Synthesis and Nuclear Magnetic Resonance Spectroscopy of Geometrical Isomers of 1,3,5-Trimethyl-2,4,6-tris(*p*-methylphenoxy)-2,4,6-trioxocyclotriphosphazane: *X*-Ray Crystal Structure of the *trans* Isomer

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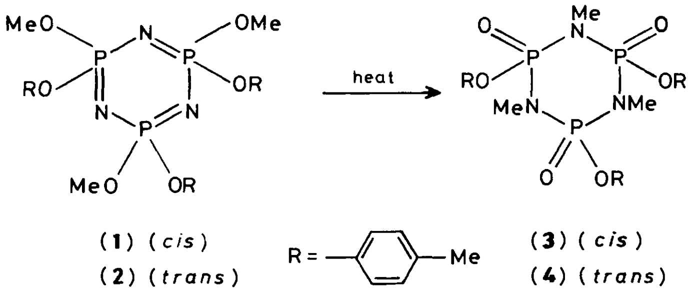
Both *cis* and *trans* isomers of tri(*N*-methyl)tris(*p*-methylphenoxy)trioxocyclotriphosphazane, $N_3Me_3P_3O_3(OC_6H_4Me\text{-}p)_3$, have been prepared by the thermal rearrangement of the respective trimethoxycyclophosphazenes, $N_3P_3(OC_6H_4Me\text{-}p)_3(OMe)_3$. The crystal and molecular structure of the *trans* isomer has been determined; it crystallises in the $P\bar{1}$ space group with a = 8.444(1), b = 11.753(1), c = 14.196(1) Å, α = 97.408(8), β = 92.487(10), γ = 102.325(10)°, and Z = 2. The structure has been solved by direct methods and refined to a R value of 0.060. The six-membered N_3P_3 phosphazane ring adopts a twist–boat confirmation. The structural data have been used to explain the n.m.r. spectroscopic features. A chair conformation is proposed for *cis*-$N_3Me_3P_3O_3(OC_6H_4Me\text{-}p)_3$ on the basis of n.m.r. data.

Alkoxycyclophosphazenes when heated alone or in the presence of an alkyl halide undergo a rearrangement to *N*-alkyloxocyclophosphazanes.[1–6] The molecular dimensions of only one *N*-alkyloxocyclotriphosphazane[7] and two isomeric *N*-alkyloxocyclotetraphosphazanes[8,9] have been reported. The two structural isomers of $N_4Me_4P_4O_4(OMe)_4$ obtained from $N_4P_4(OMe)_8$ have the 2-*trans*-4-*cis*-6-*trans*-8[8] and 2-*cis*-4-*trans*-6-*trans*-8[9] configurations of the phosphoryl groups. In contrast, the trimeric analogue, $N_3P_3(OMe)_6$, yields only a single isomer, *viz*. *trans*-$N_3Me_3P_3O_3(OMe)_3$ upon thermal rearrangement.[7] The six-membered phosphazane ring adopts a twist–boat conformation in which one oxo group occupies the axial position and the other two equatorial positions. Although the formation of the *cis* isomer is reported in the thermal rearrangement of $N_3P_3(OMe)_6$,[3–5] it is yet to be authenticated.

In this paper, we report the preparation of *cis* and *trans* isomers of tri(*N*-methyl)tris(*p*-methylphenoxy)trioxocyclotriphosphazanes (**3**) and (**4**) by the thermal rearrangement of the respective trimethoxy derivatives (**1**) and (**2**), and the structure of the *trans* isomer as determined by *X*-ray diffraction. The principal objective of the crystallographic study is to correlate the observed n.m.r. spectroscopic data for this class of compounds with the conformation of the N_3P_3-phosphazane ring and the orientation of the substituents.



(**1**) (*cis*)
(**2**) (*trans*)
(**3**) (*cis*)
(**4**) (*trans*)

Experimental

Hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, was recrystallised from light petroleum (60—80 °C) to a constant m.p. of 114 °C. Light petroleum (b.p. 60—80 °C), benzene, tetrahydrofuran (thf), and diethyl ether were purified by conventional methods.

The ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. spectra were recorded using a Bruker WH-270 MHz spectrometer. Proton-decoupled ^{31}P n.m.r. spectra were obtained from a Varian FT-80A n.m.r. spectrometer. For all n.m.r. measurements dry $CDCl_3$ was used as the solvent. Tetramethylsilane was used as the internal reference for the ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. spectra; for $^{31}P\text{-}\{^1H\}$ n.m.r. spectra, 85% H_3PO_4 was used as the external reference. Chemical shifts are quoted on the δ (p.p.m.) scale with upfield shifts negative. I.r. spectra in the region 4 000—600 cm^{-1} were recorded using a Perkin-Elmer 781 spectrophotometer. Melting points were recorded on a Reichert-Kofler microheating stage fitted with a polarising microscope.

Preparation of cis-(**1**) *and trans-*(**2**) *Isomers of* $N_3P_3(OC_6H_4Me\text{-}p)_3(OMe)_3$.—An isomeric mixture (*cis–trans* = 1:5) of trichlorotris(*p*-methylphenoxy)cyclotriphosphazene, $N_3P_3Cl_3(OC_6H_4Me\text{-}p)_3$, also containing a small quantity of the geminal isomer (< 5%), was prepared by treating $N_3P_3Cl_6$ with sodium *p*-methylphenoxide as described earlier.[10] The trichloro derivative, $N_3P_3Cl_3(OC_6H_4Me\text{-}p)_3$ (10 g, 18 mmol) was treated with an excess of sodium methoxide (5 g, 90 mmol) in boiling thf (150 cm^3) for 24 h. The reaction mixture was cooled and the precipitate of NaCl filtered off. The solvent was evaporated under reduced pressure. The residue was dissolved in diethyl ether (200 cm^3) and washed with distilled water (3 × 50 cm^3). The solution was dried over anhydrous Na_2SO_4 and the solvent evaporated to obtain an isomeric mixture of $N_3P_3(OC_6H_4Me\text{-}p)_3(OMe)_3$ as a colourless oil (7.9 g, 82%). From this mixture, the bulk of the *trans*-(**2**) isomer was isolated by fractional crystallization from dichloromethane–light petroleum (1:1); the residual mixture enriched in the *cis* and geminal isomers was subjected to multiple-development preparative t.l.c. with benzene as eluant to separate *ca*. 500 mg of the pure *cis* isomer. The R_f values for the *cis*, *trans*, and geminal isomers are 0.22, 0.28, and 0.25 respectively. The isomeric purity of the samples isolated was monitored by ^1H n.m.r. spectroscopy.

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† 1,3,5-Trimethyl-2,4,6-tris(*p*-methylphenoxy)-2,4,6-trioxo-1,3,5,2λ^5,4λ^5,6λ^5-triazatriphosphorinane.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

cis-$N_3P_3(OC_6H_4Me\text{-}p)_3(OMe)_3$ (**1**): colourless oil (Found: C, 52.4; H, 5.35. $C_{24}H_{30}N_3O_6P_3$ requires C, 52.5; H, 5.5%); i.r. (cm^{-1}) (neat): 1 185s, br (P=N), 975s (P–O); n.m.r.: δ_H, 6.90 (12 H, m, 3 C_6H_4), 3.77 [9 H, doublet with virtual coupling, *J*(PH) 12.9 Hz, 3 OMe], 2.29 (9 H, s, 3 Me-*p*); δ_C, 53.1 (s, 3 OMe), 20.7 (s, 3 Me-*p*); δ_P, 14.1 [s, 3 $P(OC_6H_4Me\text{-}p)(OMe)$].

trans-$N_3P_3(OC_6H_4Me\text{-}p)_3(OMe)_3$ (**2**): colourless crystals from light petroleum–dichloromethane (1:1), m.p. 87 °C (Found: C, 52.5, H, 5.3. $C_{24}H_{30}N_3O_6P_3$ requires C, 52.5; H, 5.5%); i.r. (cm^{-1}) (KBr disc): 1 185s (P=N), 960s (P–O); n.m.r.: δ_H, 6.95 (12 H, m, 3 C_6H_4), 3.57 [6 H, doublet with virtual coupling, *J*(PH) 13.2 Hz, 2 OMe], 3.30 [3 H, doublet with virtual coupling, *J*(PH) 13.2 Hz, 1 OMe], 2.29 (9 H, s, 3 Me-*p*); δ_C, 53.0 (s, 2 OMe), 52.8 (s, 1 OMe), 20.7 (s, 3 Me-*p*); δ_P, 14.3 [s, 3 $P(OC_6H_4Me\text{-}p)(OMe)$].

Preparation of cis-$N_3Me_3P_3O_3(OC_6H_4Me\text{-}p)_3$ (**3**).—This compound was prepared by the thermal rearrangement of (**1**). A sample of (**1**) (200 mg) was placed in a dry glass tube (length 0.2 m, outside diameter 0.02 m) fitted with a B14 cone. The tube was evacuated (pressure 13.3 N m^{-2}), sealed, and placed in an oven set at 185(±2) °C. After 5 h the tube was removed, cooled, and opened in an atmosphere of dry N_2 gas. The contents of the tube were dissolved in $CDCl_3$–CCl_4 and the solution used for spectroscopic measurements.

cis-$N_3Me_3P_3O_3(OC_6H_4Me\text{-}p)_3$ (**3**) (200 mg, 100%): highly hygroscopic crystals, m.p. 101 °C, from light petroleum–dichloromethane (1:1) (Found: C, 52.3; H, 5.7. $C_{24}H_{30}N_3O_6P_3$ requires C, 52.5; H, 5.5%); i.r. (cm^{-1}) (CCl_4 solution): 1 310s (P=O), 1 065s (P–N), 960s (P–O); n.m.r.: δ_H, 7.05 (12 H, q, 3 C_6H_4), 3.21 [9 H, t, *J*(PH) 9.9 Hz, 3 NMe], 2.30 (9 H, s, 3 Me-*p*); δ_C, 32.6 (s, 3 NMe), 20.7 (s, 3 Me-*p*); δ_P, −1.1 [s, 3 $P(O)(OC_6H_4Me\text{-}p)$].

Preparation of trans-$N_3Me_3P_3O_3(OC_6H_4Me\text{-}p)_3$ (**4**).—This compound was obtained from the thermal rearrangement of *trans*-$N_3P_3(OC_6H_4Me\text{-}p)_3(OMe)_3$ (**2**) as described above for the *cis* isomer.

trans-$N_3Me_3P_3O_3(OC_6H_4Me\text{-}p)_3$ (**4**) (200 mg, 100%): colourless crystals, m.p. 117 °C, from light petroleum–dichloromethane (1:1) (Found: C, 52.5; H, 5.4. $C_{24}H_{30}N_3O_6P_3$ requires C, 52.5; H, 5.5%); i.r. (cm^{-1}) (CCl_4 solution): 1 305s, 1 295s (P=O), 1 080s (P–N), 950s (P–O); n.m.r.: δ_H, 7.15 (12 H, m, 3 C_6H_4), 3.27 [3 H, t, *J*(PH) 9.7 Hz, 1 NMe], 3.14 [6 H, t, *J*(PH) 10.1 Hz, 2 NMe], 2.32 (3 H, s, 1 Me-*p*) 2.30 (6 H, s, 2 Me-*p*); δ_C, 33.8 (s, 1 NMe), 31.8 (s, 2 NMe), 20.7 (s, 3 Me-*p*); δ_P, −0.9 [2 $P(O)(OC_6H_4Me\text{-}p)$], 2.6 [1 $P(O)(OC_6H_4Me\text{-}p)$], *J*(PP) 22.7 Hz (AB_2 spectral pattern).

X-Ray Structural Analysis of trans-$N_3Me_3P_3O_3(OC_6H_4Me\text{-}p)_3$ (**4**).—Crystals of (**4**) were grown from light petroleum–dichloromethane (1:1) by slow evaporation of the solvent at ambient temperature (*ca.* 27 °C).

Crystal data. $C_{24}H_{30}N_3O_6P_3$, $M = 549$, triclinic, $a = 8.444(1)$, $b = 11.753(1)$, $c = 14.196(1)$ Å, $\alpha = 97.408(8)$, $\beta = 92.487(10)$, $\gamma = 102.325(10)$°, $U = 1\,361.22$ Å^3, space group $P\bar{1}$, $Z = 2$, $D_c = 1.349$ g cm^{-3}, $F(000) = 576$; crystal dimensions: 0.40 × 0.30 × 0.15 mm, $\mu(Mo\text{-}K_\alpha) = 2.14$ cm^{-1}.

Data collection. Unit-cell dimensions and their associated standard deviations were derived from at least-squares fit to the setting angles of 20 carefully selected and centred reflections on an Enraf-Nonius CAD-4 automated diffractometer. Intensity data were collected using graphite-monochromated Mo-K_α radiation in the $\omega/2\theta$ mode ($0 \leqslant \theta \leqslant 23.5$°). The stability and quality of the crystal were monitored by measuring the intensities of three standard reflections every 30 min. A total of 3 780 reflections were collected (unique data 3 619, R_{int} 0.023) of which 2 555 were considered observed [$F_o \geqslant 3\sigma(F_o)$]. The data were corrected for Lorentz and polarisation effects, but not for absorption.

Table 1. Fractional atomic co-ordinates (× 10^4) for the non-hydrogen atoms of compound (**4**) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
P(1)	7 129(2)	1 608(1)	1 831(1)
N(1)	7 152(6)	836(4)	2 730(3)
P(2)	8 679(2)	1 085(1)	3 570(1)
N(2)	8 953(6)	2 482(4)	4 005(3)
P(3)	8 489(2)	3 484(1)	3 392(1)
N(3)	8 365(6)	2 898(4)	2 251(3)
O(1)	5 318(5)	1 752(4)	1 845(3)
O(2)	7 570(6)	1 129(4)	906(3)
O(3)	10 305(5)	1 100(3)	3 045(3)
O(4)	8 373(5)	270(4)	4 257(3)
O(5)	6 648(5)	3 473(4)	3 525(3)
O(6)	9 593(6)	4 617(4)	3 604(3)
C(1)	5 791(11)	−190(7)	2 744(7)
C(2)	9 986(13)	2 889(8)	4 910(6)
C(3)	9 741(11)	3 353(8)	1 684(6)
C(11)	4 575(7)	2 314(5)	1 187(4)
C(12)	4 593(8)	3 478(6)	1 423(5)
C(13)	3 773(9)	4 017(6)	817(5)
C(14)	2 948(7)	3 414(6)	−22(4)
C(15)	3 001(9)	2 256(7)	−243(5)
C(16)	3 806(9)	1 680(6)	352(5)
C(17)	2 058(11)	4 035(10)	−659(6)
C(21)	10 782(7)	63(5)	2 673(4)
C(22)	10 856(8)	−154(6)	1 701(4)
C(23)	11 401(9)	−1 146(7)	1 332(5)
C(24)	11 888(7)	−1 875(6)	1 909(5)
C(25)	11 785(8)	−1 618(6)	2 892(5)
C(26)	11 268(8)	−630(5)	3 268(5)
C(27)	12 500(12)	−2 939(10)	1 494(9)
C(31)	5 932(7)	3 357(5)	4 405(4)
C(32)	4 656(8)	2 446(6)	4 436(5)
C(33)	3 879(9)	2 355(6)	5 267(5)
C(34)	4 347(8)	3 192(6)	6 050(5)
C(35)	5 672(9)	4 090(6)	6 011(5)
C(36)	6 491(8)	4 187(6)	5 187(5)
C(37)	3 367(13)	3 157(10)	6 912(7)

Structure analysis and refinement. The structure was solved by direct methods using the program MULTAN[11] on a DEC-1090 computer system. Refinement was carried out with SHELX 76.[12] The *R* index converged to a value of 0.078 on refining the positional parameters of the non-hydrogen atoms successively with isotropic and anisotropic thermal parameters. The positions of the hydrogen atoms were fixed from geometrical considerations. Full-matrix least-squares refinement with anisotropic thermal parameters for the non-hydrogen atoms and fixed isotropic thermal parameters for the hydrogen atoms converged at $R = 0.060$ ($R' = 0.066$).* The weighting scheme used was of the form $w = 1.0/[\sigma(F)^2 + 0.0090|F|^2]$. Atomic scattering factors were taken from International Tables.[13] Final atomic co-ordinates for the non-hydrogen atoms are given in Table 1. Selected bond distances and angles involving the non-hydrogen atoms are listed in Tables 2 and 3 respectively. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

Attempts to obtain single crystals of *cis*-$N_3Me_3P_3O_3(OC_6H_4\text{-}Me\text{-}p)_3$ (**3**) suitable for *X*-ray structure analysis were unsuccessful.

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* $R = \Sigma(F_o - |F_c|)/\Sigma F_o$, $R' = [\Sigma w(F_o - |F_c|)^2/\Sigma w F_o{}^2]^{\frac{1}{2}}$.

Table 2. Selected bond distances (Å) for the non-hydrogen atoms in compound (**4**) with e.s.d.s in parentheses

P(1)–N(1)	1.660(5)	N(2)–P(3)	1.652(5)
P(1)–N(3)	1.668(5)	N(2)–C(2)	1.485(10)
P(1)–O(1)	1.575(5)	P(3)–N(3)	1.666(4)
P(1)–O(2)	1.456(5)	P(3)–O(5)	1.572(5)
N(1)–P(2)	1.669(5)	P(3)–O(6)	1.441(5)
N(1)–C(1)	1.480(10)	N(3)–C(3)	1.487(10)
P(2)–N(2)	1.642(5)	O(1)–C(11)	1.410(7)
P(2)–O(3)	1.588(5)	O(3)–C(21)	1.410(7)
P(2)–O(4)	1.447(5)	O(5)–C(31)	1.421(7)

Table 3. Selected bond angles (°) for the non-hydrogen atoms in compound (**4**) with e.s.d.s in parentheses

N(1)–P(1)–N(3)	103.3(2)	P(2)–N(2)–P(3)	123.4(3)
N(1)–P(1)–O(1)	98.7(2)	P(2)–N(2)–C(2)	116.9(5)
N(1)–P(1)–O(2)	118.8(3)	P(3)–N(2)–C(2)	118.3(5)
N(3)–P(1)–O(1)	108.9(2)	N(2)–P(3)–N(3)	105.7(2)
N(3)–P(1)–O(2)	111.6(3)	N(2)–P(3)–O(5)	106.4(2)
O(1)–P(1)–O(2)	114.3(3)	N(2)–P(3)–O(6)	113.8(3)
P(1)–N(1)–P(2)	124.0(3)	N(3)–P(3)–O(5)	100.1(2)
P(1)–N(1)–C(1)	117.7(5)	N(3)–P(3)–O(6)	113.7(3)
P(2)–N(1)–C(1)	118.1(5)	O(5)–P(3)–O(6)	115.8(3)
N(1)–P(2)–N(2)	105.4(2)	P(1)–N(3)–P(3)	122.3(3)
N(1)–P(2)–O(3)	107.4(2)	P(1)–N(3)–C(3)	118.2(5)
N(1)–P(2)–O(4)	111.8(3)	P(3)–N(3)–C(3)	116.7(5)
N(2)–P(2)–O(3)	100.4(2)	P(1)–O(1)–C(11)	124.2(4)
N(2)–P(2)–O(4)	115.6(3)	P(2)–O(3)–C(21)	122.7(4)
O(3)–P(2)–O(4)	115.2(2)	P(3)–O(5)–C(31)	123.3(4)

Results and Discussion

Crystal Structure of trans-$N_3Me_3P_3O_3(OC_6H_4Me\text{-}p)_3$ (**4**).—*Conformation of* N_3P_3*-phosphazane ring.* The perspective view of a molecule of *trans*-$N_3Me_3P_3O_3(OC_6H_4Me\text{-}p)_3$ (**4**) down the *a* axis is shown in Figure 1. The six-membered P–N ring adopts a twist–boat conformation, as is also found for the corresponding methoxy derivative, *trans*-$N_3Me_3P_3O_3(OMe)_3$.[7] On the other hand, the P–N ring in the trimetaphosphimic acid derivative, $Na_3N_3H_3P_3O_6{\cdot}4H_2O$ assumes a chair conformation.[14] Electrostatic interactions between the sodium cation and trimetaphosphimate anion are no doubt responsible for the ring shape in $Na_3N_3H_3P_3O_6{\cdot}4H_2O$, whereas the steric effects exerted by the substituents largely determine the P–N ring shape in the methoxy and *p*-methylphenoxy derivatives.

Both mean-plane calculations and torsional angles are used to elucidate the stereochemistry of the N_3P_3-phosphazane ring in *trans*-$N_3Me_3P_3O_3(OC_6H_4Me\text{-}p)_3$ (**4**). Torsional angles of the phosphazane ring are summarised in Figure 2. Symmetries displayed by the torsional angles[15] have been used to identify the conformation of the six-membered ring. Three intersecting C_2 axes and three mirror planes are essential for the chair conformation. The presence of two orthogonal mirror planes indicates the boat conformation, whereas two orthogonal C_2 axes imply the twist–boat conformation. The degree of departure from the ideal two-fold symmetry is given by the asymmetry parameter ΔC_2, which is calculated from equation (1),

$$\Delta C_2 = \left[\frac{\sum_{i=1}^{m}(\varphi_i - \varphi_i')^2}{m}\right]^{\frac{1}{2}} \quad (1)$$

where *m* is the number of individual comparisons and φ_i and φ_i' are the symmetry-related torsion angles.[15]

The angle between the pair of opposite bonds of the N_3P_3 ring in compound (**4**) are: P(1)–N(1) and N(2)–P(3), 22°07′; N(3)–P(1) and P(2)–N(2), 29°43′; N(1)–P(2) and P(3)–N(3), 49°27′. The smallest angle observed for the P(1)–N(1) and N(2)–P(3) bonds suggested that these four atoms can be chosen to form the bottom of the twist–boat. This choice is borne out by mean-plane calculations. The deviations of the atoms forming the 'prow' and 'stern' of the twist–boat from the mean plane of the other four atoms are a maximum when P(1), N(1), N(2), P(3) is chosen as the bottom of the twist–boat compared with the other two alternatives, *viz.* P(3), N(3), N(1), P(2) and P(2), N(2), N(3), P(1). Thus, the bottom of the twist–boat is formed by P(1)–N(1) and N(2)–P(3) and 'prow' and 'stern' positions are occupied by P(2) and N(3) respectively.

Distorted tetrahedral geometry is retained around the phosphorus atoms whilst the geometry around the nitrogen atoms is nearly planar. There is a marked difference between the structure of *trans*-$N_3Me_3P_3O_3(OC_6H_4Me\text{-}p)_3$ (**4**) and that of the methoxy analogue.[7] Two oxo groups [at P(2) and P(3)] occupy axial positions and the third [at P(1)] the equatorial position in (**4**), whereas the reverse trend is observed in the methoxy analogue. Furthermore, the degree of deviation from an ideal twist–boat geometry is greater for (**4**) as reflected in the asymmetry parameters (ΔC_2) of 8.7 and 11.1 (Figure 2) compared with 1.3 and 6.4 (calculated using the fractional coordinates given in ref. 7) for the methoxy analogue. These differences may be attributed to the greater bulkiness of the *p*-methylphenoxy groups.

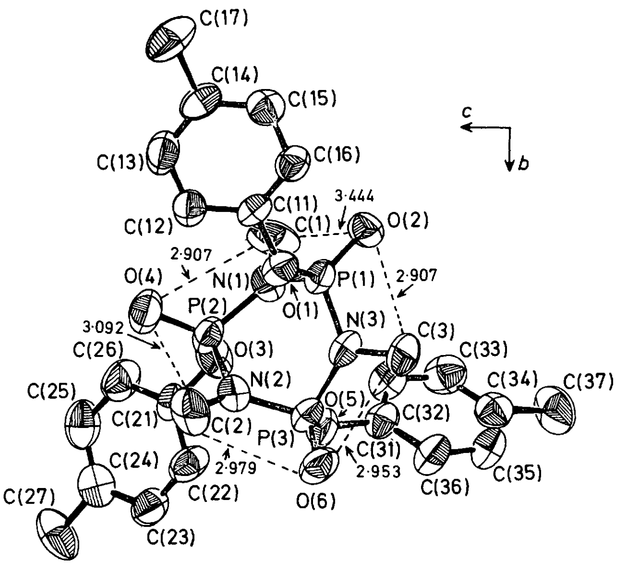

Figure 1. A molecule of *trans*-$N_3Me_3P_3O_3(OC_6H_4Me\text{-}p)_3$ (**4**) in the unit cell viewed down the *a* axis with selected intramolecular short contacts

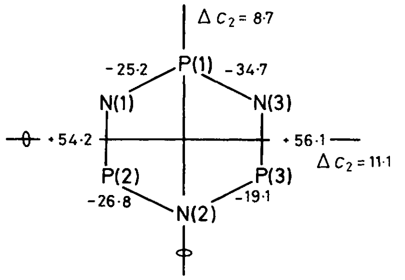

Figure 2. Torsional angles (e.s.d. 0.4°) of N_3P_3-phosphazane ring in *trans*-$N_3Me_3P_3O_3(OC_6H_4Me\text{-}p)_3$ (**4**); ΔC_2 denotes two-fold asymmetry parameters (see text)

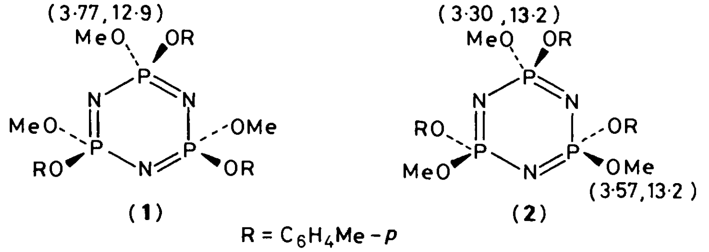

Figure 3. ^{1}H N.m.r. data (OMe protons only) for *cis*-(**1**) and *trans*-(**2**) isomers of $N_3P_3(OC_6H_4Me\text{-}p)_3(OMe)_3$; values shown are the chemical shifts with ^3J(PH) in parentheses

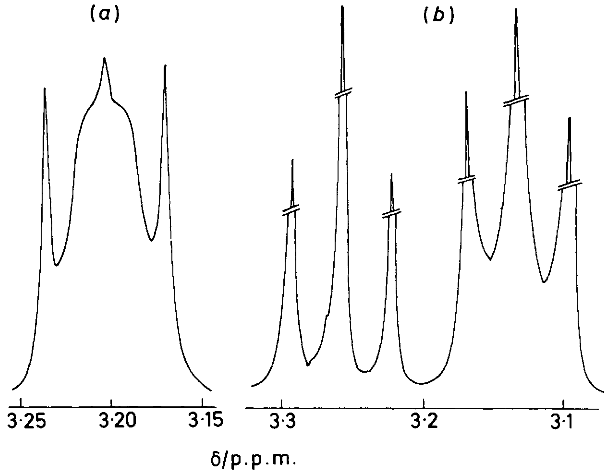

Figure 4. ^{1}H N.m.r. spectra (270 MHz, $CDCl_3$) of (*a*) *cis*-(**3**) and (*b*) *trans*-(**4**) isomers of $N_3Me_3P_3O_3(OC_6H_4Me\text{-}p)_3$ (*N*-methyl region only)

Molecular dimensions. The average bond lengths and angles for (**4**) are similar to those observed for the methoxy derivative. The average of the P–N bond lengths [1.659(2) Å] suggests that these bonds are not pure single bonds (normal P–N single bond length, 1.77 Å[16]); a certain degree of π bonding still exists in the N_3P_3-phosphazane ring skeleton. Bond lengths of the two P–N bonds flanking the N(2) atom are significantly shorter than those of the four other P–N bonds. Like the cyclic P–N bonds, the P–O bonds of the P–OC_6H_4Me-*p* units also possess a considerable degree of π bonding as evident from their bond lengths [average value, 1.578(3) Å]. The P=O bond of the oxo group attached to P(1) atom is weaker than those of the other two oxo groups as shown by its longer bond distance and smaller O–P–O bond angle. The P–N–P bond angle at the apical N(3) atom is smaller than those of the other two P–N–P units.

Packing. When the packing of the molecules in the unit cell is viewed down the '*b*' axis, stacking is observed between two centrosymmetrically related phenyl rings [attached to P(3) atoms] which are separated by an average distance of 3.44 Å.

Assignment of N.M.R. Data.—N.m.r. spectroscopic assignments for the *cis*-(**1**) and *trans*-(**2**) isomers of $N_3P_3(OC_6H_4Me\text{-}p)_3(OMe)_3$ have been made on the basis of the data for $N_3P_3(OC_6H_4Me\text{-}p)_3(NMe_2)_3$, reported earlier[10] and are shown in Figure 3.

trans-$N_3Me_3P_3O_3(OC_6H_4Me\text{-}p)_3$ (**4**) shows spectroscopic features that are similar to those of the methoxy derivative, *trans*-$N_3Me_3P_3O_3(OMe)_3$. For the latter, complete assignments of the n.m.r. resonances to the respective *N*-methyl and *O*-methyl protons have not been made.[4–6] There are two different environments for the *N*-methyl groups in compound (**4**) as shown by its ^{1}H and ^{13}C-{^{1}H} n.m.r. spectra (Figure 4 and Experimental section). Similarly the magnetic environment of one of the three phosphorus nuclei differs from those of the other two (AB_2 type ^{31}P-{^{1}H} n.m.r. spectrum).

The *X*-ray structure of the *trans* isomer (**4**) shows that all three *p*-methylphenoxy groups point away from the *N*-methyl substituents (>4.0 Å). Therefore, the 'ring current' associated with the *p*-methylphenoxy groups is unlikely to affect the magnetic environment of the *N*-methyl substituents significantly. The major factor that would determine the chemical shifts of the *N*-methyl groups in both ^{1}H and ^{13}C n.m.r. is the magnetic anisotropy associated with the phosphoryl groups. The intramolecular short contacts between the phosphoryl groups and the *N*-methyl substituents are shown in Figure 1. The oxo group attached equatorially to the P(1) atom lies below the P(1)N(1)N(2)P(3) mean plane; the other two oxo groups occupying the axial positions at P(2) and P(3) are above this mean plane. Similarly the *N*-methyl substituent attached to N(1) is below this mean plane, whereas the other two *N*-methyl substituents at N(2) and N(3) are above. The two *N*-methyl substituents [C(2) and C(3)] are therefore rendered magnetically equivalent. The two sets of resonances observed for compound (**4**) in its ^{1}H and ^{13}C-{^{1}H} n.m.r. spectra can be readily explained and assigned.

For the *cis* isomer (**3**), all three NMe groups are magnetically equivalent as shown by its ^{1}H and ^{13}C-{^{1}H} n.m.r. spectra (Figure 4 and Experimental section). The singlet observed in the ^{31}P-{^{1}H} n.m.r. spectrum reveals the equivalence of all three ring phosphorus nuclei. Either a planar structure or a chair conformation in which the three nitrogen and the three phosphorus atoms lie in two parallel planes would account for the spectroscopic features observed. The N_3P_3-cyclophosphazane ring system is more flexible compared to the corresponding phosphazene system. Torsional strain due to the presence of bulky *p*-methylphenoxy substituents on one side of the N_3P_3 ring and the less heavy oxygen atoms on the other side will tend to distort the N_3P_3 ring from planarity. Hence, a chair conformation is more likely for the *cis* isomer (**3**). However, a crystallographic investigation is necessary to confirm this inference.

Zeiss *et al.*[17] have reported the preparation of several trialkoxy-, triaryloxy-, and triamino-tri(*N*-methyl)cyclotri-λ^3-phosphazanes and indentified *cis* and *trans* isomers in solution. The ^{31}P chemical shifts of the *cis* (A_3 spin system) and *trans* (A_2B spin system) isomers are more separated for the cyclotri-λ^3-phosphazanes than for the λ^5-phosphazanes reported here and elsewhere.[6] On the other hand, the ^2J(PNP) values for *trans*-λ^5-phosphazanes are nearly double those observed for *trans*-λ^3-phosphazanes (12—14 Hz). As yet, crystal-structure data are not available for cyclotri-λ^3-phosphazanes. However, structural data for a λ^3- and λ^5-pair of cyclodiphosphazanes, $N_2Bu^t{}_2P_2Cl_2$[18] and $N_2Bu^t{}_2P_2O_2Cl_2$,[19] reveal that the skeletal P–N bonds partake of a greater degree of π bonding in the cyclodi-λ^5-phosphazane [mean P–N 1.661(5) Å] than in the corresponding λ^3-phosphazane [mean P–N 1.689(4) Å]. One may therefore anticipate a similar trend for λ^3-cyclotriphosphazanes and λ^5-trioxocyclotriphosphazanes which would explain the higher value of ^2J(PNP) observed for the latter.

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