Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

# *cis*-ansa-2,4-Dichloro-2,4-[2,2′-methylenebis(4-nitrophenoxy)]-6,6-diphenylcyclo-2$\lambda^5$,4$\lambda^5$,6$\lambda^5$-triphosphazatriene

**Tuncer Hökelek,[a]* Hakan Dal[b] and Zeynel Kılıç[b]**

[a]Hacettepe University, Department of Physics, 06532 Beytepe, Ankara, Turkey, and [b]Ankara University, Department of Chemistry, 06100 Tandoğan, Ankara, Turkey

Correspondence e-mail: merzifon@hacettepe.edu.tr

**Key indicators**

Single-crystal X-ray study
*T* = 293 K
Mean *σ*(C–C) = 0.005 Å
*R* factor = 0.067
*wR* factor = 0.258
Data-to-parameter ratio = 14.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

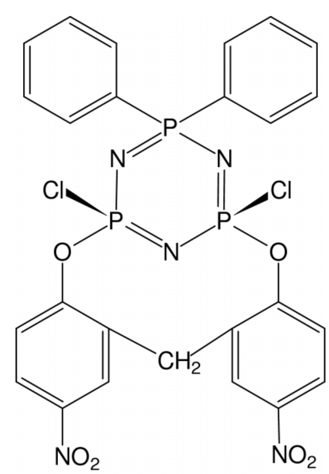


Received 4 October 2001
Accepted 12 October 2001
Online 20 October 2001

The title compound, $C_{25}H_{18}Cl_2N_5O_6P_3$, consists of a non-planar trimeric phosphazene ring, one bulky 2,2′-methylenebis(4-nitrophenoxy) side group, two *cis*-Cl atoms and two geminal phenyl groups. The P—Cl bond lengths are 1.9930 (12) and 1.9970 (12) Å, while the P—N and P—O distances are 1.568 (3)–1.617 (3) and 1.594 (2)–1.604 (2) Å. The core bond angles Cl—P—N, Cl—P—O, P—N—P, N—P—N and N—P—O are 106.9 (1)–110.2 (1), 97.9 (1)–102.5 (1), 118.8 (2)—123.1 (2), 115.6 (1)-118.7 (2) and 106.4 (1)–111.2 (1)°, respectively. In the 2,2′-methylenebis(4-nitrophenoxy) side group, the phenyl rings are almost perpendicular to each other.

## Comment

We have previously investigated the reactions of sodium 2,2′-methylenebis-(4-nitrophenoxide) and hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$. When equal amounts of the reactants were mixed, the reaction yields two different products, namely the *cis*-ansa and spiro-isomers (Hökelek, Akduran, Yıldız *et al.*, 2000). The title compound, (I), is the first *cis*-ansa-cyclophosphazene derivative, and was obtained from the reaction of $N_3P_3Ph_2Cl_4$ and 2,2′-methylenebis(4-nitrophenoxide).




(I)

$N_3P_3Cl_6$ is the starting material for the preparation of trimeric phosphazene. The crystal structures of $N_3P_3Cl_6$ (Bullen, 1971) and a few of its derivatives with bulky phenoxy groups, such as $Cl_4N_3P_3[(OC_6H_3)(NO_2)CH_2(OC_6H_3)(NO_2)]$, (II) (Hökelek, Akduran, Yıldız *et al.*, 2000), $[Cl_5N_3P_3(OC_6H_2$-2,6-$^t$Bu$_2$-4-Me], (III) (Hökelek *et al.*, 1999), $[Cl_5N_3P_3(OC_6H_2$-

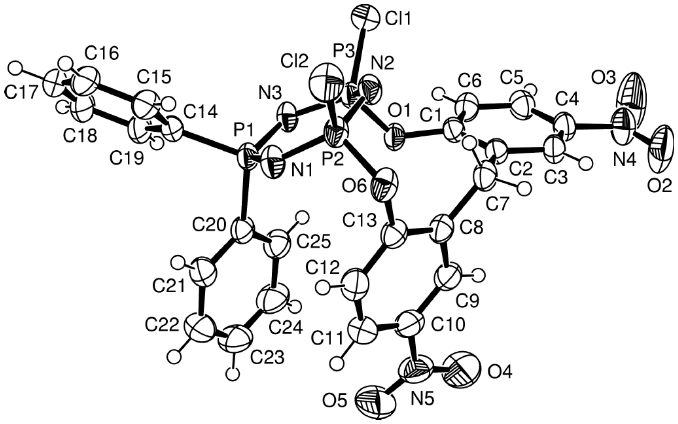



**Figure 1**
An *ORTEP*II (Johnson, 1976) drawing of the title molecule with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

2,4,6-$^{t}$Bu$_3$)], (IV) (Kılıç *et al.*, 1996), [$N_3P_3(OC_6H_4OCH_2Ph$-4)$_6$], (V) (Allcock *et al.*, 1996), [$Cl_5N_3P_3$–$P_3N_3Cl_4(OC_6H_3$-2,6-$^{t}$Bu$_2$)], (VI) (Hökelek *et al.*, 1994), [$N_3P_3Cl_4(OC_6H_3$-$Cl_2$-*o*)$_2$], (VII), and [$N_3P_3Cl_4(OC_6H_3Me_2$-*o*)$_2$], (VIII) (Allcock, Ngo *et al.*, 1992), have been reported.

The study of cyclic phosphazenes has attracted great interest with respect to their synthetic, spectroscopic and unusual structural properties (Shaw, 1980; Fincham *et al.*, 1986; Krishnamurty & Woods, 1987). The bulky phenoxy derivatives of $N_3P_3Cl_6$ (tri-P) and $N_4P_4Cl_8$ (tetra-P) have potential uses in the synthesis of small-molecule organocyclophosphazenes with inorganic backbones and aryloxy side groups (Olshavsky & Allcock, 1995; Hökelek & Kılıç, 1990). Structural studies of tri-P and tetra-P derivatives, *e.g.* [$Cl_5N_3P_3(OC_6H_2O$-2,4,6-Me)], (IX) (Hökelek, Akduran, Begeç *et al.*, 2000), [$Cl_5N_3P_3(OC_6H_2$-2,6-$^{t}$Bu$_2$-4-Me)], (X) (Hökelek *et al.*, 1999), and [$Cl_7N_4P_4(OC_6H_2$-2,6-$^{t}$Bu$_2$-4-Me)], (XI) (Hökelek *et al.*, 1996), have been the focus of interest by our group. These organocyclophosphazenes are also useful models for the related linear organopolyphosphazenes (Allcock, Dembek *et al.*, 1992). The organic, inorganic or organometallic side groups are highly effective in determining the specific physical or chemical properties of polyphosphazenes (Allcock *et al.*, 1996).

Aziridino, pyrrolidino, and primary and other secondary aminophosphazene derivatives are also useful as cancer chemotherapeutic agents (Chernov *et al.*, 1959; van der Huizen, 1984). A close relationship has been observed between the structures of the cyclophosphazene derivatives and cytostatic activity (van der Huizen, 1984). The electron donating groups in the tri-P and tetra-P phosphazenes seem to be essential for effective tumour-growth inhibition.

Compound (I) was studied 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 and 2,2′-methylenebis(4-nitrophenoxy) group, together with two *cis*–Cl atoms and two geminal phenyl groups attached to atoms P2, P3 and P1, respectively. The three N atoms are displaced on opposite sides, + and −, with respect to the plane through the P atoms as follows: N1 −0.024 (3), N2 +0.239 (3) and N3 +0.154 (3) Å.

In trimeric and tetrameric phosphazenes, the P—N bond lengths may be correlated with the orbital electronegativities of groups of atoms (Bullen & Tucker, 1972). In such structures, the lengths of the P—N bonds depend on the electronegativities of the substituents. In (I), the Cl atoms and 2,2′-methylenebis(4-nitrophenoxy) groups are slightly electron withdrawing, thus, the P—Cl and P—O bonds do not change considerably. In a given $N_3P_3R_6$ structure, the lengths of the P—N bonds are generally equal, provided all of 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 can be expected. In (I), there is a distinct difference between the electronegativities of the atoms attached to the P atoms; the P—N bond distances vary from 1.568 (3) to 1.617 (3) Å [average 1.589 (3) Å], while in a similar compound, (II), the P—N bond lengths range from 1.574 (3)–1.581 (3) Å [average 1.577 (3) Å]. In phosphazene derivatives, the P—N single and double bonds are generally in the ranges 1.63–1.69 and 1.57–1.60 Å, respectively (Allen *et al.*, 1987). In (I), the shorter P—N bonds have appreciable double-bond character (Wagner & Vos, 1968), *e.g.* in related compounds, the corresponding mean bond lengths are: 1.576 (3) Å in (II), 1.573 (3) Å in (III), 1.58 (1) Å in (IV), 1.576 (5) Å in (VI), 1.572 (3) Å in [$N_3P_3Cl_4Ph(PPh_2)$], (XII) (Allcock *et al.*, 1990), and 1.581 (3) Å in the starting material ($N_3P_3Cl_6$; Bullen, 1971). The P—Cl and P—O bonds are almost equal, with mean values of 1.995 (1) and 1.599 (2) Å, respectively.

The P—N—P bond angles range from 118.8 (2) to 123.1 (2)° and, in addition, the N—P—N bond angles vary between 115.6 (1) and 118.7 (2)°. The endocyclic N1—P1—N3 angle [115.6 (1)°] is decreased and the N1—P2—N2 [118.1 (2)°] and N2—P3—N3 [118.7 (2)°] angles are not changed significantly. On the other hand, the endocyclic P1—N1—P2 angle [123.1 (2)°] is increased and the P2—N2—P3 [118.8 (2)°] and P1—N3—P3 [120.6 (2)°] angles are decreased, while the exocyclic C14—P1—C20 [105.8 (1)°] and O1—P3—Cl1 [102.5 (1)°] angles are increased and the O6—P2—Cl2 angle [97.9 (1)°] is decreased with respect to the values [118.3 (2), 121.4 (3) and 101.2 (1)°, respectively] in the $N_3P_3Cl_6$ starting material (Bullen, 1971). The O1—P3—N3 [106.4 (1)°] angle is smaller than the other O—P—N bond angles. These variations in the *endo*- and exocyclic bond angles may be due to both the electronic and/or steric interactions (Kılıç *et al.*, 1996).

The Cl—P—N, Cl—P—O and N—P—O bond angles are in the ranges 106.9 (1)–110.2 (1) [average 108.6 (1)°], 97.9 (1)–102.5 (1) [average 100.2 (1)°] and 106.4 (1)–111.2 (1)° [average 109.5 (1)°], compared with the corresponding values in compound (II) of 108.7 (1)–109.9 (2) [average 109.2 (1)°], 99.4 (1)–103.6 (1) [average 101.5 (1)°] and 109.9 (2)–110.4 (2)° [average 110.2 (2)°].

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), which are different from the case found in tetrameric phosphazenes containing bulky phenoxy groups (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 angles 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], (XII) [114.5 (2) and 106.7 (1)°] and (III) [115.1 (1) and 106.79 (9)°], which implies less electron donation to the $N_3P_3$ ring.

## Experimental

2,2′-Methylenebis(4-nitrophenol) (10.0 g, 34.4 mmol) in tetrahydrofuran (THF, 100 ml) was added slowly over a period of 30 min to a solution of 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 (1.00 g, 2.99 mmol) was dissolved in benzene (50 ml). To this mixture, $N_3P_3Ph_2Cl_4$ (1.08 g, 2.99 mmol) in benzene (100 ml) at 253 K was added slowly and the resulting solution allowed to reach ambient temperature with constant stirring. After the mixture had been vigorously stirred and boiled under reflux for 36 h, the precipitated salt (NaCl) was filtered off and the solvent removed *in vacuo*. The *cis*-ansa product was separated by column chromatography. The crude product was crystallized from $CH_3CN$ [yield 0.92 g, 47%; m.p. 407 K (decomposed)].

*Crystal data*

$C_{25}H_{18}Cl_2N_5O_6P_3$
$M_r$ = 648.25
Triclinic, $P\overline{1}$
$a$ = 9.9482 (10) Å
$b$ = 11.2184 (10) Å
$c$ = 12.8536 (10) Å
$\alpha$ = 97.702 (7)°
$\beta$ = 105.515 (7)°
$\gamma$ = 94.503 (7)°
$V$ = 1359.9 (2) Å$^3$
$Z$ = 2
$D_x$ = 1.583 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta$ = 10–11°
$\mu$ = 0.47 mm$^{-1}$
$T$ = 293 (2) K
Rod-shaped, colorless
0.30 × 0.15 × 0.15 mm

*Data collection*

Enraf–Nonius CAD-4 diffractometer
Non-profiled $\omega$ scans
Absorption correction: refined from $\Delta F$(Walker & Stuart, 1983)
$T_{min}$ = 0.873, $T_{max}$ = 0.933
5465 measured reflections
5465 independent reflections
4666 reflections with $I > 2\sigma(I)$
$\theta_{max}$ = 26.3°
$h = -12 \rightarrow 11$
$k = -13 \rightarrow 13$
$l = 0 \rightarrow 16$
3 standard reflections
frequency: 120 min
intensity decay: 3%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.067
$wR(F^2)$ = 0.258
$S$ = 1.22
5465 reflections
378 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.20P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.28 e Å$^{-3}$
$\Delta\rho_{min}$ = −1.28 e Å$^{-3}$

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

| | | | |
|---|---|---|---|
| Cl1—P3 | 1.9970 (12) | P2—N2 | 1.589 (3) |
| Cl2—P2 | 1.9930 (12) | P2—O6 | 1.604 (2) |
| P1—N1 | 1.607 (3) | P3—N3 | 1.569 (2) |
| P1—N3 | 1.617 (3) | P3—N2 | 1.585 (3) |
| P1—C14 | 1.792 (3) | P3—O1 | 1.594 (2) |
| P1—C20 | 1.806 (3) | O1—C1 | 1.407 (4) |
| P2—N1 | 1.568 (3) | O6—C13 | 1.405 (4) |
| | | | |
| N1—P1—N3 | 115.58 (14) | N3—P3—N2 | 118.71 (15) |
| N1—P1—C14 | 107.18 (15) | N3—P3—O1 | 106.37 (13) |
| N3—P1—C14 | 110.77 (14) | N2—P3—O1 | 111.16 (13) |
| N1—P1—C20 | 109.11 (15) | N3—P3—Cl1 | 110.07 (11) |
| N3—P1—C20 | 107.95 (15) | N2—P3—Cl1 | 106.87 (11) |
| C14—P1—C20 | 105.82 (14) | O1—P3—Cl1 | 102.49 (10) |
| N1—P2—N2 | 118.13 (15) | C1—O1—P3 | 128.84 (19) |
| N1—P2—O6 | 110.74 (15) | C13—O6—P2 | 115.58 (19) |
| N2—P2—O6 | 109.57 (13) | P2—N1—P1 | 123.14 (19) |
| N1—P2—Cl2 | 110.16 (12) | P3—N2—P2 | 118.80 (16) |
| N2—P2—Cl2 | 108.42 (11) | P3—N3—P1 | 120.64 (17) |
| O6—P2—Cl2 | 97.92 (9) | | |

H atoms were positioned geometrically at a distance of 0.97 Å, for C—H bonds, from the attached C atom and a riding model was used during the refinement process. However, the two H atoms bonded to C7 were refined isotropically.

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, 1997); 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).

The authors wish to acknowledge the purchase of a CAD-4 diffractometer under Grant DPT/TBAG1 of the Scientific and Technical Research Council of Turkey and are grateful to the Ankara University Research Fund for the financial support of this work (grant number 98-05-04-05).

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