

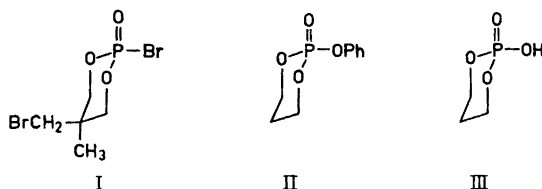
Proton Magnetic Resonance Analysis of 2-Chloro, 2-Methoxy-, and 2-Phenoxy-1,3,2-dioxaphosphorinanes

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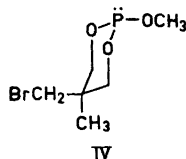
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The PMR spectra of 2-chloro-, 2-methoxy- and 2-phenoxy-1,3,2-dioxaphosphorinanes have been fully analysed by an iterative method, and the spectra show that the ring phosphites exist predominantly in one conformation with the P-Cl, P-OCH₃ and P-OPh groups in axial position. Long range coupling through four bonds of the ring has also been observed.

In the last few years six-membered rings containing quadruply linked phosphorus as hetero atom have received much attention. X-Ray analysis of three 1,3,2-dioxaphosphorinanes¹⁻³ (I-III) has confirmed that these compounds have chair-structure with the phosphoryl oxygen atom occupying the equatorial position. In the phosphate part of the ring a flattening of the chair structure is observed caused by the long P-O bonds. PMR studies of 1,3,2-dioxaphosphorinane in solution have also given evidence for a chair-like ring structure with either an equatorial or an axial phosphoryl oxygen group.⁴



X-Ray data for six-membered ring phosphites, have, so far, not been reported. Whether the lone electron pair is in equatorial or in axial position is yet unsolved. From dipole moment and PMR measurements of 2-methoxy-5-methyl-5-bromomethyl-1,3,2-dioxaphosphorinane (IV), it has been proposed that the methoxy group attached to the phosphorus atom is axial in the chair conformation of the ring.



This work reports the complete PMR analysis of the six-membered ring phosphites, 2-chloro-, 2-methoxy-, and 2-phenoxy-1,3,2-dioxaphosphorinane (V–VII). The preferred structure of the cyclic phosphites is discussed on basis of the PMR spectra.

EXPERIMENTAL

2-Chloro-1,3,2-dioxaphosphorinane (V) was prepared from 1,3-propanediol and phosphorus trichloride according to the method of Lucas *et al.*,⁷ b.p.₁₅ 67°C.

*2-Methoxy-1,3,2-dioxaphosphorinane (VI)*⁸ was prepared from V and methanol in ether solution using triethylamine as base, b.p.₁₅ 70°C.

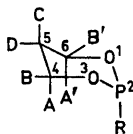
2-Phenoxy-1,3,2-dioxaphosphorinane (VII) was prepared from VI and phenol in ether solution using triethylamine as base, b.p._{1.5} 110°C, m.p. 46.5°C.

The PMR spectra of V and VI were measured as neat liquid, and VII on 80 % solution in CDCl₃. The spectra were recorded on a 60 MHz, JEOL, C-60H instrument. The samples were degassed by freezing and thawing, and the tubes were sealed under vacuum. Line positions were obtained by averaging the data from five spectra. The spectra were analyzed, using the iterative least squares computer program LACX.¹⁴ The computation were carried out on an IBM 360/50 computer, and the graphical output was obtained using a Calcomp Plotter.

SPECTRAL ANALYSIS

Gagnaire¹⁰ and coworkers report no change of the PMR spectra for a series of six-membered ring phosphites over the temperature range -50 to +160°C. The authors conclude that the results indicate the presence of rigid ring structures in the compounds. Since the rings do not undergo inversion on the PMR time scale, the molecules V, VI, and VII are well suited for PMR analysis.

The 60 MHz PMR spectra of the six-membered rings V, VI, and VII show a rather complex, but well resolved pattern. The whole spectrum can be divided into four bands, A, B, C, and D (Fig. 1). The bands A and B are assigned to the protons at carbons 4 and 6 of the ring due to the deshielding effect of the ring oxygen atoms. The bands C and D are assigned to the protons at carbon 5.



- Y: R = Cl
 VI: R = OCH₃
 VII: R = OPh

Band D appears to be a doublet of sextets with some of the signals further splitted into doublets. The larger coupling is assigned to the geminal proton coupling at carbon 5 and the sextets are assumed to arise from the coupling to the phosphorus atom and from equal coupling of the protons at carbon atoms 4 and 6. Since a strong coupling (*vicinal trans*) does not appear in band D, this indicates that the signals are due to the equatorial proton at carbon 5. Band C is accordingly assigned to the axial proton at carbon 5.

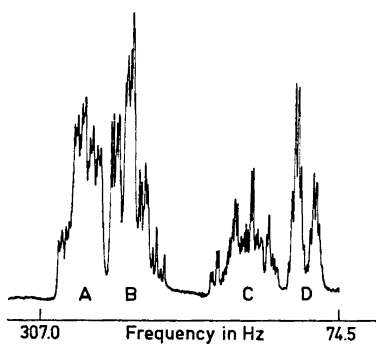


Fig. 1. 60 MHz PMR spectrum of 2-chloro-1,3,2-dioxaphosphorinane. (V)

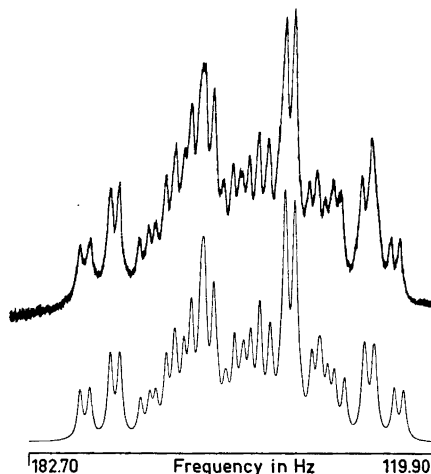


Fig. 2. The spectrum of the axial proton in position 5 (Band C) of 2-chloro-1,3,2-dioxaphosphorinane (V). Upper: Observed spectrum. Lower: Calculated spectrum.

The splitted triplet of band A indicates that there is a coupling of nearly the same magnitude as the geminal coupling, $J_{AB} = J_{A'B'}$, together with a smaller coupling. The larger coupling is assumed to be the *vicinal trans* (J_{aa}) coupling, and the smaller the coupling to the phosphorus atom. Band A is therefore assigned to the axial protons at carbon atoms 4 and 6. As the POCH coupling constant shows a substantial dihedral dependence,¹¹⁻¹³ and the appearance of a great phosphorus coupling in band B, it is reasonable to assign this band to the equatorial protons at carbon atoms 4 and 6.

The analysis of the spectra using an $(AB)_2XYP$ spin system was unsuccessful. The spectra were analysed on the basis of $(AB)_2CDX$ spin system, and a good fit between theoretical and experimental spectra were obtained (Fig. 2). The final RMS error observed was 0.1, when all 27 parameters were allowed to vary. The probable errors of the coupling constants are 0.02 to 0.03 Hz.

RESULTS AND DISCUSSION

Gagnaire¹⁵ and his co-workers claim from the PMR spectrum of VI that the difference of 3Hz of the coupling constants ${}^4J_{PH}$ (${}^4J_{PHax} = 0.5$ and ${}^4J_{PHeq} = 3.6$) that the $POCH_3$ group is situated in equatorial position. The

PMR spectra of V, VI, and VII show, however, that the ring phosphites exist predominantly in one conformation with P—Cl, P—OCH₃, and P—OPh groups in axial position. The difference between the $^4J_{\text{PHeq}}$ and $^4J_{\text{PHax}}$ in the compounds V, VI, and VII is approximately 1.5 Hz (Table 1). This agrees well with

Table 1. Chemical shift data for V, VI, and VII.^a

		V	VI	VII
H ₄ and H ₆	axial	4.59	4.41	4.52
	equatorial	3.98	3.64	3.79
H ₅	axial	2.48	2.32	2.38
	equatorial	1.69	1.56	1.48

^a Chemical shift in ppm from tetramethylsilane.

Table 2. Spin-spin coupling constants (in Hz) for V, VI, and VII.

	V	VI	VII	
$^2J_{4(6)}$	-10.95	-10.64	-10.97	J_{4e4a} OR J_{6e6a}
2J_5	-14.63	-14.16	-14.23	J_{5e5a}
$^3J_{aa}$	12.86	12.51	12.67	J_{4a6a} OR J_{5a5a}
$^3J_{ea}$	4.67	4.82	4.58	J_{4e5a} OR J_{5a6e}
$^3J_{ee}$	2.22	2.30	2.22	J_{4e5e} OR J_{5e6e}
$^3J_{ae}$	2.16	2.39	2.30	J_{4a5e} OR J_{5e6a}
$^3J_{\text{PHa}}$	5.49	4.26	3.25	J_{P4a} OR J_{P6a}
$^3J_{\text{PHe}}$	10.70	10.40	10.28	J_{P4e} OR J_{P6e}
$^4J_{ee}$	1.40	1.56	1.59	J_{4e6e}
$^4J_{ea}$	-0.60	-0.35	-0.50	J_{4e6a} OR J_{4a6e}
$^4J_{aa}$	-0.10	-0.04	-0.05	J_{4a6a}
$^4J_{\text{PHa}}$	1.46	0.47	0.64	J_{P6a}
$^4J_{\text{PHe}}$	1.78	2.15	1.83	J_{P6e}

the findings of Kainosho and Nakamura¹⁶ based on PMR analysis of 2,7,8-trioxa-1-phosphabicyclo-(3,2,1)-octane (XIV).

The axial protons on the cyclic phosphites are always observed at lower field than the corresponding equatorial protons. The same observation has also been found for the cyclic sulfite.¹⁷ The axial protons at position 5 in dioxanes are also observed at lower field than the equatorial one.³³ The relative shifts of axial and equatorial protons are thus reversed as observed for cyclohexanes.¹⁸

The PMR spectrum shows that the protons in position 4 (or 6) are differently shielded, probably due to the position of the exocyclic group attached to the phosphorus atom. In the cyclic sulfite the axial proton at positions 4 and 6 are observed with larger downfield shifts as compared to the geminal

equatorial protons when the S=O group is in the axial position.¹⁹ In the same way the chemical shifts of the axial protons (4.5 ppm) in 4 and 6 positions of V, VI, and VII as compared to the equatorial protons (3.6 ppm), might indicate an axial position of the P–Cl, P–OCH₃, or P–OPh group. In dioxanes it has been observed that the coupling J_{5e4a} is greater than J_{5e4e} which is assumed to be due to the “flattening” of the ring. In the cyclic sulfite, where the ring by X-ray^{21,22} and PMR¹⁷ analysis has been shown to be held in an almost staggered conformation, the H_{5e} is coupled equally to the H_{4e(6e)} and H_{4a(6a)}. The same observation has been found for the H_{5e} proton in IV, V, and VI.

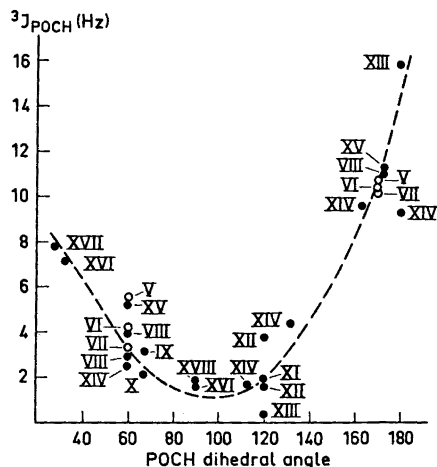
The dihedral angle in the carbon part of V, VI, and VII are calculated using the vicinal proton–proton coupling constants according to the method of Buys.²⁸ The calculated ring torsion angle of the fragment –CH₂–CH₂– is listed in Table 3. From the calculated values (V 58°, VI 57°, and VII 58°) it appears that the carbon part exists in nearly staggered conformation in six-membered ring phosphite.

Table 3. *R*-values and ring torsional angles for V, VI, and VII.

	V	VI	VII
<i>R</i>	2.205	2.055	2.175
Ψ	58.2°	57.2°	58.1°

It is known that 4J shows a maximum value when two interacting nuclei are oriented in a co-planar zigzag “W”-oriented form.²⁹ The four bond coupling between the equatorial protons in 4 and 6 positions in the ring phosphite, 1.2 Hz, is normal.^{17,23,29} Recently, several examples of non “W” coupling have

Fig. 3. Plots of POCH dihedral angles versus the range of values of $^3J_{POCH}$ in cyclic phosphites. ○ This work. ● Values taken from the literature. 5-*tert*-Butyl-2-methoxy-(VIII),⁶ 5-*tert*-butyl-2-chloro-(XV)⁶ and 4,6-dimethyl-2-methoxy-(IX–X)¹⁵. 1,3,2-dioxaphosphorinanes, 2,6,7-trioxo-1-phosphabicyclo(2,2,2)octane (XII)³¹ and the 4-methyl derivative (XI),^{9,30} 2,6,7-trioxo-1-phosphabicyclo(2,2,1)heptane (XIII),³² 2,7,8-trioxo-1-phosphabicyclo(3.2.1)octane-(XIV),¹⁶ 2-chloro-(XVI), 2-phenoxy-(XVII) and 2-methoxy(XVIII)-1,3,2-dioxaphospholanes.²⁷



been reported.^{24,26} In cyclic phosphites the four-bond coupling $J_{4bc} = -0.22$ has values similar to those reported by Hall *et al.*²⁶ for carbohydrates.

Kainosho and Nakamura¹⁶ proposed a relationship between J_{POCH} and the estimated dihedral angles. Representative values of J_{POCH} for some substituted five- and six-membered ring phosphites are presented in Fig. 3. From this figure it appears that the coupling constants J_{POCH} can be related to the dihedral angle of the fragment $-P-O-C-H$. The scattering of the data is due to the uncertainty of the dihedral angle, which in most cases is estimated from Dreiding models. The compounds V, VI, and VII, where chloro, methoxy, and phenoxy are the substituents linked to phosphorus, it may be seen that the increasing electronegativity of the substituent causes J_{POCH} to become more positive. The greater effect is observed for coupling to the axial proton as compared to the equatorial proton.

The best correlation between calculated and experimental spectra is obtained assuming a positive sign for J_{POCH} . This has also been found by Gagnaire¹⁰ for a similar compound.

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