

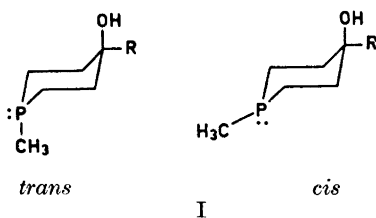
Proton Magnetic Resonance Analysis of Ring-substituted 2-Chloro-1,3,2-dioxaphosphorinanes

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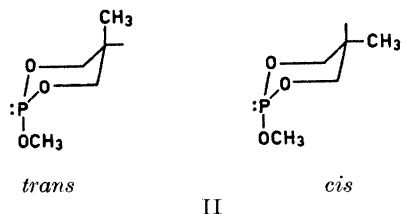
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The preferred conformation of 4-methyl-, 5-methyl-, and 5-phenyl-2-chloro-1,3,2-dioxaphosphorinanes has been determined by PMR analysis. The stable isomers of the 5-substituted phosphites exist in a chair conformation with equatorial substituent in position 5. The 4-methyl substituted phosphite occurs in an undistorted chair form with the substituent in the equatorial position. There is also evidence that the P-Cl group occupies an axial position in all compounds studied.

The chemistry of geometric isomers in six-membered ring compounds containing trivalent phosphorus as heteroatom has received much attention. Shook and Quin¹ demonstrated the existence of geometric isomers in 4-alkyl-1-methyl-1-phosphorinols (I).



The appearance of two P-CH₃ doublets in the PMR spectrum indicated that the difference in the two isomers occurs at the phosphorus atom, *i.e.* either *axial* or *equatorial* methyl substituent. Denny and Denny² found evidence from PMR spectra for the presence of geometric isomers in 5-methyl-2-methoxy-1,3,2-dioxaphosphorinane (II).

Table 1. Chemical shift data for (III), (IV), and (V).^a

		(III)	(IV)	(V)
Me ₄	eq.	1.27		
H ₄	eq.		3.89	3.97
	ax.	4.60	4.13	4.61
Me ₃	eq.		0.79	
H ₅	eq.	1.73		
	ax.	2.10	2.39	3.43
H ₆	eq.	3.98	3.89	3.97
	ax.	4.71	4.13	4.61

^a Chemical shift in ppm from tetramethylsilane.

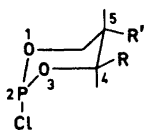
Table 2. Spin-spin coupling constants (Hz) for (III), (IV), and (V).

		(III)	(IV)	(V)
² J ₄₍₆₎		-10.85	-10.82	-11.15
² J ₅		-14.36	—	—
³ J _{aa}	(4.5) ^a	11.43	11.54	11.94
	(5.6)	12.75		
³ J _{ea}		4.53	4.30	4.62
³ J _{ee}		1.70	—	—
³ J _{ae}	(2.5)	2.40	—	—
	(2.6)	2.32		
³ J _{aCH₃}		6.30	6.70	—
³ J _{PH_a}	(5.7)	5.86	5.67	5.39
	(6.7)	5.76		
³ J _{PH_e}		10.44	10.99	10.92
⁴ J _{ee}			1.87	1.19
⁴ J _{ea}		0.20	-0.49	-0.03
⁴ J _{aa}		-0.41	-0.10	0.03
⁴ J _{PH_a}		1.34	0.82	1.03
⁴ J _{PH_e}		3.43	—	—

^a Number of ring-carbon holding the coupled nuclei.

On the appearance of two doublets ($\delta = 0.67$ and 1.28), assigned to the methyl group, the authors concluded that the difference between these isomers was due to different orientation of substituents at carbon 5. The methyl group experiences different shielding when situated in axial position as compared to equatorial position in the ring. PMR analysis of geometric isomers of ring-substituted 2-chloro-1,3,2-dioxaphosphorinanes using iterative computation was first reported by Hargis and Bentrude.³ They described a complete analysis of the *cis* and *trans* isomers of 5-*t*-butyl-2-methoxy-1,3,2-dioxaphosphorinane, and on the basis of chemical shifts and coupling constants they proposed a preferred conformation.

This work reports the complete PMR analysis of three rigid isomers of six-membered ring chloro-phosphites (III – V).



III R = Me, R' = H
 IV R = H, R' = Me
 V R = H, R' = Ph

The preferred conformation of the cyclic phosphites is proposed on basis of analysed PMR spectra.

EXPERIMENTAL

The cyclic chlorophosphites were prepared from the respective 1,3-butandiolis and phosphorus trichloride in ether solution using triethylamine as base.

4-Methyl-2-chloro-1,3,2-dioxaphosphorinane (III), b.p.₁₅ 69 – 70°C.

5-Methyl-2-chloro-1,3,2-dioxaphosphorinane (IV), b.p.₁₅ 74°C.

5-Phenyl-2-chloro-1,3,2-dioxaphosphorinane (V), b.p.₂ 122°C.

The PMR spectra of (III) and (IV) were measured as neat liquid, and (V) as 80 % solution in CCl₄. All spectra were recorded on a JEOL 60 MHz and a Varian HH – 100 instrument. The samples were degassed using the freeze-pump-thaw technique, and the tubes were sealed under vacuum. Line positions were obtained by averaging the data from several spectra. The spectra were analyzed, using the iterative least squares computer program LACX⁴ and UEATR.⁵ The computation was carried out on an IBM 360/50 computer, and the graphical output was obtained using a Calcomp Plotter.

SPECTRAL ANALYSIS

One of the isomers was always in great excess when the cyclic phosphite compounds were prepared according to the above method. No change in the PMR spectra was experienced for the cyclic phosphites over the temperature range – 60 to + 100°C, pointing to a ring structure in the temperature interval studied. The rigidity of the ring makes these compounds well suited for conformational studies with PMR spectroscopy.

The 60 MHz spectrum of (III) (Fig. 1) consists of two main regions ($\delta = 6.0$ to 4.5 and 3.5 to 2.0). The low field region can be divided into two bands and the triplet of quartets at high field is assigned to the *equatorial* proton at

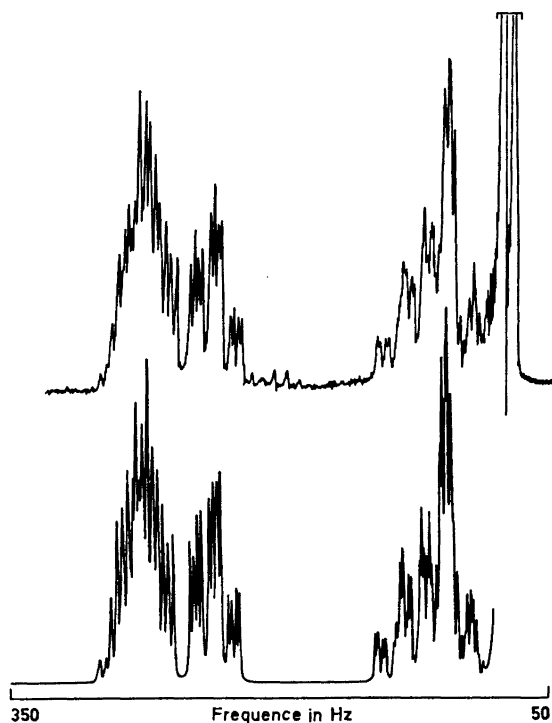


Fig. 1. 60 MHz PMR spectrum of 4-methyl-2-chloro-1,3,2-dioxaphosphorinane (III). Top, observed spectrum. Bottom, computed spectrum.

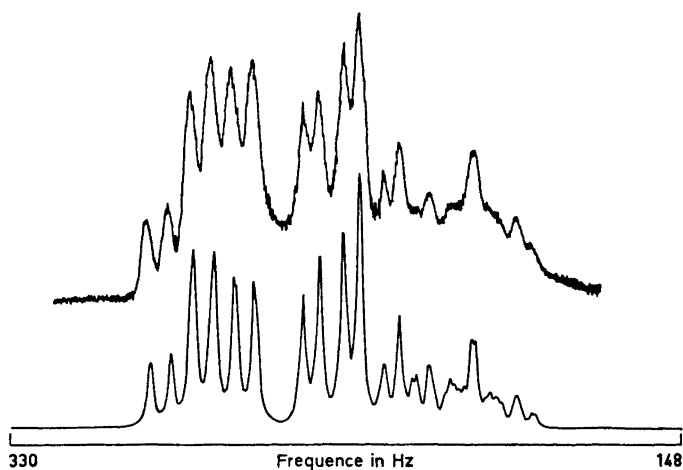
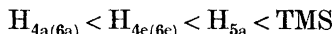


Fig. 2. Spectrum of the ring protons of 5-phenyl-2-chloro-1,3,2-phosphorinane (V). Top, observed spectrum. Bottom, computed spectrum.

carbon 6, where $|J_{\text{gem}}| \cong J_{\text{PH}} \cong 10.7$ Hz and $\frac{1}{2}|^3J_{\text{ea}}| \cong ^3J_{\text{ce}} \cong 2.4$ Hz. The complex band at low field is due to the *axial* protons at carbon 4 and 6, which is reasonable according to previous findings.⁶ The appearance of the high field bands shows, when compared with spectra of the unsubstituted compounds,⁶ that H_{5a} resonates at lower field as compared to H_{5c} . The chemical shift difference is less for the substituted compound (≈ 20 Hz) as compared to the unsubstituted compound (≈ 48 Hz). The doublet at high field in the total spectrum is assigned to the methyl group.

The PMR spectrum of (IV) consists of two complex bands ($\delta \approx 4.5$ to 3.5 and 3.0 to 1.5) and a doublet ($\delta \approx 0.75$). The low field band is assigned to the protons at carbons 4 and 6 with the *axial* protons at lower field compared to the *equatorial*. The presence of several large splittings and the width indicate that the high field band might be attributed to an *axial* proton at carbon 5. The position of the methyl group ($\delta \approx 0.75$) indicates an *equatorial* position, consistent with the observations in 5,5-dimethylsulfitcs.¹⁴

The spectrum of (V) appears to be very complex with two regions, assigned to the phenyl group ($\delta \approx 7.3$) and the ring protons ($\delta \approx 3.0$ to 5.0) (Fig. 2). The proton at carbon 5 resonates at lower field as compared to the unsubstituted molecule due to shielding caused by the phenyl group. Apparently the relative shifts of the protons are as follows:



The PMR spectra were fully analyzed by iterative computation using LACX⁴ or UEAITR.⁵ Compound (III) was analyzed on the basis of an ABCDEX₃P, (IV) as AA'BB'CX₃P and (V) as AA'BB'CP spin systems. The analysis gave a good fit between experimental and theoretical spectra for all compounds. The calculated and experimental spectra for compound (V) are shown in Fig. 2. The RMS values are less than 0.1 Hz when all parameter sets were allowed to vary. The error in line positions was 0.15 Hz or less, and the probable errors in coupling constants are about 0.02 Hz.

RESULTS AND DISCUSSION

Hargis and Bentrude^{3,14} reported the complete PMR analysis of the cyclic phosphite 5-*t*-butyl-2-chloro-1,3,2-dioxaphosphorinane, which occurs mainly in one isomer with the *t*-butyl group in the equatorial position. Their conclusion is based on the appearance of the H_5 signal, a triplet of triplets which shows that H_5 coupled unequally ($J \approx 10$ and $J' \approx 3$) to the vicinal *axial* and equatorial protons at carbons 4 and 6. The presence of a large vicinal coupling in the H_5 signal group in (IV) and (V) indicates that the stable isomer of these compounds has an *equatorial* substituent at carbon 5. The spectrum of compound (III) indicates an equatorial methyl group in position 4, due to the presence of only an axial proton at the α -carbon to oxygen. Consistent with our finding the more stable isomer of 2-ethoxy-4-methyl-1,3,2-dioxaphosphorinane⁷ has been reported to have an equatorial positioned 4-methyl group. Allbrand *et al.*¹⁰ also reported *equatorial* methyl substituents in the 4,6-dimethyl-2-chloro-1,3,2-dioxaphosphorinane.

The PMR spectra of the cyclic compounds (III), (IV), and (V) indicate that the protons in position 4 (or 6) are differently shielded, with the *axial* proton shifted to lower field compared to the *equatorial* proton. This relative shift position is the reversed as observed in cyclohexane derivatives but the same as previously reported for cyclic sulfites⁹ and phosphites.⁶ Apparently, this reversed or larger down field shift of the axial protons at carbons 4 and 6 in compounds (III), (IV) and (V), as compared to the geminal proton, indicates an *axial* position of the P-Cl group.

The *axial* proton at carbon 5 in 2-chloro-, 2-methoxy-, 2-phenoxy-, 2,6-dimethyl-2-chloro-1,3,2-dioxaphosphorinane,^{6,10} and in (III) is observed at lower field than the geminal *equatorial* proton. This observation is also reported for dioxanes,¹¹ and the cyclic trimethylene sulfite.⁹ The reason for this reversed relative shift as compared to cyclohexane might be the same as in dioxanes¹¹ for which it is assumed an interaction between H_{5e} and the *p*-orbitals of the ring oxygen in positions 1 and 3.

The geminal coupling constants for the protons at carbons 4 and 6, ${}^2J_{4(6)}$, in (IV) and (V) are smaller as compared with dioxanes, probably due to a greater geminal angle and a less ability of inductive removal of electrons by the P-Cl group. A lower value relative to dioxanes of 2J_5 in (III) is also found, and it is assumed to be caused by an increase in the H-C-H angle. Similar observation has been made in cyclic sulfites.⁹

The observation of a lower vicinal *trans* coupling from the axial proton at carbon 6 in (III) (11.4 and 12.7 Hz) is probably due to a substituent effect caused by the methyl group. From vicinal coupling constant in the $-CH_2-CH_2-$ moiety the ring torsion angle about C_5-C_6 bond can be calculated by the R-value method of Buys and Eliel.⁸ From the calculated R-value (2.10) the torsion angle is found to be about 58° , and it is reasonable to assume that the ring exists in an undistorted chair conformation. The 4-phenyl-dioxane¹⁵ is, however, reported to exist in an undistorted conformation with equal vicinal *trans* coupling from the axial proton at carbons 4 and 6.

Four bond coupling between the equatorial protons in 4 and 6 position have values similar to those reported in the literature.^{6,9,11,12} The four-bond coupling, ${}^4J_{ee}$, in (IV), 2-chloro-1,3,2-dioxaphosphorinane⁶ and (V) is 2.0, 1.4, and 1.2 Hz, respectively. This observation agrees well with the assumption that a positive contribution to ${}^4J_{ee}$ is expected upon substitution of a methyl group at carbon 5.¹³

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