2-THIOXO-1,3,2-DITHIAPHOSPHOLANES -SOLID-STATE MAS NMR AND CRYSTAL STRUCTURE INVESTIGATIONS AS WELL AS IGLO CALCULATIONS OF 31P SHIELDING TENSORS

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2-THIOXO-1,3,2-DITHIAPHOSPHOLANES — SOLID-STATE MAS NMR AND CRYSTAL STRUCTURE INVESTIGATIONS AS WELL AS IGLO CALCULATIONS OF ^{31}P SHIELDING TENSORS

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Dedicated to Prof. E. Niecke on the occasion of his 60th birthday

2-Thioxo-1,3,2-dithiaphospholanes with P-substituents R = Me, Et, *i*-Pr, *t*-Bu, Ph, 3,5-Me$_2$C$_6$H$_3$, and 4-MeOC$_6$H$_4$ were prepared and characterized by solution and high resolution solid-state ^{31}P and ^{13}C NMR spectroscopy. The influence of different alkyl and aryl substituents at the phosphorus atom on the anisotropy of ^{31}P chemical shift and on the molecular structure is discussed. The orientation of the principal axes with respect to the molecular frame is predicted from the solid-state ^{31}P NMR results. Quantum chemical calculations of the ^{31}P shielding tensors by the IGLO method confirm these results. The crystal structures of 2-*tert*-butyl-2-thioxo-1,3,2-dithiaphospholane and 2-(3,5-dimethylphenyl)-2-thioxo-1,3,2-dithiaphospholane are presented and discussed.

Keywords: 2-thioxo-1,3,2 -dithiaphospholanes; NMR; chemical shift anisotropy; IGLO calculation; crystal structure

INTRODUCTION

The high resolution MAS NMR spectroscopy of spin-½ nuclei of crystalline powders allows to determine not only the chemical shift but also its

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anisotropy. The three principal values of the chemical shift tensor, δ_{ii}, are obtained by analysis of the sideband intensities and can be converted into principal values of the shielding tensor according to σ_{ii}= 328 ppm – δ_{ii} (for ^{31}P).[1] The following definitions were used: $\delta_{11} \geq \delta_{22} \geq \delta_{33}$ or $\sigma_{11} \leq \sigma_{22} \leq \sigma_{33}$, isotropic chemical shift $\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$.[2]

The orientation of the principal axes of the shielding tensor in the molecular frame only available from single crystal investigations can be determined by quantum chemical calculations of the ^{31}P shielding tensors by the IGLO method.

In the present article, we describe new results of investigations of phosphorus containing five-membered rings, the 2-thioxo-1,3,2 -dithiaphospholanes (see Scheme 1). All synthesized compounds (**1–7**) are characterized by solution and for the first time by CP MAS NMR spectroscopy. The substituent R at the phosphorus atom was varied to determine its influence on the anisotropy of the chemical shift. It is shown that for the given class of compounds the orientation of the ^{31}P shielding tensor can be predicted from experimental data. The compound with R = 3,5-dimethylphenyl (**6**) has been prepared for the first time.

	R
1	Me
2	Et
3	*i*-Pr
4	*t*-Bu
5	Ph
6	3,5-Me$_2$C$_6$H$_3$
7	4-MeOC$_6$H$_4$
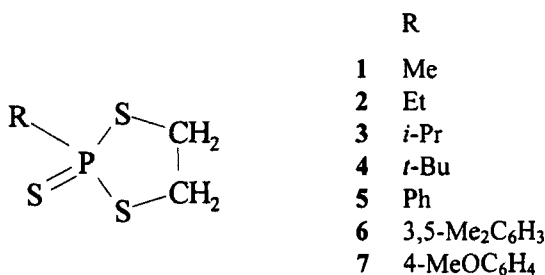
SCHEME 1 Investigated 2-thioxo-1,3,2-dithiaphospholanes

New results of quantum chemical calculations of five phospholanes (**1-5**) are also presented which are important for the interpretation of the ^{31}P MAS NMR data. In addition to the known crystal structures of 2-phenyl- and 2-chloro- 2-thioxo-1,3,2-dithiaphospholane,[3,4] we determined the structures of two other representatives of this family, of 2-*tert*-butyl- (**4**) and of 2-(3,5-dimethylphenyl)-2-thioxo-1,3,2-dithiaphospholane (**6**), which allow a better interpretation of the NMR results.

RESULTS AND DISCUSSION

^{31}P NMR

The ^{31}P NMR data of the investigated phospholanes (**1-7**) are compiled in Table I. A typical ^{31}P CP MAS spectrum is shown in Fig. 1. As expected the values of the chemical shift for the alkyl compounds in solution show an increase from the methyl to the *tert*-butyl compound. The three different aryl substituents influence the chemical shift scarcely. The measured chemical shifts agree with already published values.[5–8]

TABLE I ^{31}P NMR data (ppm) of phospholanes in solution ($CHCl_3$) and in solid state

compd	$\delta_{solution}$	δ_{iso}	σ_{11}	σ_{22}	σ_{33}
1	95.7	99.0	131	237	319
2[a]	110.0	110.6	133	218	301
3	122.0	122.0	130	198	288
4	129.7[b]	132.1	122	185	281
5	94.8	94.3	133	197	371
6	95.6	97.0	136	197	360
7	91.1[b]	91.7	142	205	362

[a] This compound is a liquid oil at ambient temperature. Therefore, the solid-state data were obtained from a static powder spectrum measured at –20°C.
[b] In C_6H_6.

The isotropic chemical shifts in the solid state, determined by CP MAS NMR spectroscopy, are very similar to the chemical shifts in solution ($CHCl_3$). The largest difference (3.3 ppm) is found for the methyl compound. This similarity of $\delta_{solution}$ and δ_{iso} can be interpreted in such a way that strong intermolecular interactions do not play an important role in the molecular lattices of the phospholanes investigated. Such strong interactions caused by short interatomic distances (especially S···S) have been reported for several dithiadiphosphetanes.[9–11]

The variation of the phosphorus substituent R has different effects on the three principal values of the shielding tensor. The largest changes are
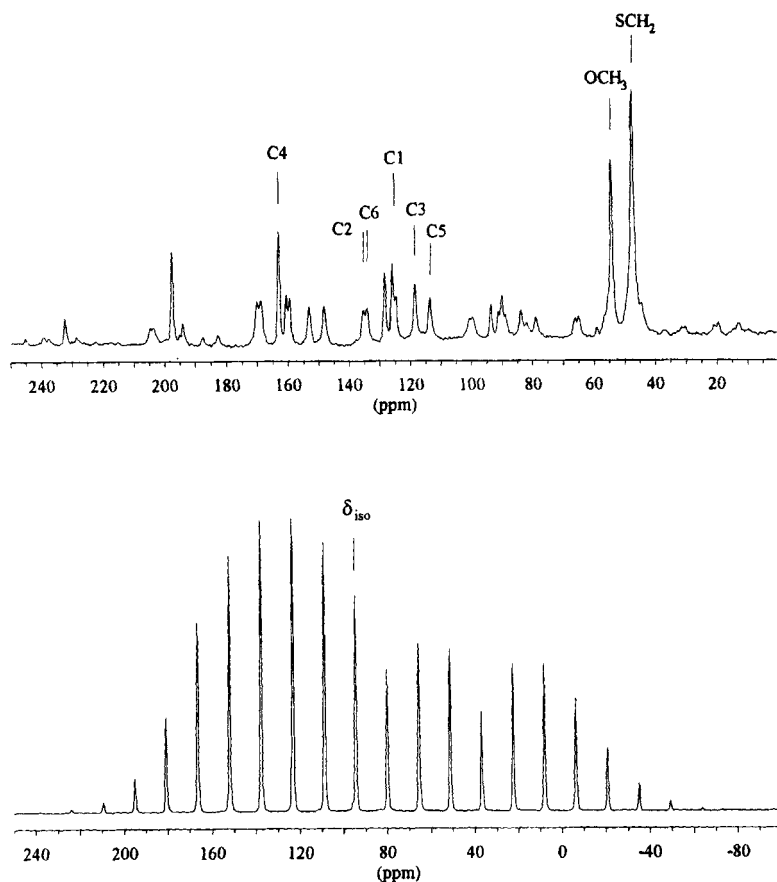
FIGURE 1 ^{31}P (bottom) and ^{13}C (top) CP MAS NMR spectra of 2-(4-methoxyphenyl)-2-thi-oxo-1,3,2-dithiaphospholane (**7**)

observed for σ_{33} ($\Delta\sigma_{33} = 90$ ppm) and the smallest for σ_{11} ($\Delta\sigma_{11} = 20$ ppm). That means the electronic situation in the plane perpendicular to axis 1 is least affected by a variation of R. Axis 1 is the most deshielded component therefore, it is almost perpendicular to the P=S double bond which causes this strong deshielding. Assuming that the structure element CP(S)S$_2$ contains a C$_s$ symmetry with the mirror plane C-P=S, then the values of $\Delta\sigma_{ii}$ allow to predict the orientation of the principal axes. For undistorted C$_s$ microsymmetry one of the principal axes must be perpen-

dicular to the mirror plane while the two other axes lie in this plane. Since σ_{11} is least sensitive to variations of R, axis 1 should be located almost along the C1-P bond.

Comparison of the four alkyl substituted compounds shows that σ_{22} and σ_{33} reflect the well-known β-effect, the most sensitive response is observed for σ_{22}. It is therefore most probably that axis 2 is perpendicular to the plane C1-P=S3. Of all three principal values σ_{33} shows the largest variations. The clear difference between aryl and alkyl compounds is mainly due to the electronic interaction between π-bond system of the aryl group and the P=S bond. Hence, axis 3 should be close to the P=S bond direction as already known from investigations of several compounds with P=S bonds.[9–12]

IGLO calculations were performed for five phospholanes 1–5 (see Table II). First a geometry optimization with a constrained symmetry (C_s) was done. Though, there is not an exact C_s symmetry in most of the phospholanes, the situation is reflected satisfactorily for our purposes. The IGLO calculations were performed for the axial as well as the equatorial position of the exocyclic sulfur. Furthermore, for compounds 1 and 2 also optimizations in C_1 symmetry were performed and for compounds 4 and 5 the molecular geometries taken from the crystal structures were used.

TABLE II Results of quantum chemical calculations for phospholanes (ppm) of different molecular geometries

| compd | C_s | | | | | | | | C_1^c or | | | |
| | S axial | | | | S equatorial | | | | crystal structure[d] | | | |
	δ_{iso}	σ_{11}	σ_{22}	σ_{33}	δ_{iso}	σ_{11}	σ_{22}	σ_{33}	σ_{iso}	σ_{11}	σ_{22}	σ_{33}
1	69	150	248	378	70	156	248	369	71[c]	143	248	379
2	85	151	224	353	91	141	233	336	83[c]	139	228	367
3	93	151	221	333	95	150	222	325				
4	114	150	177	314	120	130	193	299	92[d]	153	211	343
5[a]	78	153	206	391	82	142	223	375	79[d]	140	219	389
b	78	161	237	352	81	156	237	347				

[a]Phenyl ring is coplanar to the C-P=S plane.
[b]Phenyl ring is perpendicular to the C-P=S plane.

A satisfactory agreement between experimental (Table I) and calculated values is found. As seen in the experimental data, the calculated values show also only slight differences in σ_{11} and clear changes in σ_{22} as well as σ_{33}. An assignment to a more axial or equatorial position of the exocyclic sulfur is not possible due to very small differences between the calculated axial and equatorial values compared with the differences between calculated and experimental values.

IGLO calculations yield not only the three principal values of the shielding tensor but also the orientation of the principal axes in the molecular frame as shown in Fig. 2 for the crystal structure of compound **4**. Axis 2 is found to be nearly perpendicular to the C1-P=S3 plane and axis 3 is very close to the P=S3 bond. A similar orientation is found for all calculated structures. The results of the IGLO calculations confirm the prediction of the orientation of the principal axes concluded from the ^{31}P solid-state NMR data.
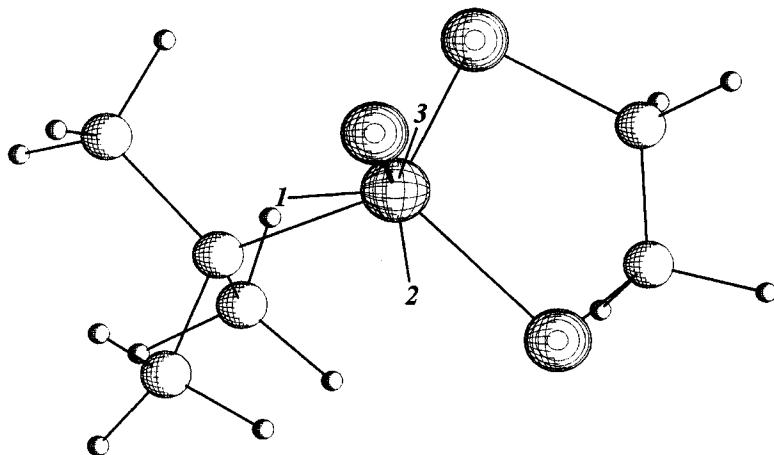
FIGURE 2 Calculated orientation of the principal axes *1, 2,* and *3* of the phosphorus nuclear magnetic shielding tensor in the molecular frame for 2-*tert*-butyl–2-thioxo-1,3,2-dithiaphospholane (4): $\angle$C1-P-*1* = 36°, $\angle$C1-P-2 = 87°, $\angle$S=P-2=85°, $\angle$S=P-*3* = 14°

^{13}C NMR

The ^{13}C NMR data are summarized in Tables III and IV, a ^{13}C CP MAS spectrum is shown in Fig. 1. A good agreement between $\delta_{solution}$ and δ_{iso}

is found. In the solution spectra (CDCl$_3$) both C atoms in the phospholane ring show only one signal. The chemical shift is approximately constant. In the solid-state spectra either one signal or two signals are observed. The ^{13}C MAS NMR data point to the ring symmetry of the phospholanes. For compound **1** two signals were found. An exact analysis and evaluation of the ^{13}C solid-state spectra of **3** and **4** is not possible due to overlap of signals (CH$_2$-CH$_2$ and C1 of the alkyl groups), but for the compound **4** two signals for the C-atoms in the phospholane ring can be observed. That indicates unsymmetrical five-membered rings for **1** and **4**. Since compound 2 is not solid at room temperature, we renounced the time-consuming measurement of a ^{13}C MAS NMR spectrum. The three aryl substituted phospholanes (**5–7**) show only one signal for both CH$_2$-groups in the five-membered ring indicating a symmetrical ring. In case of the *tert*-butyl-phospholane **4** and of the phenyl analogue **5** these conclusions are confirmed by crystal structure investigations. However, this correlation does not exist for 2-(3,5-dimethylphenyl)-2-thioxo-1,3,2-dithiaphospholane. Though the ^{13}C MAS spectrum shows only one signal for the two ring C-atoms, an unsymmetrical phospholane ring is found by crystal structure investigations. In this compound conformational changes of the phospholane ring lead to an averaged signal.

TABLE III ^{13}C NMR data (δ in ppm, J in Hz) of phospholanes in solution (CDCl$_3$)

compd	$\delta_{solution}$ $^n J_{PC}$								
	C9/10	C1	C2	C3	C4	C5	C6	C7	C8
1	42.6	35.4							
		57.7							
2	42.3	40.3	9.1						
		54.0	5.9						
3	42.2	43.9	17.7						
		51.2	2.2						
4	42.7	45.5	25.9						
		46.5	2.3						
5	42.8	137.1	131.4	128.5	132.2	128.5	131.4		
		84.1	13.0	14.8	3.7	14.8	13.0		
6	42.8	136.7	129.0	138.3	134.1	138.3	129.0	21.3	21.3
		82.3	12.9	15.7	3.7	15.7	12.9		
7	42.8	127.4	133.8	113.9	163.0	113.9	133.8	55.5	
		90.6	14.8	16.7	2.7	16.7	14.8		

TABLE IV ^{13}C NMR data (δ in ppm, J in Hz) of pholanes in solid state

compd	δ_{solid} ($^{n}J_{PC}$)								
	C9/10	C1	C2	C3	C4	C5	C6	C7	C8
1	43.4/46.3	34.9 (55)							
3	45.3[a]	45.3[a]	19.5						
4	46.4/47.3[b]	44.1[b]	26.9						
5	46.3	133.0	133.0[c]	129.6	129.6[c]	129.6	133.0[c]		
6	46.1	136.4	132.3[c]	136.4	131.2[c]	136.4	126.2[c]	23.1	20.3
7	47.2	125.2 (90)	135.4	118.4	162.9	113.9	134.1	54.0	

[a] Wide signal due to overlap of CH$_2$-CH$_2$- and C1-signals.
[b] Exact analysis and evaluation not possible, overlap of several signals (CH$_2$-CH$_2$, C1).
[c] Assignment may be exchanged.

The spectrum of compound **4** shows only one methyl signal for the tert-butyl group, hence, a sufficiently fast rotation of this group must occur in the solid state. For compound **3** also only one methyl signal was obtained for the *iso*-propyl group. In this case a rotation of the *iso*-propyl group around the C-P bond is unlikely due to the lower symmetry of this group. Therefore, the two methyl groups should be symmetrical with respect to the C1-P=S3 plane.

FIGURE 3 ORTEP[24] drawing of the molecular structure of 2-*tert*-butyl-2-thioxo1,3,2-dithiaphospholane (**4**)

The results of IGLO calculations for compound **5** predict significant differences of the principal values between coplanar and perpendicular position of the phenyl ring with respect to the C1-P=S3 plane (see Table II), but the aryl substituted phospholanes show only a very small influence on the three principal values. This indicates a similar position for the aromatic rings in all three compounds. Crystal structure analysis shows that compound **5**[3] and also compound **6** contain the aryl substituent in coplanar position. Therefore, the aromatic ring in 2-(4-methoxyphenyl)-2-thioxo-1,3,2-dithiaphospholane should also have this arrangement. The coplanar position of aromatic rings is likely caused by an interaction between the aromatic π-system and the P=S3 double bond. The aromatic ring systems cut in this position the plane perpendicular to axis 3, which is probably the reason for an increase of σ_{33} values for the aromatic compounds (Table I).

Molecular and Crystal Structure

The molecular structures of 2-*tert*-butyl-2-thioxo-1,3,2-dithiaphospholane (**4**) and 2-(3,5-dimethylphenyl)-2-thioxo-1,3,2-dithiaphospholane (**6**) are shown in the Figs. 3 and 4. Selected bond lengths and angles are given in Table V.

Both compounds **4** and **6** contain an unsymmetrical phospholane ring, resulting in differences between the two angles S1-C9-C10 and S2-C10-C9 as well as between P-S1-C9 and P-S2-C10. While **4** shows only small differences (0.3° and 0.2°), these distinctions are higher in compound **6** (ca. 2° and 5°). The five-membered ring in 2-chloro-2-thioxo-1,3,2 -dithiaphospholane[4] **8** is also unsymmetrical with differences in these angles of 2.2° and 3.9°. Only for 2-phenyl-2-thioxo-1,3,2-dithiaphospholane[3] a total symmetrical five-membered ring was found, with a mirror plane (equal to the C1-P=S3 plane) through the phospholane ring (the above mentioned angles are equal in each case).

The different symmetry of the phospholane ring becomes obviously in Fig. 5. Only in **5** the phospholane ring has an envelope conformation while in **4, 6** and **8** this ring occupies a half-chair conformation.

For the compounds **4** and **6** there was a disorder detected relevant to the five-membered phospholane ring. In case of coumpound **6** the disorder has been refined for two split positions of C9-C10 and C9'-C10' (see Fig. 3). For each position an occupation of 50% was refined. The resulting atomic
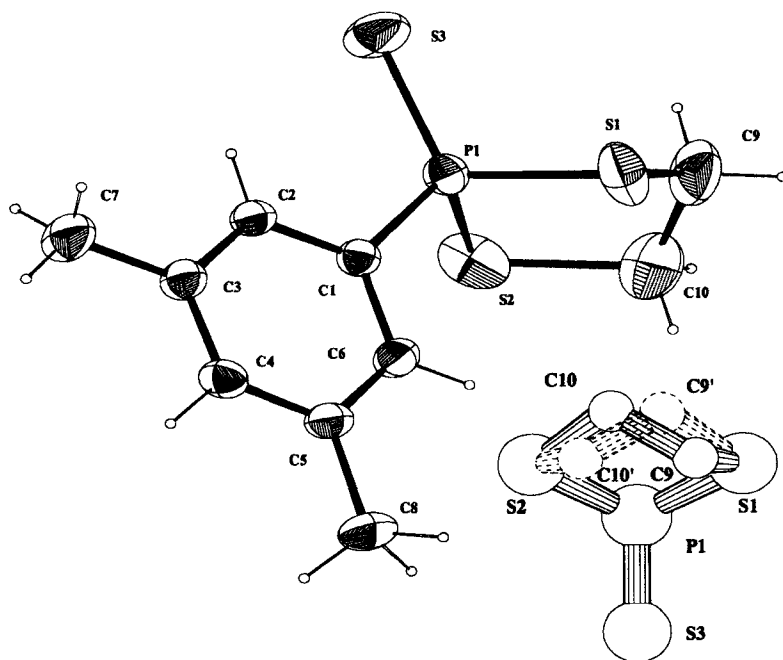
FIGURE 4 ORTEP[24] drawing of the molecular structure of 2-(3,5-dimethylphenyl)-2-thi-oxo- 1,3,2-dithiaphospholane (6)

distances (see Table V) of the two carbon atoms are 1.491(25) Å (C9-C10) and 1.445(22) Å (C9′-C10′). If the disorder is neglected a mean position of the two carbon atoms is refined and a wrong distance (1.168 Å) is obtained. The angle between the aromatic (C1-C6) and the five-membered phospholane ring is nearly right-angled (split position 1: C9-C10 / 84.7(2) °; split position 2: C9′-C10′ / 84.7(3)°). The exocyclic sulfur S3 could be assigned to an axial position (for split position 1 = 25.8°; for split position 2 = 27.3° < 30 °,[13] although it is not far from a bisectional assignment.

In case of compound 4 a refinement of a comparable splitting model for the atoms C9 and C10 was not successful, although the thermal ellipsoids (see Fig. 3) are also enlarged. But in this case the resulting atomic distance between the two carbons (C9-C10 = 1.367(8) Å) is acceptable, although it is shorter than the expected value for a normal single bond (1.54 Å). The exocyclic sulfur S3 has a bisectional (42.1° > 30°) and the carbon C1

(25.5° < 30°) an axial assignment with respect to the phospholane ring. The tetrahedral arrangement of bonds around the phosphorus is distorted in both phospholanes **4** and **6,** similar as described for the phenyl and chlorine analogues.[3,4] The three angles including the P=S3 bond are greater, while the remaining three angles are less than tetrahedral (112.6°-115.8° versus 98.5°-108.2°) as result of the shortness of the P=S3 double bond. Furthermore, the S1-P-S2 angle is reduced due to the inclusion in the five-membered ring.

TABLE V Selected bond lengths (Å) and bond angles (°) in the molecular structures of **4** and **6**

atoms	distance		atoms row	angle	
	4	6		4	6
P-S1	2.096(1)	2.084(1)	S1-P-S2	99.3(1)	98.5(1)
P-S2	2.081(1)	2.078(1)	S1-P-S3	115.8(1)	114.9(1)
P-S3	1.932(1)	1.937(1)	S2-P-S3	113.3(1)	114.6(1)
P-C 1	1.856(4)	1.810(3)	S1-P-C 1	106.6(2)	106.9(1)
S1-C9	1.769(5)	1.644(12)	S2-P-C 1	108.2(2)	106.9(2)
S1-C9′		1.991(13)	S3-P-C 1	112.6(2)	113.7(1)
S2-C10	1.775(5)	1.976(14)	P-S1-C9	98.1(2)	98.7(4)
S2-C10′		1.677(11)	P-S1-C9′		93.6(4)
C9-C10	1.367(8)	1.491(25)	P-S2-C10	97.9(2)	93.6(4)
C9-C10′		1.445(22)	P-S2-C10′		98.5(4)
			S1-C9-C10	118.3(4)	106(1)
			S2-C10-C9	118.0(5)	108(1)

The aromatic ring in compound **6** is in coplanar position with respect to the C1-P=S3 plane. The arrangement of the phenyl ring in **5** shows the same coplanar position.

CONCLUSIONS

The investigation of a series of phospholanes has shown that on certain conditions (local C_s symmetry at the P atom, significant large differences of the three principal values) the interpretation of the ^{31}P CP MAS spectra
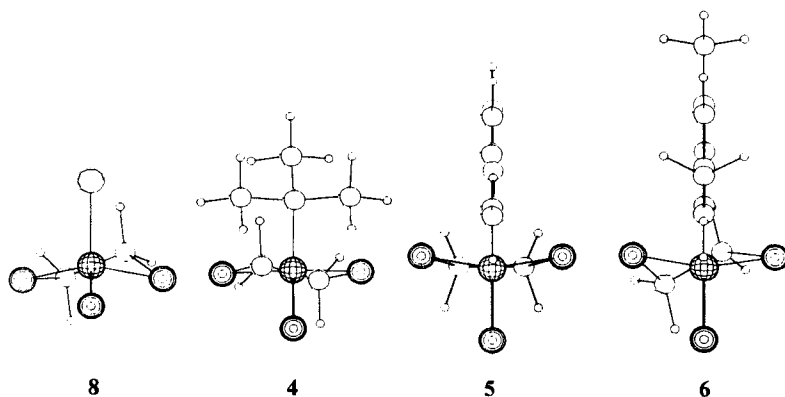
FIGURE 5 Conformation of the phospholane ring in **4, 5, 6** and **8**

allows to predict the orientation of the shielding tensor in the molecular frame. The result is in good agreement with quantum chemical IGLO calculations. The combination of NMR spectroscopy, IGLO calculations and crystal structure investigations enables a better interpretation of the obtained results and allows to draw conclusions about the molecular structures of the phospholanes.

EXPERIMENTAL

Preparations: Compounds 1,2,3,5,6

These phospholanes were obtained by reacting phosphonothioic dichloride with 1,2-ethanedithiol in dry ethyl ether in presence of triethylamine.[14] Colorless crystals of compound **6** were produced by fractional recrystallization from chloroform.

Compound 4

First the trivalent phosphorus compound, 2-*tert*-butyl-1,3,2–dithiaphospholane, was synthesized by reacting *tert*-butyl dichlorophosphine and 1,2-ethanedithiol.[15]. Afterwards the intermediate product was dissolved in dry benzene and elemental sulfur was added.[5] Fractional recrystallization from benzene gave colorless crystals.

^{31}P and ^{13}C NMR data (in CDCl$_3$) of *2-tert*-butyl-1,3,2-dithiaphospholane: $\delta_P = 73.8$, $\delta_{\underline{C}H_3} = 25.9$ ($^2J_{PC} = 19.4$), $\delta_{\underline{C}} = 36.8$ ($^1J_{PC} = 45.9$), $\delta_{\underline{C}H_2} = 41.0$.

Compound 7

This phospholane was obtained by reacting 2,4-bis(4-methoxyphenyl)– 2,4-dithioxo-1,3,2,4-dithiadiphosphetane (LAWESSON reagent) as suspension in dry benzene and ethylene sulfide.[8]

NMR Spectroscopy

The NMR spectra were run on a Bruker MSL 300 (121.50 MHz for ^{31}P and 75.48 MHz for ^{13}C). The ^{31}P chemical shifts are relative to 85% phosphoric acid and ^{13}C are relative to SiMe$_4$. For the determination of the anisotropy parameters, ^{31}P CP MAS spectra were measured at spinning frequencies of 1.5 − 2.0 kHz using cross polarization with a pulse sequence containing two contact pulses.[16] The spinning sideband systems were computed by means of the program WINMAS.[17] The uncertainties of the principal values of the chemical shift tensors are $\leq \pm 5$ ppm.

The solid state ^{31}P NMR spectrum of 2 (static powder spectrum) was run at −20°C.

IGLO Calculations

The following basis sets constructed from those of Huzinaga[18] and augmented by polarization functions were used: for hydrogen: (3)/[2], for carbon: (7,3)/[4,2], for phosphorus: (11,7,2)/[7,6,2] with $\eta_1(d) = 0.35$ and $\eta_2(d) = 1.40$ and for sulfur: (11,7,2)/[7,6,2] with $\eta_1(d) = 0.40$ and $\eta_2(d) = 1.60$ where $\eta(x)$ is the exponent of the *x*-orbital.

We have used geometrically optimized structures as well as crystal structures. Geometry optimizations were performed with the TURBOMOLE package of the Karlsruhe group.[19] In a first step only calculations with a constrained symmetry (C$_S$) were done. The following dzp-type Huzinaga basis sets[20] were used: for hydrogen: (4,1)/[2,1], for carbon: (9,5,1)/[4,2,1], for phosphorus: (12,8,1)/[6,4,1] and for sulfur: (12,8,1)/[6,4,1]. For R = Me (1) and R = Et (2) also C$_1$ optimizations were performed. For R = *t*-Bu (4) and R = Ph (5) also the crystal structures in C$_1$ symmetry were used.

TABLE VI Summary of crystal data, data collection and structure refinement for **4** and **6**

	4	*6*
formula	$C_6H_{13}PS_3$	$C_{10}H_{13}PS_3$
formula weight	212.315	251.255
crystal system	monoclinic	monoclinic
space group	$P2_1/n$ (No.14)	$P2_1/n$ (No.14)
a (Å)	6.260(2)	7.093(1)
b (Å)	10.809(2)	22.476(1)
c (Å)	15.341(2)	8.063(1)
β (deg)	95.96(2)	90.1(1)
V (Å^3)	1032.4	1285.4
Z	4	4
d_{calc} (g/cm^3)	1.366	1.345
μ (cm^{-1})	8.1	6.6
T (K)	293	288
$\lambda_{MoK\alpha}$ (Å)	0.71073	0.71073
diffractometer	ENRAF-NONIUS CAD4	
scan mode	ω-scan	ω-scan
scan angle (deg)	0.95+0.35 tg θ	1.10+0.35 tg θ
scan range (deg)	1 ≤θ≤35	1 ≤θ≤30
hkl ranges	-1/10; -17/2;-24/24	-9/2; -31/31; -3/11
max. measur. t/refl. (s)	30	60
no. of reflections collected	6676	7298
unique refl.	4515	3116
observed refl. (≥2σ(I))	4514	3116
refl. with $F_o>4\sigma(F_o)$	1470	1800
no. of parameters refined	92	172
extinction param.	0.007	0.006
weighing param. a / b	0.0608 / 0.0	0.0674 / 0.61
R1 for $F_o>4\sigma(F_o)$	0.0696	0.0449
wR2 for all (≥2σ(I))	0.1826	0.1422

TABLE VII Fractional atomic coordinates and equivalent isotropic temperature factors ($\mathring{A}^2$) for **4**

atom	x	y	z	U_{eq}
P	0.0834(2)	0.2268(1)	0.8868(1)	0.0384(3)
S1	-0.0380(2)	0.2874(1)	1.0017(1)	0.0705(4)
S2	0.3382(2)	0.1194(1)	0.9421(1)	0.0670(4)
S3	-0.1152(2)	0.1365(1)	0.8056(1)	0.0679(4)
C1	0.1957(6)	0.3651(3)	0.8363(2)	0.0450(9)
C2	0.0074(8)	0.4510(4)	0.8084(3)	0.0711(13)
C3	0.3034(8)	0.3207(4)	0.7574(3)	0.0685(13)
C4	0.3604(8)	0.4316(4)	0.9015(3)	0.0734(14)
C9	0.1364(11)	0.2028(7)	1.0779(3)	0.1172(25)
C1 0	0.3290(11)	0.1642(7)	1.0529(3)	0.1170(25)

TABLE VIII Fractional atomic coordinates and equivalent isotropic temperature factors ($\mathring{A}^2$) for **6**

atom	x	y	z	U_{eq}
P	0.2498(1)	0.1456(0)	0.1964(1)	0.0463(2)
S1	0.4724(1)	0.1915(0)	0.0869(1)	0.0841(4)
S2	0.0280(1)	0.1916(0)	0.0870(1)	0.0844(4)
S3	0.2493(2)	0.1465(0)	0.4366(1)	0.0936(4)
C1	0.2493(4)	0.0715(1)	0.1083(3)	0.0407(6)
C2	0.2497(4)	0.0230(1)	0.2135(3)	0.0447(7)
C3	0.2496(5)	-0.0346(1)	0.1494(4)	0.0488(7)
C4	0.2499(5)	-0.0413(1)	-0.0207(4)	0.0484(7)
C5	0.2495(4)	0.0067(1)	-0.1288(3)	0.0468(6)
C6	0.2494(5)	0.0635(1)	-0.0625(4)	0.0483(7)
C7	0.2492(9)	-0.0878(1)	0.2633(5)	0.0745(12)
C8	0.2495(7)	-0.0036(2)	-0.3138(4)	0.0694(10)
C9	0.3734(19)	0.2575(5)	0.0733(17)	0.0966(33)

atom	x	y	z	U_{eq}
C10	0.1958(20)	0.2495(6)	-0.0234(26)	0.0981(26)
C9′	0.3037(19)	0.2514(6)	-0.0187(23)	0.0966(33)
C10′	0.1304(17)	0.2587(4)	0.0731(16)	0.0981(26)

Crystal Structure Analysis

Single crystals of the two compounds **4** and **6** were investigated on an automatic four-circle diffractometer CAD4 (NONIUS) with MoKα radiation. The lattice constants were determined by searching and indexing 10 reflections for compound **4** and 13 reflections for compound **6**. Details of the crystallographic data and measuring conditions are summarized in Table VI. The intensity data were LP-corrected using the program XCAD4.[21] The space groups were determined by the reflection conditions. The structures were solved by direct methods using the program SHELXS86.[22] The refinements have been carried out with the program SHELXL93.[23] All non H-atoms were refined anisotropically. The positions of the H-atoms were calculated and refined under geometrical constrain. In case of the compound **6** a possible orthorhombic cell and space group (P222$_1$) has been tested for solution and refinement, but this was not successful. The main data for refinement conditions are given in Table VI. The atomic coordinates are compiled in Tables VII (**4**) and VIII (**6**). Further details of the crystal structure investigations are available from FACHINFORMATIONSZENTRUM KARLSRUHE, 76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CSD 408039 (**4**) and 408038(**6**).

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