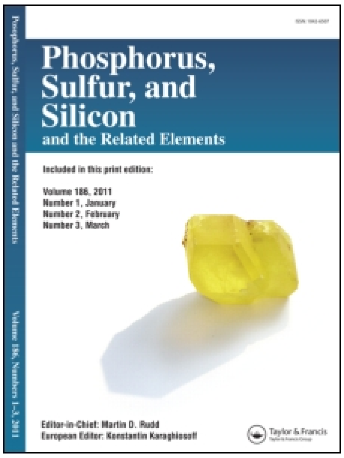

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A CONFORMATIONAL STUDY OF BIS(5,5-DIMETHYL-2-X-1,3,2-DIOXAPHOSPHORINAN-2-YL) SULFANES AND POLYSULFANES USING NMR AND IR SPECTROSCOPY

H. Kombert[ab]; G. Grossmann[a]
[a] Institute of Analytical Chemistry, Dresden University of Technology, Dresden, Germany [b] Institute of Polymer Research Dresden, Dresden, Germany

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H. KOMBER† and G. GROSSMANN
Institute of Analytical Chemistry, Dresden University of Technology, Mommsenstr. 13, D-01062 Dresden, Germany

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Bis(5,5-dimethyl-2-X-1,3,2-dioxaphosphorinan-2-yl) sulfanes and polysulfanes

$$(CH_3)_2C(CH_2O)_2P(X){-}Y{-}(X)P(OCH_2)_2C(CH_3)_2$$

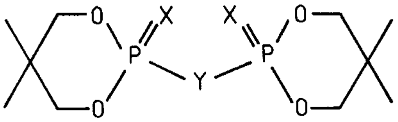
$$X = O; S \qquad Y = S_n (n = 1 - 4)$$

were synthesized and investigated by NMR and IR spectroscopy. ^{1}H, ^{13}C and ^{31}P NMR data are given. The portions of the alternative chair conformations of the dioxaphosphorinane ring are estimated from vicinal P—H coupling constants determined at room temperature in $CDCl_3$. The portion of the predominant conformer in case of all 2-oxo compounds amounts to more than 95%. For the 2-thiono compounds this portion varies with n (91 – 78%). Based on known X-ray crystallographic data and IR measurements in solid and solution state from the position of P=X stretching modes an equatorial position of the P=X bond can be suggested for the predominant conformer.

Key words: ^{31}P NMR; ^{1}H NMR; IR spectroscopy; 1,3,2-dioxaphosphorinanes; sulfanes; P—P coupling constants; ring conformation.

INTRODUCTION

Continuing our investigations on the spectroscopic characterization of bis(dialkoxythiophosphoryl) and bis(dialkoxyphosphoryl) sulfanes and polysulfanes[1–4] this report deals with NMR and IR investigations of bis(5,5-dimethyl-2-X-1,3,2-dioxaphosphorinan-2-yl) sulfanes and polysulfanes (**1**–**8**) which are the cyclic homologues of the forementioned compounds.



	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
X	S	S	S	S	O	O	O	O	S	O
Y	S	S_2	S_3	S_4	S	S_2	S_3	S_4	O	O

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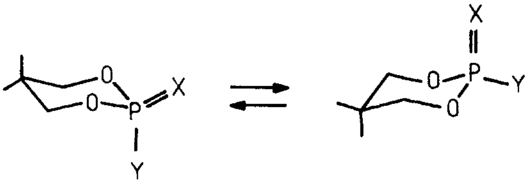
†Present address: Institute of Polymer Research Dresden, Hohe Str. 6, D-01069 Dresden, Germany.

Substituted 1,3,2-dioxaphosphorinanes (DOP) belong to the most investigated among heterocyclic organophosphorus compounds.[5,6] Especially 5,5-dialkyl substituted DPO are preferred subjects of investigation. In this case strong biasing substituents at ring positions 4, 5 and 6 are absent and the studies of ring conformation in solution are reduced to be conformational behaviour of substituents X and Y.



I II

The preferred arrangement of X and Y in solution is determined by dipole-dipole interactions as well as by steric, anomeric and solvent effects.[6]

The aim of this paper is, besides the ^{1}H, ^{13}C and ^{31}P NMR spectroscopical characterization, to study the influence of the X substituent (S or O) and of the length of the sulfane chain on the conformational equilibrium of **1**–**8** in solution by spectroscopic methods. ^{1}H NMR spectroscopy is used to determine the ratio of the two chair conformers by analysing the vicinal P—H coupling constants. By combination of IR measurements in solid and solution state and X-ray crystallographic data it can be distinguished between axial or equatorial position of substituent X.

RESULTS AND DISCUSSION

Chemical Shifts and Coupling Constants

The ^{31}P chemical shifts and P—P coupling constants of compounds **2**–**8** are in the same range as those for the corresponding derivatives with bulky dialkoxy groups[1,2] (Table I). An exception is the sulfane **1** with a ^{31}P chemical shift 14 ppm lower than that of the polysulfanes and a P—P coupling constant of -9.3 Hz (dialkoxy derivatives: ≈ -19 Hz[1]).

This high-field shift is also known from the sulfanes with dialkoxy substituents ($\Delta\delta \approx -6$ ppm) and is explained by the two *γ-gauche* interactions between one phosphorus atom and the substituents of the other one[1] (Scheme A–C). Thus only one γ-interaction is possible for the polysulfanes (D).

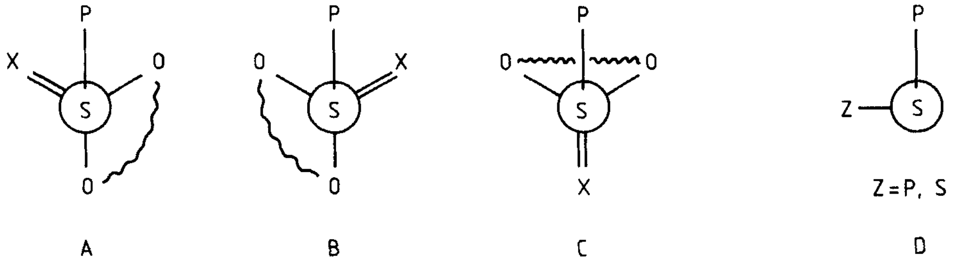


TABLE I

^{31}P and ^{13}C chemical shifts (in ppm) and some coupling constants (in Hz) of **1–8** (solvent: $CDCl_3$)

	n	$\delta_P{}^a$	$^{n+1}J_{PP}{}^b$	$\delta_{CH_3}{}^c$	δ_{CH_2}	δ_C	$^2J_{PC}{}^b$	$^3J_{PC}{}^b$
1	1	65.5	-9.3	22.4 / 20.7	79.1	32.4	9.8	7.4
2	2	79.8	3.0	22.0 / 20.8	78.9	32.4	10.2	7.7
3	3	81.0	+12.8	22.1 / 21.0	78.4	32.6	9.1	7.3
4	4	80.5	0.3	22.1 /21.1	78.5	32.6	9.1	7.3
5	1	6.4	-10.8	22.0 / 19.9	79.1	32.4	7.7	7.3
6	2	12.4	< 0.3	21.8 / 20.1	79.2	32.5	7.7	7.3
7	3	12.5	+10.9	21.8 / 20.1	78.9	32.4	7.4	7.1
8	4	12.8	< 0.3	22.0 / 20.2	79.1	32.5	7.7	7.0

[a] Data from literature: **1**: 65.5 ppm[12], **2**: 80.83 ppm[23], **5**: 6.4 ppm[9], **6**: 12.3 ppm[24].

[b] Determined from the ^{31}P coupled ^{13}C spectra (X part of a AA'X spin system)[1]. Sign as determined in Reference 1.

[c] axial CH_3-group / equatorial CH_3-group (broadened by $^4J_{PC}$)

Conformer C is unfavourable for compound **1** with equatorial P═S bond (see later) by steric reasons. Hence, the larger possibility of *γ-gauche* interactions between phosphorus and thiono sulfur causes the enhanced high-field shift of **1**. In case of the 2-oxo derivative **5** such an enhanced high-field shift is not observed for due to smaller *γ-gauche* interaction with the oxygen of the P═O bond.

The strong positivation of the geminal P—P coupling constant of **1** in comparison to those of dialkoxy derivatives is also caused by the other conformation present in the cyclic compound.

The ^{13}C NMR data of **1–8** are almost independent on the different substitution of the phosphorus (Table I). Only $^2J_{PC}$ shows the expected decrease from the 2-thiono to the 2-oxo compounds. The ^1H spectrum of the 5,5-dimethyl substituted dioxaphosphorinane ring shows for the methylene protons an AA'BB' part of an AA'BB'X spin system (X = ^{31}P). Different methyl signals are observed for the axial and equatorial arrangement, respectively. Long-range *W*-type couplings occur between the both equatorial methylene protons and between the protons of the axial methyl group and the axial methylene protons, indicating the chair conformation.[7]

The spin system of the methylene protons is more complicated if the phosphorus shows a significant P—P coupling to another phosphorus atom, i.e., for the sulfanes (**1**, **5**), trisulfanes (**3**, **7**), and oxides (**9**, **10**). This fact was not mentioned in other papers, dealing with NMR investigations on **1**[8], **5**[9] and **10**.[10]

The ^{31}P spectrum and the methylene part of the ^1H spectrum of **3** and **4** illustrate the effect of large P—P coupling constants (Figure 1). The P—P coupling of the tetrasulfane **4** is negligible and both the ^{31}P and the ^1H spectrum (Figures 1a and

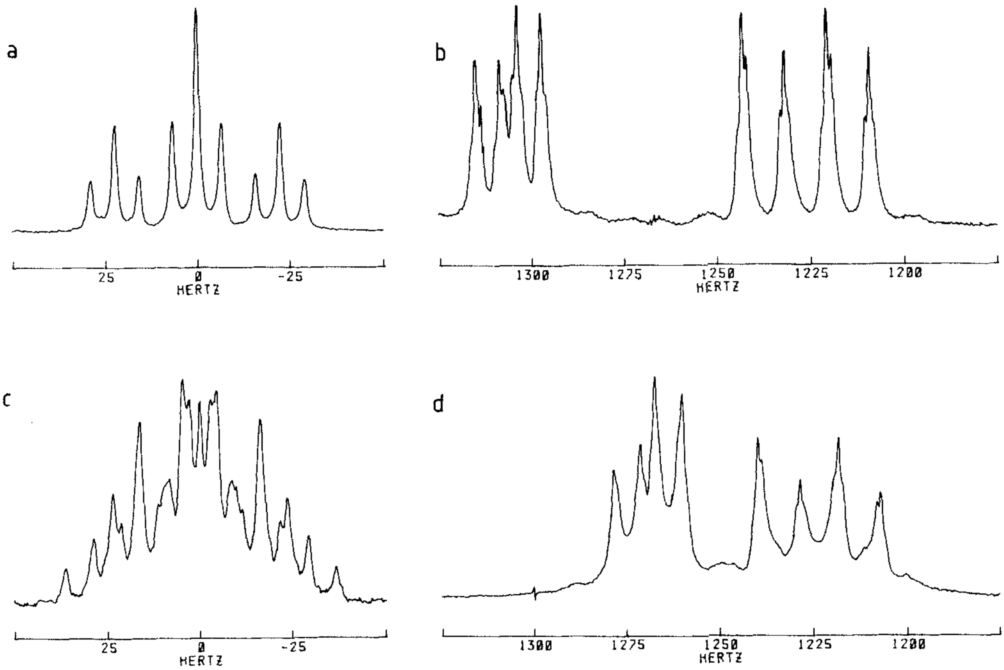


FIGURE 1 121.495 MHz ^{31}P (a, c) and 300.13 MHz ^{1}H NMR (b, d-methylene region, decoupled from axial methyl group) spectra of **4** (a: 0 Hz ≡ 80.5 ppm, b) and **3** (c: 0 Hz ≡ 81.0 ppm, d).

b) show the typical AA'BB'X pattern. Although the P—H couplings for the trisulfane **3** are nearly the same as for **4** (Table II) the P—P coupling constant of +12.8 Hz results in more complicated ^{31}P and ^{1}H spectra (Figures 1c and d).

The methylene protons (A, B) and phosphorus atoms (X) of both DPO rings are parts of a AA'BB'XX'A''A'''B''B''' spin system. As we could not simulate the ten spin system, the ^{1}H spectra of **1–8** were approximately simulated as parts of an AA'BB'X spin system. Thus, these results (Table II) are of less accuracy in case of the sulfanes and trisulfanes.

^{1}H NMR Investigations on Conformer Distribution

In the literature different methods are described to determine the conformer distribution and thermodynamic parameters of DPO ring equilibrium by ^{1}H NMR (see i.e.[9,11]). The marked stereospecificity of $^{3}J_{POCH}$, along with its Karplus-type variation of magnitude with dihedral angle, is particularly useful.

The aim of this paper is to estimate the conformer distribution for **1–8** at room temperature in CDCl$_3$ by analyzing the vicinal P—H coupling constants in a simple manner.

The measured couplings $^{3}J(\text{P—H}_A) = J_A$ and $^{3}J(\text{P—H}_B) = J_B$ ($J_A < J_B$) are weighted, time-averaged values reflecting the equilibrium of the two chair conformers I and II:

$$J_A = p_I \cdot J_a + p_{II} \cdot J_e \qquad (1)$$

$$J_B = p_I \cdot J_e + p_{II} \cdot J_a \qquad (2)$$

TABLE II

${}^{1}H$ chemical shifts (in ppm) and some coupling constants (in Hz) of **1–8** (solvent: $CDCl_3$)

	$\delta_{CH_{3e}}$	$\delta_{CH_{3a}}$[a]	$\delta_{\mathbf{CH_A}H_B}$[b]	$\delta_{CH_A\mathbf{H_B}}$[b]	J_A[b]	J_B[b]
1	0.91	1.32	4.49	3.95	4.0	26.9
2	0.94	1.27	4.38	4.01	5.4	23.2
3	0.97	1.25	4.22	4.08	7.0	21.6
4	1.01	1.27	4.30	4.04	6.5	22.6
5	0.87	1.28	4.47	3.97	2.2	26.5
6	0.87	1.29	4.41	3.95	2.5	25.1
7	0.92	1.33	4.22	4.01	2.6	23.9
8	0.91	1.31	4.30	3.98	2.9	25.0

[a] Broadened due to long-range coupling with H_A.

[b] Chemical shifts and coupling constants are obtained by AA'BB'X simulation of the methylene protons region, $J_A = {}^{3}J_{PH_A}$ and $J_B = {}^{3}J_{PH_B}$.
Further couplings: ${}^{2}J_{H_AH_B} = 11.1 - 11.4$ Hz, ${}^{4}J_{H_BH_{B'}} = 2.7 - 3.0$ Hz, other couplings negligible. The methylene region was decoupled from the axial methyl group by CW irradiation.

p_I and p_{II} are the portions of conformers I and II—we assume $p_I > p_{II}$. J_a and J_e are the vicinal P—H coupling constants for the axial and equatorial methylene proton, resp., in a fixed chair. To estimate J_a and J_e for the homologues **1–4** and **5–8**, resp., the temperature dependence of J_A and J_B for **2** and **6** was investigated (Figure 2). The spectra of these disulfanes are not complicated by large P—P couplings.

The temperature dependence of the P—H couplings is different for both compounds, and only for **6** an extrapolation is reasonable for J_A and J_B at $p_I \approx 1$. A more crude estimation of these values is necessary for **2**. Comparing with literature data[5,6,9,10] we estimate for **2**: $J_a = 1.5$ Hz and $J_e = 27.5$ Hz and for **6**: $J_a = 2.2$ Hz and $J_e = 26.0$ Hz.

As the sum $J_A + J_B$ varies with both, temperature (Figure 2) and the homologous (Table III), Equations (1) and (2) are only approximations. They neglect the influence of differences in the ring geometry of chairs I and II, temperature effects and also the effect of substituent Y on the vicinal P—H coupling constants J_a and J_e. Furthermore, the simplified analysis as AA'BB'X spectra introduces errors. To get estimations for p_I and p_{II} some assumptions have to be taken. We introduce a factor F_Y to "correct" J_a and J_e for each compound because for calculations $J_A + J_B = J_a + J_e$ must be valid:

$$F_Y = (J_A + J_B)_Y/(J_a + J_e) \qquad (3)$$

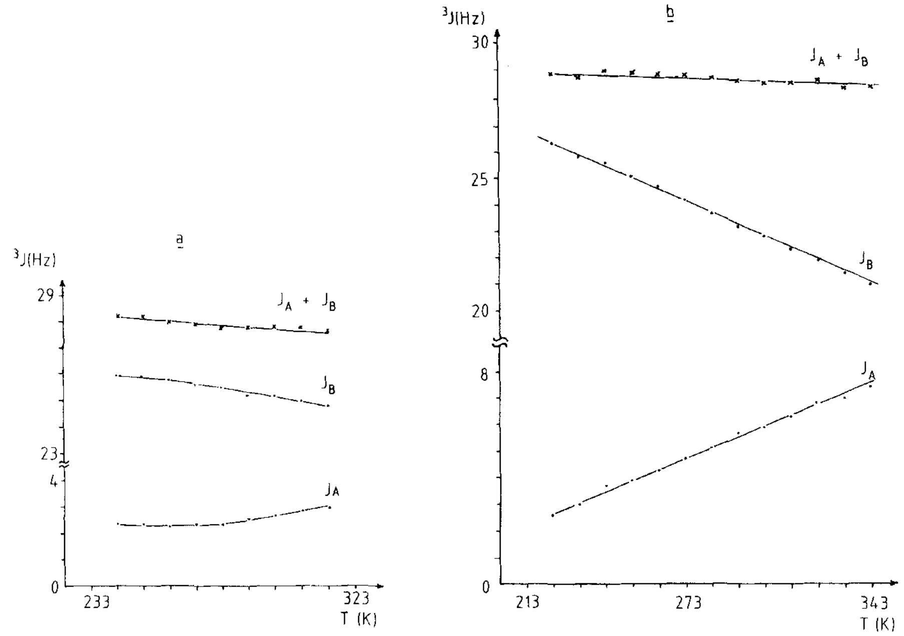


FIGURE 2 Temperature dependence of the vicinal P—H coupling constants J_A and J_B for **6** (a) and **2** (b) in an acetone-d_6 solution (0.1 M).

TABLE III

^{31}P—^{1}H coupling constants (in Hz), equilibrium conformer portions (p_I and p_{II})[a] (in percent) and methyl group chemical shift differences $\Delta\delta_{CH_3}$[b] (in ppm) for **1–8** at 300 K in $CDCl_3$, and the solvent-effect on these data for **4**

	$J_A + J_B$	F_Y	J_a^c	J_e^c	p_I	p_{II}	$\Delta\delta_{CH_3}$
1	30.9	1.06	1.6	29.3	91	9	0.41
2	28.6	0.99	1.4	27.2	84	16	0.33
3	28.6	0.99	1.4	27.2	78	22	0.28
4	29.1	1.00	1.5	27.6	81	19	0.26
4[c]	29.1	1.00	1.5	27.6	83	17	0.24
4[d]	29.0	1.00	1.5	27.5	85	15	0.21
5	28.7	1.02	2.3	26.4	99	1	0.41
6	27.6	0.98	2.2	25.4	98	2	0.42
7	26.5	0.94	2.1	24.4	98	2	0.40
8	27.9	0.99	2.2	25.7	97	3	0.41

[a] Determined from Eqs. 1 and 2 using J_a^c and J_e^c. Estimated error: ± 5%.

[b] $\Delta\delta_{CH_3} = \delta_{CH_{3a}} - \delta_{CH_{3e}}$

[c] In Acetone-d_6, J_A = 5.9 Hz and J_B = 23.2 Hz.

[d] In DMSO-d_6, J_A = 5.4 Hz and J_B = 23.6 Hz.

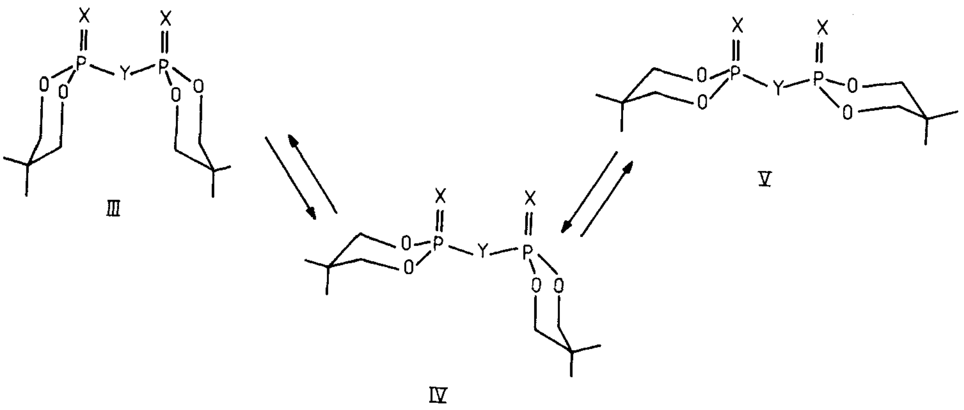
The "corrected" values J_a^c and J_c^c were used to determine p_I and p_{II} for each compound.

$$J_a^c = F_Y \cdot J_a \tag{4}$$

$$J_c^c = F_Y \cdot J_c \tag{5}$$

The effect of different J_a and J_e for chair II on the calculations is reduced due to the low part of this chair in the equilibrium (Table III).[11b] The estimations of p_I and p_{II} for **1–8** are summarized in Table III. They were obtained from Equations (1) and (2) with $p_I + p_{II} = 1$.

For the complete molecule the three conformers III–V may exist.



If Gibbs free energies of the chairs I and II do not depend on the conformation of the second DPO ring the portions of III–V in the equilibrium can be calculated easily:

$$p_{III} = (p_I)^2 \tag{6}$$

$$p_{IV} = 2 \cdot p_I \cdot p_{II} \tag{7}$$

$$p_V = (p_{II})^2 \tag{8}$$

The portion of conformers V is in the range of 2–5% for compounds **2–4**. In the other compounds investigated this portion is less than 1%.

Taking into account errors and assumptions involved from the calculated conformer distributions the following conclusions may be drawn.

In each case only one chair conformation is clearly predominant. If the two DPO rings are connected only by one atom (oxides, sulfanes) the substituents X and Y prefer strongly a distinct ring position. The preferred chair conformation is found with a portion of more than 90% for **1**, **5**,[9] and **10**.[10] The P=O and P—S_n bond prefer hardly different positions. The increasing length of the sulfur chain influences only slightly the equilibrium of the ring inversion of the 2-oxo compounds **5–8**.

The conformational preference is smaller for the 2-thiono compounds **1–4**. From $n = 1$ to $n = 2$ the portion of the second conformer increases significantly and becomes at $n > 2$ nearly constant. This reflects the decreasing influence of the second dioxaphosphorinane ring on the equilibrium and the lower difference in conformational preference between P=S and P—S_n bond ($n > 1$). These trends are also displayed in the chemical shift difference of the methyl groups of **1–8** (Table III).

However, the conformational analysis did not offer a conclusive evidence for the identity of the favoured conformers. A solvent-effect ^1H NMR study on **4** indicated only that polar solvents stabilize the favoured conformer (Table III).

The Preferred Ring Conformation—an IR Investigation

The faster time scale of IR experiments compared to NMR measurements enables to observe separate P=X stretching frequencies in conformationally non-rigid systems. As for all compounds one conformer is strongly preferred it seems possible to identify this conformer by a combination of IR investigations in solid and solution state and known crystal structures.

X-ray studies of **1**,[4] **2**[4] and **5**[13] show that for these compounds the P=X bond (X=S, O) is in equatorial position (see e.g., Figure 3).

In the IR spectrum of solid **1** we observe two P=S stretching modes at 717 and 660 cm^{-1} (Table IV). Like the C=O vibrations of organic anhydrides both P=S vibrations are coupled and result in "in phase" and "out of phase" stretching modes for the equatorial P=S bond. A smaller coupling can also be found for **2**. Only a single strong P=S band occurs for **3** and **4** at 673 and 674 cm^{-1}, respectively. Due to the intermediate frequency of these bands in comparison to the both P=S bands of **2** the P=S bonds are also expected in equatorial position for **3** and **4** in the crystalline state. Additionally, a weaker bond at 687 cm^{-1} is observed for **4** in solid state. Although we cannot assign this band, an axial P=S bond is not the reason due to its low intensity. This band is absent in solution. Furthermore, only the equatorial P=X stretching mode is significantly coupled with other vibrations in the ring plain. For this reason the higher frequency is observed for the equatorial $\nu_{(P=X)}$ (i.e., References 14–17).

Two effects are stated for the investigation of polysulfanes **1–4** dissolved in acetone. A violet shift of 4 cm^{-1} is found for all P=S bands and is attributed to solvation. Additionally, new bands or shoulders at lower frequencies appear for

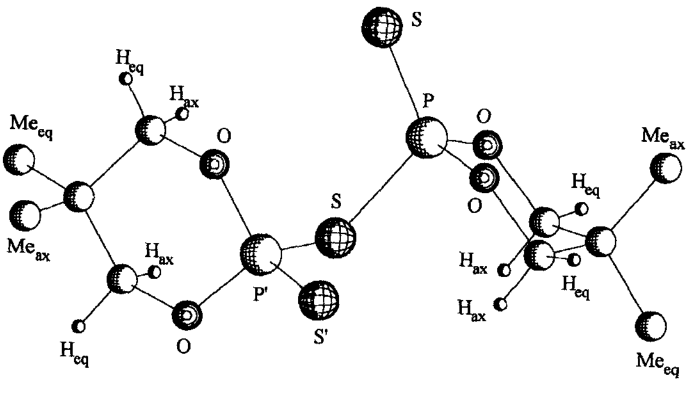


FIGURE 3 Molecular structure of **1** (protons of methyl groups are omitted).[4]

TABLE IV

The P=X stretching modes of compounds **1–8** in solid and solution state

	X	ν (P=X) [cm^{-1}]		
		Solid state	$CDCl_3$ solution	Acetone solution
1	S	717 m, 660 s		716 m, 658 s
2	S	688 s, 668 s		693 m, 685 m, 672s, 658 sh
3	S	673 s		677 s, 669 sh
4	S	687 m, 674 s		678 [a]
5	O	1287 s	1292 s	
6	O	1285 s	1289 s	
7	O	1288 s, 1280 s	1288 s	
8	O	1288 s, 1283 s	1287 s	

[a] Additional shoulders at lower wave numbers.

2–4. From the ^1H NMR investigations can be concluded that these bands and shoulders are caused by the other conformer which exists to nearly 20% in the equilibrium for **2–4**. The lower frequencies correspond with an axial position of the P=S bond in this conformer.

No such additional low frequency P=S bands were observed for **1** due to the low portion of this conformer in solution.

The discussion of the 2-oxo compounds **5–8** we start with **5**. The very strong IR-band at 1287 cm^{-1} is attributed to the equatorial P=O bond in agreement with X-ray results[13] and ^{18}O isotope effects.[18] No vibration coupling occurs due to the differences of force constants and atom masses of the P=O and P—S moieties. The P=O stretching modes for polysulfanes **6–8** were observed at nearly the same position (Table IV) and were also assigned to an equatorial P=O bond. Two bands of nearly the same intensity and a frequency difference of 8 and 5 cm^{-1}, resp., were observed for **7** and **8**. In $CDCl_3$ solution only one band is observed for both compounds and we assume that the splitting is attributed to interactions in solid state. The solvent effect of $CDCl_3$ results in a violet shift of 5 cm^{-1} and a band broadening.

In agreement with the ^1H NMR results no bands at lower frequencies are observed indicating the very small portion of the chair conformer with axial P=O bond.

Both for 2-thiono and 2-oxo compounds an equatorial P=X bond is stated for the predominant conformer from the IR investigations. These results are supported by X-ray crystallographic data of similar compounds.[19–21] Furthermore, ^1H NMR investigations of **4** indicate an increasing portion of the major conformer with increasing polarity of the solvent. This confirms the IR results taking into account that the dipole momentum of the conformer with equatorial P=S bond is larger than that with the axial one.[22]

Our results confirm the equatorial preference of the P═X bond (X = O, S) in 1, 3, 2-dioxaphosphorinanes with four-coordinated phosphorus which was observed if the remaining phosphorus substituent is a halogen, —OR or —SR group.[5,6] This effect is more pronounced for the 2-oxo compounds.

EXPERIMENTAL

Synthesis. The synthesis of sulfanes and polysulfanes **1–8** was described in Reference 1. Benzene was used as solvent. Crystalline products were obtained. The tri- and tetrasulfanes must be recrystallized at low temperature to avoid disproportionation. All products were characterized by elementar analysis and melting points (literature data for sulfanes and disulfanes). Uncorrected melting points (decomposition) of the tri- and tetrasulfanes: **3**: 148–150°C; **4**: 124–126°C; **7**: 128–130°C; **8**: 119–121°C.

Spectroscopic measurements. The NMR spectra were obtained with a Bruker MSL 300 at the working frequencies of 300.13 MHz for ^{1}H, 75.475 MHz for ^{13}C and 121.495 MHz for ^{31}P. The ^{1}H and ^{13}C chemical shifts were referenced to $CDCl_3$ at 77.00 and 7.28 ppm, respectively. 85% H_3PO_4 was used as external standard for the ^{31}P NMR spectra. The PANIC program was used for spectra simulation at a BRUKER ASPECT 3000 computer. The IR spectra were recorded by a double-beam spectrometer SPECORD 75 IR (Carl Zeiss Jena). KBr tablets were used for solid state spectra and a 128 mm cuvette of KBr for the 0.1 M solutions of **2–8** and the saturated solution of **1**.

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