

## Short Communications

## Analysis of the PMR Spectra of the 2-Methoxy- and 2-Methylthio-1,3,2-Oxathiaphospholanes

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In an earlier paper<sup>1</sup> an analysis of the PMR spectra of 2-chloro-, 2-phenyl-, and 2-phenoxy-1,3,2-oxathiaphospholanes has been reported. As a continuation of this work the PMR spectra of the ring protons of 2-methoxy- and 2-methylthio-1,3,2-oxathiaphospholanes, I and II, have been investigated. The spectra were analysed on the basis of ABXY spin-system, and a good fit between theoretical and experimental spectra were obtained, Figs. 1 and 2. The spectral parameters are listed in Table 1. The preferred conformations of the five-membered ring is proposed

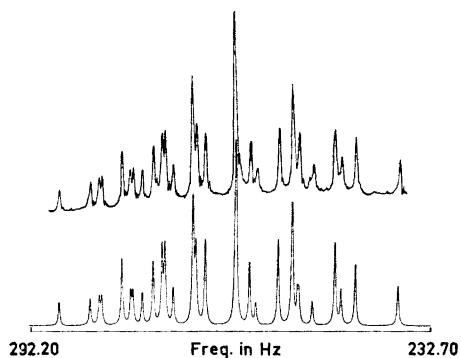
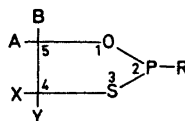


Fig. 1. 60 MHz spectrum of the X and Y protons in 2-methoxy-1,3,2-oxathiaphospholane. Upper: Observed spectrum. Lower: Calculated spectrum.

Table 1. Chemical shift data for I and II. Chemical shift in ppm from TMS.

Compound	A	B	X	Y
I	4.55	4.22	3.05	2.93
II	4.58	4.16	3.15	2.72

on the basis of the chemical shifts and coupling constants.



I: R = OCH<sub>3</sub>, II: R = SCH<sub>3</sub>.

The 60 MHz PMR spectra of I and II show a rather complex, but well resolved pattern. The spectrum can be divided into two bands, and the separation between them is large compared to the coupling constants involved. The band at low field is assigned to the AB protons at carbon 5 and the high field band to the XY protons at carbon 4. The lower field resonance of the AB protons compared to the XY protons is due to the more deshielding effect of the ring oxygen atom as compared to the sulfur atom.

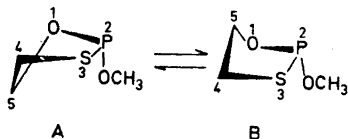
The geminal coupling constants,  $J_{AB}$  and  $J_{XY}$ , in the oxathiaphospholanes I and II are found to be in the expected ranges,<sup>1-5</sup> -8.0 to -9.6 and -10.5 to -12.5, respectively. The smaller (more negative) geminal coupling constant for the XY protons compared to the AB protons is caused by the different size and electronegativity of the sulfur atom as compared to the oxygen atom.

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

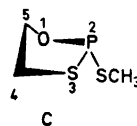
Compound	${}^3J_{AB}$	${}^3J_{AX}$	${}^3J_{AY}$	${}^3J_{AP}$	${}^3J_{BX}$	${}^3J_{BY}$	${}^3J_{BP}$	${}^3J_{XY}$	${}^3J_{XP}$	${}^3J_{YP}$
I	-9.35	5.99	6.12	4.40	6.88	6.02	8.64	-11.09	-2.11	3.17
II	-9.52	2.28	5.90	14.13	5.23	10.66	3.38	-10.50	1.70	0.25

The internal shift difference of the AB protons at carbon 5 and the XY protons at carbon 4 in I is 19.7 and 7.0 Hz, respectively, while the difference in II is equal, 25.6 Hz. The larger shift difference values for the AB protons as compared to the XY protons in I have also been found in the 2-phenyl- and 2-phenoxy-1,3,2-oxathiaphospholanes.<sup>1</sup> The reverse order is observed for the 2-chloro-1,3,2-oxathiaphospholane<sup>1</sup> and 2-chloro-1,3,2-oxathiarsolane.<sup>6</sup> Due to a rapid chlorine-exchange process resulting in inversion at phosphorus and arsenic at room temperature, the spectra of the latter compounds were observed at  $-40^\circ\text{C}$  and  $-35^\circ\text{C}$ , respectively.

The small differences between the *cis* and *trans* coupling constants in I,  $J_{AY}$ ,  $J_{BX}$  and  $J_{AX}$ ,  $J_{BY}$ , probably indicate that the oxathiaphospholane ring with the methoxy group attached to the phosphorus atom exists in an equilibrium between two envelope conformations A and B, where the carbon atom in position 5 is out of the ring plane.



The magnitude of the phosphorus-proton coupling constants is in agreement with the above assumption. However, in the 2-methylthio compound II the observed *cis* and *trans* coupling constants are quite different, which probably indicates that one conformation predominates. The phosphorus proton coupling constants observed for the AB protons in the oxygen part of the ring are found to be 14.1 and 3.4 Hz, corresponding to dihedral angles of  $180^\circ$  and  $90^\circ$ , are in agreement with the fixed conformation C.



The reason for the fixed conformation of II is probably a combination of a smaller negative inductive effect of the methylthio group<sup>7</sup> as compared to the methoxy group<sup>8</sup> and the postulated "anomeric effect",<sup>9</sup> which involved the repulsion between lone-pair orbitals of the ring sulfur atom and the sulfur atom in the axial methylthio group.

The O-C-C-S torsional angle in I and II has been calculated from the vicinal coupling constants of the  $\text{CH}_2$ - $\text{CH}_2$  moiety using the *R*-value method due to

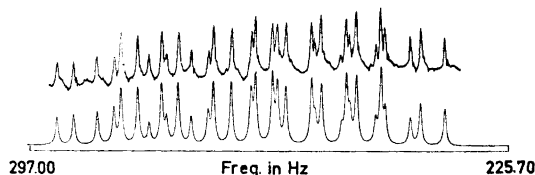


Fig. 2. 60 MHz spectrum of the A and B protons in 2-methylthio-1,3,2-oxathiaphospholane. Upper: Observed spectrum. Lower: Calculated spectrum.

Lambert<sup>10</sup> and Buys.<sup>11</sup> The calculated torsional angles are approx. 44° and 48° for I and II, respectively. Similar values have been found for 2-chloro-, 2-phenyl-, and 2-phenoxy-1,3,2-oxathiaphospholanes<sup>1</sup>.

*Experimental.* 2-Methoxy-1,3,2-oxathiaphospholane (I) was prepared from 2-chloro-1,3,2-oxathiaphospholane<sup>1</sup> and methanol in ether solution using triethylamin as base, b.p.<sub>0.1</sub> 34°.

2-Methylthio-1,3,2-oxathiaphospholane (II) was prepared from 2-chloro-1,3,2-oxathiaphospholane and methanethiol in ether solution using triethylamin as base, b.p.<sub>0.1</sub> 62°.

The PMR spectra were measured at 28°C in 50% solution of I and II in CDCl<sub>3</sub> and were recorded on a 60 MHz, JEOL, C-60H instruments. The line positions were taken as an average of several spectra. The computation was carried out using an IBM 360/50 computer. The magnitudes of the chemical shifts and coupling constants involved have been determined by the iterative computer program LAOCN3.<sup>12</sup> The final RMS error observed was 0.05, when all parameters were allowed to vary.

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## Electrophilic Bromination of 2-Methyl-4-carbethoxy-1,3,6,7-tetraazacycl[3.3.3]azine

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The preparation of 2-methyl-4-carbethoxy-1,3,6,7-tetraazacycl[3.3.3]azine, **1**, has recently been described.<sup>1</sup> Simple HMO calculations suggested<sup>1</sup> that **1** should be electrophilically substituted at C-9. (cf. Fig. 1).

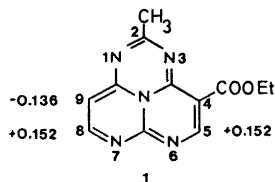


Fig. 1. Charge densities at C-5, C-8, and C-9 in 2-methyl-4-carbethoxy-1,3,6,7-tetraazacycl[3.3.3]azine.

In order to verify the theoretical predictions, **1** was treated with *N*-bromosuccinimide in chloroform at room temperature.<sup>2,3</sup> A 60% yield of 9-bromo-4-carbethoxy-2-methyl-1,3,6,7-tetraazacycl[3.3.3]azine, **2**, was isolated. The mass spectrum shows molecular ion peaks at  $m/e = 335$  and  $337$  m.u. (intensity 1:1) in agreement with the formula C<sub>12</sub>H<sub>10</sub>N<sub>6</sub>O<sub>2</sub>Br. The fragmentation pattern of **2** is entirely analogous with that of the 9-bromo derivative of **3**.<sup>3</sup> In the NMR spectrum of **1**<sup>4</sup> the H-8 and H-9 signals appear as two doublets centered at 7.75 and 5.75 ppm, respectively. In the spectrum of **2**, the signal at higher field has vanished and the lower-field signal remains as a singlet at 8.00 ppm. Therefore, substitution has occurred at C-9. The H-5 singlet is found at 8.30 ppm.

