Studies of Phosphazenes. Part 22.[1] High-field Nuclear Magnetic Resonance Investigation of Novel Isomeric Oxophosphazadienes

K. C. Kumara Swamy and Setharampattu S. Krishnamurthy*
Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560012, India

The reaction of $N_3P_3(NPPh_3)Cl_5$ with an excess of methoxide yields the 'hydroxy'-derivatives, $N_3P_3(NPPh_3)(OMe)_4(OH)$ and $N_3P_3(NPPh_3)(OMe)_3(OH)_2$, in addition to the fully methoxylated derivative $N_3P_3(NPPh_3)(OMe)_5$. The analogous reaction of *gem*-$N_3P_3(NPPh_3)(NMe_2)Cl_4$ with methoxide affords $N_3P_3(NPPh_3)(NMe_2)(OMe)_4$ and $N_3P_3(NPPh_3)(NMe_2)(OMe)_3(OH)$. The 'hydroxy'-derivatives exist in their oxophospha-za-tautomeric forms. For the 'monohydroxy'-compounds, the presence of a pair of *cis*- and *trans*-oxophosphazadienes is established from ^1H and ^{31}P n.m.r. spectroscopic data.

The mode of formation and the structures of 'hydroxy'-cyclophosphazenes is a topic of current interest.[2-7] Three types of prototropic behaviour have been reported for the oxocyclotriphosphazadiene tautomers of *gem*-$N_3P_3R_2R'_3(OH)$ (R = Ph, NHBu^t, or OMe; R' = OMe, OEt, or OPr^n); two of these involve exchange of a proton between two sites and in the third type no exchange is detected.[3] In this paper, we report the syntheses of unsymmetrically substituted 'monohydroxy'-derivatives, $N_3P_3(NPPh_3)R(OMe)_3(OH)$ (R = OMe or NMe_2), and the elucidation of their structures by high-field ^1H and ^{31}P n.m.r. spectroscopy. We also report the isolation of a 'dihydroxy'-derivative, $N_3P_3(NPPh_3)(OMe)_3(OH)_2$.

Experimental

The compounds $N_3P_3(NPPh_3)Cl_5$ (**1**) and *gem*-$N_3P_3(NPPh_3)(NMe_2)Cl_4$ (**5**) were prepared by methods reported previously.[8-10] Methanol was distilled over CaO and methyl cyanide over P_2O_5; both were preserved over molecular sieves before use. The ^1H ($CDCl_3$) and ^{31}P-{^1H} ($CHCl_3$ + $CDCl_3$) n.m.r. spectra were recorded at 270 (Bruker FT 270) and 162 MHz (Bruker FT 400) respectively. The chemical shifts are with reference to $SiMe_4$(^1H) or 85% H_3PO_4(^{31}P) and upfield shifts are negative. I.r. spectra were recorded on a Carl-Zeiss UR-10 spectrophotometer (using Nujol mulls).

Preparation of $N_3P_3(NPPh_3)(OMe)_5$ (**2**), $N_3P_3(NPPh_3)(OMe)_4(OH)$ (**3**), and $N_3P_3(NPPh_3)(OMe)_3(OH)_2$ (**4**).—A solution of sodium methoxide [75 mmol, prepared from 1.7 g of sodium and methanol (8 cm^3) using methyl cyanide (100 cm^3) as the solvent] was added to a slurry of $N_3P_3(NPPh_3)Cl_5$ (**1**) (3.0 g, 5.1 mmol) in methyl cyanide (80 cm^3) with continuous stirring during 40 min at *ca.* 25 °C. The mixture was heated under reflux for 72 h. Thin-layer chromatography [eluant, benzene–ethyl acetate (5:1)] of the reaction mixture at this stage showed the absence of (methoxy)chloro-derivatives, $N_3P_3(NPPh_3)(OMe)_nCl_{5-n}$ ($n \leqslant 4$).[11] The reaction mixture was filtered and the solvent from the filtrate evaporated *in vacuo*. The oily residue was dissolved in benzene, filtered, and washed with water (5 × 50 cm^3). The organic layer was dried over anhydrous sodium sulphate (24 h). The solvent was evaporated *in vacuo* and the resulting oil dissolved in dichloromethane–light petroleum (1:1, 60 cm^3; b.p. 60–80 °C); slow evaporation of the solvent at ambient temperature yielded first the 'hydroxy'-derivative $N_3P_3(NPPh_3)(OMe)_4(OH)$ (**3**), m.p. 215—220 °C (0.18 g, 6.4%) (Found: C, 47.6; H, 5.3. $C_{22}H_{28}N_4O_5P_4$ requires C, 47.8; H, 5.1%). I.r.: 1 175vs, 1 215vs $(PN)_{endo}$; 2 650m (NH); 1 250m, 1 280m, and 1 330s cm^{-1} (not assigned). The fully methoxylated derivative $N_3P_3(NPPh_3)(OMe)_5$ (**2**), m.p. 150 °C, was obtained from the mother-liquor (1.2 g, 41.4%) (Found: C, 48.8; H, 5.4; N, 9.6. $C_{23}H_{30}N_4O_5P_4$ requires C, 48.8; H, 5.3; N, 9.9%). I.r.: 1 175vs, 1 215vs $(PN)_{endo}$; 1 250(sh) and 1 280(sh) cm^{-1} (not assigned).

The aqueous layer obtained above was subjected to continuous liquid–liquid extraction with chloroform (150 cm^3). The chloroform extract was dried over fused calcium chloride (18 h) and the solvent evaporated from this extract *in vacuo* to obtain an oil (0.8 g). A small quantity of derivative (**3**) (0.2 g, 0.7%) was isolated from this oil. The residual mixture was then subjected to column chromatography over silica gel (12 g) using acetone–methanol (8:1) as the eluant. The first fraction (150 cm^3) consisting of impure (**3**) (0.01 g) was rejected. From the next fraction (150 cm^3), the 'dihydroxy'-derivative $N_3P_3(NPPh_3)(OMe)_3(OH)_2$ (**4**), m.p. 150—160 °C (0.12 g, 4.4%) (Found: C, 45.6; H, 5.6. $C_{21}H_{26}N_4O_5P_4$ requires C, 46.8, H, 5.0%), was isolated. The compound is highly hygroscopic and the lower carbon analysis found is in accord with the presence of a molecule of water ($C_{21}H_{28}N_4O_6P_4$ requires C, 45.3%). Proton n.m.r. for (**4**) (OMe region) [δ, ^3J(P–H)/Hz]: 3.64, 12.7; 3.62, 12.7; 3.58, 10.5; 3.57, 12.5; 3.55, 13.6; 3.37, 12.7; 3.34, 11.8; and 3.21, 12.7. The doublet at δ 3.58 had an intensity almost twice that of the remaining ones. I.r.: 1 190vs, 1 210vs $(PN)_{endo}$; 2 640m (NH); 3 200br (water); 1 260m and 1 330s cm^{-1} (not assigned).

A similar reaction with *gem*-$N_3P_3(NPPh_3)(NMe_2)Cl_4$ (**5**) (0.30 g, 0.5 mmol) yielded $N_3P_3(NPPh_3)(NMe_2)(OMe)_3(OH)$ (**7**), m.p. 230—234 °C (0.06 g, 21%) (Found: C, 48.7; H, 5.4; N, 12.6. $C_{23}H_{31}N_5O_4P_4$ requires C, 48.8; H, 5.5; N, 12.4%) [i.r.: 1 180vs, 1 230vs $(PN)_{endo}$; 2 690m (NH); 1 250m and 1 280s cm^{-1} (not assigned)] and $N_3P_3(NPPh_3)(NMe_2)(OMe)_4$ (**6**) (0.06 g, 21%) (^1H n.m.r.: integrated intensities for Ph:NMe_2:OMe 15:6:12) [i.r.: 1 190(sh), 1 220vs $(PN)_{endo}$; and 1 260s cm^{-1} (not assigned)].

Attempted Hydrolysis of $N_3P_3(NPPh_3)(OMe)_5$ (**2**).—Treatment of compound (**2**) (1 mmol) dissolved in methanol (50 cm^3) with an aqueous KOH solution (1 mol dm^{-3}, 15 cm^3) and subsequent heating of the mixture under reflux for 120 h did not yield compound (**3**); the starting material was recovered quantitatively by extraction with benzene.

Results and Discussion

Five possible structures (**A**)—(**E**) can be envisaged for compound (**3**) as shown in Figure 1; only the oxophosphazadiene tautomeric forms are considered.[2] The ^1H n.m.r. spectrum (methoxy-region only) of (**3**) is shown in Figure 2. Two sets of four doublets are observed which indicate the presence of two

Table. The ^{31}P-{^1H} n.m.r. data for compounds (2) and (3)

Compound	Chemical shift (δ) PPh_3 (a)	$P(NPPh_3)(OMe)$ (b)	$P(OMe)_2$ (c)	$P(O)(OMe)$ (d)	Coupling constants (Hz) ab	bc	bd	cd	ac	ad
(2)	9.42	13.48	21.01	—	37.0	70.9	—	—	2.0	—
(3a) (major isomer)	14.32	7.18	14.45	2.65	33.7	67.0	28.4	62.0	<2	<2
(3b) (minor isomer)	13.20	7.11	14.06	3.15	36.5	68.0	26.0	62.3	<2	<2

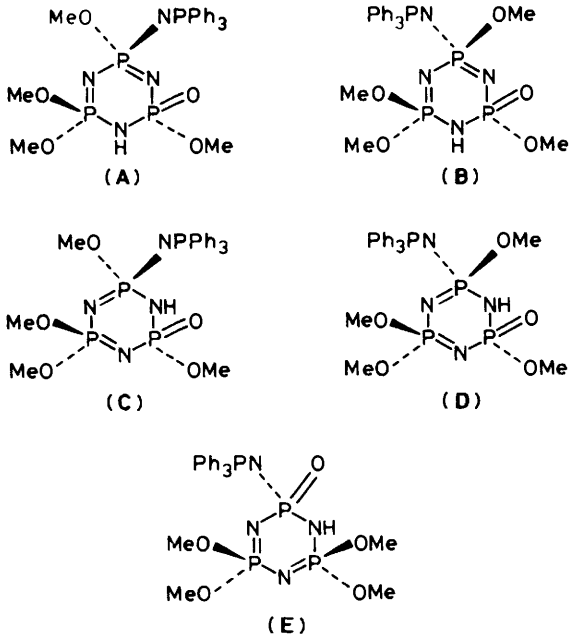

Figure 1. The five possible oxophosphazadiene structures for $N_3P_3(NPPh_3)(OMe)_4(OH)$ (3)

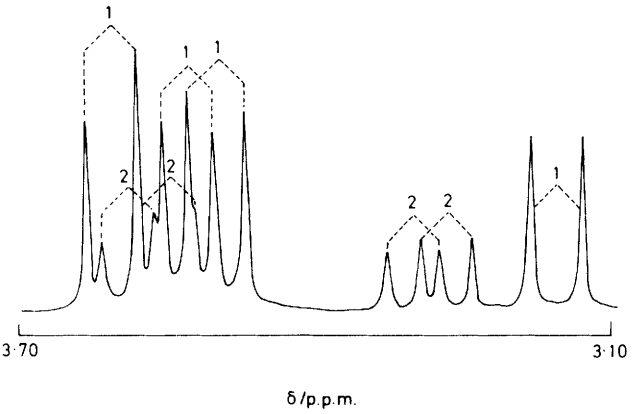

Figure 2. The ^1H n.m.r. spectrum of compound (3) (methoxy-region only); peaks 1 are due to the *cis* isomer (3a), 2 to the *trans* isomer (3b)

isomers. The corresponding ^{31}P-{^1H} n.m.r. spectrum (Figure 3) confirms the presence of two isomers. The phosphorus chemical shifts and coupling constants are listed in the Table. The pair of doublet of doublets centred at δ 2.65 and 3.15 are readily assigned to =P(O)(OMe) groups.[3] The assignment of signals due to $\equiv P(NPPh_3)(OMe)$ (δ 7.18 and 7.11), $\equiv P(OMe)_2$ (δ 14.45 and 14.06), and $=PPh_3$ (δ 14.32 and 13.20) can be made by examining the splitting patterns. Hence structure (E) is excluded. Structures (A) and (B) can be discounted from the observed ^2J(P–P) values. The magnitude of ^2J(P–P) across a ≡P–N(H)–P≡ unit would be expected to be smaller than those across a ≡P=N–P≡ unit.[3,12,13] The very low values observed for $^2J[P(NPPh_3)(OMe)–P(O)(OMe)]$ (28.4 and 26.0 Hz) as compared to $^2J[P(OMe)_2–P(O)(OMe)]$ (62.0 and 62.3 Hz) for both isomers (3a) and (3b) unambiguously establish that the proton resides at the ring nitrogen adjacent to the $\equiv P(NPPh_3)(OMe)$ site. Thus only isomeric structures (C) and (D) are possible for (3).

The assignments of the observed methoxy-peaks in the ^1H n.m.r. spectrum (Figure 2) to the respective isomers (3a) and (3b) (relative abundance 3:1 as determined from the intensities of the spectral lines) are shown in Figure 4 along with data for compounds (2), (6), and (7). These assignments are based upon the criteria established earlier for other cyclophosphazene derivatives containing the $-NPPh_3$ substituent.[10,11,14] In particular, the $-NPPh_3$ group exerts a pronounced shielding effect on the protons of the *cis* substituent and hence the more abundant isomer is assigned a structure in which the P=O and $-NPPh_3$ groups are *cis* to each other, (3a). The doublets centred at δ 3.55 [for (3a)] and 3.60 [for (3b)] have the largest ^3J(P–H) values (13.6 Hz each) and are ascribed to the methoxy-protons of the $\equiv P(NPPh_3)(OMe)$ group on the basis of coupling-constant data for (2) (Figure 4). The ^{31}P n.m.r. assignments to the individual isomers (3a) and (3b) follow from the relative intensity of the two sets of signals (Figure 3).

Further proof for the absence of a $=P(O)(NPPh_3)$ group in compound (3) is obtained by the synthesis of $N_3P_3(NPPh_3)(NMe_2)(OMe)_3(OH)$ (7) from *gem*-$N_3P_3(NPPh_3)(NMe_2)Cl_4$ (5).[9] The dimethylamino-derivative (7) also exists in solution as an isomeric pair [(7a) and (7b) in the ratio 3:2] as shown by its ^1H n.m.r. (270-MHz) data which are very similar to those for compound (3) (Figure 4).

The likely site of protonation in compounds (3) and (7) can be predicted from a knowledge of the relative electron densities at the ring nitrogen atoms which can be calculated by using the substituent constants derived from basicity measurements.[3,7] Since the electron-releasing character of the relevant substituents decreases in the order $NPPh_3 \gg NMe_2 > OMe$,[7,15] it can easily be shown that protonation should occur at the nitrogen adjacent to the $\equiv P(NPPh_3)R$ (R = OMe or NMe_2) group as established from n.m.r. data.

For the 'dihydroxy'-compound (4) there are eight possible dioxocyclotriphosphaza-1-ene structures including geometrical and positional isomers. The ^1H n.m.r. spectrum is complex and shows more than eight methoxy-doublets. The presence of at least three isomers is therefore indicated. The doublet centred at δ 3.55 with a ^3J(P–H) value of 13.6 Hz (see Experimental section) is presumably due to an isomer containing the $\equiv P(NPPh_3)(OMe)$ group.

The present study thus demonstrates the existence of geometrical isomerism for oxophosphazadienes. This novel behaviour arises as a result of unsymmetrical substitution at the phosphorus centre adjacent to the site of protonation.

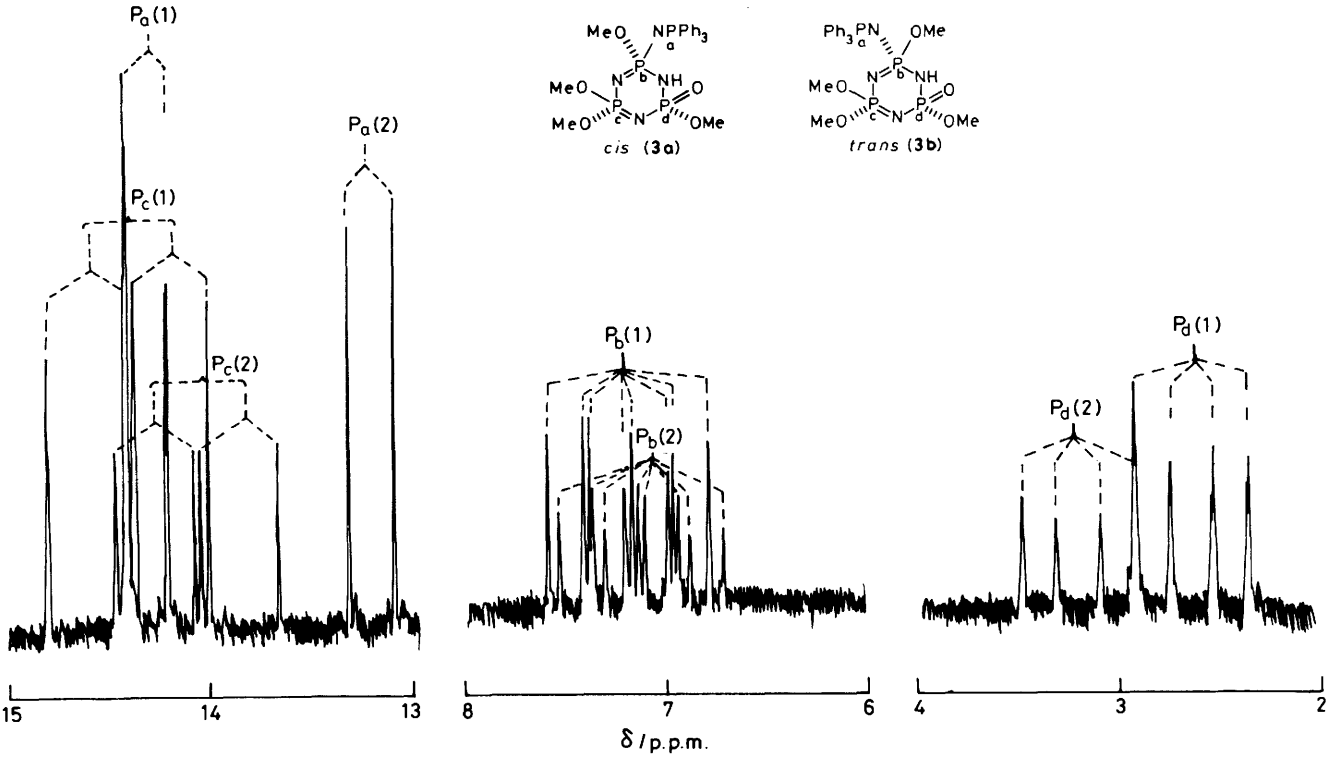

Figure 3. The ^{31}P n.m.r. spectrum (162 MHz, $CDCl_3$) of compound (3)

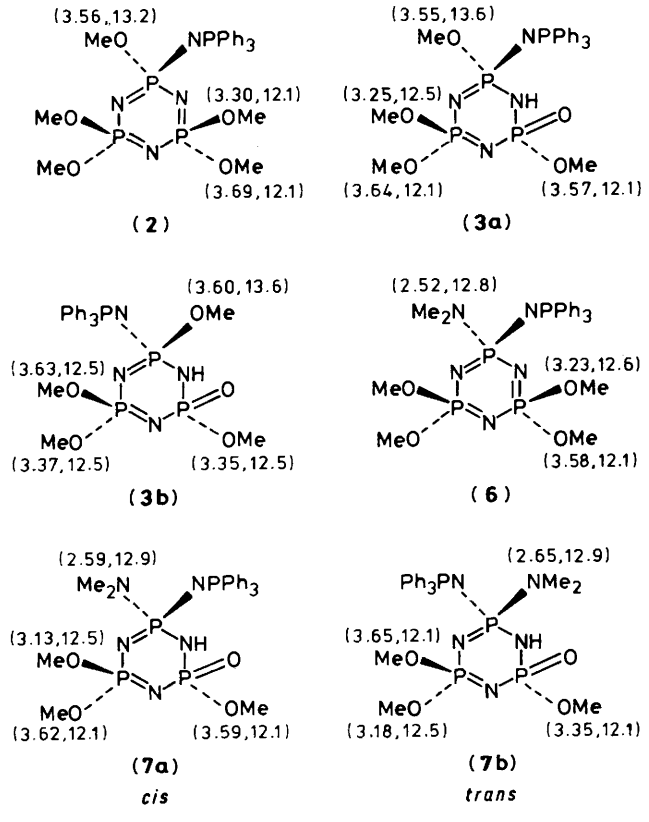

Figure 4. The structures of compounds (2), (3), (6), and (7) along with ^1H n.m.r. data; chemical shifts (δ/p.p.m.) and $^3J(P-H)$ values (Hz) for the methoxy-protons are given in parentheses

Acknowledgements

We thank Professor A. R. Vasudeva Murthy for his interest, and the Council of Scientific and Industrial Research, New Delhi for a fellowship (to K. C. K. S.). Our thanks are also due to Dr. J. Mason for providing the $^{31}P-\{^1H\}$ n.m.r. spectra.

References

1 Part 21, K. V. Katti and S. S. Krishnamurthy, *J. Chem. Soc., Dalton Trans.*, 1985, 285.
2 K. S. Dhathathreyan, S. S. Krishnamurthy, A. R. Vasudeva Murthy, T. S. Cameron, C. Chan, R. A. Shaw, and M. Woods, *J. Chem. Soc., Chem. Commun.*, 1980, 231.
3 K. S. Dhathathreyan, S. S. Krishnamurthy, A. R. Vasudeva Murthy, R. A. Shaw, and M. Woods, *J. Chem. Soc., Dalton Trans.*, 1982, 1549.
4 D. M. Kok, A. M. G. Kok-Hettinga, and J. C. Van de Grampel, *Inorg. Chim. Acta*, 1982, **59**, 107.
5 B. de Ruiter, H. Winter, T. Wilting, and J. C. Van de Grampel, *J. Chem. Soc., Dalton Trans.*, 1984, 1027.
6 H. R. Allcock and T. J. Fuller, *J. Am. Chem. Soc.*, 1981, **103**, 2250; H. R. Allcock, J. J. Fuller, and K. Matsumara, *Inorg. Chem.*, 1983, **21**, 515.
7 R. A. Shaw, *Pure Appl. Chem.*, 1980, **52**, 1063.
8 R. Keat, M. C. Miller, and R. A. Shaw, *J. Chem. Soc. A*, 1967, 1404.
9 M. Biddlestone and R. A. Shaw, *J. Chem. Soc., Dalton Trans.*, 1973, 2740.
10 S. S. Krishnamurthy, P. Ramabrahmam, A. R. Vasudeva Murthy, R. A. Shaw, and M. Woods, *Z. Anorg. Allg. Chem.*, in the press.
11 K. C. Kumara Swamy and S. S. Krishnamurthy, *Phosphorus Sulfur*, 1983, **18**, 241.
12 K. S. Dhathathreyan, S. S. Krishnamurthy, A. R. Vasudeva Murthy, R. A. Shaw, and M. Woods, *J. Chem. Soc., Dalton Trans.*, 1981, 1928.
13 B. Thomas and G. Grossmann, *Phosphorus Sulfur*, 1981, **10**, 375.
14 K. C. Kumara Swamy, M. Damodara Poojary, S. S. Krishnamurthy, and H. Manohar, *Z. Naturforsch., Teil B*, 1984, **39**, 615.
15 R. A. Shaw, *Z. Naturforsch., Teil B*, 1976, **31**, 641.

Received 31*st August* 1984; *Paper* 4/1507