

# Analysis of the High Resolution $^1\text{H}$ NMR Spectra of 2-Phenyl-1,3,2-dithiaphosphorinane

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$^1\text{H}$  NMR studies of 1,3,2-dioxaphosphorinanes with tervalent phosphorus atom have received much attention the last years.<sup>1-5</sup> Most of the six-membered ring phosphites show no change of the NMR spectra over the temperature range  $-90$  to  $+160^\circ\text{C}$ . This observation indicates anancomeric ring structure of the compounds and is therefore well suited to NMR analysis. NMR studies have also confirmed that the compounds have chair-structure and that the ring phosphites exist predominantly in one conformation with the group attached to the phosphorus atom in axial position. This paper reports the  $^1\text{H}$  NMR analysis of 2-phenyl-1,3,2-dithiaphosphorinane, I, where the conformation

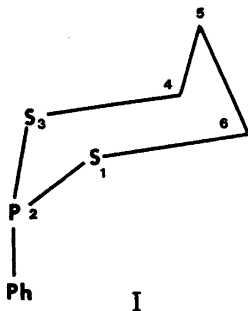


Table 1. 100 MHz spectral parameters (in Hz) of 2-phenyl-1,3,2-dithiaphosphorinane.

Chemical shift <sup>a</sup>	Coupling constants				
	$\nu$ Hz	$J$	Hz	$J$ Hz	
4a	275.22	4a4e	-14.09	4e6a	0.06
4e	235.58	5a5e	-17.11	4a6a	0.01
5a	212.79	4a5a	12.01	P4a	2.36
5e	172.95	4e5a	2.52	P4e	-0.08
		4e5e	5.60	P5a	2.68
		4a5e	2.19	P5e	2.52
		4e6e	1.02		

<sup>a</sup> Downfield from TMS.

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is discussed on the basis of spectral properties. The iterated spectral parameters of I are listed in Table 1.

The  $^1\text{H}$  NMR spectrum of I was analyzed as an AA'BB'CDP spin system by means of the computer programs LAOCN3<sup>6</sup> and KOMBIP.<sup>7</sup> The latter sub-routine generated "stick"- and Lorentzian line-shape plots.

The 100 MHz  $^1\text{H}$  NMR spectrum of I, Fig. 1, shows a more complex pattern as compared to the dioxo analog which was divided into four well resolved bands. However, the splitted triplet observed in the lower field region of the spectrum indicates that there is a coupling of nearly the same magnitude as the geminal coupling, together with a smaller coupling. The larger coupling is assumed to be the vicinal *trans* ( $J_{aa}$ ) coupling, and the smaller coupling to the equatorial proton in position 5. The low field part is therefore assigned to the axial protons at carbon 4 and 6. As a consequence the equatorial protons at C(4) and C(6) are therefore shifted to higher field compared to the axial protons. This relative shift position is reversed as observed in cyclohexane derivatives,<sup>8</sup> but the same as reported for 1,3,2-dioxaphosphorinanes<sup>3</sup> and cyclic sulfites.<sup>9-10</sup> Apparently, this reversed or larger down field shift of axial protons at carbon 4 and 6, as compared to the geminal proton, indicates an axial position of the P-Ph group. The high field part of the spectrum is very complex and is due to the equatorial protons at carbon 4 and 6 and the protons at carbon 5.

It has been found that the axial proton at carbon 5 in trimethylenesulfide,<sup>9</sup> 2-chloro-, 2-methoxy- and 2-phenoxy-1,3,2-dioxaphosphorinane,<sup>3</sup> 2-chloro-1,3,2-dithiarsenane,<sup>11</sup> and also now 2-phenyl-1,3,2-dithiaphosphorinane (I) is always observed at lower field than the corresponding geminal equatorial proton. These compounds resemble the dioxanes with respect to relative shift positions of geminal protons at carbon 5, which also show this reversed relative position.<sup>12</sup> The reason for this observation is probably an interaction between  $H_{5e}$  and the *p*-orbitals of the ring oxygen and ring sulfur atoms.<sup>13</sup>

The vicinal coupling constants,  $J_{4a5a}$  and  $J_{4e5e}$ , found for 2-phenyl-1,3,2-dithiaphosphorinane are in the expected ranges<sup>14</sup> and are also consistent with a chair conformation of the ring. The rather large value of  $J_{4e5e}$  in I and 2-chloro-1,3,2-dithiarsenane<sup>11</sup> probably indicates a high ring puckering of the C(4)-C(5)-C(6) moiety of the ring.<sup>15</sup> In dioxanes, where the ring is assumed to be somewhat "flattened",  $J_{5e4a}$  is observed to be greater than  $J_{5e4e}$ .<sup>13,16</sup>

The geminal coupling constants in six-membered rings<sup>17</sup> are in the ranges  $-13$  to  $-14$  Hz and  $-12$  to  $-18$  Hz in C-CH<sub>2</sub>-S- and C-CH<sub>2</sub>-C, moieties, respectively. The observed values for I are in the expected range, and the magnitude of  $J_{4a4e}$  is close to the cor-

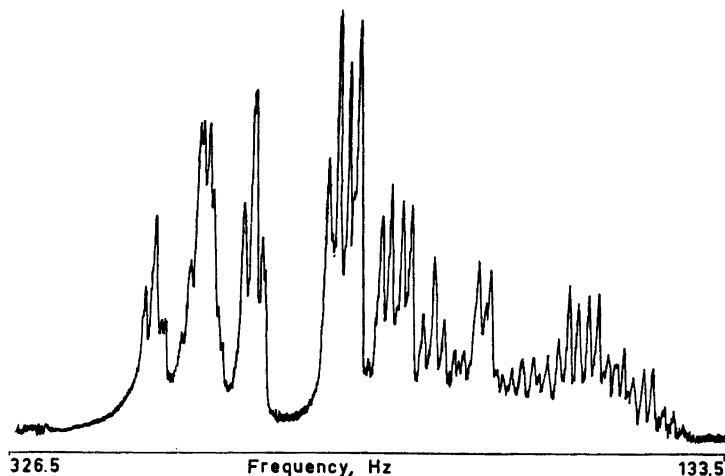


Fig. 1. Experimental 100 MHz spectrum of compound I in benzene solution.

responding coupling constant in 2-phenyl-5-*tert*-butyl-1,3,2-dithiaphosphorinane<sup>18</sup> and 2-chloro-1,3,2-dithiarsenane.<sup>11</sup>

The four-bond coupling of 1.02 Hz between the equatorial protons in 4 and 6 positions is an expected value for this type.<sup>13</sup>

The dihedral angle in the carbon part of the 1,3,2-dithiaphosphorinane is calculated using the vicinal proton-proton coupling constants according to the method of Buys.<sup>19</sup> The calculated ring torsion angle of the fragment  $-\text{CH}_2-\text{CH}_2-$  is found to be  $59^\circ$ , which indicates that the carbon part exists in nearly staggered conformation.

Further analysis of ring substituted 1,3,2-dithiaphosphorinanes are in progress in this laboratory.

**Experimental.** 2-Phenyl-1,3,2-dithiaphosphorinane (I), was prepared from propanedithiol and dichlorophenyl-phosphine in benzene solution using triethylamine as base. B.p.  $100^\circ\text{C}/0.5$  mm Hg.

The NMR spectrum was recorded on a 100 MHz, Varian HA-100 spectrometer at  $28^\circ\text{C}$  in 50 % solution of I in benzene. The spectrum was analysed on the basis of AA'BB'CDP spin system using the iterative computer program LAOCN3<sup>6</sup> with some modification. Line positions was taken by averaging the data of four spectra. The computations were carried out on an UNIVAC 1110 computer. The r.m.s. deviation of 197 experimental and calculated transitions were less than 0.1, and the probable errors of the coupling constants are 0.02 to 0.03 Hz.

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