organic papers

2,2-[2,2′-Methylenebis(4-nitrophenoxy)]-4,6-[2,2′-methylenebis(4-nitrophenoxy)]-4,6-dichloro-1,3,5,2λ⁵,4λ⁵,6λ⁵-triazatriphosphorine (spiro-ansa) acetonitrile

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The title compound, $C_{26}H_{16}Cl_2N_7O_{12}P_3 \cdot C_2H_3N$, consists of a non-planar trimeric phosphazene ring and two bulky 2,2′-methylenebis(4-nitrophenoxy) side groups, two cis-Cl atoms, and an acetonitrile molecule as solvent. With respect to the corresponding values in the reference compound $N_3P_3Cl_6$, the endocyclic angles around the P atoms are slightly changed, while two of the exocyclic angles are increased and the remaining one is decreased. This situation is different from that in other reported phosphazene derivatives.

Comment

We have previously investigated the reactions of sodium 2,2′-methylenebis(4-nitrophenoxide) and hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$. When equal amounts of these compounds were reacted, the reaction yielded two different products, namely the cis-ansa and spiro isomers (Hökelek, Akduran, Yıldız et al., 2000). On the other hand, when one equivalent of $N_3P_3Cl_6$ and two equivalents of phenoxide were reacted, two different products, namely the cis-(ansa-spiro), (I), and dispiro, (II), isomers were isolated. The title compound, (I), was separated from the reaction mixture by column chromatography. Although a series of spiro and ansa cyclophosphazene derivatives have been reported, there is only a very limited number of spiro–ansa cyclophosphazene derivatives (Labarre & Labarre, 1993). The title compound, (I), is the first cis-(ansa-spiro) cyclophosphazene derivative to be reported.
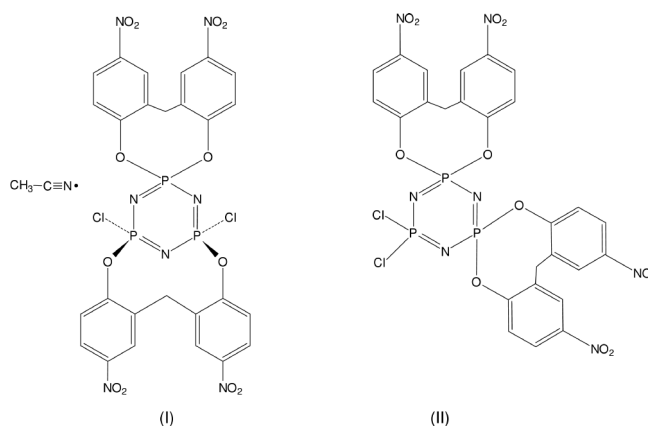
The investigation of cyclic phosphazenes has attracted great interest in their synthetic, spectroscopic and unusual structural properties and dramatic advances have been observed in this area during the past decade of the millennium (Allcock, 1985; Shaw, 1980; Fincham et al., 1986; Krishnamurty & Woods, 1987). The bulky phenoxy derivatives of hexachlorocyclo-
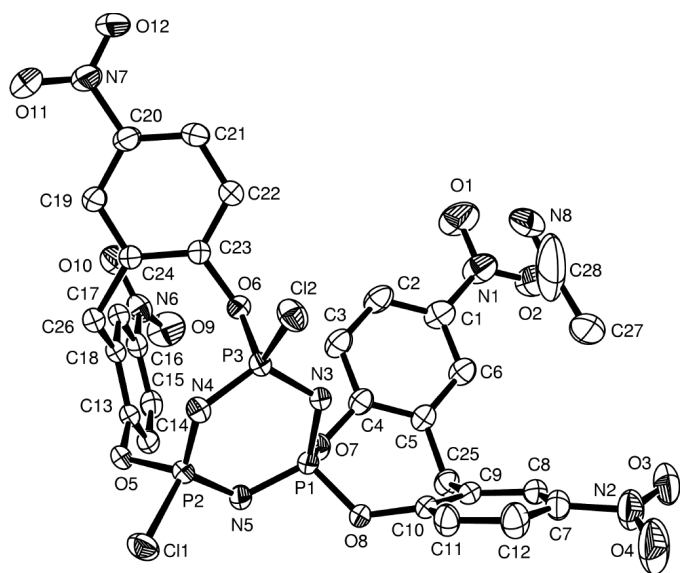
Figure 1
An *ORTEP*-3 (Farrugia, 1997) drawing of the title molecule with the atom-numbering scheme. The displacement ellipsoids are drawn at the 30% probability level.

$2\lambda^5,4\lambda^5,6\lambda^5$-triphosphazatriene ($N_3P_3Cl_6$) and octachloro-cyclo-$2\lambda^5,4\lambda^5,6\lambda^5, 8\lambda^5$-tetraphosphazatetraene ($N_4P_4Cl_8$), have potential use in the synthesis of new, small-molecule organo-cyclophosphazenes with inorganic backbones and aryloxy side groups which have many different uses (Allcock, 1985; Allcock *et al.*, 1987; Olshavsky & Allcock, 1995; Hökelek & Kılıç, 1990; Hökelek *et al.*, 1996). The small-molecule organocyclophosphazenes are also small-molecule models for the corresponding linear organo-polyphosphazenes (Allcock, Dembek *et al.*, 1992; Allen, 1994). Some of the amino-phosphazenes are thought to be useful as cancer chemotherapeutic agents (Chernov *et al.*, 1959; Huizen, 1984).

The structures of the organic, inorganic or organometallic side groups are highly effective in determining the specific physical or chemical properties of phosphazene derivatives (Allcock *et al.*, 1996). The organophosphazene derivatives are used in polymer synthesis and the resulting polymers are expected to have unique physical properties (Allcock, 1972; Allcock *et al.*, 1987).

$N_3P_3Cl_6$ 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 [$Cl_5N_3P_3(OC_6H_2O-2,4,6–Me)$], (III) (Hökelek, Akduran, Kılıç *et al.*, 2000), [$Cl_5N_3P_3(OC_6H_2-2,6-^tBu_2-4-Me)$], (IV) (Hökelek *et al.*, 1999), [$Cl_7N_4P_4(OC_6H_2-2,6-^tBu_2-4-Me)$], (V) (Hökelek *et al.*, 1996), $Cl_4N_3P_3[(OC_6H_3)(NO_2)$-$CH_2(OC_6H_3)(NO_2)]$, (VI) (Hökelek, Akduran, Yıldız *et al.*, 2000), $Cl_2N_3P_3[(OC_6H_3)(NO_2)CH_2(OC_6H_3)(NO_2)](Ph)_2$, (VII) (Hökelek *et al.*, 2001), [$Cl_5N_3P_3(OC_6H_2-2,4,6-^tBu_3)$], (VIII) (Kılıç *et al.*, 1996), [$N_3P_3(OC_6H_4OCH_2Ph-4)_6$], (IX) (Allcock *et al.*, 1996), [$Cl_5N_3P_3–P_3N_3Cl_4(OC_6H_3-2,6-^tBu_2)$], (X) (Hökelek *et al.*, 1994), [$N_3P_3Cl_4(OC_6H_3Cl_2-o)_2$], (XI), and [$N_3P_3Cl_4(OC_6H_3Me_2-o)_2$], (XII) (Allcock, Ngo *et al.*, 1992), have been reported.

The study of (I) was undertaken in order to understand the influence of the highly hindered 2,2′-methylenebis(4-nitrophenoxy) side groups on the structure of the cyclic trimeric phosphazene ring (Fig. 1). The structure consists of a non-planar trimeric phosphazene ring with 2,2′-methylenebis(4-nitrophenoxy) groups attached to atoms P3, P2 and P1, respectively, and an acetonitrile molecule which is used as a solvent in the synthesis. The phenyl ring *A* (C1—C6) is planar while *B* (C7—C12), *C* (C13—C18) and *D* (C19—C24) are nearly planar, with the largest displacements from the least-squares planes −0.014 (7) Å for C12, −0.014 (4) Å for C18 and −0.019 (5) Å for C24.

The dihedral angles between the phenyl ring planes are *A*/*B* = 65.5 (2), *A*/*C* = 70.7 (2), *A*/*D* = 28.2 (1), *B*/*C* = 81.2 (1), *B*/*D* = 87.9 (1) and *C*/*D* = 82.8 (2)°. The three N atoms are displaced on opposite sides (+ and −) with respect to the plane through the P atoms as follows: N3 −0.168 (4), N4 −0.298 (4) and N5 +0.104 (4) Å.

The P—N—P bond angles range from 118.6 (3) to 121.8 (2)°. In addition, the variation in the N—P—N bond angles, ranging from 117.4 (2) to 118.7 (2)°, is small. The endocyclic N3—P1—N5 angle [118.7 (2)°] is a little increased and N4—P2—N5 [117.5 (2)°] and N3—P3—N4 [117.4 (2)°] angles are a little decreased, while the exocyclic O6—P3—Cl2 [104.1 (1)°] and O7—P1—O8 [104.9 (2) °] angles are increased and the O5—P2—Cl1 angle [97.4 (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 the standard compound, $N_3P_3Cl_6$ (Bullen, 1971).

In trimeric phosphazenes, it has been observed that endocyclic N—P—N angles about P decrease while exocyclic R—P—Cl angles increase (Contractor *et al.*, 1985; Fincham *et al.*, 1986; Hökelek *et al.*, 1994; Kılıç *et al.*, 1996); these results are different from the findings in the tetrameric phosphazenes containing bulky phenoxy groups (Allcock *et al.*, 1995; Allcock, Dembek *et al.*, 1992; Hökelek *et al.*, 1996; Hökelek & Kılıç, 1990). In (I), the N—P—N angles are larger and the O—P—Cl angles are smaller than the corresponding ones in $N_3P_3Cl_5(NPPh_3)$, (XIII) [114.4 (1) and 107.2 (1)°; Fincham *et al.*, 1986], $N_3P_3Cl_4(NPPh_3)_2$, (XIV) [109.2 (4) and 110.9 (4)°; Fincham *et al.*, 1986], $N_3P_3Cl_4Ph(PPh_2)$, (XV) [114.5 (2) and 106.7 (1)°; Allcock *et al.*, 1990] and (IV) [115.1 (1) and 106.79 (9)°; Hökelek *et al.*, 1999], which implies less electron donation to the N_3P_3 ring.

The O6—P3—N3 [106.1 (2)°] and O5—P2—N5 [109.5 (2)°] angles have different values, while O6—P3—N4 [111.6 (2)°], O5—P2—N4 [110.4 (2)°], O8—P1—N3 [110.6 (2)°] and O7—P1—N3 [109.1 (2)°] have nearly the same values. The P1—N3—P3, P2—N4—P3 and P1—N5—P2 angles [119.3 (2), 118.6 (2) and 121.8 (2)°, respectively] may be compared with 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 the bond angles are more reliable guides to electronic shifts than the changes in bond lengths (Fincham *et al.*, 1986; Contractor *et al.*, 1985).

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) groups seem to be slightly electron-with-drawing. Thus, the P—Cl and P—O bonds are not seen to change substantially. 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 the ring 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 1.570 (3) to 1.588 (4) Å.

In related compounds, the corresponding mean bond lengths are: 1.576 (3) Å in (VI) (Hökelek, Akduran, Yıldız *et al.*, 2000), 1.573 (3) Å in (IV) (Hökelek *et al.*, 1999), 1.58 (1) Å in (VIII) (Kılıç *et al.*, 1996), 1.576 (5) Å in (X) (Hökelek *et al.*, 1994), 1.572 (3) Å in [$N_3P_3Cl_4Ph(PPh_2)$], (XVI) (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 1.683 (5) Å (Allen *et al.*, 1987). The short bonds in the ring have appreciable double-bond character; this is generally observed for phosphazene derivatives (Wagner & Vos, 1968).

In the acetonitrile solvent molecule the bond lengths and angles (Table 1) are in accordance with the conventional values (Allen *et al.*, 1987).

Experimental

2,2′–Methylenebis(4-nitrophenol) (10.00 g, 34.4 mmol) in tetra-hydrofuran (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 being passed over the reaction mixture. The solvent was removed under reduced pressure and the residue was dried. The sodium phenoxide (2.00 g, 5.98 mmol) was dissolved in CH_3CN (100 ml). To this mixture, $N_3P_3Cl_6$ (0.96 g, 2.76 mmol) in CH_3CN (100 ml) was added slowly and the resulting solution allowed to come to ambient temperature with constant stirring. After the mixture had been vigorously stirred and boiled under reflux for 15 h, the precipitated salt (NaCl) was filtered off and the solvent removed *in vacuo*. The products *cis*-(ansa-spiro), (I), and dispiro, (II), were separated by column chromatography. The isomer (I) was crystallized from CH_2Cl_2/n-hexane (3:2) [m.p. 553 K (decomposition)].

Crystal data

$C_{26}H_{16}Cl_2N_7O_{12}P_3 \cdot C_2H_3N$	$Z = 2$
$M_r = 823.32$	$D_x = 1.565$ Mg m^{-3}
Triclinic, $P\bar{1}$	Cu $K\alpha$ radiation
$a = 11.549\ (1)$ Å	Cell parameters from 25
$b = 11.857\ (1)$ Å	reflections
$c = 15.024\ (1)$ Å	$\theta = 16$–$42°$
$\alpha = 97.49\ (1)°$	$\mu = 3.63$ mm^{-1}
$\beta = 109.99\ (1)°$	$T = 293\ (2)$ K
$\gamma = 109.78\ (1)°$	Block-like, colorless
$V = 1747.5\ (2)$ Å^3	$0.30 \times 0.25 \times 0.20$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.034$
Non-profiled ω scans	$\theta_{max} = 74.2°$
Absorption correction: ψ scans (*MolEN*; Fair, 1990)	$h = 0 \to 14$
	$k = -14 \to 13$
$T_{min} = 0.388$, $T_{max} = 0.484$	$l = -18 \to 17$
7549 measured reflections	3 standard reflections
7127 independent reflections	frequency: 120 min
4690 reflections with $I > 2\sigma(I)$	intensity decay: 1%

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.067$	$w = 1/[\sigma^2(F_o^2) + (0.1313p)^2]$
$wR(F^2) = 0.194$	where $p = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} < 0.001$
6411 reflections	$\Delta\rho_{max} = 1.10$ e Å^{-3}
469 parameters	$\Delta\rho_{min} = -0.56$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

P2—N5	1.573 (4)	P1—O7	1.592 (3)
P2—N4	1.588 (4)	Cl2—P3	1.9864 (15)
P2—O5	1.596 (3)	N4—P3	1.581 (3)
P2—Cl1	1.9799 (14)	N3—P3	1.571 (3)
P1—O8	1.566 (3)	C28—N8	1.12979 (18)
P1—N5	1.570 (3)	C28—C27	1.5125 (3)
P1—N3	1.580 (3)	P3—O6	1.581 (3)
N5—P2—N4	117.47 (17)	N3—P1—O7	109.05 (17)
N5—P2—O5	109.49 (18)	P1—N5—P2	121.8 (2)
N4—P2—O5	110.35 (17)	P3—N4—P2	118.6 (2)
N5—P2—Cl1	111.03 (15)	P3—N3—P1	119.28 (19)
N4—P2—Cl1	109.24 (14)	N8—C28—C27	173.445 (1)
O5—P2—Cl1	97.43 (11)	N3—P3—N4	117.38 (18)
O8—P1—N5	106.24 (17)	N3—P3—O6	106.06 (16)
O8—P1—N3	110.62 (16)	N4—P3—O6	111.59 (16)
N5—P1—N3	118.67 (18)	N3—P3—Cl2	109.30 (13)
O8—P1—O7	104.85 (16)	N4—P3—Cl2	107.66 (14)
N5—P1—O7	106.49 (18)	O6—P3—Cl2	104.05 (12)

The H atoms were positioned geometrically at distances of 0.96, 0.97 and 0.93 Å for CH_3, CH_2 and CH bonds, respectively, from the corresponding atoms and a riding model was used during the refinement process.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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