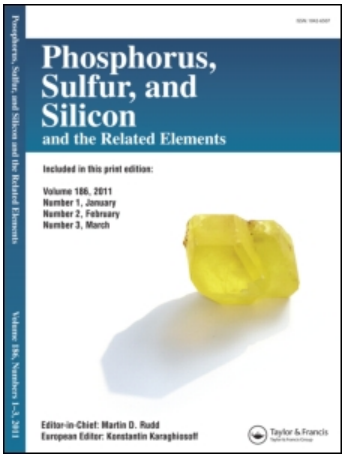


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# CONFORMATIONS OF (ARYLOXY)-δ³-CY CLOTRIPHOSPHAZANES. SINGLE CRYSTAL X-RAY STRUCTURES OF $[EtNP(OR)]_3$ [R=$C_6H_4$Br-2 (CIS), $C_6H_3Me_2$-2,6 (TRANS)]

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# CONFORMATIONS OF (ARYLOXY)-$\lambda^3$-CYCLOTRIPHOSPHAZANES. SINGLE CRYSTAL X-RAY STRUCTURES OF [EtNP(OR)]$_3$ [R = $C_6H_4$Br-2 (*CIS*), $C_6H_3Me_2$–2,6 (*TRANS*)]*

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*(Received 30 January, 1997; In final form 31 March, 1997)*

The reaction of the $\lambda^3$-cyclotriphosphazane, $(EtNPCl)_3$ with 2-bromo or 2-nitro phenol in the presence of diazabicyclooctane yields a *cis-trans* isomeric mixture of [EtNP($OC_6H_4X$-2)]$_3$ (X = Br or $NO_2$) from which the *cis*-[EtNP($OC_6H_4$Br-2)]$_3$ or *trans*-[EtNP($OC_6H_4NO_2$-2)]$_3$ is isolated in a pure state by fractional crystallisation. The two compounds have been characterised by elemental analysis and NMR ($^{31}$P, $^{13}$C, and $^1$H) spectroscopic data. Variable temperature (303–363 K) $^{31}$P NMR studies on *cis*-[EtNP($OC_6H_4$Br-2)]$_3$ indicate its slow conversion to the *trans*-analogue with increasing temperature. The structure of *cis*-[EtNP($OC_6H_4$Br-2)]$_3$ and the previously known *trans*-[EtNP($OC_6H_3Me_2$-2,6)]$_3$ have been determined by single crystal X-ray analysis. The six-membered $P_3N_3$ ring adopts a chair and a twist conformation in *cis*-[EtNP($OC_6H_4$Br-2)]$_3$ and *trans*-[EtNP($OC_6H_3Me_2$-2,6)]$_3$ respectively. The structural features are compared with those observed for other $\lambda^3$-cyclotriphosphazanes.

*Keywords:* $\lambda^3$-cyclotriphosphazanes; $P_3N_3$ ring conformation; "Negative hyperconjugation"; C-H...X (X = O, Br) hydrogen bonds

## INTRODUCTION

The chemistry of $\lambda^3$-cyclotriphosphazanes, $(RNPX)_3$ unlike that of the dimeric analogue $\lambda^3$-cyclodiphosphazanes, $(RNPX)_2$ is of recent origin[1] and there is only one detailed study on the conformations of the six-membered ring in $\lambda^3$-cyclotriphosphazanes[2]. In this paper, we report the synthesis and NMR

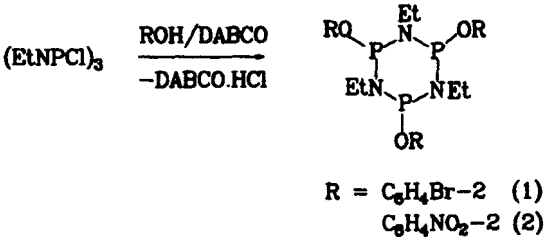
* Dedicated to Prof. Robert Wolf for his many fine contributions to phosphorus chemistry.

spectra of *cis*-[EtNP($OC_6H_4Br$-2)]$_3$, **1a** and *trans*-[EtNP($OC_6H_4NO_2$-2)]$_3$, **2b**. We also report the crystal structure analysis of **1a** and *trans*-[EtNP($OC_6H_3Me_2$-2,6)]$_3$ **3**[2] in order to gain an insight into the nature of the P-N bonding as well as the factors that determine the conformation of the six-membered ring in $\lambda^3$-cyclotriphosphazanes.

## RESULTS AND DISCUSSION

### Synthesis and Spectroscopic data

The new (aryloxy)cyclotriphosphazanes [EtNP(OR)]$_3$ (R = $C_6H_4X$-2; X = Br or $NO_2$) are obtained by the reaction of the chloro precursor (EtNPCl)$_3$ with the respective phenol in the presence of diazabicyclooctane (DABCO) as HCl acceptor (Scheme 1). The $^{31}$P NMR spectrum of the reaction mixture in each case shows the presence of *cis* and *trans* isomers in ~1:4 ratio. The *cis* isomer of [EtNP(OR)]$_3$ (R = $C_6H_4Br$-2), **1a** can be separated from the reaction mixture by fractional crystallisation from $CH_2Cl_2$/petrol (9/1, v/v). Similarly, the *trans* isomer of [EtNP(OR)]$_3$ (R = $C_6H_4NO_2$-2), **2b** is obtained in a pure state by fractional crystallisation from diethyl ether. The *trans* and *cis* analogues of **1a** and **2b,** however, could not be obtained in a pure state.




SCHEME 1

The $^{31}P\{^1H\}$ NMR spectrum of **1a** shows a single peak at 93.0 ppm indicating that all the three phosphorus nuclei are equivalent. The spectrum of **2b** shows an $A_2X$ pattern ($\delta_A$ = 122.7, $\delta_X$ = 119.3; $^2J_{PP}$ = 8.8 Hz) which indicates the presence of two different kinds of phosphorus nuclei. The $^{31}$P chemical shifts and P-P coupling constants are comparable to those observed for other $\lambda^3$-cyclotriphosphazanes[2]. The chemical shift of the *cis* isomer occurs at a higher field compared to that of *trans* isomer. The $^1$H NMR spectrum of **1a** shows the presence of equivalent $CH_2CH_3$ groups; the methyl protons resonate at 1.23 ppm as a triplet ($^3J_{HH}$ = 7.2 Hz) and the methylene protons resonate as unresolved multiplet at 3.70 ppm. The spectrum of **2b**, on the other hand, shows the

presence of two types of both methyl [1.24, 1.26 ppm each triplet, $^3J_{HH}$ = 7.1, 7.0 Hz] and methylene [3.46 and 3.63 ppm (m)] protons with an intensity ratio 2:1. The equivalence of all the $CH_2CH_3$ groups in **1a** is also evident from its $^{13}C$ NMR spectrum which shows only a singlet at 18.2 ppm for the methyl carbons and a triplet at 47.5 ppm ($^2J_{PC}$ = 44.0 Hz) for the methylene carbons. The $^{13}C$ NMR spectrum of **2b** shows two singlets at 17.3 and 18.4 ppm for the methyl carbon nuclei and a triplet at 45.6 ppm ($^2J_{PC}$ = 42.9 Hz) and a doublet of doublet at 44.8 ppm ($^2J_{PC}$ = 29.1, 40.6 Hz) for the methylene carbon nuclei.

A variable temperature $^{31}P$ NMR (303–363 K) study on **1a** shows its slow conversion to the *trans* isomer **1b.** The relative intensity of **1b** increases with increasing temperature and it reaches 1:1 at 363 K. Cooling the sample to 303 K, however, does not alter the isomeric ratio suggesting that *cis* → *trans* isomerisation is irreversible and hence presumably thermodynamic in origin. During this experiment apart from *cis* → *trans* isomerisation, substantial decomposition of the cyclotriphosphazane is also noted. This situation may be contrasted with the earlier observation that the $\lambda^3$-cyclotriphosphazane, *cis*-[EtNP($OC_6H_4Br$-*4*)]$_3$ does not undergo isomerization even after heating it at 373 K for two hours[2]. The steric strain imposed by the presence of bromine atoms in the *ortho* position of the aryloxy rings in **1a** is probably responsible for its greater ease of isomerization as compared to the *4*-bromo phenoxy derivative, *cis*-[EtNP($OC_6H_4Br$-*4*)]$_3$. It is to be noted that $\lambda^3$-cyclodiphosphazanes undergo *cis-trans* isomerization much more readily than $\lambda^3$-cyclotriphosphazanes[3]. The *cis-trans* isomerisation in $\lambda^3$-cyclodiphosphazanes can occur either by pyramidal inversion at phosphorus or dissociation into a monomeric $\lambda^3\sigma^2$-iminophosphane intermediate[4]. Murugavel *et al,* have pointed out that pyramidal inversion in $\lambda^3$-cyclotriphosphazanes is subject to a high energy barrier[2]. At present there is no definitive evidence for the presence of monomeric intermediates in the isomerisation of $\lambda^3$-cyclodiphosphazanes. Presumably pyramidal inversion is more rapid in $\lambda^3$-cyclo*di*phosphazanes compared to $\lambda^3$-cyclo*tri*phosphazanes as a result of greater strain in the former; the NPN and PNP angles (~ 80 and 100 °) in cyclodiphosphazanes[1] are very much less than those in cyclotriphosphazanes (~100 and 130°)(see below and also ref. 2 ).

## CRYSTALLOGRAPHIC STUDIES

The structures of **1a** and **3** have been determined by X-ray crystallography. Perspective views of the molecules are shown in Figures 1 and 2. Pertinent bond lengths and bond angles are listed in Table Ia & Ib. The structural features of **1a** and **3** are compared with those reported for other $\lambda^3$-cyclotriphosphazanes and are summarised in Table II.

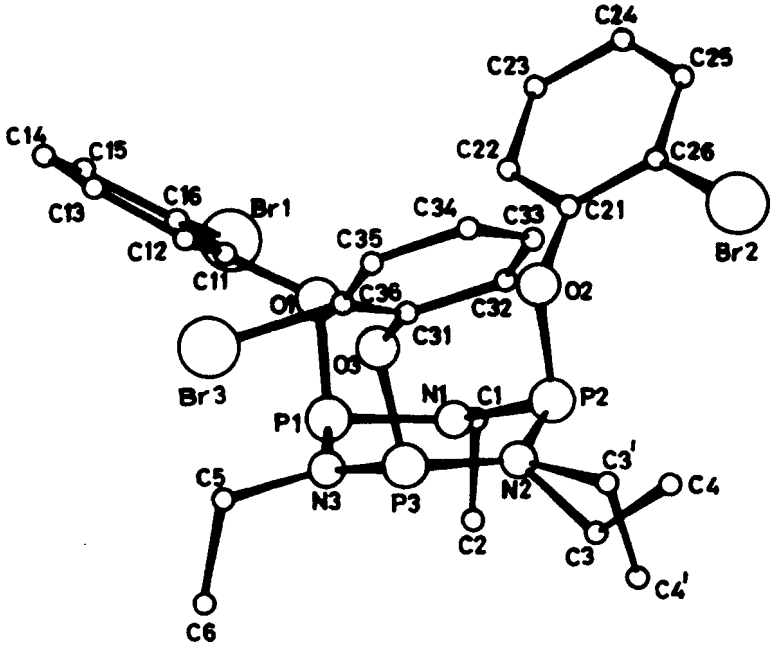



FIGURE 1 Molecular Structure of *cis*-[EtNP($OC_6H_4Br$-2)]$_3$ **1a** ("statistical disorder" of ethyl group is shown at N2) (hydrogen atoms omitted for clarity)

TABLE Ia

*Selected bond lengths (Å) and bond angles (deg) for* ***1a***

| | | | |
|---|---|---|---|
| P(1)-O(1) | 1.665(6) | N(3)-P(1)-N(1) | 101.8(3) |
| P(1)-N(3) | 1.681(7) | N(2)-P(2)-N(1) | 101.9(4) |
| P(1)-N(1) | 1.686(8) | N(3)-P(3)-N(2) | 101.9(4) |
| P(2)-O(2) | 1.680(7) | C(1)-N(1)-P(1) | 113.0(6) |
| P(2)-N(2) | 1.688(8) | C(1)-N(1)-P(2) | 114.6(6) |
| P(2)-N(1) | 1.690(8) | P(1)-N(1)-P(2) | 131.5(4) |
| P(3)-O(3) | 1.675(6) | C(3)-N(2)-P(2) | 115.1(9) |
| P(3)-N(3) | 1.692(7) | C(3)-N(2)-P(3) | 113.0(9) |
| P(3)-N(2) | 1.695(7) | C(3')-N(2)-P(2) | 113.0(1) |
| N(1)-C(1) | 1.503(11) | C(3')-N(2)-P(3) | 113.4(1) |
| N(2)-C(3) | 1.55(2) | P(2)-N(2)-P(3) | 130.9(4) |
| N(2)-C(3') | 1.55(2) | C(5)-N(3)-P(1) | 113.4(6) |
| N(3)-C(5) | 1.528(11) | C(5)-N(3)-P(3) | 111.1(6) |
| | | P(1)-N(3)-P(3) | 133.0(4) |

*Hydrogen bond parameters (Å, °)*

| D-H...A | H...A | D...A | D-H...A |
|---|---|---|---|
| C(12)-H(12)..O(3) | 2.618 | 3.430 | 146.0 |
| C(22)-H(22)..O(1) | 2.411 | 3.186 | 140.7 |
| C(32)-H(32)..O(2) | 2.720 | 3.445 | 135.4 |
| C(5)-H(5A)..Br(3) | 2.880 | 3.963 | 152.6 |

TABLE Ib

| *Selected bond lengths (Å) and bond angles (deg) for 3* | | | |
|---|---|---|---|
| P(1)-O(1) | 1.671(2) | N(3)-P(1)-N(1) | 98.8(1) |
| P(1)-N(3) | 1.716(3) | N(2)-P(2)-N(1) | 101.3(1) |
| P(1)-N(1) | 1.688(3) | N(3)-P(3)-N(2) | 101.1(1) |
| P(2)-O(2) | 1.655(3) | C(1)-N(1)-P(1) | 114.1(2) |
| P(2)-N(2) | 1.696(3) | C(1)-N(1)-P(2) | 114.8(2) |
| P(2)-N(1) | 1.704(3) | P(1)-N(1)-P(2) | 131.0(2) |
| P(3)-O(3) | 1.676(3) | C(3)-N(2)-P(2) | 116.0(2) |
| P(3)-N(3) | 1.689(3) | C(3)-N(2)-P(3) | 114.7(2) |
| P(3)-N(2) | 1.689(3) | P(2)-N(2)-P(3) | 128.4(2) |
| N(1)-C(1) | 1.489(4) | C(5)-N(3)-P(1) | 112.3(3) |
| N(2)-C(3) | 1.496(4) | C(5)-N(3)-P(3) | 113.2(2) |
| N(3)-C(5) | 1.533(5) | P(1)-N(3)-P(3) | 125.0(2) |
| *Hydrogen bond parameters (Å, °)* | | | |
| D-H..A | H..A | D..A | D-H..A |
| C(27)-H(27A)..O(3')[a] | 2.545 | 3.484 | 166.1 |

[a] symmetry code of 0(3'): y + 1/4, -x + 1/4 + 1, z + 1/4



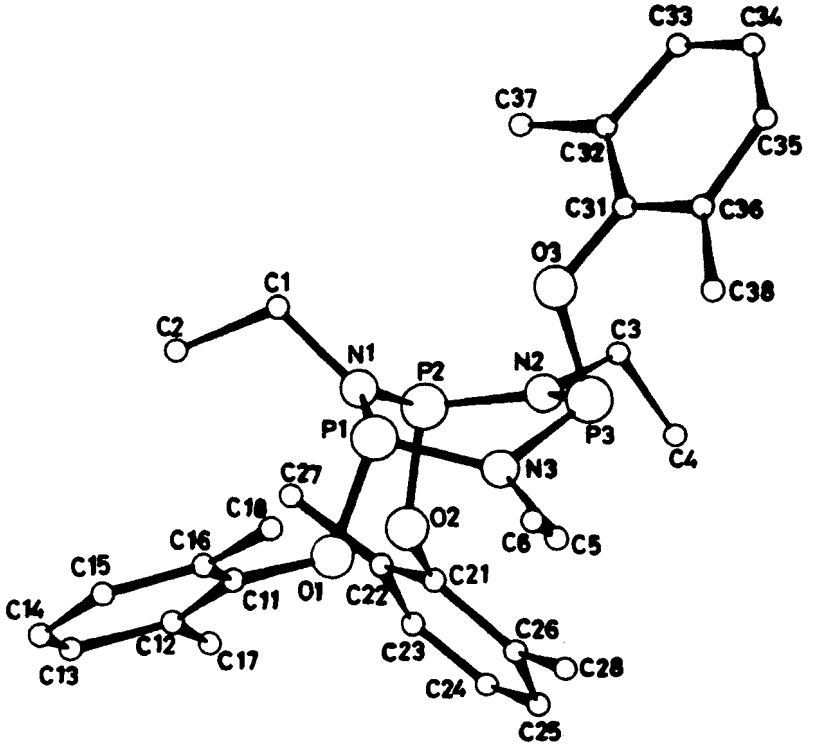



FIGURE 2 Molecular Structure of *trans*-[EtNP($OC_6H_3Me_2$-2,6)]$_3$ **3** (hydrogen atoms omitted for clarity)

TABLE II Comparison of Structural Data for $\lambda^3$-Cyclotriphosphazanes

| *Structural Feature* | *Compounds* | | | |
|---|---|---|---|---|
| | *cis* | *trans* | *cis* | *trans* |
| | $[EtNP(OC_6H_4Br\text{-}2)]_3$ | $[EtNP(OC_6H_3Me_2\text{-}2,6)]_3$ | $[EtNP(OC_6H_4Br\text{-}4)]_3$ | $[EtNP(OC_6H_4Br\text{-}4)]_3$ |
| $P_3N_3$ ring conformation | chair | twist | chair | boat |
| av (P-N), Å | 1.689(7) | 1.697(3) | 1.68(1) | 1.66(2) |
| av (P-O), Å | 1.673(6) | 1.667(3) | 1.66(1) | 1.63(2) |
| av (P-N-P), deg | 131.8(4) | 128.1(2) | 132.8(9) | 131.3(9) |
| av (N-P-N), deg | 101.9(4) | 100.4(1) | 101.7(8) | 99.4(9) |
| range, (P-N-P), deg | 130.9 – 133.0 | 125.0 – 131.0 | 130.0 – 134.9 | 128.9 – 133.0 |
| (N-P-N), deg | 101.8 – 101.9 | 98.8 – 101.3 | 101.2 – 102.0 | 99.0 – 100.0 |
| geometry of nitrogen atoms | planar | planar except N3 ($\Sigma N^\circ = 350.5$) | planar | planar |
| asymmetry parameters | | | | |
| $\Delta C_2$ | 5.6, 2.7, 2.9 | 11.4, 12.5 | 4.5, 4.5, 9.0 | – |
| $\Delta C_s$ | 4.0, 3.9, 0.2 | – | 6.3, 0.0, 6.3 | 5.3, 5.7 |
| reference | this work | this work | 2 | 2 |

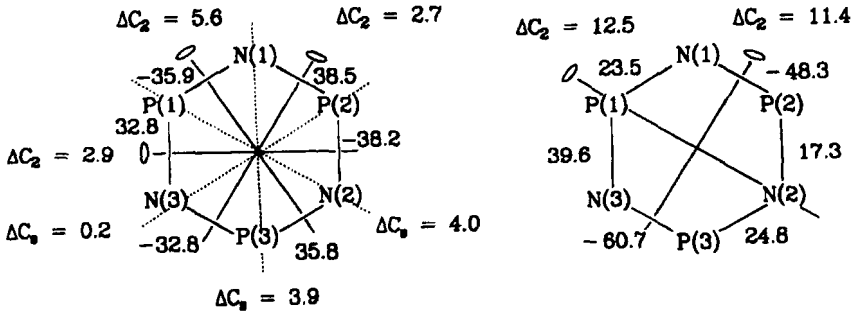



FIGURE 3 $P_3N_3$ ring torsion angles and asymmetry parameters ($\Delta C_2$ and $\Delta C_s$) for *cis*-[EtNP($OC_6H_4Br$-*2*)]$_3$ **1a** and *trans*-[EtNP($OC_6H_3Me_2$-*2,6*)]$_3$ **3**

$$\Delta C_2 = \left[\sum_{i=1}^{m} (\phi_i - \phi'_i)^2/m\right]^{1/2}$$

$$\Delta C_s = \left[\sum_{i=1}^{m} (\phi_i + \phi'_i)^2/m\right]^{1/2}$$

where m = the number of individual comparisons
$\phi_i, \phi_i'$ = symmetry related torsion angles[5]

Both mean plane calculations and torsion angles are used to define the ring conformations of the $P_3N_3$ in cyclophosphazanes **1a** and **1b**. Symmetries displayed by the torsion angles have been used to identify the conformations of six-membered rings in carbocyclic systems[5]. Three intersecting $C_2$ axes and three mirror planes are essential for the chair conformation, while twist conformation requires two $C_2$ axes. However, in the ring systems formed by heteroatoms there may be deviations from the ideal conformations; the degree of departure from ideal 2-fold symmetry ($\Delta C_2$) and mirror planes ($\Delta C_s$) calculated for **1a** and **3** is shown in Fig 3. The six-membered ring in the *cis*-compound **1a** adopts a chair conformation; the four atoms P1, N2, P2, and N3 lie in a plane with P3 and N1 lying above and below the weighted least-squares mean plane at 0.45 and 0.41 Å respectively. On the other hand, in the *trans*-compound **3**, the six-membered ring assumes a twist conformation. The atoms P1, P2, N2, and N3 lie in a plane while N1 and N3 are located above and below this weighted least-squares mean plane at 0.52 and 0.67 Å respectively. The degree of departure from ideal chair conformation in **1a** is less than that observed for the *4*-bromo phenoxy derivative, *cis*-[EtNP($OC_6H_4Br$-*4*)]$_3$. The extent of deviation from an ideal twist conformation in **3** is much higher than that observed for the corresponding *4*-bromo phenoxy derivative, *trans*-[EtNP($OC_6H_4Br$-*4*)]$_3$ in which the $P_3N_3$ ring displays a boat conformation[2]. This difference presumably arises due to the presence of bulky aryloxy substituents in **3**. Despite the pres-

ence of bulky substituents on phenyl rings, the aryloxy groups still prefer an axial orientation. Such an orientation would maximise "negative hyperconjugative" interactions involving nitrogen lone pairs and P-X σ* orbitals. This point is discussed elsewhere[2].

The P-N bond distances in both **1a** and **3** span a narrow range, 1.681(7)–1.695(7) and 1.688(3)–1.716(3) Å respectively. The average P-N bond distance in both **1a** and **3** is ~ 1.69 Å which is close to the average P-N distance in *cis*-[EtNP($OC_6H_4Br$-*4*)]$_3$. A slightly lower average P-N distance has been observed for the *trans*-[EtNP($OC_6H_4Br$-*4*)]$_3$. The mean P-O distance in **1a** [1.673(6) Å] is comparable to the that observed in *cis*-[EtNP($OC_6H_4Br$-*4*)]$_3$ but the average P-O distance for **3** [1.667(3) Å] is longer than that observed in *trans*-[EtNP($OC_6H_4Br$-*4*)]$_3$[2].

The PNP (130.9–133.0°) and NPN (101.8–101.9°) angles for **1a** do not vary much; the variations are less than those observed for **3** and other $\lambda^3$-cyclotriphosphazanes. The variations of NPN (98.8–101.3° ) and PNP (125.0–131.0°) angles are the largest for **3** among $\lambda^3$-cyclotriphosphazanes for which structural data are available (Table II). The average PNP angles are widened and the NPN angles are shortened when compared to the corresponding values for $\lambda^5$-cyclotriphosphazanes of the type [RNP(O)(OR')]$_3$[6]. The geometry around all the nitrogen atoms in **1a** is planar but in **3**, two nitrogen atoms N1 and N2 display planar geometry while the third nitrogen N3 deviates slightly from planarity (ΣN = 350.5°). Accordingly, the longest P-N bond (P1-N3 1.716(3) Å) involves the nitrogen atom N3. The variation in the P-N bond lengths and the deviation of the geometry of one of the nitrogen from planarity can be attributed to the varying degrees of "negative hyperconjugative" interactions between nitrogen lone pairs and P-N σ* orbitals caused by the presence of sterically demanding 2,6-dimethyl phenoxy groups. As noted earlier, a C-N-P-N (or C-N-P-O) torsion angle of 90° would result in maximum "negative hyperconjugation" while any departure from this value would reduce this interaction[2]. Some of the torsion angles involving N3 tend more toward 180° compared to the torsion angles involving N1 or N2.

The molecules in the unit cell are stabilised by *inter* and *intra*molecular hydrogen bonds. In **1a,** three *intra*molecular C-H..O hydrogen bonds are observed between the oxygen atom of an aryloxy group and an *ortho*-hydrogen atom of an adjacent aryloxy group; in addition, a C-H..Br *intra*molecular hydrogen bond[7] is observed between the bromine atom Br(3) of an aryloxy group and a hydrogen atom attached to C(5) of the adjacent NEt group. It may be noted that in the structure of the analogous *4*-bromo phenoxy derivative, *cis*-[EtNP($OC_6H_4Br$-*4*)]$_3$, only one *intra*molecular C-H..O hydrogen bond can be discerned[8]. These hydrogen bonds probably give extra stability for the *cis* chair conformation for **1a**, despite the presence of bulky bromine atom in the *ortho*- position of the aryloxy

group. Only one *inter*molecular C-H..O hydrogen bond is observed in the structure of **3** between a hydrogen atom of one of the *ortho* methyl groups and the oxygen atom of another symmetry related molecule (Table Ib).

## EXPERIMENTAL

All experimental manipulations were performed under an atmosphere of nitrogen using Schlenk techniques[9]. Benzene, dichloromethane, diethyl ether and petrol (b.p. 60–80 °C) were purified by conventional procedures and freshly distilled prior to use[10]. 2-Bromo phenol (Aldrich) and 2-nitro phenol (BDH) were used as purchased. The $^{1}H$, $^{13}C$($Me_4Si$-internal standard) and $^{31}P$(85% $H_3PO_4$-external standard) NMR spectra were recorded on a Bruker AMX 400 or ACF–200 spectrometers. Chemical shifts downfield from the standard were assigned positive values. The chlorocyclotriphosphazane, $(EtNPCl)_3$ was prepared and purified as described previously[11]. The preparation of *trans*-$[EtNP(OC_6H_3Me_2\text{-}2,6)]_3$ is reported earlier[2]. The synthesis of the other (aryloxy)cyclotriphosphazanes are described below.

**Preparation of *cis*-$[EtNP(OC_6H_4Br\text{-}2)]_3$ 1a:** $(EtNPCl)_3$ (5.0 g, 0.0153 mol) in benzene (20 ml) was slowly added to an ice-cold solution of 2-bromo phenol (7.90 g, 0.046 mol) and diazabicyclooctane, DABCO (3.4 g, 0.031 mol) dissolved in benzene (25 ml). Stirring was continued for 2 h. The reaction mixture was heated under reflux for 12 h and cooled under nitrogen atmosphere. The $^{31}P$ NMR spectrum of the reaction mixture showed the presence of *cis* and *trans*-$[EtNP(OC_6H_4Br\text{-}2)]_3$ and impurities arising from the oxidation of $\lambda^3$-cyclotriphosphazanes (signals in the range –10 to 15 ppm). DABCO.HCl was removed by filtration and solvent evaporated from the filtrate. The viscous oily residue was dissolved in petrol-benzene (1/1, v/v) mixture and the solution passed through a silica gel column to remove excess phenol and oxidised products. Solvent was evaporated from the eluent to obtain a colourless oil containing a mixture of *cis* and *trans*-$[EtNP(OC_6H_4Br\text{-}2)]_3$(6.9 g) in 60% yield. Slow crystallisation of the mixture from $CH_2Cl_2$/petrol (9/1, v/v) at 0 °C yields **1a** (1.24 g) in 11% yield. M.p. 153–157 °C. Elemental analysis calc. for $C_{24}H_{27}Br_3N_3O_3P_3$: C 39.02, H 3.66, N 5.70; found C 38.98, H 3.68, N 5.64. $^{1}H$ NMR ($CDCl_3$): δ 1.23 (t, $CH_3$, 9 H, $^{3}J_{HH}$ = 7.2 Hz), 3.70 (br, $CH_2$, 6 H ), 6.90–7.70 (mult, $C_6H_4Br$–2, 12 H). $^{13}C$ NMR ($CDCl_3$): δ 18.2 (s, $CH_3$, 3 C), 47.5 (t, $CH_2$, 3 C, $^{2}J_{PC}$ = 44.0 Hz), 124.2, 124.4, 128.0, 132.6 (carbon nuclei of aryl rings). $^{31}P$ NMR ($CDCl_3$): δ 93.0.

The *trans* isomer of $[EtNP(OC_6H_4Br\text{-}2)]_3$ **1b** could not be isolated in a pure form but was identified by the $^{31}P$ NMR spectrum of the mixture [$\delta_A$ = 124.6, $\delta_X$ = 120.5; $^{2}J_{AX}$ = 8.3 Hz].

**Preparation of *trans*-[EtNP($OC_6H_4NO_2$-*2*)]$_3$ 2b:** The reaction of $(EtNPCl)_3$ with *2*-nitro phenol was carried out as described above to give a *cis-trans* mixture of [EtNP($OC_6H_4NO_2$-2)]$_3$ in 72% yield. Crystallisation of the mixture from diethyl ether gave yellow crystals of *trans*-[EtNP($OC_6H_4NO_2$-*2*)]$_3$ **2b** (6.2 g) in 64% yield. M.p. 99 °C. Elemental analysis calc. for $C_{24}H_{27}N_6O_9P_3$: C 45.28, H 4.24, N 13.21; found C 45.21, H 4.06 , N 13.23. $^1$H NMR ($CDCl_3$): δ 1.24 (t, $CH_3$, 6 H, $^3J_{HH}$ = 7.1 Hz), 1.26 (t, $CH_3$, 3 H, $^3J_{HH}$ = 7.0 Hz), 3.46 (br, $CH_2$ 4 H), 3.63 (br, $CH_2$, 2 H), 7.00–7.80(mult, $C_6H_4NO_2$–2, 12 H). $^{13}$C NMR ($CDCl_3$): δ 17.3 ($CH_3$, s, 2 C), 18.4 ($CH_3$, s, 1C), 45.6 (t, $CH_2$ 1C, $^2J_{PC}$ = 42.9 Hz), 44.8 (dd, $CH_2$, 2 C, $^2J_{PC}$ = 29.1, 40.6 Hz), 122.0, 122.1, 122.2, 122.6, 122.7, 125.3, 125.5, 133.5, 133.9 (carbon nuclei of the aryl ring). $^{31}$P NMR($CDCl_3$): $\delta_A$ = 122.7, $\delta_X$ = 119.3; $J_{AX}$ = 8.8 Hz.

The *cis*-isomer of [EtNP($OC_6H_4NO_2$-*2*)]$_3$ **2a** could not be isolated in a pure state but identified by its $^{31}$P NMR spectrum [$\delta_P$ = 97.4].

### X-ray Crystal Structures of *cis*-[EtNP($OC_6H_4$Br-*2*)]$_3$ 1a and *trans*-[EtNP($OC_6H_3Me_2$-*2,6*)]$_3$ 3

Colourless rectangular plates of **1a** and **3** (recrystallized from petrol at 0 °C) were encapsulated in a Lindemann capillary as the crystals were moisture- and air-sensitive. Intensity data were collected on an Enraf-Nonius CAD–4 diffractometer. A total of 25 reflections in the range $24 \leq 2\theta \leq 32$ were used to derive the lattice parameters. The data were corrected for Lorentz and polarisation effects. Absorption correction was applied for **1a** using DIFABS[12] program. The structures were solved by Direct Methods using SHELXS–86[13]. Full matrix least-squares refinement was carried out on $|F_0|^2$ using SHELXL–93[14]. In **1a**, the carbon atoms C(3) and C(4) bonded to N(2) showed high thermal vibrations as well as some residual electron density near them. A positional disorder of the ethyl carbon atoms attached to N(2) was suspected and refinement was carried out by assigning equal occupancy factors for the two positions of C(3) and C(4). This "statistical disorder" is a necessary consequence of a "pseudo mirror plane" passing through N(2), P(1), and O(1). The carbon atom C(6) in **3** showed a positional disorder and taking into account the thermal parameters, site occupancy factors of 0.6 and 0.4 were assigned to the two positions of this carbon atom during refinement. All the non-hydrogen atoms(except disordered atoms) were refined anisotropically. The hydrogen atoms were placed on the respective atoms (except those on C(3) and C(4) in **1a** and C(5) and C(6) in **3**) in their calculated positions and were allowed to ride on the attached atoms during refinement. The position of the hydrogen atom H(5A) involved in C-H...Br hydrogen bonding was ensured by locating it from a difference Fourier map. The details pertaining to data collection, structure solution and refinement are summarised in Table III. The final fractional atomic coordinates with the associated equivalent isotropic temperature factors are listed in Table IV & V.

TABLE III Crystallographic Data for **1a** and **3**

| | *1a* | *3* |
|---|---|---|
| chemical formula | $C_{24}H_{27}Br_3N_3O_3P_3$ | $C_{30}H_{42}N_3O_3P_3$ |
| formula weight | 738.13 | 585.58 |
| crystal system | triclinic | tetragonal |
| crystal size, mm | 0.25 × 0.20 × 0.15 | 0.55 × 0.45 × 0.40 |
| space group | $P\bar{1}$ | $I4_1/a$ |
| a, Å | 10.480(5) | 34.072(6) |
| b, Å | 11.262(5) | |
| c, Å | 15.10(2) | 11.208(3) |
| α, deg | 78.85(6) | |
| β, deg | 73.55(5) | |
| γ, deg | 62.96(3) | |
| V, Å$^3$ | 1518(2) | 13011(5) |
| $\rho_{calcd}$, g cm$^{-3}$ | 1.615 | 1.196 |
| Z | 2 | 16 |
| temperature, K | 294 | 294 |
| λ (Mo-Kα), Å | 0.7107 | 0.7107 |
| μ (Mo-Kα), cm$^{-1}$ | 41.74 | 2.16 |
| transmission coefft. | 0.898–1.161 | |
| scan method | ω–2θ | ω |
| 2θ range, deg | $2 \le 2\theta \le 50$ | $2 \le 2\theta \le 50$ |
| index range | $-11 \le h \le 12$ | $-40 \le h \le 40$ |
| | $-12 \le k \le 13$ | $0 \le k \le 40$ |
| | $0 \le l \le 17$ | $0 \le l \le 13$ |
| reflections, unique | 5350 | 5729 |
| with [I >2σ(I)] | 2961 | 3547 |
| parameters refined | 325 | 359 |
| F(000) | 732 | 4992 |
| residual (negative) peak, e Å$^{-3}$ | 0.636 (–0.973) | 0.451 (–0.203) |
| final $R_1$[a] | 0.0739 | 0.0552 |
| $wR_2$[b] | 0.1680 | 0.1294 |
| S on F[2c] | 1.063 | 1.057 |

[a] $R_1 = \Sigma \, ||F_0|-|F_c||/\Sigma|F_0|$. [b] $wR_2 = [\Sigma[w(F_0^2-F_c^2)^2] / \Sigma[w(F_0^2)^2]]^{1/2}$.
[c] $S = [\Sigma[w(F_0^2-F_c^2)^2]/(n-p)]^{1/2}$

Lists of structure factors, complete bond lengths and angles and thermal parameters have been deposited with the Cambridge Crystallographic Centre, University Chemical Laboratory, Lensfield Road, Cambridge, U. K.

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TABLE IV Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **1a**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

| *ATOM* | *x* | *y* | *z* | *U(eq)* |
|---|---|---|---|---|
| P(1) | −1324(3) | 11381(2) | 7083(2) | 63(1) |
| P(2) | 261(3) | 13219(2) | 6339(2) | 70(1) |
| P(3) | 2020(3) | 10175(2) | 6235(2) | 66(1) |
| N(1) | −1182(7) | 12817(7) | 6624(5) | 65(2) |
| N(2) | 1652(8) | 11803(7) | 5903(5) | 66(2) |
| N(3) | 314(8) | 10226(7) | 6582(5) | 63(2) |
| O(1) | −1160(6) | 11434(6) | 8138(4) | 62(1) |
| O(2) | 757(7) | 13019(6) | 7342(4) | 70(2) |
| O(3) | 2307(6) | 9940(6) | 7304(4) | 61(1) |
| C(1) | −2648(11) | 13988(10) | 6624(8) | 91(3) |
| C(2) | −3254(16) | 14070(15) | 5819(10) | 142(6) |
| C(3) | 2600(21) | 12003(21) | 4945(14) | 70(5) |
| C(3') | 3014(29) | 12020(33) | 5304(22) | 129(10) |
| C(4) | 3826(22) | 12295(21) | 5025(15) | 82(6) |
| C(4') | 2565(48) | 12441(46) | 4427(29) | 187(17) |
| C(5) | 379(12) | 8822(11) | 6702(8) | 95(3) |
| C(6) | 100(22) | 8526(16) | 5906(10) | 153(7) |
| C(11) | −1455(11) | 10574(9) | 8869(6) | 65(2) |
| C(12) | −301(12) | 9411(10) | 9086(6) | 73(3) |
| C(13) | −552(16) | 8566(11) | 9850(8) | 92(3) |
| C(14) | −1932(19) | 8864(14) | 10376(8) | 110(4) |
| C(15) | −3068(16) | 9993(14) | 10156(8) | 102(4) |
| C(16) | −2852(12) | 10886(10) | 9404(7) | 81(3) |
| C(21) | 54(12) | 14002(9) | 7936(7) | 70(2) |
| C(22) | −1287(13) | 14171(9) | 8529(7) | 83(3) |
| C(23) | −1956(14) | 15122(12) | 9184(7) | 97(4) |
| C(24) | −1314(19) | 15912(12) | 9232(11) | 116(5) |
| C(25) | 20(18) | 15738(12) | 8635(10) | 108(4) |
| C(26) | 709(12) | 14790(10) | 7994(8) | 85(3) |
| C(31) | 3698(9) | 9556(10) | 7421(6) | 66(2) |
| C(32) | 4232(12) | 10505(11) | 7318(7) | 82(3) |
| C(33) | 5605(14) | 10119(16) | 7485(8) | 101(4) |
| C(34) | 6412(14) | 8842(20) | 7764(10) | 121(5) |
| C(35) | 5895(12) | 7896(13) | 7858(9) | 105(4) |
| C(36) | 4541(12) | 8257(10) | 7690(8) | 83(3) |
| Br(1) | −4420(2) | 12482(2) | 9131(1) | 127(1) |
| Br(2) | 2548(2) | 14568(2) | 7228(1) | 133(1) |
| Br(3) | 3823(2) | 6943(1) | 7852(1) | 115(1) |

TABLE V Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters ($Å^2$ x$10^3$) for **3**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

| *ATOM* | *x* | *y* | *z* | *U(eq)* |
|---|---|---|---|---|
| P(1) | 8585(1) | 3847(1) | 405(1) | 52(1) |
| P(2) | 7934(1) | 3414(1) | -985(1) | 57(1) |
| P(3) | 8785(1) | 3145(1) | -1120(1) | 58(1) |
| N(1) | 8189(1) | 3813(1) | -497(2) | 54(1) |
| N(2) | 8302(1) | 3118(1) | -1451(2) | 57(1) |
| N(3) | 8772(1) | 3385(1) | 197(2) | 58(1) |
| O(1) | 8437(1) | 3767(1) | 1805(2) | 54(1) |
| O(2) | 7818(1) | 3243(1) | 351(2) | 61(1) |
| O(3) | 8942(1) | 3516(1) | -1976(2) | 64(1) |
| C(1) | 8064(1) | 4194(1) | -1027(4) | 66(1) |
| C(2) | 7740(1) | 4390(1) | -353(4) | 86(1) |
| C(3) | 8203(1) | 2841(1) | -2443(3) | 69(1) |
| C(4) | 8085(2) | 2441(1) | -2033(4) | 101(2) |
| C(5) | 9134(2) | 3308(2) | 977(4) | 105(2) |
| C(6) | 9048(3) | 2965(3) | 1773(10) | 125(4) |
| C(6') | 9221(6) | 2907(4) | 1318(18) | 139(6) |
| C(11) | 8336(1) | 4083(1) | 2544(3) | 54(1) |
| C(12) | 7951(1) | 4097(1) | 2961(3) | 59(1) |
| C(13) | 7849(1) | 4399(1) | 3725(4) | 79(1) |
| C(14) | 8116(2) | 4675(2) | 4071(4) | 98(2) |
| C(15) | 8494(2) | 4648(1) | 3678(4) | 87(1) |
| C(16) | 8620(1) | 4352(1) | 2913(3) | 66(1) |
| C(17) | 7661(1) | 3788(1) | 2621(4) | 80(1) |
| C(18) | 9043(1) | 4322(1) | 2570(4) | 86(1) |
| C(21) | 7552(1) | 2934(1) | 453(3) | 61(1) |
| C(22) | 7161(1) | 2990(1) | 184(4) | 74(1) |
| C(23) | 6911(2) | 2671(2) | 309(4) | 100(2) |
| C(24) | 7050(2) | 2318(2) | 714(5) | 113(2) |
| C(25) | 7439(2) | 2275(1) | 1027(5) | 102(2) |
| C(26) | 7699(1) | 2583(1) | 893(3) | 72(1) |
| C(27) | 6997(1) | 3383(2) | -173(5) | 104(2) |
| C(28) | 8119(2) | 2543(1) | 1250(4) | 95(2) |
| C(31) | 9112(1) | 3443(1) | -3081(4) | 65(1) |
| C(32) | 8896(1) | 3530(1) | -4112(4) | 75(1) |
| C(33) | 9080(2) | 3479(1) | -5200(4) | 99(2) |
| C(34) | 9459(2) | 3354(2) | -5278(6) | 117(2) |
| C(35) | 9667(2) | 3281(2) | -4267(6) | 109(2) |
| C(36) | 9502(1) | 3320(1) | -3131(4) | 82(1) |
| C(37) | 8487(1) | 3691(1) | -4051(4) | 91(1) |
| C(38) | 9736(1) | 3250(2) | -2002(5) | 110(2) |

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