

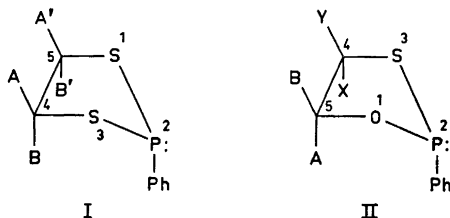
PMR Analysis of 2-Phenyl-1,3,2-dithiaphospholane and 2-Phenyl-1,3,2-oxathiaphospholane

KNUT BERGESEN, MALVIN BJØRØY and THOR GRAMSTAD

Chemical Institute, University of Bergen, N-5014 Bg-U, Bergen, Norway

The high resolution magnetic resonance spectra of 2-phenyl-1,3,2-dithiaphospholane and 2-phenyl-1,3,2-oxathiaphospholane have been completely analysed. The geminal *cis* and *trans* and the phosphorus proton coupling constants and the shift values are reported. The spin-system of the dithiaphospholane ring confirms the existence of pseudorotation with a pseudo-axial phenyl group, while the oxathiaphospholane ring exists mainly in an equilibration between two envelope conformations. Good fits are observed between experimental and calculated spectra.

Analysis of the PMR spectra of five-membered rings with heteroatoms in the ring has received considerable attention in recent years.¹⁻⁷ Dioxalanes are suitable test compounds for the conformational investigation of five-membered rings. The PMR spectra are simplified because the oxygen atoms cause different chemical shifts for the protons on carbon 2 compared to those on carbon atoms 4 and 5. It is well established that the presence of two different substituents on carbon 2 gives rise to an AA'BB' spectrum of the protons on carbon 4 and 5. Haake and co-workers⁵ have reported the complete analysis of the PMR spectra for 2-chloro-, 2-methoxy- and 2-phenoxy-1,3,2-dioxaphospholane in benzene and deuteriochloroform. Devillers and co-workers⁷ have analysed the ³¹P decoupled PMR spectra of 2-methoxy- and 2-phenoxy-2-oxo-1,3,2-oxazaphospholanes which give rise to well resolved ABXY patterns. This paper reports the complete PMR analysis of 2-phenyl-1,3,2-dithiaphospholane (I) and 2-phenyl-1,3,2-oxathiaphospholane (II). The conformation is discussed on the basis of the spectral properties.



EXPERIMENTAL

2-Phenyl-1,3,2-dithiaphospholane (I) was prepared from ethanedithiol and dichlorophenylphosphine in benzene solution using triethylamine as base b.p._{0.5} 146°.

2-Phenyl-1,3,2-oxathiaphospholane (II) was prepared from mercaptoethanol and dichlorophenylphosphine in benzene solution using triethylamine as base b.p._{0.5} 106°.

The PMR spectra were measured at 28°C in 50 % solution of I and II in CDCl₃ and were recorded on a 60 MHz JEOL, C-60 H instrument. Line position was taken by averaging the data of four spectra. 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.

SPECTRAL ANALYSIS

The PMR spectrum of I shows two bands at $\delta = 3.0$ and $\delta = 7.5$ (Fig. 1). The lower band is assigned to the protons of the phenyl group attached to the phosphorus atom and the band at higher field is due to the ring protons at carbon atoms 4 and 5.

It has been observed^{8,9} that addition of paramagnetic complexing agents such as nickel(II)acetylacetonate (Ni(AA)₂), NiCl₂, or COCl₂, causes a decoupling of the phosphorus nuclei in the PMR spectra of phosphites, phosphonates, and phosphates. The complete decoupling of the protons of I is obtained by using 0.01 M Ni(AA)₂ in CDCl₃. The PMR spectrum of the ring protons is changed to an AA'BB' spin system. This spin system has been fully described in the literature,¹⁰⁻¹² and the parameters obtained from the analysis of an AA'BB' spectrum are,

$$\begin{aligned} N &= J_{AB} + J_{AB'} & K &= J_{AA} + J_{BB'} \\ L &= J_{AB} - J_{AB'} & M &= J_{AA} - J_{BB'} \end{aligned}$$

The PMR spectrum of the ring protons of II shows a rather complex, but a well resolved pattern. The spectrum can be divided into two bands. The band at lower field is assigned to the protons at carbon 5 due to the more deshielding effect of the ring oxygen atom compared to the sulfur atom. Consequently, the band at higher field is assigned to the proton at carbon 4. Addition of Ni(AA)₂ reduces the PMR spectrum to an ABXY spin system. Diehl and Chuck¹³ have developed, by using sub-spectral and direct methods, a systematic analysis of an ABXY spin system. Using the parameters obtained from the ABXY spin system the coupling constants and chemical shifts can be calculated. The undecoupled spectra of I and II were analyzed using the iterative

Table 1. Chemical shift data for I and II.^a

	A = A'	B = B'	A	B	X	Y
I	3.06	2.84				
II			4.21	3.92	2.75	2.53

^a Chemical shift in ppm from tetramethylsilane.

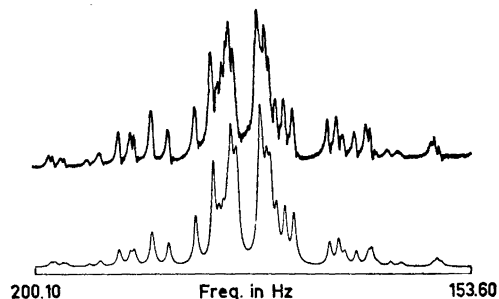


Fig. 1. 60 MHz PMR spectrum of 2-phenyl-1,3,2-dithiaphospholane (I). The phenyl group not recorded. Upper: Observed spectrum. Lower: Calculated spectrum.

least squares computer programs LACX²³ and LAOCN3.¹⁹ A reasonable correlation between theoretical and experimental spectra was obtained, as shown in Figs. 1, 2, and 3. Chemical shifts and coupling constants of the computed compounds are listed in Tables 1 and 2.

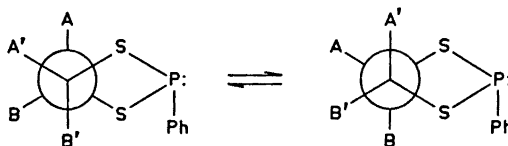
Table 2. Spin-spin coupling constants (in Hz) for I and II.

	${}^2J_{AB}$	${}^3J_{BB'}$	${}^3J_{AA'}$	${}^3J_{BA'}$	${}^3J_{AP}$	${}^3J_{BP}$	${}^3J_{AX}$	${}^3J_{AY}$	${}^3J_{BX}$	${}^3J_{BY}$	${}^2J_{XY}$	${}^3J_{XP}$	${}^3J_{YP}$
I	-11.36	5.40	6.13	6.66	1.88	-1.05							
II	-9.26				3.27	7.26	4.27	6.78	5.87	8.38	-11.26	3.12	-0.49

RESULT AND DISCUSSION

The *cis* ($J_{AA'} \neq J_{BB'}$) and *trans* ($J_{AB'} = J_{A'B}$) coupling constants of I are found to have a positive sign, and the geminal ($J_{AB} = J_{A'B'}$) negative sign. This observation is in agreement with that found for dioxalanes¹⁻³ and sulfites.⁵ The phosphorus-proton coupling is found to be positive and negative.

The ring is non-planar and the equality $J_{AB'} = J_{A'B}$ originates from a rapid interconversion of two equally populated families of pseudorotation conformer.



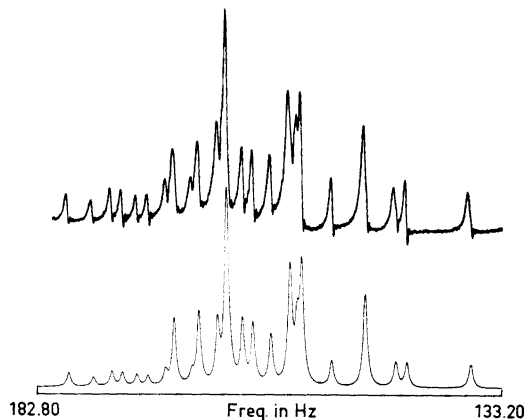


Fig. 2. 60 MHz PMR spectrum of the X and Y protons in 2-phenyl-1,3,2-thioxaphospholane (II). *Upper*: Observed spectrum. *Lower*: Calculated spectrum.

Each form represents the average of a range of conformations of practically equal energy, pseudolibration.^{14,15} There is no direct information available about the important average torsional angle of the fragment S-CH₂-CH₂-S in 1,3,2-dithiaphospholanes.

Ring torsional angles of the fragment -CH₂-CH₂- in six-membered rings are calculated using the vicinal proton-proton coupling constants according to the method of Lambert²⁰ and Buys.²¹ The torsional angle θ is given by the expression $\cos \theta = [3/(2 + 4R)]^{1/2}$ where the measurable R is obtained from the equation $R = (J_{aa} + J_{cc}) / (J_{ac} + J_{ca})$. By this method, a quantitative determination of the dihedral arrangements within the XCH₂CH₂Y fragment may be made. The calculated torsional angle of the fragment S-CH₂-CH₂-S in I by this method is approx. 48°. This is not in agreement with the calculated torsional angle for the cyclic sulfite (33°) and 2-phenyl-1,3,2-dioxaphospholane⁵ (27°). Here the calculation was based on the method of $\cos^2 \theta$ relation.

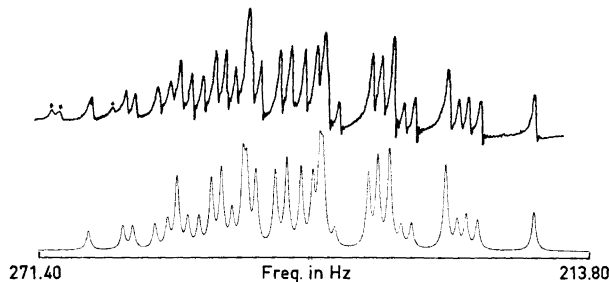


Fig. 3. 60 MHz PMR spectrum of the A and B protons in 2-phenyl-1,3,2-thioxaphospholane (II). *Upper*: Observed spectrum. *Lower*: Calculated spectrum.

In dioxanes,¹⁻³ sulfites,⁵ and 1,3,2-dioxaphospholanes⁵ the geminal coupling constant is found to be in the range of approx. -7.3 to -8.6 Hz. In the 1,3,2-dithiaphospholane the geminal coupling is smaller (more negative), -11.4 , which is apparently due to a combination of (a) a reduced H-CH- angle and (b) smaller electron withdrawal effect of sulfur as compared with oxygen.

The *cis* coupling in 1,3-dioxalanes,¹⁻³ sulfite,⁵ and 1,3,2-dioxaphospholanes⁵ has been observed to be larger than the *trans* coupling. However, in compound I the *cis* coupling constants are found to be smaller than the *trans*. Such reverse observation is also found in 2-phenyl-1,3,2-dithiarsolane.²²

Kainosho and Nakamura¹⁶ 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 a Karplus plot type.¹⁷ From this plot coupling constants of about 2 Hz and 9 Hz correspond to dihedral angles of 90° and 180° , respectively. A similar dependence of the $J_{\text{PSC-H}}$ with the dihedral angle of the fragment $-P-S-C-H$ is also found.¹⁸ However, the phosphorus-proton coupling constant is much smaller, probably due to the longer P-S bond as compared to the P-O bond. The difference in the phosphorus proton coupling constants in I, 1.88 and -1.05 Hz, probably indicates that the ring prefers twist-envelope forms.

The chemical shift of the A proton in the AB part of the spectrum of II is found to be downfield due to the deshielding effect of the pseudo-axial phenyl group. The same observation is also found for the X proton in the XY part of the spectrum. The geminal coupling constant, J_{XY} , in the sulfur part of the ring is found to be larger than the geminal coupling in 1,3,2-dioxaphospholanes and 1,3,2-oxazaphospholanes, probably due to the same effect as proposed for 2-phenyl-1,3,2-dithiaphospholane. The phosphorus-proton coupling constants, J_{AP} , J_{BP} , J_{XP} , and J_{YP} are found to be 3.2, 7.3, 3.1, and -0.4 Hz, indicating different dihedral angles in the two P-O-C-H coupling paths, respectively, in the two P-S-C-H coupling paths. This observation probably indicates that the five-membered oxathiaphospholane ring exists mainly in an equilibration between two envelope conformations, where the carbon atom in position 5 is out of the ring plane.

The best correlation between calculated and experimental spectra of II is obtained assuming a negative sign for J_{YP} and a positive sign for the other phosphorus proton coupling constants.

Acknowledgement. The authors express their thanks to cand. real. Per Albriktsen for valuable discussions of the PMR spectra.

REFERENCES

1. Alderweireldt, F. and Anteunis, M. *Bull. Soc. Chim. Belges* **74** (1965) 488.
2. Matthiason, B. *Acta Chem. Scand.* **17** (1963) 2133.
3. Abraham, B. J. *J. Chem. Soc.* **1964** 256.
4. Gagnaire, D. and Robert, J. B. *Bull. Soc. Chim. France* **1965** 3646.
5. Haake, P., McNeal J. P. and Goldsmith E. J. *J. Am. Chem. Soc.* **90** (1968) 715.
6. Gagnaire, D., Robert, J. B. and Verrier, J. *Bull. Soc. Chim. France* **1966** 3719.
7. Devillers, J., Navech, J. and Albrand J. P. *Org. Magn. Resonance* **3** (1971) 177.
8. Kaonosho, M. *J. Phys. Chem.* **73** (1969) 3516.
9. Engel, R. and Jung, A. *J. Chem. Soc. C* **1971** 1761.

10. Dischler, B. and Maier, Z. *Naturforsch.* **16a** (1961) 318.
11. Poble, J. A., Schneider, W. G. and Bernstein H. J. *High-Resolution Nuclear Magnetic Resonance*, McGraw, New York 1959.
12. Garbisch, E. W., Jr. *J. Chem. Educ.* **45** (1968) 480.
13. Diehl, P. and Chuck, R. J. *Mol. Phys.* **13** (1968) 417.
14. Altona, C., Buys, H. R. and Havinga E. *Rec. Trav. Chim.* **85** (1966) 973 and 983.
15. Buys, H. R., Altona C. and Havinga E. *Rec. Trav. Chim.* **85** (1966) 988.
16. Kainosho, M. and Nakamura, A. *Tetrahedron* **25** (1969) 4071.
17. Bergesen, K. and Albrigtsen, P. *Acta Chem. Scand.* **25** (1971) 2257.
18. Bergesen, K. and Albrigtsen, P. *Unpublished results*.
19. Castellano, S. and Bothner-By, A. A. *J. Phys. Chem.* **41** (1964) 3863.
20. Lambert, J. B. *Accounts Chem. Res.* **4** (1971) 87.
21. Buys, H. R. and Eliel, E. L. *Tetrahedron Letters* **1970** 2779.
22. Aksnes, D. and Vikane, O. *Private communication*.
23. Haigh, C. W. *Private communication*.

Received December 27, 1971.