On the Ring Size of Cyclopolyphosphines

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Summary The ring size of cyclopolyphosphines, $(RP)_n$, in solution may be determined by observing the proton decoupled ^{31}P n.m.r. spectrum.

The determination of ring size of cyclopolyphosphines has been problematical. Cryoscopic, ebullioscopic, and isopiestic molecular weight determinations have yielded, for reasons not perfectly clear, particularly erroneous results. The mass spectra of cyclopolyphosphines normally do not indicate a parent peak. *X*-Ray crystallography has been the only reliable method for ascertaining the number of phosphorus atoms incorporated into a particular cyclopolyphosphine ring.[1] The nature of the problem is particularly well illustrated by the confusion which existed over the phenylcyclopolyphosphine system until the structures were solved by *X*-ray crystallography.[2]

We have found that four- and five-membered cyclopolyphosphine rings, which constitute all known cyclopolyphosphines except for hexaphenylcyclohexaphosphine,[2] can be distinguished in solution simply by recording the ^{31}P n.m.r. spectrum of the sample while decoupling all other nuclei in the molecule with spin (normally only protons). The phosphorus atoms in four-membered rings have lone pairs which alternate in a *trans* manner around the ring. This is to be expected in order to minimize lone pair–lone pair and R-group–R-group interactions, it is also the case for all known crystal structures.[3,4] Assuming only that the pendant R groups are symmetry equivalent on the n.m.r. time scale, then the four phosphorus atoms all belong to a single set of magnetically equivalent nuclei. The undecoupled ^{31}P n.m.r. spectrum is a complex second-order spectrum due to long range phosphorus coupling.

However, by decoupling the pendent R group, the ^{31}P n.m.r. spectrum should collapse to a singlet because the magnetically equivalent set of phosphorus atoms are coupled to no other nuclei.

TABLE

Proton decoupled ^{31}P n.m.r. spectra[a] of cyclopolyphosphines $(RP)_n$

R	Ring size	Method of preparation	Solvent	Chemical shift[b]	Multiplicity
Me	5	A	C_6D_6	−17·3	complex multiplet
Me	5	A	neat[c]	−18·8	complex multiplet
Ph	5	B	THF[c]	+ 4·7	complex multiplet
Bu	5	C	neat[c]	−13·4	complex multiplet
Et	5	C	neat[c]	−16·0	complex multiplet
Pr^i	4	C	C_6D_6	+62·4	singlet
Cyclohexyl	4	C	C_6D_6	+68·3	singlet

[a] Measured on a Varian XL-100-15 FT spectrometer operating at 40·5 MHz, ^2H lock. [b] In p.p.m. relative to 85% H_3PO_4. [c] Spectrometer locked on internal C_6D_6 capillary. [d] A: $RPCl_2$ + Li.[7] B: $RPCl_2 + RPH_2$.[7] C: P_4 + RMgX + RX.[8]

A five-membered cyclopolyphosphine ring cannot have symmetric *trans* alternation of phosphorus lone pairs around the ring. The phosphorus nuclei belong, then, to an AA′BB′C spin system. Decoupling of the pendant R groups will not yield a singlet, but rather a second order AA′BB′C spectrum. One such system, pentamethylcyclopentaphosphine has recently been analyzed.[5]

We have examined the tetracyclopolyphosphines $(RP)_4$, where R = isopropyl and cyclohexyl, which have been shown to be tetrameric by *X*-ray crystallography.[4] These both collapse to sharp singlets (width at half-height of *ca.* 2 Hz) upon ^1H decoupling. The pentacyclopolyphosphines $(RP)_5$, R = phenyl and methyl, yield AA′BB′C spectra upon ^1H decoupling. Ethylcyclopolyphosphine was originally believed to be tetrameric and more recent investigations concluded that possibly both four- and five-membered rings existed.[6] We find evidence only for the existence of pentaethylcyclopentaphosphine. Upon ^1H decoupling only a complex ^{31}P multiplet is apparent. If, indeed, any tetramer exists, it is less than *ca.* 5%. We also believe that the n-butylcyclopolyphosphine is a pentamer, not a tetramer as previously reported.[7] Furthermore, by correcting the reported ring size of ethyl and n-butyl cyclopolyphosphines, we find that the ^{31}P n.m.r. chemical shift of cyclopolyphosphines to be indicative of ring size. Four-membered rings all occur between +50 and +70 p.p.m. relative to 85% H_3PO_4, five-membered rings all occur between −20 and +10 p.p.m.

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[4] J. W. Bart, *Acta Cryst.*, 1969, B**25**, 762; It may be argued that the integrity of the ring size in the solid is lost in solution. However, for both the phenyl and perfluoromethyl systems, both of which occur in two ring sizes (n = 5 & 6 for phenyl, n = 4 & 5 for perfluoromethyl), the ring size appears to be unaltered upon dissolution.

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