

## Preparation and PMR Analysis of *cis* and *trans* Isomers of 2-Chloro-5-methyl-1,3,2-oxathiaphospholane and 2-Phenyl-5-methyl-1,3,2-oxathiaphospholane

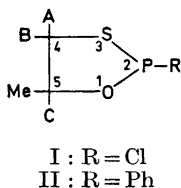
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The high resolution magnetic resonance spectra of the *cis* and *trans* isomers of 2-chloro- and 2-phenyl-5-methyl-1,3,2-oxathiaphospholane have been completely analysed. The geminal *cis*, *trans* and the proton phosphorus coupling constants and the shift values are reported. The *trans* isomer is found mainly to exist in an equilibrium between two envelope conformations, while only one conformation predominates in the *cis* isomer. In both isomers the carbon atom 5 is found to be out of the ring plane.

Five membered ring compounds, such as 1,3,2-oxathiaphospholanes,<sup>1-3</sup> are suitable for conformational investigation. The PMR spectra are simplified because of the large chemical shift difference of the ring protons caused by the more deshielding effect of the ring oxygen atom as compared to the sulfur atom. From the PMR analysis of phosphorus substituted 1,3,2-oxathiaphospholanes<sup>1-2</sup> the ring was found to exist mainly in an equilibrium between two envelope conformations, where the carbon atom in position 5 is out of the ring plane. However, in 2-methylthio-1,3,2-oxathiaphospholane<sup>3</sup> the ring was found to exist in a fixed conformation, in agreement with the large difference in the *cis* and *trans* coupling constants and the large difference of the phosphorus proton coupling constants observed for the protons in the oxygen part of the ring.

In order to obtain useful information about the 1,3,2-oxathiaphospholane ring when substituted in the 5 position, the *cis* and *trans* isomers of 2-chloro- (I) and 2-phenyl-5-methyl-1,3,2-oxathiaphospholane (II) were prepared and their PMR spectra analysed in detail with respect to both coupling constants and chemical shifts. The PMR spectra of I and II indicate the presence of two isomers in the ratio 1:2, which complicated the analysis to some extent. 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 from the major *trans* isomer can be separated from the rest of the spectrum as it appears to be an ABMX<sub>3</sub>P spin system.

The 60 MHz spectrum of the ring protons of I consists of four main regions ( $\delta = 2.5 - 3.0$ ,  $3.0 - 3.5$ ,  $4.0 - 4.6$ , and  $4.6 - 5.3$ ). The two low field bands are assigned to the methine proton at carbon 5 because of the deshielding effect of the group attached to the phosphorus atom. The methine proton of the *trans* isomer is found to resonance at lower field as compared to the methine proton of the *cis* isomer.

The complex band at high field of the spectrum is due to the protons at carbon 4 of the two isomers. The B proton of the *cis* and *trans* isomers is observed to give resonance at higher field as compared to the A protons. The two doublets at high field in the total spectrum is assigned to the methyl group.

The 60 MHz spectrum of the ring protons of II consists of two main regions ( $\delta = 1.8 - 3.0$  and  $3.7 - 4.7$ ). The low field band is assigned to the methine proton of the two isomers, while the high field band is due to the protons at carbon 4.

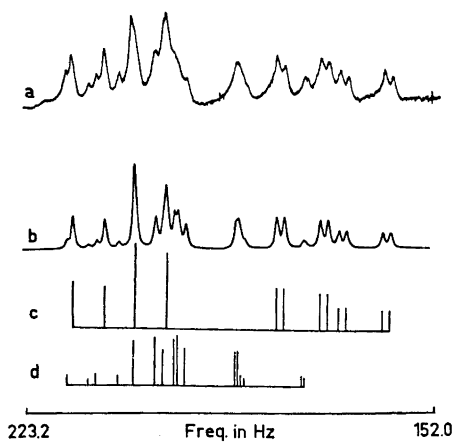


Fig. 1. The AB part of the 60 MHz spectrum of the *cis* and *trans* isomers of I: (a) experimental spectrum; (b) computed total lineshape spectrum; (c) computed stickplot of the AB protons in the *trans* isomer; (d) computed stick-plot of the AB protons in the *cis* isomer.

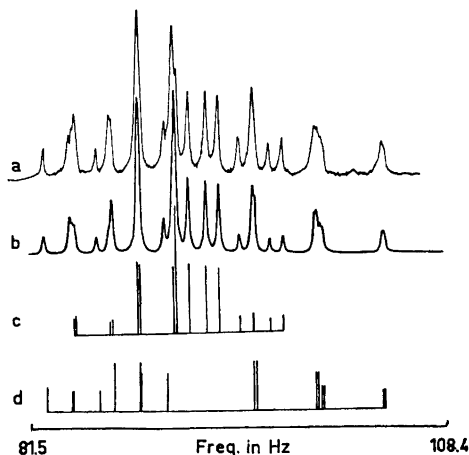


Fig. 2. The AB part of the 60 MHz spectrum of the *cis* and *trans* isomers of II: (a) experimental spectrum; (b) computed total line-shape spectrum; (c) computed stick-plot of the AB protons in the *trans* isomer; (d) computed stick-plot of the AB protons in the *cis* isomer.

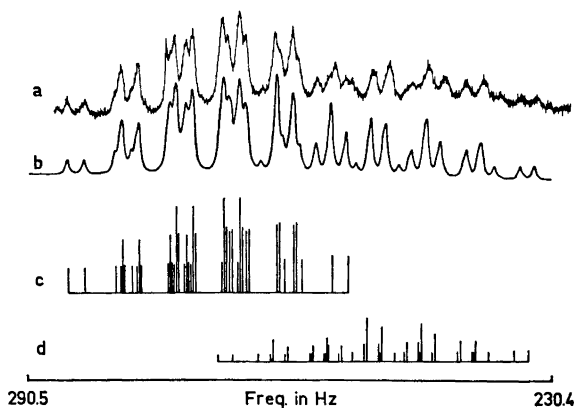


Fig. 3. The C part of the 60 MHz spectrum of the *cis* and *trans* isomers of II: (a) experimental spectrum; (b) computed total line-shape spectrum; (c) computed stick-plot of the C proton in the *trans* isomer; (d) computed stick-plot of the C proton of the *cis* isomer.

The PMR spectra of I and II were analysed as an  $ABMX_3P$  spin system by means of the computer program UEAITR<sup>4</sup> and KOMBIP.<sup>5</sup> The fully computer analysed 60 MHz and 100 MHz spectra resulted in a good correlation between calculated and experimental spectra, Figs. 1, 2, and 3. The final RMS error observed was 0.06 or less when all parameters were allowed to vary. The probable errors of the coupling constants are 0.02 to 0.03 Hz. The spectral parameters are listed in Table 1.

Recent articles on geminal coupling constants in 1,3,2-dithiaphospholanes<sup>1,6-9</sup> and 1,3,2-dithiaarsolanes<sup>10</sup> indicate the range  $-11.0$  to  $-12.5$  Hz in the C-CH<sub>2</sub>-S-moiety. The observed values for I and II are in the expected range. These coupling constants are smaller (more negative) than those found in the 1,3,2-dioxaphospholanes and 1,3,2-dioxaarsolanes, which probably is due to a combination of a reduced H-C-H angle and a smaller electron withdrawal effect of sulfur as compared to oxygen.

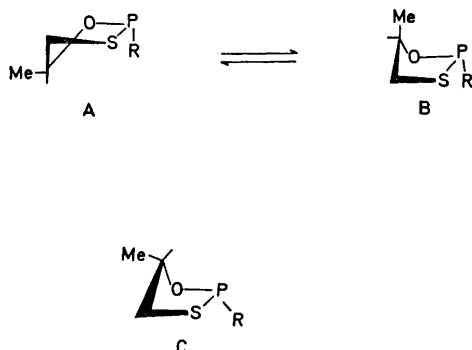


Table 1. Chemical shifts and coupling constants for the *cis* and *trans* isomers of I and II.

Com- pound	Isomer	CH <sub>3</sub>	A	B	C
I	<i>cis</i>	1.60	3.38	3.12	4.59
	<i>trans</i> <sup>a</sup>	2.23	3.09	2.48	4.80
II	<i>cis</i>	1.40	2.79	2.19	4.17
	<i>trans</i>	1.19	2.71	2.47	4.49

Com- pound	Isomer	Coupling constants, Hz							
		J <sub>AB</sub>	J <sub>AC</sub>	J <sub>AP</sub>	J <sub>BC</sub>	J <sub>BP</sub>	J <sub>CP</sub>	J <sub>CH<sub>3</sub>-C-H</sub>	J <sub>P-O-C-CH<sub>3</sub></sub>
I	<i>cis</i>	-11.79	4.82	4.24	11.13	0.13	4.53	6.10	-0.01
	<i>trans</i> <sup>a</sup>	-10.90	5.53	-0.01	7.65	1.36	3.22	6.20	0.03
II	<i>cis</i>	-11.97	4.66	4.69	11.11	0.31	1.73	6.36	0.34
	<i>trans</i>	-11.31	6.60	0.17	5.14	2.57	1.89	6.10	0.04

<sup>a</sup>Values obtained from 100 MHz spectra.

The vicinal coupling constants for 1,3,2-oxathiaphospholanes<sup>1-3</sup> are in the range  $J_{cis} = 4.3 - 7.4$  Hz and  $J_{trans} = 5.9 - 6.9$  Hz for most of the compounds studied, except for 2-methylthio-1,3,2-oxathiaphospholane,<sup>3</sup> where the *cis* and *trans* coupling constants are quite different in magnitude. The *cis* and *trans* coupling constants in the *trans* isomer of I and II are very similar in magnitude to those found for most of the 1,3,2-oxathiaphospholanes,<sup>1-2</sup> which probably indicates that this five-membered oxathiaphospholane mainly exists in an equilibrium between two envelope conformation A and B with carbon atom 5 out of the ring plane.

This is also in agreement with the small difference between the phosphorus proton coupling constant observed for the AB protons in the sulfur part of the ring.

The *cis* and *trans* coupling constants observed in the *cis* isomer of I and II are quite different (Table 1), which probably indicates that only one conformer predominates, C.

This assumption is in agreement with that found from the Dreiding stereo-models where the carbon in position 5 is out of the ring plane and with an equatorial position of both the methyl group and the substituent attached to the phosphorus atom. The difference in the phosphorus proton coupling constant for the AB protons in the *cis* isomer is also in agreement with conformation C. The same relation has been found for the *cis* isomers of 2-chloro- and 2-phenyl-4-methyl-1,3,2-dithiaphospholane<sup>9</sup> and 2-chloro- and 2-phenyl-4-methyl-1,3,2-dithiarsolane.<sup>11</sup> Further analyses of other ringsubstituted 1,3,2-oxathiaphospholanes are in progress in this laboratory.

## EXPERIMENTAL

*2-Chloro-5-methyl-1,3,2-oxathiaphospholane (I)* was prepared from 3-mercapto-propan-2-ol and phosphorus trichloride in ether solution using triethylamine as base, b.p.<sub>10</sub> 68°C.

*2-Phenyl-5-methyl-1,3,2-oxathiaphospholane (II)* was prepared from 3-mercapto-propan-2-ol and dichlorophenylphosphine in ether solution using triethylamin as base, b.p.<sub>0.5</sub> 93°C.

The PMR spectra of I and II were measured as 50 % solution in CDCl<sub>3</sub>. The spectra were recorded on a 60 MHz JEOL, C-60 H and a 100 MHz Varian HA-100 spectrometer. In the PMR sample tubes, small amounts of TMS were added to serve as reference and locking substance. The tubes were degassed and sealed under vacuum. The spectra were recorded in internal lock mode with frequency sweep at approx. 50 Hz sweep width and calibrated every 5 Hz using a frequency counter. The counter is accurate to 0.1 Hz to a 10 sec count. Line positions were taken by averaging the data from four spectra, and are assumed to be correct to about 0.05 Hz. The computation was carried out using a UNIVAC 1110 computer and graphical output was obtained using a Calcomp Plotter.

## REFERENCES

1. Bergesen, K., Bjorøy, M. and Gramstad, T. *Acta Chem. Scand.* **26** (1972) 3037.
2. Bergesen, K., Bjorøy, M. and Gramstad, T. *Acta Chem. Scand.* **26** (1972) 2156.
3. Bergesen, K. and Bjorøy, M. *Acta Chem. Scand.* **27** (1973) 357.
4. Johannessen, R. B., Fenetti, I. A. and Harris, R. K. *J. Magn. Resonance* **3** (1970) 84.
5. Aksnes, D. W. KOMBIP, Quantum Chemistry Program Exchange, Indiana University, Chemistry Department, Indiana, U.S.A.
6. Albrand, J. P., Cogne, A., Gagnaire, D., Martin, J., Robert, J. B. and Verrier, J. *Org. Magn. Resonance* **3** (1971) 75.
7. Peake, S. C., Fild, M., Schmutzler, R., Harris, R. K., Nichols, J. M. and Rees, R. G. *J. Chem. Soc. Perkin Trans. 2* **1971** 380.
8. Albrand, J. P., Gagnaire, D., Martin, J. and Robert, J. B. *Org. Magn. Resonance* **5** (1973) 33.
9. Bergesen, K. and Bjorøy, M. *Acta Chem. Scand.* **27** (1973) 1103.
10. Aksnes, D. W. and Vikane, O. *Acta Chem. Scand.* **27** (1973) 1337.
11. Aksnes, D. W. and Vikane, O. *Acta Chem. Scand.* **27** (1973) 2135.

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