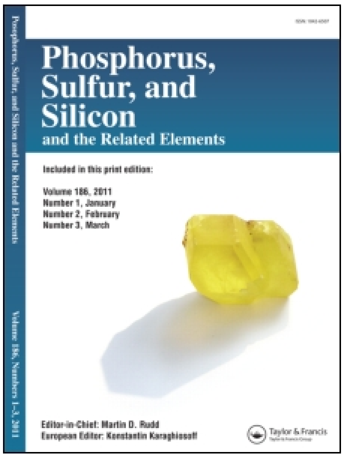

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THE ^{31}P NMR SPECTRA OF ISOMERIC DIAMINOHEXACHLOROCYCLOTETRAPHOSPHAZATETRAENES; EXAMPLES OF A_2B_2 AND AA′BB′ SPIN SYSTEMS

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The ^{31}P nmr spectra of 2,4- and 2,6-diamino-derivatives of octachlorocyclotetraphosphazatetraene, $N_4P_4Cl_6(NR^1R^2)_2$ (R^1 = H, R^2 = Bu^t; R^1 = H, R^2 = CH_2Ph; R^1 = Me, R^2 = Ph), have been measured. The 2,4- and 2,6-isomers were analysed as AA′BB′ and A_2B_2 spin systems respectively. In the 2,4-isomers the spin-spin couplings $^2J(PNP)$ and $^4J(PNPNP)$ were of opposite sign.

Relatively few examples of the ^{31}P nmr spectra of derivatives of octachlorocyclotetraphosphazatetraene have been reported, but it has been shown that the technique is extremely useful for distinguishing positional isomers.[1–3] For example, derivatives of the type, $N_4P_4Cl_6(NRR^1)_2$ (R and R^1 = H, alkyl, or aryl), could exist as positional isomers with amino-groups in 2,2- 2,4- or 2,6-positions which can be characterized by their AB_2C, AA′BB′, and A_2B_2 ^{31}P spectra respectively. Of these spectra, those of the A_2B_2 type are easiest to analyse, although surprisingly few examples have been reported where true magnetic equivalence of A and B groups is encountered.[4] We now compare these spectra with those of the AA′BB′ type, examples of which are provided by 2,4-amino-derivatives, $N_4P_4Cl_6(NR^1R^2)_2$ (R^1 = H, R^2 = Bu^t; R^1 = H, R^2 = CH_2Ph; R^1 = Me, R^2 = Ph).

The ^{31}P chemical shifts are characteristically to high field of analogous amino-derivatives of $N_3P_3Cl_6$. The 2,4-isomers all have PCl_2 signals to high field of the analogous 2,6-isomers, but the reverse is true of the $PClNR^1R^2$ signals. In all cases except that of 2-*trans*-6-$N_4P_4Cl_6(NMePh)_2$ the shift δ_{AB} was sufficient to analyse the spectra (e.g. Figure 1) by conventional methods.[4] The two bond couplings $^2J(PNP)$ are generally less positive than those of the analogous trimeric derivatives which is surprising[5] when it is considered that bond angles at endocyclic nitrogen atoms are larger[6] in these (tetramer) derivatives. Both $^2J(AA')$ and $^2J(BB')$, (see table for definitions), which are not distinguished in the analyses, are relatively small considering that one must pertain to the $-Cl_2P{=}N{-}PCl_2{=}$ fragment and that the replacement of amino- by chloro-substituents might be expected to increase $^2J(PNP)$.[7] In fact the relative constancy of $^2J(BB')$ implies that this coupling applies to the $-Cl_2P{=}N{-}PCl_2{=}$ grouping.

It is interesting to find that $^4J(PP)$ [$=J(AB')$] is opposite in sign to all the two-bond couplings, the latter of which must be positive.[1] Small negative and positive couplings, $^4J(PP)$, have also been reported for phosphazenylcyclotriphosphazatrienes and related to their conformations,[8] but it does not appear that any related reasoning can be applied here. P···P spin couplings in aminocyclotetraphosphazatetraenes are not influenced by substituents in the same way as in aminocyclotriphosphazatrienes.[7]

TABLE 1

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

Compound[b]	mp °C	δ_A[c]	δ_B[c]	$^2J(AB)$	$^4J(AB')$	$^2J(BB')$	$^2J(AA')$
					(in Hz[c,d])		
$N_4P_4Cl_6(NHBu^t)_2$ (2,4:)	128	−7.3	−8.7	37.4	−0.7	33.0	33.9
$N_4P_4Cl_6(NHBu^t)_2$ (2,6:)	171	−10.6[e]	−6.1[e]	38.3[e]			
$N_4P_4Cl_6(NHCH_2Ph)_2$ (2,4:)	liquid	−0.8	−6.1	38.1	−1.1	33.3	36.9
$N_4P_4Cl_6(NHCH_2Ph)_2$ (2,6:)	149–150	−2.6	−5.2	38.8			
$N_4P_4Cl_6(NMePh)_2$[f] (2,4:)	105–106	−3.2	−7.2	41.6	−0.8	32.8	44.0
$N_4P_4Cl_6(NMePh)_2$[f] (2,6:)	145	−5.3[e] (singlet)					

[a] Spectra obtained using $CDCl_3$ solutions on a Varian XL-100 at 40.5 MHz, except for the *N*-methylanilino-derivatives which were recorded on a Jeol C60HL at 24.3 MHz. Chemical shifts downfield from the standard are reported as positive.

[b] The preparation of *t*-butylamino[3] and *N*-methylanilino[9] derivatives has been reported; the preparation of benzylamino derivatives (K. Ramachandran, unpublished work) will be reported elsewhere.

[c] A = $PClNR^1R^2$, B = PCl_2; $^2J(AA')$ and $^2J(BB')$ are not distinguished in the analysis of these spectra.

[d] All positive except where otherwise stated (±0.5 Hz) AA′BB′ simulations obtained using the SIMEQ II programme of C. W. F. Kort and M. J. A. de Bie.

[e] Spectra previously reported in Ref. 2.

[f] Structures confirmed by x-ray crystallography (2,6-isomer: K. K. Bhandari, H. Manohar, and Y. S. Babu, *Acta Cryst.* **B33**, 3548 (1977); 2,4-isomer: Y. S. Babu, and H. Manohar, *Cryst. Struct. Comm.* **6**, 803 (1977).

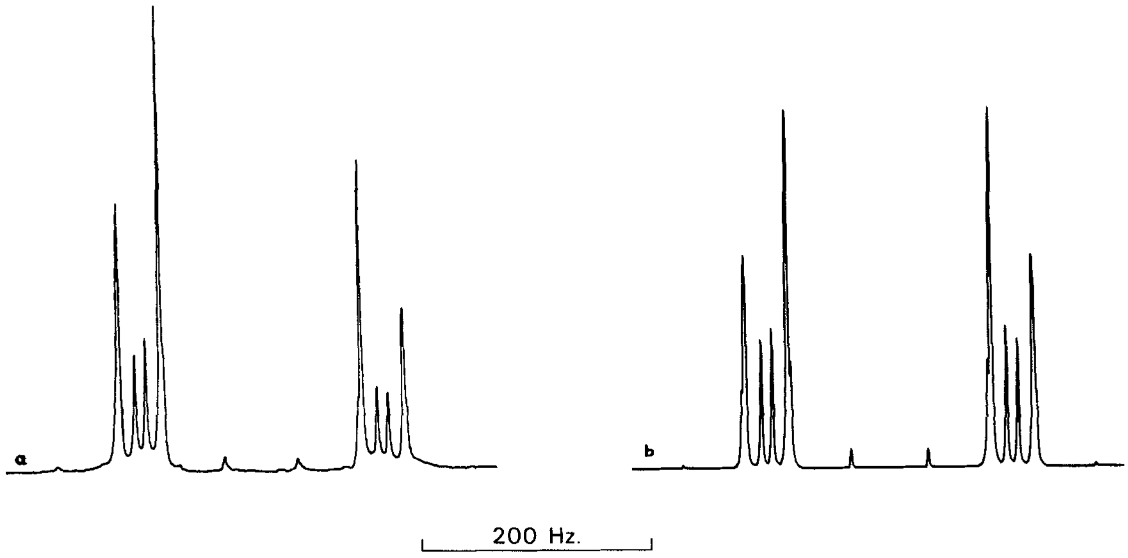

FIGURE 1 ^{31}P nmr spectrum of $2,4\text{-}N_4P_4Cl_6(NHCH_2Ph)_2$ with ^1H noise decoupling. (*a*) observed, (*b*) simulated, using the parameters in the table.

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