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2,4-[2,2′-Methylenebis(4-nitrophenoxy)]-2,4,6,6-tetrachlorocyclo-2λ^5,4λ^5,6λ^5-triphosphazatriene (ansa)

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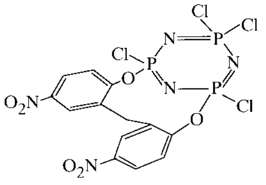
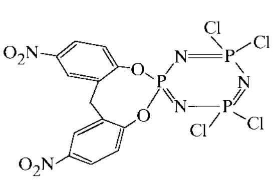
The title compound, $C_{13}H_8Cl_4N_5O_6P_3$, consists of a non-planar trimeric phosphazene ring and a bulky 2,2′-methylenebis(4-nitrophenoxy) side group which predominantly determines the molecular shape. With respect to the corresponding values in the reference compound $N_3P_3Cl_6$, the endocyclic angle around one P atom is the same, but the exocyclic angle is increased, while the endocyclic and exocyclic angles about another P atom are both decreased. This situation is different from that in other reported phosphazene derivatives.

Comment

During the last two decades, 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 ($N_4P_4Cl_8$), have found applications in the synthesis of new, small-molecule organocyclophosphazenes (Allen, 1994) and polymeric phosphazene derivatives 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.*, 1995), liquid crystalline materials (Allcock & Kim, 1991), biomedical materials (Cohen *et al.*, 1990) and small molecule models for the corresponding linear phosphazene macromolecules. 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). $N_3P_3Cl_6$ 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 $[Cl_5N_3P_3(OC_6H_2\text{-}2,6\text{-}{}^t\text{Bu}_2\text{-}4\text{-Me})]$ (Hökelek *et al.*, 1999), $[Cl_5N_3P_3(OC_6H_2\text{-}2,4,6\text{-}{}^t\text{Bu}_3)]$ (Kılıç *et al.*, 1996), $[N_3P_3(OC_6H_4\text{-}4\text{-}OCH_2Ph)_6]$ (Allcock *et al.*, 1996), $[Cl_5N_3P_3\text{–}P_3N_3Cl_4(OC_6H_3\text{-}2,6\text{-}{}^t\text{Bu}_2)]$ (Hökelek *et al.*, 1994), $[N_3P_3Cl_4(OC_6H_3Cl_2\text{-}o)_2]$ and $[N_3P_3Cl_4(OC_6H_3Me_2\text{-}o)_2]$ (Allcock *et al.*, 1992), have been reported. We have investigated the reaction of sodium [2,2′-methylenebis(4-nitrophenoxide)] and hexachlorocyclotriphosphazene, $N_3P_3Cl_6$. The reaction yielded two different products, namely the *cis*-ansa, (I), and spiro, (II), isomers.



(I)



(II)

The title compound, (I), was separated from the reaction mixture by column chromatography. The study of (I) was undertaken in order to understand the influence of the highly hindered 2,2′-methylenebis(4-nitrophenoxy) side group on the structure of the cyclic trimeric phosphazene ring (Fig. 1).

The structure consists of a non-planar cyclic trimeric phosphazene ring with 2,2′-methylenebis(4-nitrophenoxy) group attached to P2 and P3; the phenyl rings are apparently not strictly planar, but the largest displacements from the least-squares planes are only −0.016 (4) Å for C1 and 0.014 (5) Å for C13. The dihedral angle between the phenyl ring planes is 78.5 (1)°. The three N atoms are displaced from the plane through the P atoms as follows: N1 by −0.187 (4), N2 by +0.290 (3) and N3 by −0.088 (3) Å. The P—N—P bond angles range from 119.9 (2) to 120.9 (2)°. In addition, the variation in the N—P—N bond angles, ranging from 117.0 (2) to 118.2 (2)°, is small. The endocyclic N1—P2—N2 angle is the same [118.1 (2)°] and the N2—P3—N3 angle is decreased [117.0 (2)°], while the exocyclic O6—P2—Cl4 angle [103.6 (1)°] is increased and the O1—P3—Cl3 angle [99.4 (1)°] is decreased with the variations in the electron supply and the repulsion of the substituents with respect to the values [118.3 (2) and 101.2 (1)°, respectively] in $N_3P_3Cl_6$ (Bullen, 1971). In (I), the N1—P2—N2 and N2—P3—N3 angles are larger and the O—P—Cl angles are smaller than the corre-

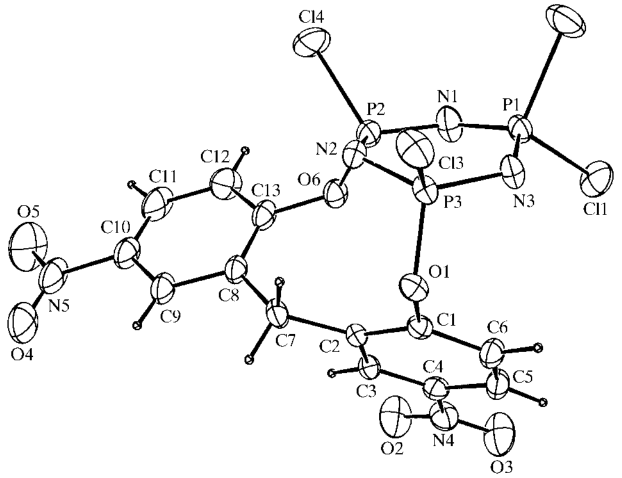


Figure 1
An *ORTEP*II (Johnson, 1976) drawing of the title molecule with the atom-numbering scheme. The displacement ellipsoids are drawn at the 30% probability level.

sponding ones 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), $N_3P_3Cl_4Ph(PPh_2)$ [114.5 (2) and 106.7 (1)°; Allcock *et al.*, 1990], [$Cl_5N_3P_3(OC_6H_2$-2,6-^{t}Bu$_2$-4-Me)] [115.1 (1) and 106.79 (9)°; Hökelek *et al.*, 1999] and [$Cl_5N_3P_3(OC_6H_2$-2,4,6-^{t}Bu$_3$)] [115.8 (1) and 104.5 (6)°; Kılıç *et al.*, 1996], which implies less electron donation to the N_3P_3 ring. The exocyclic O1—P3—Cl3 [99.4 (1)°] angle is smaller, while the O6—P2—Cl4 [103.6 (1)°] angle is larger than the exocyclic Cl1—P1—Cl2 angle [101.86 (7)°] due to the replacement of the bulky 2,2′-methylenebis(4-nitrophenoxy) group by Cl atoms which may be attributed to the steric or the bulky group effect. The P1—N1—P2, P2—N2—P3 and P1—N3—P3 angles [119.9 (2), 120.8 (2) and 120.9 (2)°, respectively] appear to increase slightly with increasing electron supply to the N_3P_3 ring; they are little different from the corresponding value [121.4 (3)°] in $N_3P_3Cl_6$ (Bullen, 1971).

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 atoms and 2,2′-methylenebis(4-nitrophenoxy) group attached to P2 and P3 seem to be slightly electron withdrawing. Thus, the P—Cl and P—O bonds are not seen to change considerably. 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 (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 1.573 (4) to 1.581 (3) Å. In related compounds, the corresponding mean bond lengths are: 1.58 (1) Å in [$Cl_5N_3P_3(OC_6H_2$-2,4,6-^{t}Bu$_3$)] (Kılıç *et al.*, 1996), 1.572 (3) Å in $N_3P_3Cl_4Ph(PPh_2)$ (Allcock *et al.*, 1990), 1.581 (3) Å in $N_3P_3Cl_6$ (Bullen, 1971), 1.573 (3) Å in [$Cl_5N_3P_3(OC_6H_2$-2,6-^{t}Bu$_2$-4-Me)] (Hökelek *et al.*, 1999) and 1.576 (5) Å in [$Cl_5N_3P_3$–$P_3N_3Cl_4(OC_6H_3$-2,6-^{t}Bu$_2$)] (Hökelek *et al.*, 1994). 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 2,2′-methylenebis(4-nitrophenoxy) group is very effective in determining the shape of the molecule.

Experimental

2,2′-Methylenebis(4-nitrophenol) (10.00 g, 3.44 mmol) in tetrahydrofuran (THF) (100 ml) was added slowly over a period of 30 min to NaH (1.65 g, 6.88 mmol) in THF (50 ml) with stirring at 298 K, with argon passed over the reaction mixture. The solvent was removed under reduced pressure and the residue was dried. To this mixture (1.00 g, 2.99 mmol), $N_3P_3Cl_6$ (0.96 g, 2.76 mmol) in CH_3CN (150 ml) was added slowly and the resulting solution allowed to equilibrate to ambient temperature with constant stirring. After the mixture had been vigorously stirred and boiled under reflux for 12 h, the precipitated salt (NaCl) was filtered off and the solvent removed *in vacuo*. The products were separated by *cis*-ansa-(I) and spiro-(II) column chromatography. The title compound (I) was crystallized from chloroform–petroleum ether (3:2) [m.p. 515 K, R_f 0.33, 0.46 g (3%) yield].

Crystal data

$C_{13}H_8Cl_4N_5O_6P_3$
$M_r = 564.97$
Monoclinic, $P2_1/n$
$a = 16.317$ (1) Å
$b = 8.047$ (1) Å
$c = 16.802$ (1) Å
$\beta = 96.97$ (1)°
$V = 2189.8$ (1) Å^3
$Z = 4$
$D_x = 1.71$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 21$–$42°$
$\mu = 7.391$ mm^{-1}
$T = 298$ K
Block, colourless
0.30 × 0.25 × 0.20 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans (*MolEN*; Fair, 1990)
$T_{\min} = 0.156$, $T_{\max} = 0.228$
4457 measured reflections
4457 independent reflections
3072 reflections with $F > 3\sigma(F)$
$\theta_{\max} = 74.3°$
$h = 0 \rightarrow 19$
$k = 0 \rightarrow 9$
$l = -20 \rightarrow 20$
3 standard reflections
frequency: 120 min
intensity variation ±1%

Refinement

Refinement on F
$R = 0.045$
$wR = 0.052$
$S = 0.85$
3072 reflections
280 parameters
H atoms constrained
$w = 1/[\sigma(F)^2 + (0.02F)^2 + 1]$
$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 0.34$ e Å^{-3}
$\Delta\rho_{\min} = -0.54$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cl1—P1	1.971 (2)	P2—O6	1.587 (3)
Cl2—P1	1.987 (2)	P2—N1	1.578 (4)
Cl3—P3	1.976 (1)	P2—N2	1.575 (3)
Cl4—P2	1.988 (2)	P3—O1	1.593 (3)
P1—N1	1.573 (4)	P3—N2	1.574 (3)
P1—N3	1.574 (3)	P3—N3	1.581 (3)
Cl1—P1—N3	109.0 (1)	Cl3—P3—N2	108.9 (1)
Cl2—P1—N1	109.9 (2)	Cl3—P3—N3	109.9 (1)
Cl2—P1—N3	108.7 (1)	O1—P3—N2	110.4 (2)
N1—P1—N3	118.2 (2)	O1—P3—N3	109.9 (2)
Cl4—P2—O6	103.6 (1)	N2—P3—N3	117.0 (2)
Cl4—P2—N1	109.7 (2)	P3—O1—C1	113.9 (2)
Cl4—P2—N2	107.9 (1)	P2—O6—C13	123.8 (2)
O6—P2—N1	105.4 (2)	P1—N1—P2	119.9 (2)
O6—P2—N2	111.3 (2)	P2—N2—P3	120.8 (2)
N1—P2—N2	118.1 (2)	C2—C7—C8	116.8 (3)
Cl3—P3—O1	99.4 (1)	P1—N3—P3	120.9 (2)
N3—P1—N1—P2	19.3 (4)	N3—P3—N2—P2	21.0 (3)
N1—P1—N3—P3	−15.2 (3)	N2—P3—N3—P1	−4.6 (3)
N2—P2—N1—P1	−3.5 (4)	C1—C2—C7—C8	133.6 (4)
N1—P2—N2—P3	−17.1 (3)	C3—C2—C7—C8	−49.7 (5)

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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: BM1373). Services for accessing these data are described at the back of the journal.

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