comment

Over the last two decades, there have been a number of studies of the bulky phenoxy derivatives of hexachlorocyclo-2λ^5,4λ^5,6λ^5-triphosphazatriene ($N_3P_3Cl_6$) and octachlorocyclo-2λ^5,4λ^5,6λ^5,8λ^5-tetraphosphazatetraene ($N_4P_4Cl_8$). These phosphazene derivatives have potential use in the preparation of new small-molecule organocyclophosphazenes (Allcock, Dembek *et al.*, 1992; Allen, 1994), and high polymeric phosphazene derivatives with inorganic backbones and aryloxy side groups. These classes of polymers 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), biomedical materials (Cohen *et al.*, 1990) and small-molecule models for the corresponding linear phosphazene macromolecules. The structures of the organic, inorganic or organometallic side groups are highly effective in determining the specific physical or chemical properties of phosphazene polymers (Allcock *et al.*, 1996; Allcock, 1985).

$N_3P_3Cl_6$ is a standard compound for trimeric phosphazene derivatives. The crystal structures of $N_3P_3Cl_6$ (Bullen, 1971) and only a few of its derivatives with bulky phenoxy groups, such as $[Cl_5N_3P_3\text{–}P_3N_3Cl_4(OC_6H_3\text{-}2,6\text{-}{}^t\mathrm{Bu}_2)]$ (Hökelek *et al.*, 1994), $[N_3P_3Cl_5(OC_6H_3Cl_2\text{-}o)]$, $[N_3P_3Cl_4(OC_6H_3Cl_2\text{-}o)_2]$ and $[N_3P_3Cl_4(OC_6H_3Me_2\text{-}o)_2]$ (Allcock, Ngo *et al.*, 1992), and $[N_3P_3(OC_6H_4OCH_2Ph\text{-}4)_6]$ (Allcock *et al.*, 1996), have been reported. The study of the title structure, (I), was undertaken in order to understand the influence of the highly hindered side group on the structure of the cyclic trimeric phosphazene ring and is part of a study of the effects of the steric and electronic factors on the nucleophilic substitution patterns found for cyclic trimeric phosphazenes.



(I)

The title molecule is shown in Fig. 1. The structure consists of a non-planar cyclic trimeric phosphazene ring with one 2,6-di-*tert*-butyl-4-methylphenoxy group attached to the P2 atom; the phenyl ring is not strictly planar, the largest displacements from its least-squares plane being *ca* 0.06 Å for C1, C4 and C6. The total puckering amplitude of the phosphazene ring is 0.166 (2) Å (Cremer & Pople, 1975). The three N atoms are displaced on opposite sides (+ and −) with respect to the plane through the P atoms as follows: N1 +0.203 (3), N3 +0.084 (3) and N5 −0.075 (3) Å.

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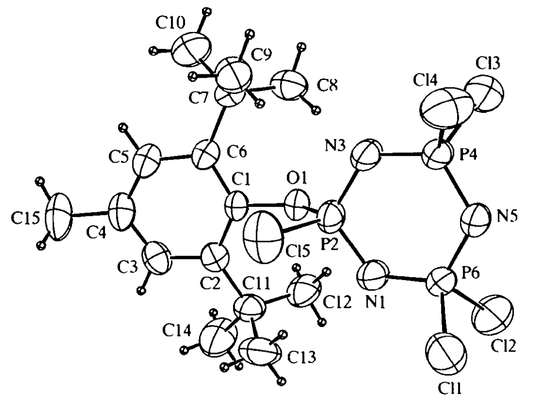

Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of a molecule of (I) with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

The P—N—P bond angles range from 119.9 (2) to 122.5 (2)°. In addition, the variation in the N—P—N bond angles, ranging from 115.1 (1) to 118.9 (2)°, is large. In tetrameric phosphazenes, the P—N—P bond angles range from 133.6 (2) to 139.3 (2)°, as found in 2-(2,6-di-*tert*-butyl-4-methylphenoxy)-2,4,4,6,6,8,8-heptachlorocyclo-$2\lambda^5,4\lambda^5,6\lambda^5,8\lambda^5$-tetraphosphazatetraene (Hökelek *et al.*, 1996). It has been reported that such large angles appear to be characteristic of tetrameric phosphazene derivatives containing chlorine or fluorine (George *et al.*, 1972).

The endocyclic N1—P2—N3 angle is decreased [115.1 (1)°], while the exocyclic O1—P2—Cl5 angle [104.79 (9)°] is increased with the increase in the electron supply and the repulsion of substituents with respect to the values [118.3 (2) and 101.2 (1)°, respectively] in the standard $N_3P_3Cl_6$ compound (Bullen, 1971). Hence, the endocyclic P2—N3—P4 angle [122.5 (2)°] also shows the maximum increase among the P—N—P angles in the phosphazene ring. Similar behaviour of the endocyclic (N—P—N) and exocyclic (ArO—P—Cl) angles is observed in other trimeric phosphazene derivatives containing a bulky side group (Fincham *et al.*, 1986; Hökelek *et al.*, 1994; Kılıç *et al.*, 1996).

In the title compound, the N1—P2—N3 angle is larger and the O1—P2—Cl5 angle is smaller than the corresponding angles in $N_3P_3Cl_5(NPPh_3)$ [114.4 (1) and 107.2 (1)°; Fincham *et al.*, 1986], $N_3P_3Cl_4(NPPh_3)_2$ [109.2 (4) and 110.9 (4)°; Fincham *et al.*, 1986] and $N_3P_3Cl_4Ph(PPh_2)$ [114.5 (2) and 106.7 (1)°; Allcock *et al.*, 1990], which implies less electron donation to the N_3P_3 ring. The exocyclic Cl5—P2—O1 angle [104.79 (9)°] is larger than that of the exocyclic Cl3—P4—Cl4 and Cl1—P6—Cl2 angles [100.81 (6) and 101.61 (6)°, respectively] due to replacement of the bulky tri-*tert*-butylphenoxy group by chlorine, which may be expressed as the steric or the bulky group effect.

The P4—N5—P6, P2—N1—P6 and P2—N3—P4 angles [119.9 (2), 121.9 (2) and 122.5 (2)°, respectively] are seen to change considerably and seem to increase with increasing electron supply to the N_3P_3 ring; they are a little different from the corresponding value [121.4 (3)°] in $N_3P_3Cl_6$ (Bullen, 1971). In the benzene ring, the endocyclic angles are also decreased when the substituents are electron-releasing and increased when the substituents are electron-withdrawing groups (Table 1). As in the benzene ring, the changes in bond angles were more reliable guides to electronic shifts than the changes in bond lengths (Fincham *et al.*, 1986; Contractor *et al.*, 1985).

The interatomic distances O1···H82 = 2.226 (5) Å and O1···H123 = 2.197 (4) Å indicate possible hydrogen bonds. In trimeric phosphazenes, the P—N bond lengths may be correlated with the orbital electronegativities of groups of atoms, as in the tetrameric phosphazenes (Bullen & Tucker, 1972). In such structures, the lengths of the P—N bonds depend on the electronegativities of the substituents. In the present structure, the Cl atom seems to be electron withdrawing and the bulky group attached to P2 slightly electron donating. Thus, P2—Cl5 [1.998 (1) Å] is the longest of the P—Cl bonds. In a given $N_3P_3R_6$ structure, the lengths of the P—N bonds are generally equal, provided all the substituents (R) are the same. If R is a difunctional bulky substituent (Kubono *et al.*, 1994) or contains different substituents, the P—N bonds may show significant variations in lengths (Fincham *et al.*, 1986; Contractor *et al.*, 1985). When electron-donating groups are present, different P—N distances in the cyclotri(phosphazene) ring could be expected, but there is no clear difference in the present structure between the electronegativities of the atoms attached to the P atoms; the P—N bond distances vary from 1.563 (3) to 1.581 (3) Å. In related compounds, the corresponding mean bond lengths are: 1.57 (1)–1.60 (1) Å in $N_3P_3Cl_5(OAr)$ (Kılıç *et al.*, 1996), 1.554 (3)–1.590 (4) Å in $N_3P_3Cl_5Ph$ (Allcock *et al.*, 1990) and 1.581 (3) Å in $N_3P_3Cl_6$ (Bullen, 1971). These values for P—N bonds are considerably smaller than the P—N single-bond length of 1.78 (6) Å [*cf.* Table 4.1.4 in *International Tables for X-ray Crystallography* (1968, Vol. III)]. The short bonds in the ring have appreciable double-bond character; this is generally observed for phosphazene derivatives (Wagner & Vos, 1968). The phenoxy group is very effective in determining the shape of the molecule.

Experimental

2,6-Di-*tert*-butyl-4-methylphenol (2.68 g, 0.012 mol) in THF (20 ml) was added slowly over a period of 30 min to small pieces of Na (0.500 g, 0.022 mol) in THF (10 ml) with stirring at 298 K, with argon being passed over the reaction mixture. Excess Na was removed by filtration and the solution obtained was cooled. To this mixture, $N_3P_3Cl_6$ (4.235 g, 0.012 mol) in THF (40 ml) was added slowly and the resulting solution allowed to equilibrate to ambient temperature with constant stirring. After the mixture had been vigorously stirred for 72 h at room temperature, the precipitated salt (NaCl) was filtered off and the solvent removed *in vacuo*. The residue was dissolved in *n*-hexane and set aside to crystallize (m.p. 398 K).

Crystal data

$C_{15}H_{23}Cl_5N_3OP_3$
$M_r = 531.56$
Monoclinic
$P2_1/n$
$a = 10.386\,(1)$ Å
$b = 22.501\,(1)$ Å
$c = 11.114\,(1)$ Å
$\beta = 110.08\,(3)^\circ$
$V = 2439.4\,(3)$ Å^3
$Z = 4$
$D_x = 1.447$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10$–18°
$\mu = 0.8$ mm^{-1}
$T = 298$ K
Block
0.28 × 0.25 × 0.22 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (*MolEN*; Fair, 1990)
$T_{\min} = 0.799$, $T_{\max} = 0.839$
5369 measured reflections
4938 independent reflections

3076 reflections with $F > 3\sigma(F)$
$R_{\rm int} = 0.017$
$\theta_{\max} = 26.3^\circ$
$h = -12 \rightarrow 0$
$k = -28 \rightarrow 0$
$l = -13 \rightarrow 13$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F
$R = 0.038$
$wR = 0.050$
$S = 1.60$
3076 reflections
244 parameters
H-atom parameters constrained

$w = 1/[\sigma(F)^2]$
$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 0.28$ e Å^{-3}
$\Delta\rho_{\min} = -0.13$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

Cl1—P6	1.987 (1)	P4—N5	1.581 (3)
Cl2—P6	1.978 (1)	P4—N3	1.563 (3)
Cl3—P4	1.992 (2)	P2—O1	1.554 (2)
Cl4—P4	1.985 (1)	P2—N3	1.581 (3)
Cl5—P2	1.998 (1)	P2—N1	1.581 (3)
P6—N5	1.569 (3)	O1—C1	1.435 (3)
P6—N1	1.565 (3)		
Cl1—P6—Cl2	101.61 (6)	Cl5—P2—O1	104.79 (9)
Cl1—P6—N5	108.4 (1)	Cl5—P2—N3	108.5 (1)
Cl1—P6—N1	109.4 (1)	Cl5—P2—N1	109.2 (1)
Cl2—P6—N5	108.4 (1)	O1—P2—N3	109.2 (1)
Cl2—P6—N1	108.79 (9)	O1—P2—N1	109.5 (1)
N5—P6—N1	118.9 (1)	N3—P2—N1	115.1 (1)
Cl3—P4—Cl4	100.81 (6)	P2—O1—C1	130.4 (2)
Cl3—P4—N5	109.2 (1)	P6—N5—P4	119.9 (2)
Cl3—P4—N3	108.3 (1)	P4—N3—P2	122.5 (2)
Cl4—P4—N5	108.6 (1)	P6—N1—P2	121.9 (2)
Cl4—P4—N3	109.5 (1)	O1—C1—C2	117.3 (2)
N5—P4—N3	118.9 (2)	O1—C1—C6	118.4 (3)

The title compound was solved by direct methods. The H-atom positions were calculated geometrically and a riding model was used during the refinement process.

Data collection: *MolEN* (Fair, 1990). Cell refinement: *MolEN*. Data reduction: *MolEN*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1395). Services for accessing these data are described at the back of the journal.

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