

## A SOLUTION AND SOLID STATE CONFORMATION OF 2-PHOSPHORYL SUBSTITUTED 1,3-OXATHIANES

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**Summary:** Analysis of  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra of 2-dimethoxyphosphoryl and 2-diphenylphosphinoyl-substituted 1,3-oxathianes revealed that they exist in solution almost exclusively in a chair conformation with the phosphoryl group being equatorial. The equatorial orientation of the  $\text{Ph}_2\text{P}(\text{O})$ -group in 2-(diphenylphosphinoyl)-5,5-dimethyl-1,3-oxathiane was also found in the crystal state.

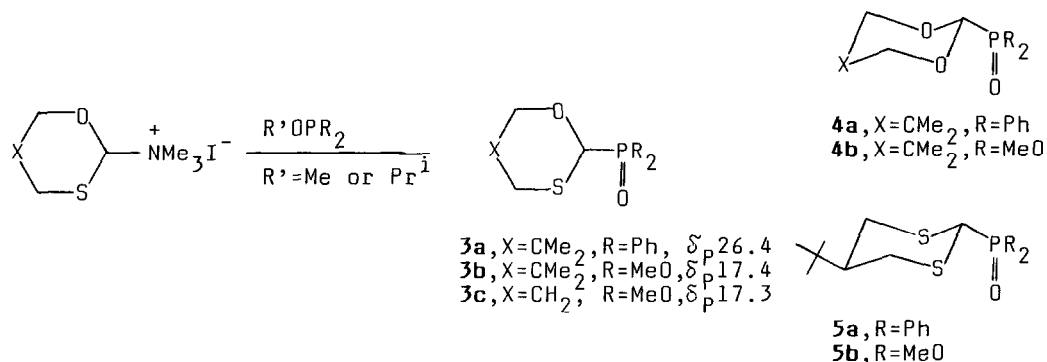
The determination of conformational preferences of substituents at the carbon atom 2 in 1,3-heteroananes is interesting especially from the point of view of understanding the origin of the anomeric effect observed very often in these heterocyclic systems<sup>1-3</sup>. Recently, we described<sup>4</sup> a contrasting conformational behaviour of 2-phosphoryl substituted 1,3-dithianes **1** and 1,3-dioxanes **2**. Thus, whereas the former compounds exist in a chair conformation with the axial phosphoryl group, in the latter it is equatorial.



According to molecular mechanics calculations<sup>5</sup>, a strong anomeric effect operating in **1**, i.e. the axial preference of the  $\text{R}_2\text{P}(\text{O})$ -group, is mainly due to repulsive interactions occurring in the equatorial conformation of **1** between the lone electron pairs on sulphur and the phosphoryl oxygen. In the case of 1,3-dioxanes **2**, owing to a short C-O bond distance, 1,3-syn-axial interactions in the axial conformation of **2** are stronger than stereoelectronic effects and are responsible for the equatorial position of the  $\text{P}(\text{O})$ -group.

The findings briefly presented above prompted us to study the conformational behaviour of 2-phosphoryl substituted 1,3-oxathianes **3**. The predominant orientation of the phosphoryl group in **3** should be determined by a more complex combination of the steric and stereoelectronic effects because of the simultaneous presence of the oxygen and sulphur atom in this six-membered ring.

The required 1,3-oxathianes **3a-c** were prepared in low to moderate yields (15 to 30%) by the Arbusov reaction of isopropyl diphenylphosphinite or trimethyl phosphite with an appropriate (1,3-oxathian-2-yl)-trimethylammonium iodide<sup>6</sup>.



Analysis of their <sup>1</sup>H and <sup>13</sup>C NMR spectra and especially comparison with those for 1,3-dioxanes **4** and 1,3-dithianes **5** bearing the equatorial phosphoryl group clearly point to a strong preferential equatorial orientation of the P(O)-group in the 1,3-oxathiane ring in solution. Some selected spectroscopic data for **3**, **4** and **5** are collected in Table.

Table. Selected NMR Data for 2-Phosphoryl-1,3-Heteroanes **3**, **4** and **5**<sup>a</sup>

No	<sup>1</sup> H-NMR						<sup>13</sup> C NMR			
	$\delta_{4,6\text{-ax}}$		$\delta_{4,6\text{-eq}}$		$\Delta\delta$		$\gamma$ -effect		$^3J_{\text{C-P}}$	
	CH <sub>2</sub> S	CH <sub>2</sub> O	CH <sub>2</sub> S	CH <sub>2</sub> O	CH <sub>2</sub> S	CH <sub>2</sub> O	CH <sub>2</sub> S	CH <sub>2</sub> O	CH <sub>2</sub> S	CH <sub>2</sub> O
<b>3a</b>	2.82	3.28	2.64	3.75	0.18	0.47	0.23	0.41	6.0	9.6
<b>3b</b>	2.76	3.29	2.68	3.78	0.08	0.49	-0.28	-0.13	6.9	11.7
<b>3c</b> <sup>b</sup>							0.03	0.41	6.4	10.9
<b>4a</b> <sup>c</sup>	-	3.48	-	3.74	-	0.26	-	-0.72	-	10.4
<b>4b</b> <sup>d</sup>	-	3.45	-	3.76	-	0.31	-	-0.46	-	13.8
<b>5a</b> <sup>e</sup>	2.55	-	3.07	-	0.52	-	1.21	-	7.1	-
<b>5b</b> <sup>e</sup>	2.69	-	2.96	-	0.27	-	0.67	-	8.7	-

<sup>a</sup>)  $\delta$ -values in ppm; J-values in Hz; <sup>1</sup>H (300.13 MHz) and <sup>13</sup>C (75.47 MHz) NMR spectra, measured in CDCl<sub>3</sub>; <sup>b</sup>) full analysis of <sup>1</sup>H NMR spectra is under current investigation; <sup>c</sup>) data from ref.4; <sup>d</sup>) this work; <sup>e</sup>) data from ref.7;  
<sup>f</sup>)  $\Delta\delta = |\delta_{4,6\text{-ax}} - \delta_{4,6\text{-eq}}|$ .

Two multiplets centered at about 2.7 and 3.5 ppm in the <sup>1</sup>H NMR spectrum of **3a** and **3b** were ascribed to the methylene protons connected with the sulphur and oxygen atom, respectively. This assignment is strongly supported by comparison of these values with those recorded for 1,3-dioxanes **4** and 1,3-dithianes **5**. The coupling pattern of the CH<sub>2</sub>O protons in **3a** and **3b** is very similar

to that observed for 1,3-dioxanes **4**. For example, in **3b** a low-field part of the AB system, which is assigned to the equatorial proton, appears in the spectrum as a doublet of triplets due to two long-range, W-type couplings with phosphorus and with the equatorial CH<sub>2</sub>S-proton equal to 1.7 and 1.6 Hz, respectively. The up-field shifted part of the CH<sub>2</sub>O-resonance attributed to the axial proton is a doublet with the geminal coupling constant,  $^2J_{\text{H-H}}=11.6$  Hz. However, in contrast to 1,3-dithianes **5**<sup>7</sup>, the resonance positions of the axial and equatorial CH<sub>2</sub>S-protons in **3** are reversed. Whereas a low-field part of the CH<sub>2</sub>S-resonance centered at 2.8 ppm, appears only as a doublet with  $^2J_{\text{H-H}}=13.2$  Hz for **3a** and 13.3 Hz for **3b**, the high-field signal at 2.7 ppm is more complex due to additional, W-type couplings with phosphorus ( $^4J_{\text{H-P}}=4.6$  Hz for **3a** and 5.9 Hz for **3b**) and with the equatorial CH<sub>2</sub>O-proton. Therefore, the latter signal corresponds to the equatorial CH<sub>2</sub>S-proton.

The observed coupling of the CH<sub>2</sub>O- and CH<sub>2</sub>S-protons with phosphorus and a very small chemical shift difference ( $\Delta\delta$ ) between axial and equatorial methylene protons are best rationalized by assuming the equatorial position of the phosphoryl group in the oxathiane chair conformation. This conclusion is further corroborated by the <sup>13</sup>C NMR spectra of **3**. Both the  $\nu$ -effect values and the  $^3J_{\text{C-P}}$  coupling constants are typical for 1,3-heteroanes with a strong preferential equatorial orientation of the P(O) group<sup>7</sup>. In accord with this, the low-temperature <sup>31</sup>P NMR spectra of **3a-c** (down to -120°C) did not show decoalescence and the presence of two conformers.

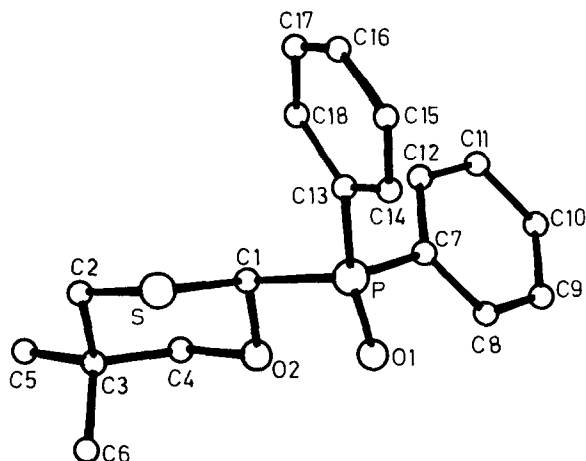


Fig. 1. The solid-state conformation of **3a** with the numbering system

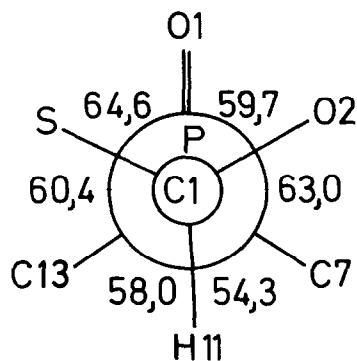


Fig. 2. Newman projection along C1-P bond showing the relevant torsion angles (°) in **3a**

In this context, it is interesting that **3a** exists also in the crystal state<sup>8</sup> in the equatorial conformation. A view of its solid-state conformation is shown in Fig. 1 and a Newman projection along carbon-phosphorus bond in Fig. 2. The six-membered ring adopts a slightly deformed chair conformation with the lowest asymmetry parameters:  $\Delta C_5^{(\text{S-C4})}=5.1^\circ$  and  $\Delta C_2^{(\text{S-C2})}=2.5^\circ$ . This is a consequence of the presence of two heteroatoms in the ring with different bond dis-

tances (S-C1=1.826(4)Å; O-C1=1.563(4)Å) and valence angles equal to 93.4° and 104.2° for sulphur and oxygen, respectively.

In conclusion, the results presented above show that, in contrast to 1,3-dithianes, the phosphoryl group at the anomeric carbon atom in 1,3-oxathianes strongly prefers to be equatorial like in 1,3-dioxanes. Further studies to synthesize diastereoisomeric cis- and trans-systems and to evaluate  $\Delta G^\circ$ -values for 1,3-oxathianes are in progress in this Laboratory.

**Acknowledgements:** This work was financially supported by the projects CPBP-01-13 and RP-II-10

### References and Notes

1. A.J.Kirby, *The Anomeric Effect and Related Stereoelectronic Effects at Oxygen*, Springer Verlag, Berlin, Heidelberg, New York, 1983.
2. E.Juaristi, I.Valle, B.A.Valenzuela and M.A.Aguilar, *J.Am.Chem.Soc.*, **1986**, 108, 2000 and references cited therein.
3. M.Mikołajczyk, *Pure Appl.Chem.*, **1987**, 59, 983 and references cited therein.
4. M.Mikołajczyk, P.Graczyk, M.W.Wieczorek, G.Bujacz, Y.T.Struchkov and M.Y.Antipin, *J.Org.Chem.*, **1988**, 53, 3609.
5. M.Mikołajczyk, P.Graczyk, M.I.Kabachnik and A.P.Baranov, *J.Org.Chem.*, submitted.
6. Optimization of the reaction conditions and yields is being investigated.
7. M.Mikołajczyk, P.Graczyk and P.Bałczewski, *Tetrahedron Lett.*, **1987**, 28,573.
8. Crystal data of **3a**: mp.142-143°C (acetone), C<sub>18</sub>H<sub>21</sub>PSO<sub>2</sub>(332.40), orthorhombic; space group *Pbca*; *a*=10.959(6)Å, *b*=17.234(5)Å, *c*=18.683(3)Å; *V*=3528.5(34)Å<sup>3</sup>, *Z*=8, *F*(000)=1408, *d*<sub>calc</sub>=1.25 gcm<sup>-3</sup>,  $\mu(\text{MoK}\alpha)=2.683 \text{ cm}^{-1}$ . The intensities of 3510 reflections were measured on an Enraf-Nonius CAD-4 diffractometer using MoK $\alpha$  radiation ( $\lambda=0.71073 \text{ \AA}$ ), graphite monochromator; range of measurements  $1 \leq \theta \leq 25^\circ$ ;  $\omega/2\theta$  scan; empirical absorption correction was applied. The structure was solved by direct methods. The coordinates of all non-hydrogen atoms were used from the E-map. Hydrogen atoms were located in a difference map in the expected positions. After application of the acceptance criterion  $I \geq 3\sigma(I)$ , 1960 reflections were retained for the refinement by full-matrix least-squares method for non-H atoms with anisotropic temperature factors and with isotropic temperature factors for H atoms. Convergence was reached at *R*=0.074 (*R*<sub>w</sub>=0.079). All the crystallographic data of **3a** are deposited with the Cambridge Crystallographic Data Centre, U.K.

(Received in UK 11 October 1988)