# Synthesis, Spectral Characterisation and Single-crystal Structure of a Bicyclic Tetraphosphapentazane Tetraoxide, $N_5P_4Et_5O_4(OC_6H_3Me_2\text{-}2,6)_2$†

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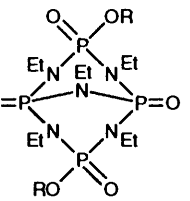
Reaction of the bicyclic phosphazane $N_5P_4Et_5Cl_2$ with 2,6-dimethylphenol and subsequent oxidation of the product by aqueous hydrogen peroxide yields $N_5P_4Et_5O_4(OC_6H_3Me_2\text{-}2,6)_2$ in 85% yield. Its structure has been established by NMR spectroscopy and single-crystal X-ray diffraction. The compound crystallises in the monoclinic space group $C2/c$ with $a = 21.245(5)$, $b = 10.879(2)$, $c = 16.450(6)$ Å, $\beta = 123.94(2)°$, $Z = 4$, $R = 0.066$. The structural features are compared with those of bicyclic $\lambda^5$-phosphazenes of type $N_5P_4R^3(NR^1R^2)_5(NHR^3)$ ($R^1,R^3$ = Me or Et, $R^2$ = H or Me). The observed conformation of the $N_3P_3$ rings in the present compound is mainly dictated by the maximisation of the stabilising influence of 'negative hyperconjugative interactions' between the nitrogen lone pairs and the adjacent P–X $\sigma^*$ orbitals.

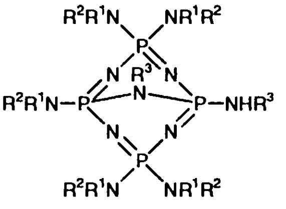
Bulloch and Keat,[1] in an effort to prepare the still unknown cyclodiphosphazane $(MeNPCl)_2$ from the reaction of $NMe(PCl_2)_2$ and methylamine, observed the formation of the bicyclic tetraphosphapentazane $N_5P_4Me_5Cl_2$ **1** along with other products. Compound **1** was characterised by phosphorus-31 NMR and mass spectral data. Almost simultaneously but independent of this work, Wannagat and Autzen[2] observed the formation of **1** in the reaction of $NMe(PCl_2)_2$ with $SiMe_2(NHMe)_2$. Subsequently, Zeiss and Endrass[3] reported the preparation and isolation of the bicyclic tetraphosphapentazane $N_5P_4Me_5Br_2$ from the reaction of $(MeNPBr)_3$ with $NMe(SiMe_3)_2$. Later, Keat and co-workers[4] prepared the analogous *N*-ethyl compound $N_5P_4Et_5Cl_2$ **2** from the direct reaction of ethylamine hydrochloride and $PCl_3$. Murray and Woodward[5] have reported the preparation and crystal structure of a bicyclic $\lambda^5$-phosphazane, $N_5P_4Ph_5Cl_2O_4$, but no details have been published.

Bicyclic tetraphosphapentazanes can exist in a series of conformers[4,6] which are analogous to those of bicyclo[3.3.1]-nonanes in carbocyclic chemistry. The preferred molecular shapes and ring conformations of the former type of compounds have not been clearly established as no crystallographic data are available. In this paper, we report the synthesis of a bicyclic $\lambda^5$-tetraphosphapentazane $N_5P_4Et_5O_4(OC_6H_3Me_2\text{-}2,6)_2$ **3** and its NMR and IR spectroscopic data. The solid-state structure of **3** has been determined by single-crystal X-ray diffraction. The structural features are compared with those of the analogous bicyclic $\lambda^5$-phosphazenes of the type **I** derived from cyclotetraphosphazenes.[7]



R = $C_6H_3Me_2$-2,6

**3**



| | R¹ | R² | R³ |
|---|---|---|---|
| **a** | Me | Me | Et |
| **b** | Me | H | Me |
| **c** | Me | Me | Me |
| **d** | Et | H | Et |

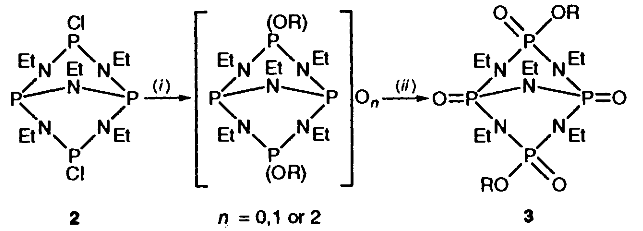
**I**

## Results and Discussion

*Synthesis and NMR Spectra.*—The reaction of phosphorus trichloride with ethylamine hydrochloride in 1:1 molar ratio following the procedure of Keat and co-workers[4] yields the cyclotriphosphazane $(EtNPCl)_3$ as the major product along with small quantities (< 5%) of the bicyclic tetraphosphapentazane $N_5P_4Et_5Cl_2$ **2**. However, substantial quantities (≈45%) of **2** can be obtained by changing the $PCl_3{:}NH_2Et{\cdot}HCl$ ratio to 5:4. The chloro bicyclic phosphazane is highly moisture- and air-sensitive.

Treatment of compound **2** with 2,6-dimethylphenol in the presence of 1,4-diazabicyclo[2.2.2]octane (dabco) as HCl acceptor yields a highly viscous oil. This oil gives a complex $^{31}P$ NMR spectrum. Most of the peaks could be assigned to a mixture of bicyclic tetraphosphapentazane and its mono- and di-oxides, $N_5P_4Et_5O_n(OC_6H_3Me_2\text{-}2,6)_2$ ($n$ = 0, 1 or 2):[4] $\delta_P$ +2 to −10 (P=O), +44 and +62 ($\lambda^3$-$_P$ centres at the bridge) and +95 to +155 ($\lambda^3$-$_P$ terminal). Attempts to separate these components of the mixture by fractional crystallisation or column chromatography were unsuccessful. However, on treatment with aqueous $H_2O_2$ the pure tetraoxide $N_5P_4Et_5O_4(OC_6H_3Me_2\text{-}2,6)_2$ **3** is readily obtained as the only product in 85% yield (Scheme 1).

Compound **3** has been characterised by elemental analysis,



**2** $n$ = 0,1 or 2 **3**

**Scheme 1** (*i*) ROH, dabco; (*ii*) $H_2O_2$

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† *Supplementary data available:* see Instruction to Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

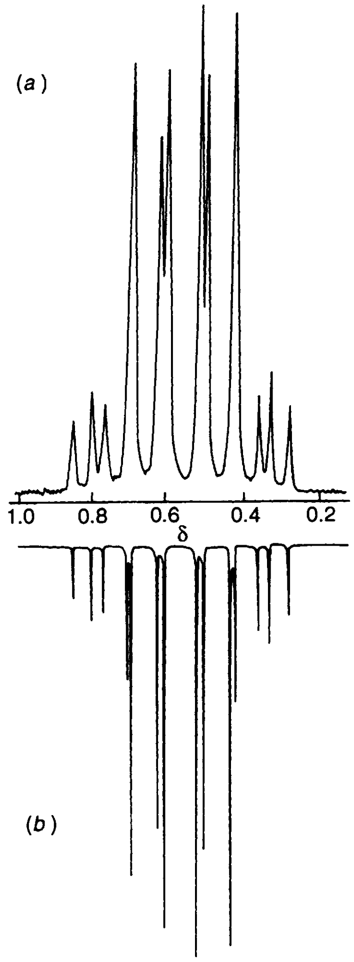

**Fig. 1** The experimental (*a*) and simulated (*b*) $^{31}P$ NMR spectra (162 MHz, $CDCl_3$) of compound **3**

IR, $^{1}H$, $^{13}C$ and $^{31}P$ NMR spectroscopy. The IR spectrum shows two very strong absorptions at 1269 and 1326 cm$^{-1}$ assignable to P=O and O–C(aryl) stretching vibrations respectively. The $^{1}H$ NMR spectrum shows two sets of resonances for the NEt protons. The methyl protons resonate at δ 1.37 and 1.47 ($^{3}J_{HH}$ = 7.1 Hz) in 4 : 1 ratio. The $NCH_2$ protons also appear as two sets of signals at δ 3.57 and 3.78; however the various coupling constants are unresolved even when the spectrum is recorded at 400 MHz. The methyl protons attached to the phenyl rings resonate at δ 2.49 as a singlet. The $^{13}C$ NMR spectrum shows a similar non-equivalence of both $NCH_2$ and $CH_3$ carbon nuclei. Resonances due to four methyl groups ($NCH_2CH_3$) appear as a singlet at δ 16.3 while that of the methyl group of the bridging NEt group appears as a singlet at δ 17.4. Similarly the methylene carbons appear at δ 41.6 and 40.8 respectively; however, two-bond P–C coupling is not observed. The carbon atoms of the 2,6-methyl groups (aryl) resonate at δ 18.3.

The $^{31}P$ NMR spectrum recorded at 81 MHz shows only a single broad resonance at δ 0.55. However, at 162 MHz an $A_2B_2$ pattern ($\delta_A$ = 0.42, $\delta_B$ = 0.69, $J_{AB}$ = 18.3 Hz) was observed. The observed and computer-simulated spectra are shown in Fig. 1. The closeness in the chemical shift values for the two kinds of phosphorus nuclei in this molecule is surprising because of the entirely different chemical environments around them. The small difference would explain the complex $^{1}H$ NMR spectrum in the $NCH_2$ region owing to 'virtual coupling'.[8]

*Molecular Structure of Compound* **3**.—In order to ascertain the molecular geometry, the ring conformations and the disposition of exocyclic phosphorus substituents, the structure of compound **3** has been determined by single-crystal X-ray diffraction. A perspective view of the molecule with the atom labelling scheme is shown in Fig. 2. Selected structural parameters are listed in Table 1.

The molecule is made up of two $P_3N_3$ rings fused by a common PNP fragment. Surprisingly, the six-membered rings do not display any of the commonly observed ring con-

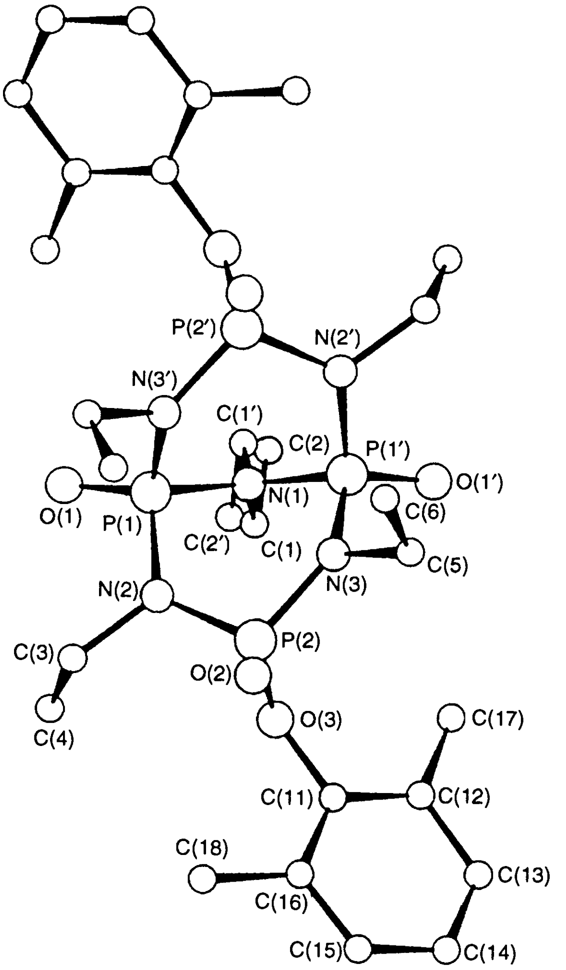

**Fig. 2** Molecular structure of compound **3** with the atom labelling scheme

**Table 1** Selected bond distances (Å) and angles (°) involving non-hydrogen atoms for compound **3**

| | | | |
|---|---|---|---|
| N(1)–P(1) | 1.647(3) | P(1)–N(2) | 1.665(4) |
| P(1′)–N(3) | 1.660(4) | N(2)–P(2) | 1.664(3) |
| P(2)–N(3) | 1.657(5) | P(1)–O(1) | 1.462(4) |
| P(2)–O(2) | 1.463(4) | P(2)–O(3) | 1.595(4) |
| N(1)–C(1) | 1.57(1) | N(2)–C(3) | 1.516(7) |
| N(3)–C(5) | 1.492(5) | O(3)–C(11) | 1.413(9) |
| P(1′)–N(1)–C(1) | 118.4(4) | P(1)–N(1)–C(1) | 118.8(4) |
| P(1)–N(1)–P(1′) | 118.2(1) | N(1)–P(1)–O(1) | 116.1(2) |
| N(1)–P(1)–N(2) | 102.5(1) | N(2)–P(1)–O(1) | 115.2(2) |
| N(1)–P(1′)–N(3) | 104.3(2) | P(1)–N(2)–C(3) | 113.7(2) |
| P(1)–N(2)–P(2) | 130.4(2) | P(2)–N(2)–C(3) | 115.6(3) |
| N(2)–P(2)–O(3) | 110.0(2) | N(2)–P(2)–O(2) | 110.8(2) |
| N(2)–P(2)–N(3) | 104.8(2) | O(2)–P(2)–O(3) | 112.8(2) |
| N(3)–P(2)–O(3) | 100.4(2) | N(3)–P(2)–O(2) | 117.3(2) |
| P(1′)–N(3)–P(2) | 123.6(2) | P(2)–N(3)–C(5) | 116.7(3) |
| P(1′)–N(3)–C(5) | 119.5(3) | P(2)–O(3)–C(11) | 124.2(3) |
| N(1)–C(1)–C(2) | 107(1) | N(2)–C(3)–C(4) | 113.4(5) |
| N(3)–C(5)–C(6) | 113.7(4) | | |

**Table 2** Comparison of the structures of bicyclic phosphazane 3 and phosphazenes I

| Structural feature | 3 | Bicyclic phosphazenes I<br>a | <br>b | <br>c |
|---|---|---|---|---|
| $N_3P_3$ ring conformation | Irregular (see text) | Sofa | Sofa | Sofa |
| Dihedral angle/° | 125.0 | 121.2 | 122.4 | 115.0 |
| P–N length at the bridge/Å | 1.647 | 1.74 | 1.716 | 1.716 |
| Geometry of bridging nitrogen | Trigonal planar | Pyramidal | Pyramidal | Pyramidal |
| $\Sigma\hat{N}_{(bridge)}$/° | 355.4 | 336.8 | 337.5 | 336.8 |
| Ref. | This work | 12 | 11 | 10 |

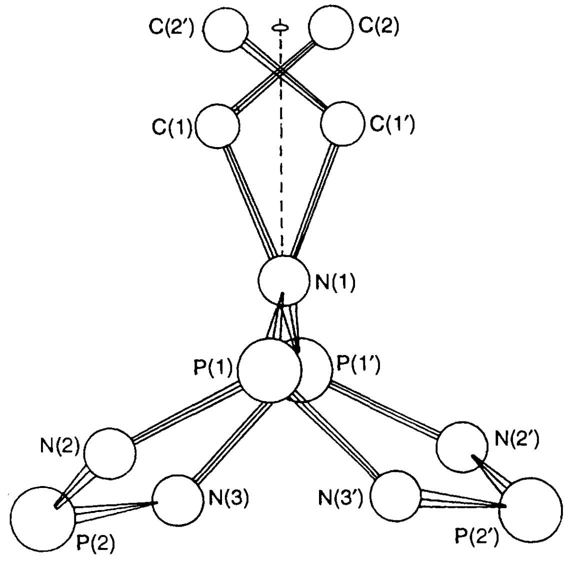

**Fig. 3** Structure of the bicyclic core of compound 3 showing the ring conformation and disorder of the ethyl group at the bridging nitrogen

formations for carbocyclic systems,[9] *viz* chair, boat, half-chair, twist-boat and sofa. The atoms N(2), P(2), N(3) and P(1') which form part of a six-membered ring lie in a plane; the remaining two atoms P(1) and N(1) are located above this plane at 0.647 and 1.078 Å respectively. It is interesting to compare the ring conformations displayed by this compound with those of a series of (amino)bicyclic tetraphosphapentazenes of the type **I** discovered in our laboratory several years ago,[7] wherein the six-membered rings display a sofa conformation.[10–13] The similarities and the differences between these two types of compounds are summarised in Table 2. The dihedral angle of 125° between the best least-squares planes of the two six-membered rings in **3** is larger than that observed for bicyclic $\lambda^5$-phosphazenes, $N_5P_4R^3(NR^1R^2)_5(NHR^3)$ **I**. The two phenoxy groups adopt pseudo-axial positions on their respective phosphorus atoms; the P=O bonds are in the equatorial positions.

The molecule would have a two-fold axis passing through the bridging nitrogen N(1) but for the ethyl group attached to it (Fig. 3). However, in the crystal, there is a crystallographic two-fold axis passing through the bridging nitrogen atom N(1) as a result of a 'rotational disorder' which stems from two positions for the carbon atoms C(1) and C(2) with equal occupancy factors. In addition, the thermal parameters of C(2) are large indicating that this ethyl group is undergoing a large thermal motion. However, the main focus of the study, the central tetraphosphapentazane ring, appears well behaved.

The P–N bond lengths in the molecule vary over a small range (1.647–1.665 Å) and are much shorter than the accepted value of 1.77–1.80 Å for a P–N single bond,[10–12] indicating partial double-bond character (see below). In particular, the two P–N bonds (1.647 Å) at the bridging nitrogen atom N(1) are significantly shorter than the remainder (1.657–1.665 Å). The average P–N distance of 1.659 Å in **3** is comparable with the value found for the $\lambda^5$-cyclotriphosphazane $N_3P_3Me_3O_3(OC_6H_4Me\text{-}4)_3$ [1.659(2) Å].[14] However this value is much shorter than the average value observed for the cyclotriphosphazane *cis*-$[EtNP(OC_6H_4Br\text{-}4)]_3$ (1.69 Å).[15] This observation is consistent with the values obtained for the $\lambda^3$- and $\lambda^5$-cyclodiphosphazanes, $N_2P_2Bu^t{}_2Cl_2$ [1.689(4) Å][16] and $N_2P_2Bu^t{}_2Cl_2O_2$ [1.661(5) Å].[17] Like the cyclic P–N bonds, the P–O bonds are also shortened to a considerable extent [1.595(4) Å]. The P=O bonds attached to two different kinds of phosphorus atoms have nearly same lengths [1.462(4) and 1.463(4) Å].

The geometry around the bridging nitrogen N(1) deviates only slightly from planarity ($\Sigma\hat{N}$ = 355.4°), in contrast to the considerable pyramidalisation ($\Sigma\hat{N}$ = 335°) around the bridging nitrogen atom in bicyclic $\lambda^5$-phosphazenes of the type **I**.[10–13] This difference is reflected in the short P–N distances at the bridging nitrogen [1.647(3) Å] in **3** compared to the longer P–N distances at the bridging nitrogen atoms of **I** (1.71–1.76 Å). The P–N distances in the latter are close to the accepted value for a P–N single bond.[10] The geometry around the other nitrogen atoms in the molecule is strictly planar ($\Sigma\hat{N}$ = 359.8°). The P–N–P angle at the bridging nitrogen in **3** is smaller [118.2(1)°] than the other P–N–P angles.

*Electronic Origin of the Ring Conformations and the* P–N *Bond Lengths*.—Shaw and co-workers[18] have attributed the electronic origin of the observed conformations of phosphazenylcyclophosphazenes of the type $N_3P_3R_3(N{=}PPh)_3$ and aminocyclophosphazenes of the type $N_3P_3Cl_{6-n}(NMe_2)_n$ to an interaction between the nitrogen lone pair and the adjacent P–X σ* orbitals following the postulation of a similar kind of stabilising interaction in phosphoric acid and phosphate esters by Lehn and Wipff.[19] This interaction has been recently[20] termed 'negative hyperconjugation' and provides an alternative basis to conventional theoretical models involving d orbitals to explain the bonding of main group elements.[21] It would appear that the electronic origin of the structural differences between the two types of bicyclic $N_5P_4$ systems represented by **3** and **I** lies in the maximisation of negative hyperconjugative interactions between the nitrogen lone pairs and the adjacent P–X σ* (X = N or O) orbitals. These negative hyperconjugative interactions will be maximal in **3** only if the nitrogen lone pairs are parallel to the P–O bonds (or P=O bonds). However, such a relationship is not possible in any of the usually observed ring conformations of the six-membered rings.[9] Hence the molecule twists around one of the ring P–N bonds and in the resulting conformation the nitrogen lone pairs have an orthogonal relationship with the P=O bonds and a parallel disposition with the P–O bonds. From the X-ray structural data for **3** and $\lambda^5$-cyclotriphosphazanes[14,22,23] of the type $[RNP(O)X]_3$, it is evident that the nitrogen lone pair prefers a parallel orientation with a P–X bond rather than with a P=X bond. This preference implies that negative hyperconjugative interactions are more effective with P–X σ* orbitals than P=X σ* orbitals. This preference is in fact reflected in the pyramidal geometry of the bridging nitrogen atom of the bicyclic phosphazenes **I** (see Table 2); if the nitrogen atom in **I** were to adopt a trigonal-planar geometry, its lone pair would be oriented parallel to the

**Table 3** Fractional atomic coordinates for compound **3**

| Atom | *X*/*a* | *Y*/*b* | *Z*/*c* |
|---|---|---|---|
| N(1) | 0.5000 | −0.1725(5) | 0.2500 |
| P(1) | 0.5081(1) | −0.0947(1) | 0.3413(1) |
| N(2) | 0.4431(2) | 0.0151(3) | 0.2835(2) |
| P(2) | 0.3729(1) | 0.0289(1) | 0.1659(1) |
| N(3) | 0.4078(2) | −0.0268(3) | 0.1051(2) |
| O(1) | 0.5024(2) | −0.1664(3) | 0.4121(2) |
| O(2) | 0.3439(2) | 0.1549(3) | 0.1435(2) |
| O(3) | 0.3085(2) | −0.0702(3) | 0.1380(2) |
| C(1)* | 0.5323(6) | −0.3073(9) | 0.2694(8) |
| C(2)* | 0.4685(10) | −0.3885(11) | 0.2117(11) |
| C(3) | 0.4447(3) | 0.1109(5) | 0.3516(3) |
| C(4) | 0.4879(3) | −0.2232(5) | 0.3607(5) |
| C(5) | 0.3577(3) | −0.0204(5) | −0.0040(3) |
| C(6) | 0.3168(4) | −0.1389(7) | −0.0515(4) |
| C(11) | 0.2457(3) | −0.0489(4) | 0.1442(4) |
| C(12) | 0.2476(3) | −0.1068(5) | 0.2208(4) |
| C(13) | 0.1839(4) | −0.0899(6) | 0.2247(5) |
| C(14) | 0.1231(4) | −0.0224(6) | 0.1547(7) |
| C(15) | 0.1224(3) | 0.0287(6) | 0.0790(6) |
| C(16) | 0.1840(3) | 0.0162(5) | 0.0711(4) |
| C(17) | 0.3108(4) | −0.1850(6) | 0.2920(4) |
| C(18) | 0.1802(3) | 0.0675(7) | −0.0160(5) |

* Disordered atom, site occupancy factor = 0.5.

phosphazenic formal P=N double bond, unlike in the case of **3** where the lone pair on the bridging nitrogen atom is oriented parallel to a formal P–N single bond.

The stabilising influence of negative hyperconjugative interactions introduces multiple bonding in the P–N bonds. The average P–N distance of 1.659 Å in **3** is consistent with this reasoning. The shortest P–N distance of 1.647(3) Å at the bridging nitrogen is due to the effective participation of the lone pair on N(1) in negative hyperconjugation. On the other hand, the longer P–N distances at the bridging nitrogen in bicyclic phosphazenes **I** (see Table 2) can be attributed to the inability of the nitrogen lone pair to take part in negative hyperconjugation.

The results reported here provide convincing evidence for 'negative hyperconjugation' as a dominant feature of multiple bonding involving phosphorus and nitrogen. Quantitative theoretical calculations on the electronic structures of this class of molecules represented by **3** and **I** or appropriately modelled systems would shed further light on the nature of the P–N bond.[24]

## Experimental

*Apparatus and Chemicals*.—All manipulations were carried out under a nitrogen atmosphere using standard vacuum-line or Schlenk-tube techniques.[25] The bicyclic phosphazane $N_5P_4Et_5Cl_2$ was prepared and purified as described previously.[4] Ethylamine hydrochloride (Fluka), dabco (E. Merck), $PCl_3$ (Fluka) and 2,6-dimethylphenol were used as supplied. Light petroleum (b.p. 60–80 °C), chloroform, tetrahydrofuran, benzene and 1,1,2,2-tetrachloroethane were purified by conventional procedures.

The $^1H$, $^{13}C$ and $^{31}P$ NMR spectra were recorded on a Bruker AMX-400 spectrometer operating at 400.1, 100.6 and 162 MHz respectively. The $^1H$ and $^{13}C$ chemical shifts were measured with $SiMe_4$ as the internal standard, the $^{31}P$ chemical shifts with external 85% $H_3PO_4$. Chemical shifts downfield from the standard are assigned positive δ values. The infrared spectrum was recorded on a Hitachi Shimadzu spectrometer. Microanalysis was carried out on a Hereaus CHN-O-Rapid elemental analyser.

*Preparation of* $N_5P_4Et_5O_4(OC_6H_3Me_2\text{-}2,6)_2$ **3**.—A benzene solution (100 $cm^3$) of 2,6-dimethylphenol (20 mmol) and dabco (11 mmol) was added dropwise over 2 h to a stirred solution of $N_5P_4Et_5Cl_2$ (10 mmol) in benzene (50 $cm^3$) at 25 °C. The mixture was stirred for 8 h, heated under reflux for 2 h then cooled. The precipitated diazabicyclooctane hydrochloride was filtered off and solvent evaporated from the filtrate *in vacuo* to obtain a viscous oil. A large excess of 20% $H_2O_2$ solution (50 $cm^3$) was added dropwise to a vigorously stirred solution of the oil in tetrahydrofuran (thf) (50 $cm^3$) at 0 °C. The reaction mixture was brought to room temperature over 3 h then stirred for 2 h. Removal of thf and water *in vacuo* yielded a waxy solid, which was dissolved in $CHCl_3$ (100 $cm^3$). The solution was dried over anhydrous $Na_2SO_4$ and filtered. The filtrate was concentrated to ≈25 $cm^3$ and poured into light petroleum (200 $cm^3$) to precipitate $N_5P_4Et_5O_4(OC_6H_3Me_2\text{-}2,6)_2$ **3** in 85% yield (based on $N_5P_4Et_5Cl_2$).

The product was recrystallised from toluene–light petroleum (1:1), m.p. 183 °C (Found: C, 48.4; H, 6.7; N, 10.8. $C_{26}H_{43}N_5O_6P_4$ requires C, 49.8; H, 7.1; N, 10.4%). IR (Nujol): 1470s, 1380s, 1365w, 1326s, 1269vs, 1169m, 1152s, 1092s, 1071s, 1038s, 993s, 966s, 942s, 912vs, 777s, 711w, 681w and 657m $cm^{-1}$. NMR ($CDCl_3$): $^1H$, δ 1.37 (t, 12 H, $CH_3$, $^3J_{HH}$ = 7.1), 1.47 (t, 3 H, $CH_3$, $^3J_{HH}$ = 7.1), 2.49 (s, 12 H, $CH_3$), 3.57 (br, complex m, 2 H, $CH_2$), 3.78 (br, complex m, 8 H, $CH_2$), and 6.97–7.05 (m, 6 H, aryl); $^{13}C$, δ 16.26 (s, 4 C, $CH_3$), 17.36 (s, 1 C, $CH_3$), 18.30 (s, 4 C, $CH_3$), 40.84 (s, 1 C, $CH_2$), 41.63 (s, 4 C, $CH_2$), 125.55, 129.68, 130.28 and 148.60 (aromatic); $^{31}P$, $A_2B_2$ pattern, $\delta_A$ =0.42, $\delta_B$ = 0.69, $J_{AB}$ = 18.3 Hz.

*Crystallography*.—Colourless crystals of compound **3** were obtained from toluene–light petroleum solution.

*Crystal data*. $C_{26}H_{43}N_5O_6P_4$, $M$ = 645.5, monoclinic, space group *C*2/*c*, crystal size 0.2 × 0.15 × 0.15 mm, $a$ = 21.245(5), $b$ = 10.879(2), $c$ = 16.450(6) Å, β = 123.94(2)°, $U$ = 3154(2) $Å^3$ (derived and refined by using 25 randomly selected well centred reflections in the range $40 < 2\theta < 80°$); $Z$ = 4, $D_c$ = 1.359 g $cm^{-3}$, $F(000)$ = 1368, μ(Cu-Kα) = 26.3 $cm^{-1}$, $T$ = 294 K.

*Data collection and processing*. Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer using Cu-Kα radiation (λ = 1.5418 Å) and a ω–2θ scan mode was employed; octants collected $+h$, $+k$, $\pm l$, 2θ range 2–120°, no crystal or intensity decay. Of 2964 unique reflections, 1878 [$I > 3\sigma(I)$] were considered observed. The data were corrected for Lorentz, polarisation, absorption and extinction[26] effects.

*Structure solution and refinement*. Intensity data revealed that the space group should be either *Cc* or *C*2/*c*. The structure was initially solved in the non-centrosymmetric space group *Cc*. This resulted in erratic bond lengths (for example the ring P–N bond lengths varied from 1.598 to 1.733 Å without any trend) and high thermal parameters for C(1) and C(2). Hence, the structure was redetermined in the centrosymmetric space group *C*2/*c*. This resulted in uniform and meaningful bond lengths with two positions for both C(1) and C(2) which are related by a crystallographic two-fold axis. A test for second harmonic generation of the crystals also gave negative results consistent with a centrosymmetric space group.

The structure was solved by direct methods using SHELXS 86.[27a] The hydrogen atoms were located from successive difference maps and included in subsequent calculations. Least-squares refinement was carried out using SHELX 76.[27b] All non-hydrogen atoms were refined anisotropically and the hydrogen atoms isotropically. The final $R$ value was 0.066 for 273 parameters refined. The final shift/e.s.d. and residual electron density were 0.066 and 0.24 e $Å^{-3}$ respectively. Final fractional atomic coordinates of the non-hydrogen atoms are given in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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