

between tetrahedral (sp^3) and trigonal (sp^2) in aniline is obtained.

Comparison of the reported $J(^{13}\text{C}-^{15}\text{N})$ values with $^{13}\text{C}-^{31}\text{P}$ couplings in phenyl phosphorus compounds^{1c} (e.g. phenylphosphine) will form part of a subsequent paper.

Experimental. ^{13}C spectra were recorded on a Varian XL-100-15 spectrometer operating in the c.w. mode at 25.2 MHz. Internal field-frequency lock was provided by the ^2H resonance of acetone- d_6 used as solvent. Carbon line positions were measured relative to the carbon resonance of internal TMS using a sweep width of 0.5 Hz/cm. Noise-modulated and single-frequency proton decoupling experiments were performed by means of the Varian Gyrocode spin decoupler. The sample solution was contained in a 12 mm tube sealed under vacuum.

[^{15}N]-Aniline (98 % enriched) was obtained from Ministerio de Industria Junta de Energia Nuclear, Spain.

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Received April 17, 1972.

Proton Magnetic Resonance Analysis of the *trans* Isomer of 2-Chloro-4-methyl-1,3,2-dioxaphospholane and the *cis* and *trans* Isomers of 2-Chloro-4,5-dimethyl-1,3,2-dioxaphospholane

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Goldwhite¹ has found evidence from PMR spectra for the presence of geometric isomers in 2-chloro-4-methyl-1,3,2-dioxaphospholane (I). The mixed isomers showed two doublets for the C-CH₃ absorption at 0.95 and 1.20 ppm, indicating different environment around the methyl group in the two isomers. The C-CH₃ absorption of the corresponding phosphate isomers seemed to indicate similar position of the 4-methyl substituent. Gagnaire and co-workers² have reported the PMR spectra of the isomers of 2-chloro-4,5-dimethyl-1,3,2-dioxaphospholane (II), where the *cis* and *trans* forms were prepared from *meso*- and *D,L*-2,3-dimethylbutandiol, respectively. The proton-proton coupling constants and the phosphorus-proton coupling constants involved were obtained from double resonance experiments. This paper reports the PMR analysis of the *trans*-isomer of I and the *cis* and *trans* isomers of II, using the iterative computer program UEATR.³ This program adds iterative evaluation of input parameters to an earlier program (UEA-NMRII), which makes use of magnetic equivalence factoring to reduce the size of certain matrices.

The PMR spectrum of 2-chloro-4-methyl-1,3,2-dioxaphospholane (I) shows that there are two kinds of methyl groups in magnetically different environments in the ratio 1:4. It is unlikely that the different environments arise from a stable nonplanar conformation of the ring, since studies of 1,3-dioxalanes^{4,5} and 1,3-dioxasulfolanones⁶ suggest that flexing of these five-membered rings is rapid. The most reasonable interpretation of the spectrum is that a relatively stable pyramidal stereochemistry at phosphorus leads to two kinds of methyl groups in the compound, *cis* and *trans* to the 2-chloro-substituent. The

ring protons resonance at lower field as compared to the methyl protons. The total spectra of the ring protons were extremely complex due to the overlapping of the protons of the isomers. However, the signals of the ring protons of the *trans* isomer can easily be recognized from the rest of the spectrum.

The higher field region of the spectrum of the ring protons of the *trans* isomer is assigned to one of the protons at carbon 5. The low field region is due to the other proton at carbon 5 and the methine proton at carbon 4. The downfield shifts of these protons are caused by the deshielding effect of the chlorine atom attached to the phosphorus atom, which is found to prefer a pseudo-axial orientation. These observations are in agreement with those found for 2-chloro-4-methyl-1,3,2-dioxazepane⁷ and 4-methyl-1,3-dioxasulfolane.⁸

The PMR spectrum of 2-chloro-4,5-dimethyl-1,3,2-dioxaphospholane (II) shows the existence of *cis* and *trans* isomers, since the resonances are observed at four distinct regions, integrating to 2:2:6:6. The bands in the low field region ($\delta=3.95$ and $\delta=4.55$) may be assigned to the methine protons and the high field bands ($\delta=1.06$ and $\delta=1.22$) are due to the methyl protons. The two isomers result from the mixture of the *meso* and D,L forms in 2,3-dimethylbutandiol.

Temperature studies of the *cis* and *trans* isomer of II show that the best spectra of the *cis* isomer are observed at 35°C and the *trans* isomer at 125°C. At these temperatures both isomers can be analysed as an $X_3AA'X_3P$ spin system. Reducing the temperature to -40°C, using toluene as solvent, the spin system of the *trans* isomer changes to an ABX_3Y_3P system, which is expected. The change of the spin system of the *trans* isomer when the temperature is lowered is a chemical chlorine exchange process. In agreement with this observation Fondal and Goldwhite⁹ have found that 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane shows a singlet in neat liquid at room temperature, which broadens and finally splits into two peaks when the temperature is

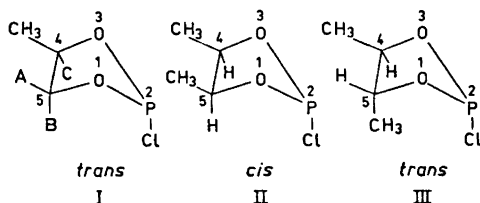


Table 1. Chemical shifts and coupling constants for the *trans* isomer of I.

Isomer	δ_{CH_3}	δ_A	δ_B	δ_C	Coupling constants, Hz							
					J_{AB}	J_{AC}	J_{AP}	J_{BC}	J_{BP}	J_{CB}	J_{CH_3-H}	$J_{P-O-C-H}$
<i>trans</i>	1.39	3.71	4.46	4.81	-9.40	8.27	7.01	6.71	2.53	0.89	6.20	0.42

Table 2. Chemical shifts and coupling constants for the *cis* and *trans* isomers of II.

Isomer	δ_{CH_3} ppm	$\delta_{H_4(H_5)}$ ppm	Coupling constant, Hz.
<i>cis</i>	1.06	4.55	$J_{H-CH_3}=6.42$, $J_{P-C-CH_3}=0.56$ $J_{H-H}=6.59$, $J_{POCH}=2.73$
<i>trans</i>	1.22	3.95	$J_{H-CH_3}=6.06$, $J_{P-C-CH_3}=0.49$ $J_{H-H}=8.81$, $J_{P-O-CH_3}=2.61$

lowered. The chlorine exchange process is also found for the isomers of I when introducing small amounts of tetraphenylarzonium chloride.

The geminal coupling constants in the *trans* isomer of I and the isomers of II are found to have negative sign and the *cis* and *trans* coupling positive sign. This is in agreement with what was found for 1,3-dioxalanes¹⁰⁻¹² and 1,3-dioxasulfolanones.^{8,13} The best correlation between calculated and experimental spectra is obtained assuming a positive sign for the phosphorus proton coupling constants in the isomers.

The *trans* coupling in the isomers is always found to be greater than the *cis* coupling. This observation is the reverse of that found for 1,3-dioxalanes,¹⁰⁻¹² but is in agreement with that found for 2-phenyl-1,3,2-dithiazolane⁷ and 2-phenyl-1,3,2-dithiaphospholane.¹⁴

The succession of the chemical shifts for the methyl groups in the *trans* isomer of I and the isomers of II is found to be the reverse of that for the corresponding methine protons. This effect arises from the pseudo-axial orientation of the chloro substituent. The *cis* protons exhibit the same shielding as the axial protons at carbons 4 and 6 in 2-chloro-1,3,2-dioxaphosphorinanes,¹⁵ which are always to low field compared to the equatorial protons.

The coupling constants observed in the *cis* isomer of II show only small differences as compared to the values found by Gagnaire and co-workers.² Table 2. In the *trans* isomer the coupling constants show a larger difference compared to Gagnaire's values. This is due to the earlier mentioned chlorine exchange process at the evaluated temperature, which makes the methine protons lie in the same magnetic environments. A similar observation is made for the methyl groups. At lower temperatures (-40°) the exchange process stopped and the chemical shifts and coupling constants observed are in agreement with those found by Gagnaire and co-workers.²

Kainosho and Nakamura¹⁶ have 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 have been presented in an earlier paper¹⁵ and 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 phosphorus-proton coupling constant in the *cis* isomer of II

is found to be 2.7 Hz, which indicates a dihedral angle of about 90° . In the *trans* isomer the phosphorus-proton coupling observed is 2.6 Hz for both methine protons. This changes to 4.1 Hz and 0.2 Hz at -40° , indicating different dihedral angles in the two P-O-C-H systems. Different phosphorus-proton coupling constants are also observed in the *trans* isomer of I.

Experimental. 2-Chloro-4-methyl-1,3,2-dioxaphospholane (I) was prepared from 1,2-propandiol and phosphorus trichloride in ether solution using triethylamine as base, b.p._{0.1} 32°C .

2-Chloro-4,5-dimethyl-1,3,2-dioxaphospholane (II) was prepared from 2,3-butandiol and phosphorus trichloride in ether solution using triethylamine as base, b.p._{0.1} 34°C .

The PMR spectra of I were measured as 50% solution in CDCl_3 and II as neat liquid at 35° and 125° . The spectra were recorded on a JEOL, C-60H spectrometer operating at 60 MHz. The spectrometer was operated in the field-frequency lock mode with frequency sweep. The samples were degassed by the usual freezing and thawing procedure using a vacuum line, and the tubes were sealed under vacuum. Line positions were taken by averaging the data from five spectra using a frequency counter. The counter is accurate to 0.1 Hz for a 10 sec count. The computations were carried out on an IBM 360/50 computer and the graphical output was obtained using a Calcomp Plotter. The final RMS error observed was 0.1 when all parameters were allowed to vary. The probable errors of the coupling constants are 0.02 to 0.03 Hz.

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Received May 5, 1972.

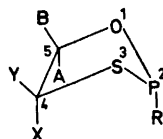
PMR Study of the Conformation of 1,3,2-Oxathiaphospholanes

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Five-membered rings containing heteroatoms in the ring are suitable for conformational investigation. The PMR spectra of 1,3-dioxasulfolanes,^{1,2} 1,3-oxathiolanes,^{3,4} 1,3-dithiolanes,⁵ 1,3,2-dioxaphospholanes,^{1,6} and 1,3,2-dithiaphospholanes⁷⁻⁹ are simplified because of the large chemical shift difference of the ring protons. The 1,3,2-dioxasulfolanes exist in twist-envelope conformation with the sulfur atom above the ring plane. In 2-substituted 1,3-oxathiolanes⁴ it has been possible to conclude that there is one highly preferred conformation, but that rapid pseudorotation is occurring. The 1,3-dithiolane rings are found to be more puckered than the 1,3-dioxalanes, and the rings exist preferentially in a C₂ "half-chair" rather than a C_s "envelope" conformation. Haake *et al.*¹ investigated 1,3,2-dioxaphospholanes and assumed twist-envelope conformation with pseudo axial position of the substituent at phosphorus. In this paper the complete PMR analysis of the ring protons of 2-chloro-, 2-phenyl-⁷

and 2-phenoxy-1,3,2-oxathiaphospholanes (I-III) has been carried out.



I: R = Cl, II: R = Ph, III: R = OPh

The PMR spectrum of the ring protons of I, II, and III consists of two main regions, where the separation between the two regions is large compared to the coupling constants involved. The band at lower field is assigned to the protons at carbon 5 due to the more deshielding effect of the ring oxygen atom as compared to the sulfur atom. Consequently, the band at higher field is assigned to the protons at carbon 4.

Table 1. Chemical shift data for I, II, and III. Chemical shift in ppm from tetramethylsilane.

Compound	A	B	X	Y
I	4.71	4.59	3.40	3.22
II ⁷	4.21	3.92	2.75	2.53
III	4.39	4.14	2.71	2.66

The spectra of I, II, and III in deuteriochloroform at room temperature are expected to constitute an ABXYP spin system. However, this is found only for II and III, while the spectrum of I is of the AA'XX'P type. Chemical exchange of chlorine is therefore expected to occur at room temperature and to be the reason for the observed type of spectrum in I. Reducing the temperature to -40°C the spin system of the ring protons of I changes to an ABXYP system. At that temperature the PMR analysis of I has been carried out. The fully computer analysed 60 MHz spectra resulted in a good agreement between calculated and experimental spectra (Fig. 1).

In 1,3-dioxalanes,^{10,11} 1,3,2-dioxasulfolanes,^{1,2} 1,3,2-dioxaphospholanes,^{1,6} and 1,3,2-diazaphospholanes¹² the geminal