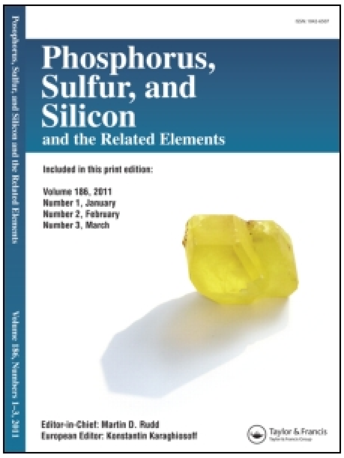

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THE STRUCTURES OF PENTAPHENYLCYCLOTRIPHOSPHAZATRIENE-DERIVATIVES; A ^{31}P N.M.R. INVESTIGATION

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THE STRUCTURES OF PENTAPHENYLCYCLOTRIPHOSPHAZATRIENE-DERIVATIVES; A ^{31}P N.M.R. INVESTIGATION

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A ^{31}P n.m.r. study of a compound, previously thought to be a hydroxyphosphazene, $N_3P_3(OH)Ph_5$, shows that it is present in solution as an oxophosphazane, $N_3HP_3(O)Ph_5$. Its condensation product, $(N_3P_3Ph_5)_2O$, gives a ^{31}P spectrum which can be analysed as an $A_2BB'A'_2$ spin system, confirming that it has an oxygen-bridged phosphazene structure.

Some time ago, two of reported[1] that the hydrolysis of the chloropentaphenyl-derivative (**1**) results in the formation of a hydroxy-phosphazene (**2**). Evidence for the latter structure came from infrared spectroscopy, but in view of recent ^{31}P n.m.r. results on related compounds,[2] the possibility of oxophosphazane structures (**3**) and (**4**) requires further consideration. At ambient temperature the $^{31}P-\{^1H\}$ pulsed Fourier transform n.m.r. spectrum of the hydrolysis product gave a series of three broadened signals. At −60°C, two of these signals were sharp see Figure 1, and P...P spin coupling readily measured (Table I). The reason for the broad PPh$_2$-signal is not clear. These results are only consistent with the oxophosphazane structure (**3**), in which the ambient temperature ^{31}P signals are broadened by exchange of the NH proton and/or incomplete removal of coupling to the ^{14}N quadrupole. Consistent with this assignment, it has also been found[3] that (**3**) can be obtained by the reaction:

$$Ph_2(H_2N)P{=}N{-}\overset{+}{P}(NH_2)Ph_2Cl^- + PhP(O)Cl_2 \xrightarrow[\text{reflux}]{\text{PhCl}} (3) + 3HCl$$

The foregoing evidence is in line with that on other so-called hydroxyphosphazenes, which, with the possible exception of $N_4P_4Ph_6(OH)_2$,[4] are known to exist in the oxophosphazane form.[5]

The condensation of (**1**) and (**3**), induced by a pyridine/water mixture,[1] results in the linking of two cyclophosphazene rings to form a compound

TABLE I

^{31}P n.m.r. data[a]

Compound	$\delta P\mathrm{Ph}_2^b$	$\delta P\mathrm{Ph}^b$	$\lvert J(PNP)\rvert$ /Hz
$N_3P_3ClPh_5$	16.8	28.6	2.5
$N_3HP_3(O)Ph_5$	16.7	2.7	—
	24.0		
" (at −60°C)	17.2[c]	3.7	2.5
	24.7		5.5
$[N_3P_3Ph_5]_2O$	15.4	10.1	11.4
			$\lvert J(POP)\rvert = 37.9$
			$\lvert J(PNPOP)\rvert = 0.2$

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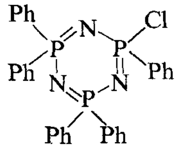
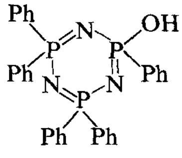
[a] Obtained on $CDCl_3$ solutions on a Varian XL–100 at 40.5 MHz and *ca* 25°C unless otherwise stated.

[d] Relative to external 85% H_3PO_4; downfield shifts are positive.

[c] Broad, $W_{\frac{1}{2}}$ *ca* 30 Hz.



(1)



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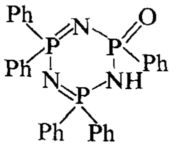

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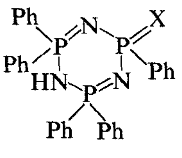

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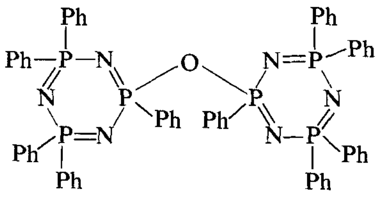

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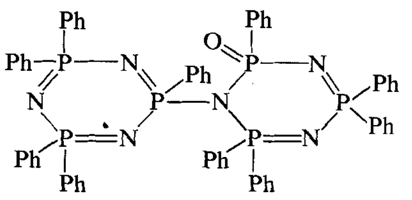

(6)

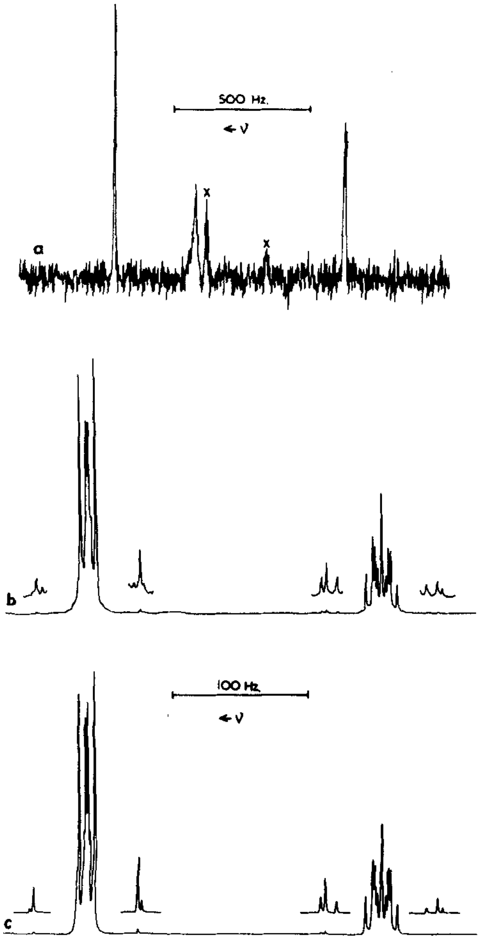

FIGURE 1 a) ^{31}P-$\{^1H\}$n.m.r. spectrum of (3) at −60°C, X = impurity (compound 5) b) ^{31}P-$\{^1H\}$n.m.r. spectrum of (5) c) Simulated spectrum of (5), using the parameters in the Table. The weak outer lines in b) and c) are also shown with the amplitude increased by *ca* 10X.

which was formulated as (**5**), but the alternative structure (**6**) is also possible. The $^{31}P - \{^1H\}$ n.m.r. spectrum of this compound is quite complex, although it can be simulated in terms of an $A_2BBA'_2$ spin system with particular attention being paid to the weak lines using the parameters in Table I. This confirms that the structure is (**5**); compound (**6**) would have at least five chemically shifted ^{31}P signals. ^{31}P n.m.r. data for (**1**) are also included in the table for comparison. Whilst the *PNP* spin-couplings are generally relatively small, as expected,[6] the *POP* coupling is the largest that we have encountered. The latter coupling, involving two quinquivalent phosphorus nuclei, is generally less than 35 Hz (sign not considered).[7]

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