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2-(2,6-Di-*tert*-butyl-4-methylphenoxy)-2,4,4,6,6,8,8-heptachlorocyclo-2λ^5,4λ^5,6λ^5,8λ^5-tetraphosphazatetraene

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Abstract

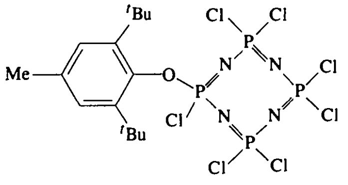
The title compound, $C_{15}H_{23}Cl_7N_4OP_4$, consists of a saddle-shaped cyclic tetrameric phosphazene ring and a bulky 2,6-di-*tert*-butyl-4-methylphenoxy side group. The bulky group substituent is instrumental in determining the molecular shape. The exo- and endocyclic angles about the P atoms both decrease on substitution whereas the P—N—P angles increase.

Comment

In recent years, there have been many studies of the bulky phenoxy derivatives of hexachlorocyclo-2λ^5,4λ^5,6λ^5-triphosphazene, $N_3P_3Cl_6$, and octachlorocyclo-2λ^5,4λ^5,6λ^5,8λ^5-tetraphosphazene, $N_4P_4Cl_8$, for a number of reasons. Firstly, they have potential use in the synthesis of new small molecule organocyclophosphazenes (Allcock, Dembek *et al.*, 1992) and high polymeric phosphazenes with inorganic backbones and aryloxy side groups which may be useful as high refractive index glasses (Olshavsky & Allcock, 1995), ferroelectric and non-linear optical polymers (Allcock *et al.*, 1991), liquid-crystalline materials (Allcock & *Kim*, 1991) and biomedical materials (Cohen *et al.*, 1990). Secondly, these compounds are also small-molecule models for the corresponding linear phosphazene macromolecules. The specific physical or chemical properties of phosphazene polymers are imposed by the structure of the organic, inorganic or organometallic side groups (Allcock, 1985).

$N_4P_4Cl_8$ is a standard compound for tetrameric phosphazenes. Two crystal modifications of this compound, generally called the *K* and *T* forms, are known (Hazekamp, Migchelsen & Vos, 1962; Wagner & Vos, 1968). The crystal structures of some $N_4P_4Cl_8$ derivatives such as *cis*-$N_4P_4Cl_4Ph_4$ (Bullen & Tucker, 1972*a*), β-*trans*-$N_4P_4Cl_4(NMe_2)_4$ (Bullen & Tucker, 1972*b*), β-*trans*-$N_4P_4(NHMe)_4Ph_4$ (Bullen & Mallinson, 1972), $N_4P_4Cl_4(NEt_2)_4$ (Hökelek & Kılıç, 1990) and $N_4P_4Cl_7(NPPh_3)$ (Babu & Manohar, 1979) have been examined. Only a few derivatives of $N_3P_3Cl_6$ and $N_4P_4Cl_8$ with bulky phenoxy groups have been reported (Allcock, Ngo, Parvez & Visscher, 1992; Allcock, Dembek *et al.*, 1992; Allcock, Al-Shali, Ngo, Visscher & Parvez, 1995; Allcock, Fuller & Matsumara, 1981). In an earlier paper (Hökelek, Kılıç & Kılıç, 1994), we reported the structure of 2-(2,6-di-*tert*-butylphenoxy)-2′,4,4,4′,4′,6,6,6′,6′-nonachloro-2,2′-bi(*cyclo*-λ^5-phosphazene) $[Cl_5N_3P_3\text{-}P_3N_3Cl_4(OC_6H_3\text{-}2,6\text{-}{}^tBu_2)]$ which has a 2,6-di-*tert*-butylphenoxy side group.

The main objective of this study was to determine the influence of the highly hindered side group on the structure of the cyclic tetraphosphazene ring as part of a study of the effects of the steric and electronic factors on the nucleophilic substitution patterns found for cyclic tetrameric phosphazenes.



(I)

The title molecule, (I), is shown in Fig. 1. Its structure consists of a cyclic tetrameric phosphazene ring in a saddle conformation with one 2,6-di-*tert*-butyl-4-methylphenoxy group attached to the P1 atom. The four P atoms are coplanar and the four N atoms are displaced above (+) and below (−) their plane by approximately equal amounts [N1 +0.498 (3), N2 −0.484 (3), N3 +0.517 (3) and N4 −0.316 (3) Å]. The bulky group is not in a pseudo-equatorial position since the dihedral angles between the least-squares plane through the P atoms and those through atoms P1, O1, C1 and the benzene ring are 39.8 (2) and 65.8 (1)°, respectively. The phosphazene ring has approximate mirror symmetry with the mirror plane through N2···N4, as indicated by the torsion angles of the ring bonds in which a mirror operation reverses the sign of a torsion angle (shown in Fig. 2).

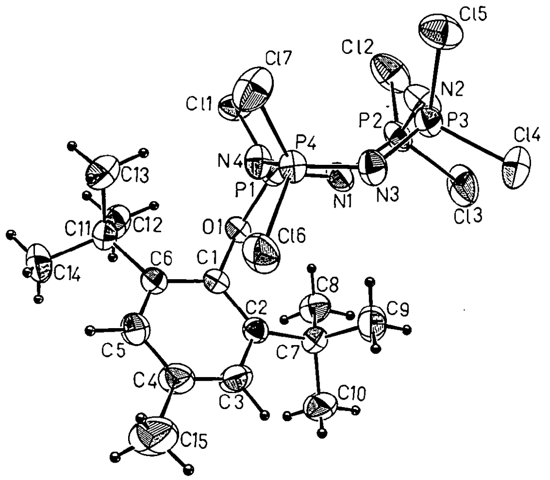


Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of the title molecule with the atomic numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

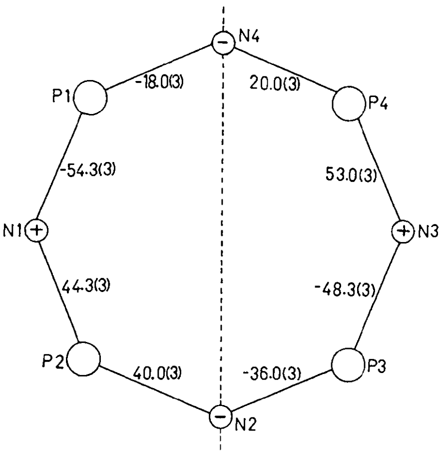


Fig. 2. Shape of the phosphazene ring with torsion angles (°).

The P—N—P bond angles range from 133.6 (2) to 139.3 (2)° [average 135.8 (2)°]. Similar spreads of P—N—P angles were found in *cis*-$N_4P_4Cl_4Ph_4$ (Bullen & Tucker, 1972*a*), *β-trans*-$N_4P_4Cl_4(NMe_2)_4$ (Bullen & Tucker, 1972*b*) and $N_4P_4Cl_4(NEt_2)_4$ (Hökelek & Kılıç, 1990) and it was reported that such large angles appear to be characteristic of molecules containing chlorine or fluorine (George, Mackay & Stobart, 1972). In addition, the variation in the N—P—N bond angles is small, ranging from 119.3 (1) to 121.4 (1)° with an average of 120.7 (1)°. In trimeric phosphazenes, it has been observed that endocyclic (N—P—N) angles about P decrease while exocyclic (*R*—P—Cl) angles increase (Contractor, Hursthouse, Shaw, Shaw & Yılmaz, 1985; Fincham, Hursthouse, Parkes, Shaw & Shaw, 1986; Hökelek, Kılıç & Kılıç, 1994; Kılıç *et al.* 1996). The title compound and other tetrameric phosphazenes containing bulky phenoxy groups (Allcock, Al-Shali, Ngo, Visscher & Parvez, 1995; Allcock, Ngo, Parvez & Visscher, 1992; Allcock, Dembek *et al.*, 1992) are different. The exocyclic Cl—P—O [101.0 (1)°] and endocyclic N1—P1—N4 [119.3 (1)°] angles are less affected by the phenoxy group bonded to P1 atom, while the P1—N4—P4 [139.3 (2)°] and P1—N1—P2 [136.0 (1)°] angles are expanded compared to the corresponding angle in $N_4P_4Cl_8$ [131.3 (6)°; Hazekamp, Migchelsen & Vos, 1962].

The interatomic distances C8···O1 [2.833 (4) Å], H83···O1 [2.231 (2) Å], C12···O1 [2.897 (5) Å] and H122···O1 [2.242 (2) Å] may indicate possible hydrogen bonds, causing a decrease in the exocyclic O1—P1—Cl1 [101.0 (1)°] angle compared to the corresponding value in $N_4P_4Cl_8$ [102.8 (2)°; Hazekamp, Migchelsen & Vos, 1962]. In tetrameric phosphazenes, the P—N bond lengths have been correlated with the orbital electronegativities of groups of atoms (Bullen & Tucker, 1972*a*). In such structures, the lengths of the P—N bonds depend on the electronegativities of the substituents. In the present structure, the Cl atom and the bulky group attached to the P1 atom seem to be electron withdrawing and a slightly electron-donating group, respectively. Thus, P1—Cl1 [2.005 (1) Å] is the longest of the P—Cl bonds; the average length of the remaining P—Cl bonds is 1.987 (1) Å.

When electron-donating groups are present, different P—N distances in the cyclotetra(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 1.549 (2) to 1.563 (3) Å [average 1.558 (3) Å]. In related compounds, the corresponding mean bond lengths are 1.58 Å [$N_4P_4(NMe_2)_8$; Bullen, 1962], 1.561 (6) Å [$N_4P_4Cl_4(NEt_2)_4$; Hökelek & Kılıç, 1990] and 1.56–1.57 Å ($N_4P_4Cl_8$; Hazekamp, Migchelsen & Vos, 1962; Wagner & Vos, 1968). These values for P—N bonds are considerably smaller than the single P—N bond length of 1.77 Å (Cruickshank, 1964; Hobbs, Corbridge & Raistrick, 1953) and 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 an appreciable double-bond character; this is generally observed for phosphanitrilic molecules (Wagner & Vos, 1968). The average P—N and the P1—O1 and C1—O1 bond lengths are comparable with reported values [P—

N 1.560 (2), P—O 1.582 (1) and C—O 1.399 (2) Å in $N_4P_4(OC_6H_5)_8$ (Allcock *et al.*, 1992)].

The benzene ring is non-planar with a maximum deviation from the least-squares plane of −0.083 (3) Å for C1. In the crystal packing, the 2,6-di-*tert*-butyl-4-methylphenoxy groups are close to each other owing to van der Waals interactions and they are packed parallel to *c* axis of the unit cell. The phenoxy group is very effective in determining the shape of the molecule.

Experimental

In this study, 2,6-di-*tert*-butyl-4-methylphenoxide was prepared from the reaction of 2,6-di-*tert*-butyl-4-methylphenol (1.90 g, 8.63 mmol) with metallic sodium (0.50 g, 21.73 mmol) (Çetinkaya, Gümrükçü & Lappert, 1980). The title compound was then synthesized by the reaction of $N_4P_4Cl_8$ (4.00 g, 8.63 mmol) with the prepared sodium 2,6-di-*tert*-butyl-4-methylphenoxide in 120 cm^3 THF and separated from the reaction mixture by column chromatography. The compound crystallized from a chloroform–heptane mixture (1:2), m.p. 399 K, 2.18 g (39%) yield.

Crystal data

$C_{15}H_{23}Cl_7N_4OP_4$
$M_r = 647.44$
Triclinic
$P\bar{1}$
$a = 10.029 (1)$ Å
$b = 11.051 (1)$ Å
$c = 13.794 (1)$ Å
$\alpha = 71.81 (1)^\circ$
$\beta = 73.87 (1)^\circ$
$\gamma = 73.61 (1)^\circ$
$V = 1362.9 (2)$ Å^3
$Z = 2$
$D_x = 1.58$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10$–18°
$\mu = 0.98$ mm^{-1}
$T = 298$ K
Block-like
0.64 × 0.40 × 0.40 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
5665 measured reflections
5428 independent reflections
3898 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int} = 0.014$

$\theta_{\rm max} = 26.3^\circ$
$h = 0 \rightarrow 12$
$k = -12 \rightarrow 13$
$l = -16 \rightarrow 17$
3 standard reflections monitored every 250 reflections frequency: 120 min intensity decay: 1%

Refinement

Refinement on F
$R = 0.033$
$wR = 0.043$
$S = 1.45$
3898 reflections
303 parameters
$w = 1/[\sigma(I)^2 + (0.04F^2)^2]^{1/2}$
$(\Delta/\sigma)_{\rm max} = 0.01$

$\Delta\rho_{\rm max} = 0.41$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.08$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Cl1	0.58375 (8)	0.14609 (7)	0.46530 (5)	3.78 (2)
Cl2	0.6461 (1)	0.3756 (1)	0.58563 (6)	5.77 (2)
Cl3	0.7487 (1)	0.59697 (7)	0.40062 (7)	6.24 (2)
Cl4	1.1682 (1)	0.44481 (8)	0.33030 (7)	6.45 (2)
Cl5	1.18970 (8)	0.17085 (8)	0.48399 (6)	4.62 (2)
Cl6	1.07089 (9)	0.15088 (8)	0.12765 (6)	4.79 (2)
Cl7	1.10915 (8)	−0.03670 (7)	0.34389 (7)	4.69 (2)
P1	0.70661 (6)	0.24300 (6)	0.34131 (5)	2.31 (1)
P2	0.77059 (8)	0.40480 (7)	0.44408 (5)	3.16 (2)
P3	1.06830 (7)	0.29832 (7)	0.38954 (5)	2.97 (1)
P4	1.01065 (7)	0.14277 (6)	0.27937 (5)	2.60 (1)
O1	0.6152 (2)	0.2798 (2)	0.2560 (1)	2.43 (4)
N1	0.7092 (2)	0.3706 (2)	0.3664 (2)	3.20 (5)
N2	0.9234 (3)	0.3380 (2)	0.4627 (2)	4.15 (6)
N3	1.0752 (2)	0.2472 (2)	0.2945 (2)	3.17 (5)
N4	0.8494 (2)	0.1455 (2)	0.3146 (2)	3.02 (5)
C1	0.6736 (2)	0.2731 (2)	0.1500 (2)	2.35 (5)
C2	0.7160 (3)	0.3832 (2)	0.0769 (2)	2.56 (5)
C3	0.7944 (3)	0.3630 (3)	−0.0195 (2)	3.55 (7)
C4	0.8207 (3)	0.2467 (3)	−0.0447 (2)	4.00 (8)
C5	0.7576 (3)	0.1485 (3)	0.0256 (2)	3.67 (7)
C6	0.6786 (3)	0.1579 (2)	0.1245 (2)	2.72 (6)
C7	0.6819 (3)	0.5227 (2)	0.0913 (2)	3.07 (6)
C8	0.5457 (3)	0.5530 (3)	0.1718 (2)	3.98 (7)
C9	0.8093 (3)	0.5465 (3)	0.1187 (2)	4.53 (8)
C10	0.6568 (4)	0.6221 (3)	−0.0117 (2)	4.91 (9)
C11	0.6001 (3)	0.0492 (2)	0.1932 (2)	3.18 (6)
C12	0.4517 (3)	0.1052 (3)	0.2496 (3)	4.20 (8)
C13	0.6835 (3)	−0.0500 (3)	0.2723 (2)	4.12 (8)
C14	0.5754 (4)	−0.0267 (3)	0.1249 (3)	6.03 (9)
C15	0.9123 (5)	0.2268 (4)	−0.1493 (3)	7.4 (1)

Table 2. *Selected geometric parameters (Å, °)*

Cl1—P1	2.005 (1)	P1—N4	1.559 (2)
Cl2—P2	1.989 (1)	P2—N1	1.556 (3)
Cl3—P2	1.983 (1)	P2—N2	1.556 (3)
Cl4—P3	1.981 (1)	P3—N2	1.558 (2)
Cl5—P3	1.983 (1)	P3—N3	1.559 (3)
Cl6—P4	1.991 (1)	P4—N3	1.563 (3)
Cl7—P4	1.996 (1)	P4—N4	1.549 (2)
P1—O1	1.574 (2)	O1—C1	1.434 (3)
P1—N1	1.562 (3)		
Cl1—P1—O1	101.0 (1)	Cl6—P4—N3	105.3 (1)
Cl1—P1—N1	107.0 (1)	Cl6—P4—N4	109.2 (1)
Cl1—P1—N4	107.6 (1)	Cl7—P4—N3	110.6 (1)
O1—P1—N1	108.7 (1)	Cl7—P4—N4	106.4 (1)
O1—P1—N4	111.5 (1)	N3—P4—N4	121.4 (1)
N1—P1—N4	119.3 (1)	P1—O1—C1	124.0 (1)
Cl2—P2—Cl3	102.7 (1)	P1—N1—P2	136.0 (1)
Cl2—P2—N1	110.8 (1)	P2—N2—P3	133.6 (2)
Cl2—P2—N2	104.7 (1)	P3—N3—P4	134.3 (1)
Cl3—P2—N1	105.8 (1)	P1—N4—P4	139.3 (2)
Cl3—P2—N2	110.0 (1)	O1—C1—C2	118.4 (2)
N1—P2—N2	121.3 (1)	O1—C1—C6	117.7 (2)
Cl4—P3—Cl5	102.7 (1)	C2—C1—C6	123.8 (2)
Cl4—P3—N2	110.9 (1)	C1—C2—C3	115.3 (2)
Cl4—P3—N3	105.0 (1)	C1—C2—C7	127.1 (2)
Cl5—P3—N2	104.9 (1)	C3—C2—C7	117.6 (2)
Cl5—P3—N3	111.2 (1)	C1—C6—C5	114.8 (2)
N2—P3—N3	120.7 (1)	C1—C6—C11	125.8 (2)
Cl6—P4—Cl7	102.5 (1)	C5—C6—C11	119.3 (3)
N4—P1—O1—C1	−24.8 (2)	O1—C1—C6—C11	13.5 (4)
O1—P1—N1—P2	176.3 (2)	N1—P1—O1—C1	108.8 (2)
P1—O1—C1—C6	93.7 (3)	O1—P1—N4—P4	110.1 (2)
O1—C1—C2—C7	−12.7 (4)	P1—O1—C1—C2	−89.3 (3)

The structure was solved by direct methods. H-atom positions were calculated geometrically and a riding model was used in the refinement.

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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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1378). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1,1,3,3-Tetramethylurea

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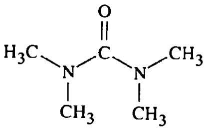
Abstract

Molecules of 1,1,3,3-tetramethylurea, $C_5H_{12}N_2O$, exhibit twofold symmetry and the geometry at the N atom deviates slightly from planarity.

Comment

The structure of 1,1,3,3-tetramethylurea, (I), was determined to investigate the degree of planarity at the N atoms. The molecule lies on a crystallographic twofold axis, as shown in Fig. 1. Bond lengths and angles are generally as expected (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). The N atom, N(1), lies 0.201 (1) Å out of the plane defined by C(1), C(2) and C(3). The geometrical data correspond well with the structure of aqua-dioxo-bis(μ_2-hydrophosphito)uranium bis(1,1,3,3-tetramethylurea) (Mistryukov, Kanishcheva & Mikhailov, 1983) in which the 1,1,3,3-tetramethylurea is present as molecules of solvation. Other related structures are hexakis(1,1,3,3-tetramethylurea) trihydrophosphido-tetracontaoxa-dodeca-molybdenum (Prosser-Mccartha, Kadkhodayan, Williamson, Bouchard & Hill, 1986), triiodo-(1,1,3,3-tetramethylurea-*O*)iron (Pohl, Opitz, Saak & Haase, 1993) and trichloro-(1,1,3,3-tetramethylurea-*O*)aluminium (Bittner, Mannig & Noth, 1986). The first of these contains 1,1,3,3-tetramethylurea bonded through the O atom *via* a bifurcated hydrogen bond, the last two contain 1,1,3,3-tetramethylurea directly bonded to iron and aluminium, respectively, through the O atom. This has the effect of increasing the C—O distance from 1.226 (6) Å as found in the



(I)