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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-dithiaphospholanes [7-9] 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-oxathiolanes [4] 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 C_2 "halfchair" 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.
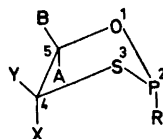
I: R = Cl, II: R = Ph, III: R = OPh

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-diazaphospholanes [12] the geminal
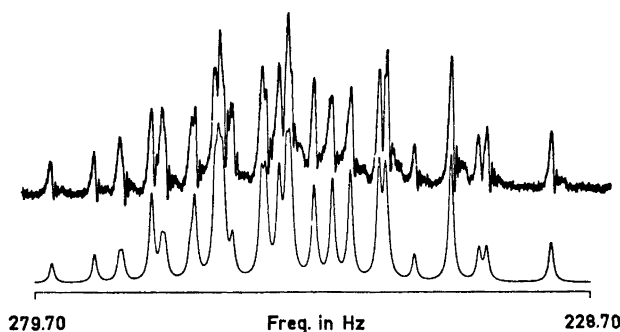
Fig. 1. 60 MHz PMR spectrum of the A and B protons in 2-phenoxy-1,3,2-oxathiaphospholane (III). Upper: observed spectrum. Lower: calculated spectrum.

Table 2. Spin-spin coupling constants (in Hz) for I, II, and III.

Compound	$^2J_{AB}$	$^3J_{AX}$	$^3J_{AY}$	$^3J_{AP}$	$^3J_{BX}$	$^3J_{BY}$	$^3J_{BP}$	$^2J_{XY}$	$^3J_{XP}$	$^3J_{YP}$
I	− 9.27	5.83	6.08	5.23	6.63	6.70	10.67	− 11.22	− 0.41	2.08
II[7]	− 9.26	4.27	6.78	3.27	5.87	8.38	7.26	− 11.26	3.12	− 0.49
III	− 9.24	6.35	6.16	3.43	5.89	6.84	9.62	− 11.06	2.18	− 0.09

coupling constant is found to be in the range from − 7.3 to − 9.2 Hz, while in 1,3-dithiolanes [5] and 1,3,2-dithiaphospholanes [7–9] the range is between − 11.3 and − 11.5 Hz. In agreement with these observations, the geminal coupling constants, J_{AB} and J_{XY}, in I, II, and III are found to be in the same ranges (Table 2). The greater geminal coupling for the XY protons compared to the AB protons, $J_{XY} > J_{AB}$, is probably caused by the different size and electronegativity of the sulfur atom as compared to the oxygen atom.

The $\cos^2 \theta$ relation has been used in the examination of the dihedral angle in five-membered rings. Lemieux *et al.*[13] conclude that 2,2-dimethyl-1,3-dioxalane has a dihedral angle of 41°. Abraham [14] found evidence for a dihedral angle of 38° in 2-methyl-1,3-dioxalane. Haake *et al.*[1] found dihedral angles of 27° and 33° in 2-phenyl-1,3,2-dioxaphospholane and 2-oxo-1,3,2-dioxasulfolane, respectively. However, the uncertainty in dihedral angle calculations by this method is the determination of the constants involved in the Karplus equa-

tion. Lambert [15] has observed that the ratio J_{trans}/J_{cis}' defined as the R value, for the $- CH_2 - CH_2 -$ fragment in six-membered rings, may be used in predicting molecular ring shape. Buys [16,17] has used this criterion and found a relation, $\cos \theta = [3/(2 + 4R)]^{1/2}$, for the dihedral angle in which the Karplus factor A is no longer present. The application of this equation to the PMR data obtained for the 1,3,2-oxathiaphospholanes gives values of approximately 45° for the torsional angles (Table 3).

A relationship has been postulated between J_{POCH} and the estimated dihedral

Table 3. R-Values and ring torsional angle for I, II, and III.

	I	II	III
R	1.095	1.000	0.913
ψ	47°	45°	43°

angles.[18] Coupling constants of about 2 Hz and 9 Hz correspond to dihedral angles of 90° and 180°, respectively. A similar dependence of the J_{P-S-CH} with dihedral angle is also found.[19] The different phosphorus proton coupling constants found in both the AB and XY part of the spectra of I, II, and III, Table 2, indicate different dihedral angles in the two $P-O-C-H$ and $P-S-C-H$ paths, respectively. This observation probably indicates that the five-membered oxathiaphospholane ring exists mainly in an equilibrium between two envelope conformations, A and B, where the carbon atom in position 5 is out of the ring plane. This is in agreement with that found from Dreiding models, and may be attributed to be different bond length of the $P-S$ bond compared to the $P-O$ bond.

A   **B**
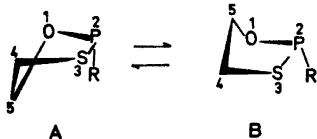
Experimental. *2-Chloro-1,3,2-oxathiaphospholane* (I) was prepared from mercaptoethanol and phosphorus trichloride in benzene solution using triethylamine as base, b.p.$_{0.4}$ 57°.

2-Phenyl-1,3,2-oxathiaphospholane (II)[7] was prepared from mercaptoethanol and dichlorophenylphosphine in benzene solution using triethylamine as base, b.p.$_{0.5}$ 105°.

2-Phenoxy-1,3,2-oxathiaphospholane (III) was prepared from 2-chloro-1,3,2-oxathiaphospholane (I) and phenol in benzene solution using triethylamine as base, b.p.$_{0.5}$ 123°.

The PMR spectra were measured at 28°C and -40°C in 50 % solution of I, II, and III in $CDCl_3$ and were recorded on a 60 MHz, JEOL, C-60H instrument. The spectra were recorded in internal lock mode with frequency sweep at approximately 50 Hz sweep width and calibrated every 5 Hz using a frequency counter. The counter is accurate to 0.1 Hz. The line positions were taken as an average of several spectra, and are assumed to be correct to about 0.05 Hz. The computation was carried out using an IBM 360/50 computer

and graphical output was obtained using a Calcomp Plotter. The magnitudes of the chemical shifts and coupling constants involved have been determined by the iterative computer program LAOCN3.[20] The final RMS error observed was 0.05, when all parameters were allowed to vary. The probability errors of the coupling constants are 0.02 to 0.03 Hz.

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