Phosphorus Nuclear Magnetic Shielding Anisotropy and Crystal Structure of (1-Hydroxyalkyl)dimethylphosphine Sulfides

Gisbert Grossmann,*,† Kerstin Krüger,† Gisela Ohms,† Axel Fischer,‡ Peter G. Jones,‡ Jens Goerlich,‡ and Reinhard Schmutzler*,‡

Institut für Analytische Chemie, Technische Universität Dresden, Mommsenstrasse 13, D-01062 Dresden, Germany, and Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, D-38023 Braunschweig, Germany

For a series of (1-hydroxyalkyl)dimethylphosphine sulfides $Me_2P(S)C(OH)R^1R^2$ the molecular structures have been determined. The crystallographic results obtained are as follows. $Me_2P(S)C(OH)Me_2$; monoclinic, $P2_1/n$, $a = 10.910(3)$ Å, $b = 6.340(2)$ Å, $c = 11.886(3)$ Å, $\beta = 96.47(2)°$, $V = 816.9$ Å^3, $Z = 4$. $Me_2P(S)C(OH)(CH_2)_5$: orthorhombic, $P2_12_12_1$, $a = 8.683(3)$ Å, $b = 9.474(3)$ Å, $c = 12.730(3)$ Å, $V = 1047.2$ Å^3, $Z = 4$. $Me_2P(S)C(OH)(Me)C(O)Me$: orthorhombic, $P2_12_12_1$, $a = 7.664(3)$ Å, $b = 10.354(2)$ Å, $c = 11.838(3)$ Å, $V = 939.4$ Å^3, $Z = 4$. $Me_2P(S)C(OH)(Ph)C(O)Ph$: monoclinic, $P2_1/n$, $a = 8.400(3)$ Å, $b = 10.343(3)$ Å, $c = 17.784(4)$ Å, $\beta = 101.97(3)°$, $V = 1511.5$ Å^3, $Z = 4$. $Me_2P(S)C(OH)(H)C(O)(OH)$: triclinic, $P\bar{1}$, $a = 6.145(2)$ Å, $b = 11.268(4)$ Å, $c = 12.126(3)$ Å, $\alpha = 110.64(2)°$, $\beta = 103.64(2)°$, $\gamma = 94.88(2)°$, $V = 750.4$ Å^3, $Z = 4$. The principal values of the phosphorus nuclear magnetic shielding tensor have been determined by ^{31}P solid-state CP MAS NMR spectroscopy. The similar structures of the compounds around the P atom and symmetry considerations allow a prediction of the orientation of the shielding tensor principal axes in the molecular framework. Quantum chemical calculations applying the IGLO method support these results. By application of three independent methods (X-ray structure analysis, solid-state NMR spectroscopy, and quantum chemical calculations) the influence of intermolecular interactions on the nuclear magnetic shielding can be clearly shown.

Introduction

The modern NMR techniques of solid-state magic angle spinning (MAS) and high-power proton decoupling permit the investigation of the chemical shift anisotropy of the respective nucleus studied in polycrystalline samples. Because of the high NMR sensitivity of the ^{31}P nucleus, the large variety of phosphorus compounds forms suitable subjects for such investigations. Since the nuclear magnetic shielding depends on the electronic structure (and its modification by the magnetic field) in the vicinity of the nucleus investigated, it is reasonable to correlate the shielding tensor with the molecular structure. Unfortunately, the MAS sideband spectra and also the static spectra of crystalline powders allow only the determination of the principal values of the tensor σ_{11}, σ_{22}, and σ_{33}; the orientation of the principal axes remains unknown.[1]

The knowledge of the local symmetry around the ^{31}P nucleus can provide useful information[2] about the orientation of the principal axes. Thus, the shielding tensor must be an axial tensor with one value $\sigma_{\parallel}$ and two values $\sigma_{\perp}$ if the local symmetry is C_3 or higher. The presence of a mirror plane suggests that one axis is perpendicular to this plane, but it is not known which. Additional information can be gained if a second magnetic nucleus has a substantial dipole−dipole interaction with the nucleus investigated.[3] Complete information about the shielding tensor, including the orientation of the principal axes, is available by NMR investigation of a sufficiently large single crystal with

a goniometer probehead[4] or, approximately, by theoretical calculations of the nuclear magnetic shielding of an isolated molecule.[5]

The results of previous investigations suggest that in all four-coordinated thiophosphoryl compounds the principal axis 3, which corresponds to the direction of greatest shielding, approximately coincides with the P=S bond.[6] The investigations of five (1-hydroxyalkyl)dimethylphosphine sulfides described in this paper are intended to support this result. Furthermore, it is shown that the investigation of a series of compounds of similar structures allows the prediction of the orientation of the principal axes 1 and 2, provided that the differences between the three principal values are large enough.

(3) See, for example: Wasylishen, R. E.; Curtis, R. D.; Eichele, K.; Lumsden, M. D.; Penner, G. H.; Power W. P.; Wu, G. Applications of Dipolar NMR Spectroscopy in Characterizing Nitrogen and Phosphorus Shielding Tensors. In *Nuclear Magnetic Shieldings and Molecular Structure*; Tossel, J. A., Ed.; NATO ASI Series C, Vol. 386; Kluwer Academic Publishers: Boston, 1993; pp 297−314.
(4) Kennedy, M. A.; Ellis, P. D. *Concepts Magn. Reson.* **1989**, *1*, 35, 109.
(5) Webb, G. A. An Overwiev of Nuclear Magnetic Shielding. In *Nuclear Magnetic Shieldings and Molecular Structure*; Tossel, J. A., Ed.; NATO ASI Series C, Vol. 386; Kluwer Academic Publishers: Boston, 1993; pp 1−25.
(6) (a) Krüger, K; Grossmann, G.; Fleischer, U.; Franke, R.; Kutzelnigg, W. *Magn. Reson. Chem.* **1994**, *32*, 596. (b) Uhlig, F.; Herrmann, E.; Schädler, D.; Ohms, G.; Grossmann, G.; Besser, S.; Herbst-Irmer, R. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1962. (c) Potrzebowski, M. J.; Grossmann, G.; Blaszcyk, J.; Wieczorek, M. W.; Sieler, J.; Knopik, P.; Komber, H. *Inorg. Chem.* **1994**, *33*, 4688. (d) Fleischer, U.; Krüger, K.; Grossmann, G.; Kutzelnigg, W. *Phosphorus, Sulfur Silicon Relat. Elem.* **1994**, *93*, *94*, 217. (e) Ohms, G.; Fleischer, U.; Kaiser, V. *J. Chem. Soc., Dalton Trans.* **1995**, 1297. (f) Grossmann, G.; Beckmann, H.; Rademacher, O.; Krüger, K.; Ohms, G. *J. Chem. Soc., Dalton Trans.* **1995**, 2797. (g) Grossmann, G.; Ohms, G.; Krüger, K.; Jeschke, G.; Jones, P. G.; Fischer, A. *Phosphorus, Sulfur Silicon Relat. Elem.* **1995,** *107*, 57.

† Technische Universität Dresden.
‡ Technische Universität Braunschweig.
(1) Haeberlen, U. *High Resolution NMR in Solids. Selective Averaging*; Academic Press: New York, 1976.
(2) Buckingham, A. D.; Malm, S. M. *Mol. Phys.* **1971**, *22*, 1127.

Table 1. Crystallographic Data for Compounds $Me_2P(S)C(OH)R^1R^2$

	R^1, R^2				
	Me, Me	$(-CH_2-)_5$	Me, C(O)Me	Ph, C(O)Ph	H, COOH
formula	$C_5H_{13}OPS$	$C_8H_{17}OPS$	$C_6H_{13}O_2PS$	$C_{16}H_{17}O_2PS$	$C_4H_9O_3PS$
fw	152.18	192.25	180.19	304.33	168.14
T, °C	-100	-130	-100	-100	-130
space group	$P2_1/n$	$P2_12_12_1$	$P2_12_12_1$	$P2_1/n$	$P\bar{1}$
a, Å	10.910(3)	8.683(3)	7.664(3)	8.400(3)	6.145(2)
b, Å	6.340(2)	9.474(3)	10.354(2)	10.343(3)	11.268(4)
c, Å	11.886(3)	12.730(3)	11.838(3)	17.784(4)	12.126(3)
α, deg	90	90	90	90	110.64(2)
β, deg	96.47(2)	90	90	101.97(3)	103.64(2)
γ, deg	90	90	90	90	94.88(2)
V, Å³	816.9	1047.2	939.4	1511.5	750.4
Z	4	4	4	4	4
d_{calc}, g/cm³	1.237	1.219	1.274	1.337	1.488
μ, cm^{-1}	5.1	4.1	4.6	3.2	5.8
R_{int}	0.029	0.030	0.033	0.050	0.101
$wR(F^2)^a$	0.082	0.064	0.070	0.101	0.104
$R(F)^b$	0.033	0.025	0.030	0.041	0.039

^{a} $wR(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ (all reflections). ^{b} $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ $[F > 4\sigma(F)]$.

The assignment of the principal axes in the molecular framework is verified by comparison with quantum chemical calculations.

In this paper we present crystal structures determined by X-ray diffraction, principal values of the phosphorus nuclear magnetic shielding tensors obtained by solid-state crystal powder ^{31}P MAS NMR spectroscopy, and also the results of theoretical shielding tensor calculations using the IGLO method[7] for five (1-hydroxyalkyl)dimethylphosphine sulfides $Me_2P(S)C(OH)$-R^1R^2:

compd	R^1, R^2		
		3	Me, C(O)Me
1	Me, Me	**4**	Ph, C(O)Ph
2	$(-CH_2-)_5$	**5**	H, COOH

It is shown how the nuclear magnetic shielding of the ^{31}P nucleus is affected by chemical bonds and electron lone pairs. The influence of neighboring molecules in the crystal lattice is considered.

Experimental Section

Preparation. The dimethyl(1-hydroxyalkyl)phosphine sulfides **1**−**4** were prepared as described in the literature.[8]

Synthesis of Dimethyl(carboxyhydroxymethyl)phosphine 5. A mixture of 1.88 g (20 mmol) of dimethylphosphine sulfide and 1.90 g (20.6 mmol) of glyoxylic acid in 40 mL of THF was stirred at room temperature for 5 h. Subsequently, the solid product which was precipitated was collected by filtration, was washed with three 10 mL portions of *n*-hexane, and was dried *in vacuo*. Yield: 2.94 g (84.9%). Mp: 112−114 °C. Crystals suitable for an X-ray structure determination were obtained by slow evaporation of a solution of the product in dichloromethane. $C_4H_9O_3PS$ (168.15), calcd (found): C, 28.57 (28.57); H, 5.39 (5.44); S, 19.07 (18.36). ^1H NMR (CD$_3$CN): 1.72 [d, ^2J(PH) = 12.82, 3 H, CH_3]; 1.79 [d, ^2J(PH) = 13.02, 3 H, CH_3]; 3.75 [s, C(OH)H]; 4.65 [d, ^2J(PH) = 5.81, 1 H, C(OH)H]. A signal due to the C(:O)OH proton was not observed. ^{31}P NMR: 45.61 (s). IR (in hexane): 2810 [s, b, (OH)]; 732 (s, P(:S)]. Mass spectrum (70 eV): m/z (relative intensity) = 168 (72) [M]$^+$; 111 (81) [M − C_2O_2H]$^+$; 93 (100) [(CH$_3$)$_2$PS]$^+$; 79 (19) [CH$_3$PSH]$^+$.

Structural Determinations. Crystallographic data of all investigated compounds are presented in Table 1. Data were collected with Mo Kα radiation (λ = 0.710 73 Å) at low temperature on Siemens R3 or Stoe STADI-4 diffractometers. Structures were solved by direct methods and refined anisotropically on F^2, using the program SHELXL-93.[9] H atoms were included in rigid groups (OH, Me) or with a riding model. Weighting schemes were of the form $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $3P = (2F_c^2 + F_o^2)$ and a and b are constants optimized by the program.

NMR Measurements. Solid-state ^{31}P NMR spectra were recorded using a BRUKER MSL 300 spectrometer (121.5 MHz for ^{31}P) by magic angle spinning of the sample at frequencies between 1.4 and 2.5 kHz using a cross polarization (CP) technique with a pulse sequence containing two contact pulses.[10] The length of the 90° pulses was 5 μs, the contact time 1 ms, and the repetition time including two contact pulses 10 s. The MAS spectra were analyzed using the program WINMAS.[11] The principal values of the chemical shift tensor were obtained with a standard deviation of 5 ppm. The ^{31}P chemical shifts determined with external reference to 85% H$_3$PO$_4$ were converted to the absolute nuclear magnetic shieldings using the data of Jameson et al.:[12] $\sigma(^{31}P) = 328$ ppm $- \delta(^{31}P)$. The data are reported following the convention $\sigma_{33} \geq \sigma_{22} \geq \sigma_{11}$.

IGLO Calculations. First, the electronic ground state was calculated with the TURBOMOLE package[13] using dzp basis sets. The calculations were performed with coordinates from crystal structure data (CS) without geometry optimization but with modified C−H (1.09 Å) and O−H bond lengths (0.95 Å) and alternatively with coordinates obtained from TURBOMOLE geometry optimization (GO).

The ^{31}P shielding tensors were calculated with the direct IGLO program (DIGLO)[14] using Huzinaga basis sets.[15] For **1**, **2** (GO), **3**, **5** basis set II: (5s 1p) contracted to [3 1 1, 1] with a p exponent of 0.65 for H, (9s 5p 1d) contracted to [5 1 1 1 1, 2 1 1 1, 1] with a d exponent of 1.0 for C and O, and (11s 7p 2d) contracted to [5 1 1 1 1 1 1, 2 1 1 1 1, 1 1] with d exponents of 0.35 and 1.40 for P and 0.40 and 1.60 for S. For the atoms of the substituents R^1 and R^2 in **2** (CS) and **4** reduced basis sets are used (basis set II′): (3s) contracted to [2 1] for H, and (7s 3p) contracted to [4 1 1 1, 2 1] for C and O.

Results and Discussion

Structural Characterization. The bond lengths and angles for the investigated compounds lie in the ranges indicated in

(7) (a) Kutzelnigg, W. *Isr. J. Chem.* **1980**, *19*, 193. (b) Schindler, M.; Kutzelnigg, W. *J. Chem. Phys.* **1982**, *76*, 1919. (c) Kutzelnigg, W.; Fleischer, U.; Schindler, M. In *NMR Basic Principles and Progress*; Diehl, P., Fluck, E., Günther, H., Kosfeld, R., Seelig, J., Eds.; Springer-Verlag: New York, 1991; Vol. 23, pp 165−262.

(8) Well, M.; Schmutzler, R. *Phosphorus, Sulfur Silicon Relat. Elem.* **1992**, *72*, 171.

(9) Sheldrick, G. M. *SHELXL-93, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, FRG, 1993.

(10) Jeschke, G.; Grossmann, G. *J. Magn. Reson., Ser. A* **1993**, *103*, 323.

(11) WIN-MAS is available commercially from BRUKER-FRANZEN ANALYTIK GmbH, Fahrenheitstrasse 4, D-28359 Bremen, Germany.

(12) Jameson, C. J.; de Dios, A. C.; Jameson, A. K. *Chem. Phys. Lett.* **1990**, *167*, 575.

(13) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Klömel, C. *Chem. Phys. Lett.* **1989**, *162*, 165. TURBOMOLE is available commercially from BIOSYM Technologies, San Diego, CA.

(14) Meier, U.; van Wüllen, Ch.; Schindler, M. *J. Comput. Chem.* **1992**, *13*, 551.

(15) Huzinaga, S. *Approximate Atomic Wave Functions*; University of Alberta: Edmonton, 1971.

Table 2. Range of Selected Bond Lengths (Å) and Angles (deg) for the Investigated (1-Hydroxyalkyl)dimethylphosphine Sulfides

|	
P=S	1.963–1.975
P–C (methyl)	1.788–1.809
P–C (1–hydroxyalkyl)	1.846–1.898
C–O (hydroxy)	1.406–1.431
C–C (1–hydroxyalkyl)	1.502–1.545
S=P–C (methyl)	109.9–114.5
S=P–C (1–hydroxyalkyl)	110.0–116.3
C–P–C (both methyl)	105.3–107.2
C–P–C (1–hydroxyalkyl)	102.6–109.9
P–C–O	105.4–109.5
P–C–C	109.0–110.8

Table 2. In compound **2** the P(S)Me$_2$ group is equatorial at the cyclohexane ring and the OH group axial. As the centrosymmetric space groups for **1**, **4**, and **5** indicate the presence of racemate crystals, the first compound contains conformational enantiomers and the others configurational enantiomers. Compound **3** crystallizes as enantiomeric twins. Compound **5** shows two crystallographically independent molecules in the unit cell, which are however essentially identical; a least-squares fit of the molecules **A** and **B** gives a mean deviation of 0.09 Å.

The molecules **1**, **2**, and **3** are stabilized by an *anti* conformation of sulfur and oxygen around the P–C$_{hy}$ (hy: 1-hydroxyalkyl) bond, whereas the molecules **4**, **5A**, and **5B** have a *gauche* conformation for these atoms. The absolute S=P–C–O torsion angles are 175.0, 172.2, 172.3, 49.6, 69.5, and 67.8°, respectively.

The molecular structures of **1**, **3**, and **5** are shown in Figure 1 and of **2** and **4** in Figure 2. For better comparison all structures are drawn in a similar manner. The molecules **1** and **2** approximate closely to mirror symmetry both in the gaseous and in the liquid state. In the solid state this symmetry is distorted by the crystal packing due to the formation of hydrogen bonds. The molecules of **1** are linked in chains by a *y* axis translation, with O···S = 3.309(2) Å, O–H···S = 169°, and the molecules of **2**, related by a 2$_1$ operator, form chains parallel to the *x* axis, with O···S = 3.256(1) Å, O–H···S = 160°.

Although the other investigated compounds have a chiral center and hence no mirror plane, the Me$_2$P(S)C$_{hy}$ fragment of the molecules shows marked similarities. In all compounds the S=P–C$_{hy}$ plane is approximately a local mirror plane with respect to the methyl groups attached to phosphorus. For the center of gravity of the carbon atoms of these two methyl groups, the absolute deviation from the S=P–C$_{hy}$ plane is very small. For the molecules **1**, **2**, **3**, **4**, **5A**, **5B** this value amounts to 0.010, 0.010, 0.021, 0.025, 0.091, and 0.029 Å, respectively. This fact is important in order to discuss the direction of the principal axes of the ^{31}P shielding tensor in these compounds.

The formation of O–H···S hydrogen bonds is also observed for compounds **3** and **4**. The molecules of **3** are related by a 2$_1$ operator and form chains parallel to the *y* axis with O1···S = 3.447(2) Å, O1–H1···S = 148°, and the molecules of **4** are arranged in pairs related by inversion centers, with O1···S = 3.195(2) Å, O1–H1···S = 153°. In compound **5** four H atoms are available for hydrogen bonding (see Figure 3) in the two independent molecules **A** (unprimed) and **B** (primed). Of these, one is involved in an intramolecular hydrogen bond [O3···O2 = 2.700 Å, O3–H3···O2 = 117°]. The intermolecular H bonds are characterized as follows: (i) a "carboxylic acid dimer" type linking molecules **B** across inversion centers [O1′···O2′ = 2.685(3) Å, O1′–H1′···O2′ = 180°]; (ii) O–H···S interactions linking molecules **A** across inversion centers [O1···S = 3.097(2) Å, O1–H1···S = 161°]; (iii) hydroxyl OH to carboxylic acid O=C, linking molecules **A** and **B** [O3′···O2 = 2.858(3) Å, O3′–H3′···O2 = 157°].
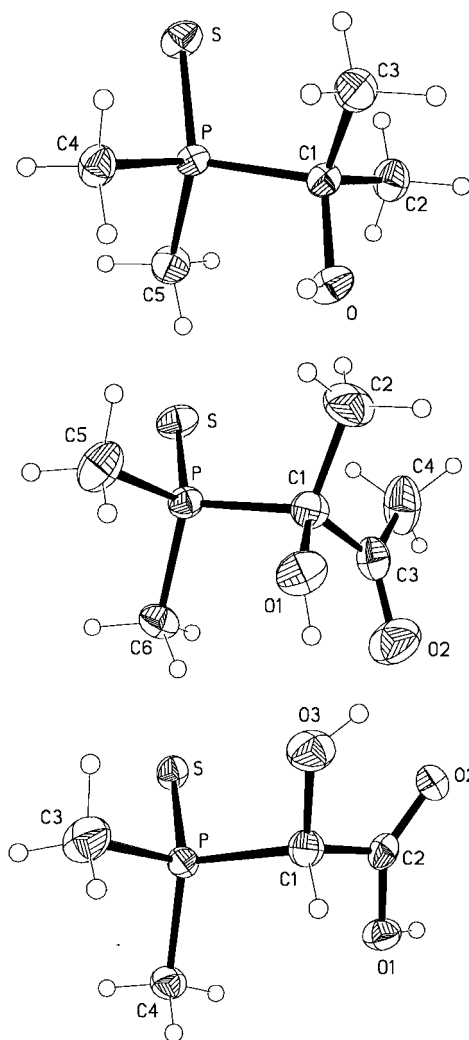
Figure 1. Molecular structures of compounds Me$_2$P(S)C(OH)R^{1}R^2 with R^1, R^2 = Me, Me (**1**, top); Me, C(O)Me (**3**, middle); and H, COOH (**5A**, bottom).

^{31}P Shielding Tensor Characterization. ^{31}P CP MAS spectra of compounds **1**–**4** show one sideband system as demonstrated in Figure 4a. For compound **5** two isotropic lines with their sidebands are visible (Figure 4b), according to the two crystallographically independent molecules present in the unit cell (see Figure 3). In solutions of **5** only one chemical shift is determined, indicating the chemical equivalence of all molecules in this state.

The similarity of the chemical shifts δ_{iso} and $\delta_{solution}$ of compounds **1**–**4** and of molecule **5B** is a consequence of the fact that the intermolecular interactions in the solid state caused by the crystal packing and the time-averaged interactions of a molecule with the solute lead to comparable nuclear magnetic shieldings at the observed nucleus (see Table 3). The δ_{iso} value of the other crystallographically independent molecule **5A** shows a low-field shift of about 4 ppm in comparison with $\delta_{solution}$. It may be assumed that some other intermolecular interactions are responsible for this deviation. As has already been shown for some dithiadiphosphetanes,[6f,g] intermolecular S···S distances shorter than the sum of the the van der Waals radii are the reason for large low-field shifts. An inspection of the crystal packing of compound **5** shows no such short S···S distances, but one relatively short O···S distance between two **A** molecules is observed (see Figure 3). This is the shortest hydrogen bond O1–H1···S (distance O···S = 3.097 Å) of all five investigated compounds. Therefore, the larger δ_{iso} value (49.7 ppm) is assigned to the **A** molecules of **5**.
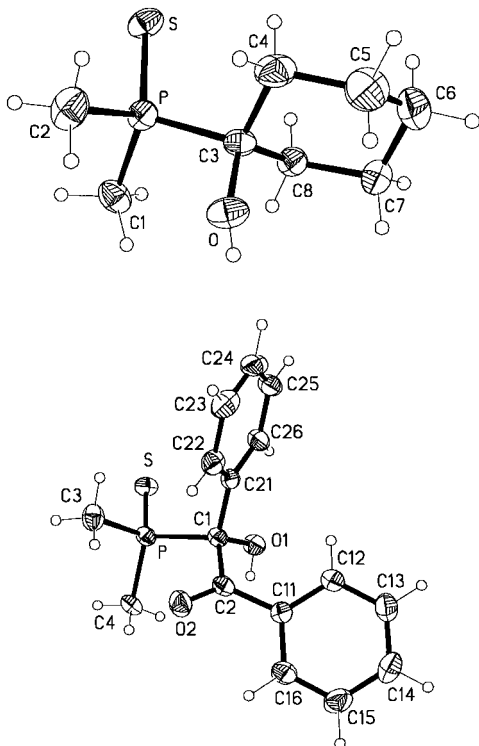
Figure 2. Molecular structures of compounds $Me_2P(S)C(OH)R^1R^2$ with R^1, $R^2 = (-CH_2-)_5$ (**2**, top) and Ph, C(O)Ph (**4**, bottom).
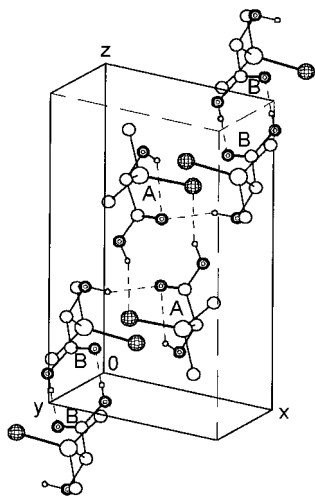
Figure 3. Molecular packing of $Me_2P(S)C(OH)R^1R^2$ with R^1, $R^2 =$ H, COOH (**5**). The two crystallographically independent molecules in the unit cell are marked with **A** and **B**, hydrogen bonds with dashed lines. Hydrogen atoms bonded to carbon are omitted.

Figure 4. ^{31}P CP MAS spectra of compounds $Me_2P(S)C(OH)R^1R^2$: (a) R^1, $R^2 =$ Me, Me (**1**), $\nu_{rot} = 1400$ Hz; and (b) R^1, $R^2 =$ H, COOH (**5**), $\nu_{rot} = 2300$ Hz. Two scales are given: for chemical shift δ and for the absolute nuclear magnetic shielding σ.

The ^{31}P principal values of the nuclear magnetic shielding tensor σ_{11}, σ_{22}, and σ_{33}, available by analysis of the sideband CP MAS spectra, are summarized in Table 3. All investigated compounds have similar experimental principal values σ_{22}. The difference $\Delta\sigma_{22}$ between maximal and minimal σ_{22} values is 12 ppm, whereas for $\Delta\sigma_{11}$ and $\Delta\sigma_{33}$ these values are 47 and 26 ppm, respectively. Accordingly, the contributions of the different substituents R^1 and R^2 are minimal for σ_{22}.

From the crystal structures the conclusion may be drawn that the S=P—C_{hy} plane is approximately a local mirror plane in compounds **1**−**5**. Perpendicular to this plane, one of the principal axes must pass through the phosphorus nucleus. The principal value of this axis must include contributions from atoms lying in the S=P—C_{hy} plane and in its vicinity,[16] e.g., from R^1 and R^2. This is probably the value σ_{11}, because from

earlier investigations[6,17] of four-coordinated P(S) compounds, it is known that the principal axis 3 coincides approximately with the P=S bond. Therefore, by investigating a series of chemically similar compounds and analyzing their solid-state powder NMR spectra it is possible to estimate the orientation of the principal axes in the molecular framework.

The IGLO calculations of the nuclear magnetic shielding tensors are performed with atomic coordinates of the crystal structure and also with coordinates resulting from geometry optimization by the TURBOMOLE program. This geometry optimization gives slightly different coordinates (differences in bond lengths ≤ 0.03 Å, in bond angles $\leq 3°$) whereby for the molecules **1** and **2** a C_s symmetry with a mirror plane coincident with the S=P—C_{hy} plane was assumed. The results of the IGLO calculations are essentially the same when using the two sets of coordinates (differences in the principal values ≤ 11 ppm). Only in case of molecule **4** is a larger difference found for σ_{33} (24 ppm), since the geometry optimization leads to a different conformation of the phenyl groups than does the X-ray diffraction.

The principal values σ_{ii} and some angles to the principal axes 1, 2, and 3 calculated on the base of X-ray coordinates are compiled in Table 3. Considering the large differences between experimental and calculated isotropic chemical shift values (calculated values in parentheses), the quality of the calculations seems to be unsatisfactory. However, the three principal values σ_{ii} show distinct differences for the experimental as well as the calculated data.

The differences $\Delta\sigma_{22}$ between calculated maximal and minimal σ_{22} values of 12 ppm correspond well with the

(16) Zilm, K. W.; Conlin, R. T.; Grant, D. M.; Michl, J. *J. Am. Chem. Soc.* **1980**, *102*, 6672.
(17) Dutasta, J. P.; Robert, J. B.; Wiesenfeld, L. *Chem. Phys. Lett.* **1981**, *77*, 336.

Table 3. Experimental and Calculated[a] ^{31}P NMR Data for Compounds Me$_2$P(S)C(OH)R^{1}R^2

| R^1, R^2 | method | δ_{iso} | $\delta_{solution}$ | σ_{11} | σ_{22} | σ_{33} | angles to the principal axes | | |
							S=P−3	C(OH)−P−2	norm−1[b]
Me, Me	CP MAS	55.2	53.5	229	249	341			
	IGLO (II)	(18)		252	281	397	8.7	34.8	14.5
(−CH$_2$−)$_5$	CP MAS	52.9	53.2	224	251	352			
	IGLO (II′)	(24)		235	278	397	9.7	34.2	3.4
Me, C(O)Me	CP MAS	51.8	51.6	213	250	366			
	IGLO (II)	(17)		243	282	409	2.8	29.1	2.2
Ph, C(O)Ph	CP MAS	59.7	61.4	188	261	356			
	IGLO (II′)	(24)		214	290	407	4.4	20.8	4.3
H, COOH **A**	CP MAS	49.7	45.6	235	260	340			
	IGLO (II)	(12)		257	289	401	2.8	22.1	9.5
B	CP MAS	47.5	45.6	230	253	360			
	IGLO (II)	(11)		258	288	406	1.2	25.5	14.2

[a] Data for crystal structure geometry. II and II′: Abbreviations for the basis sets used in the IGLO calculations (see Experimental Section). [b] Norm−1 is the angle between the normal to the S=P−C$_{hy}$ plane and the principal axis 1.
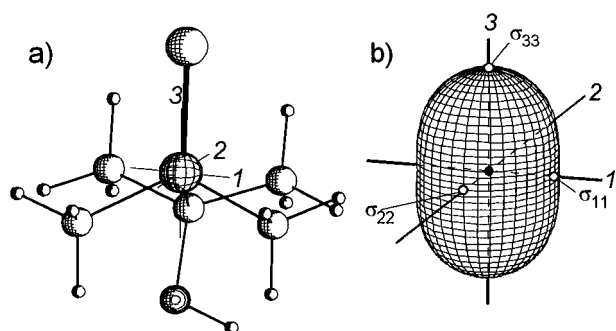

Figure 5. ^{31}P nuclear magnetic shielding tensor of Me$_2$P(S)C(OH)-Me$_2$ (**1**): (a) orientation of the principal axes 1, 2, and 3 in the molecular framework calculated by the IGLO method, (b) ovaloid pictorial representation of the shielding based on the experimental principal values σ_{11}, σ_{22}, and σ_{33} of the tensor.

experimental value mentioned above. The same result is obtained for the calculated $\Delta\sigma_{11}$ values of 43 ppm and for the $\Delta\sigma_{33}$ values of 12 ppm. These similarities of calculated and experimental differences $\Delta\sigma_{ii}$ confirm that the calculated orientation of the principal axes in the molecular framework is a good approximation. The angles in Table 3, characterizing the orientation of the shielding tensor principal axes in the molecular framework, support the assumption derived from NMR powder investigations: the principal axis 3 shows a slight deviation from the P=S bond and the principal axis 1 a slight deviation from the normal to the S=P−C$_{hy}$ plane. For **1** the calculated orientation of the principal axes in the molecular framework is shown in Figure 5a (see the same for **4** in the Table of Contents graphic).

The calculated difference of the principal values $\Delta\sigma_{33} = 5$ ppm of isolated molecules **5A** and **5B** does not explain the large experimental difference $\Delta\sigma_{33} = 20$ ppm. This is a second indication of significantly different intermolecular O···S interactions of molecules **A** and **B**. The short intermolecular O···S distance and the large deviation of the O1···S=P arrangement from linearity lead to a decrease of the symmetry of the lone-pair electron distribution and hence to a larger deshielding. This confirms that molecule **5A**, showing the shortest intermolecular O···S distance, has to be assigned to the shielding tensor with the more (20 ppm) deshielded σ_{33} value. In case of the well-known Lawesson reagent, for instance, intermolecular S···S interactions in the solvent-free crystals give an additional deshielding in σ_{33} of more than 70 ppm in comparison with crystals containing solvate molecules.[6g]

The nuclear magnetic shielding situation can be visualized by drawing an ovaloid.[18] This is a surface showing the measurable shielding σ_{zz} as a function of the orientation of the

principal axes to the direction of the magnetic field. If the direction of the magnetic field is parallel to one of the principal axes 1, 2, or 3, the nuclear magnetic shielding is equal to σ_{11}, σ_{22}, and σ_{33}, respectively.

Such an ovaloid is shown for **1** in Figure 5b and for **4** in the Table of Contents graphic. For the ovaloid calculation the experimental values σ_{ii} given on an absolute scale[12] must be used. The orientation of the principal axes to the molecular geometry is taken from the quantum chemical molecule calculations and therefore can differ somewhat from the orientation in the solid state.

The application of local molecular orbitals (LMOs) within the IGLO scheme[7c] allows an analysis of individual bond contributions σ_{ii}(LMO) to σ_{ii}. If one considers that the deshielding contributions to a given σ_{ii} depend on the electronic structure in a plane perpendicular to the principal axis i, bonds almost perpendicular to a certain principal axis should make the main deshielding contributions to σ_{ii}. This fact is well demonstrated for three of the investigated compounds in Table 4 (the data for the compounds **2** and **3** are similar).

The P=S bond provides deshielding contributions mainly to σ_{11} and σ_{22}, the P−Me bonds contribute preferentially to σ_{22} and σ_{33}, and the P−C$_{hy}$ bond contributes to σ_{11} and σ_{33}. The S= lone pairs provide a *shielding* contribution to σ_{33}, probably due to their symmetrical electron density distribution with respect to the P−S axis. This symmetry is perturbed by the O···S interaction between molecules **5A** leading to a decrease of the shielding of the experimental σ_{33} value.

For a discussion of the LMO contributions, the following facts must be considered. Although the sums of the given contributions $\sigma_{ii}(\Sigma)$ are close to the values of σ_{ii}(total), it is not correct to conclude that only atoms directly bonded to the phosphorus atom determine its nuclear magnetic shielding or, more precisely, its deshielding. More distant atoms, causing the well-known β, γ, and δ effects in the solution NMR, influence the electron distribution in the phosphorus environment and modify the contributions of the LMOs of the P−X bonds and the lone pairs of the directly bonded atoms. This fact becomes obvious on considering the σ_{11}(LMO) contributions for **4**. Experimental and calculated σ_{11} values of **4** differ significantly from the corresponding values found for the other compounds. According to the data given in Table 4, this difference is caused mainly by the contribution σ_{11}(P=S). A more detailed inspection of the crystal structure data shows that, not the slightly different P=S bond strengths (bond lengths), but rather the close vicinity of a β atom is responsible for this result. In **4** the oxygen atom in a position β to the phosphorus is closer to the center of the

(18) Radeglia, R. *Solid State Nucl. Magn. Reson.* **1995**, *4*, 317.

Table 4. Main IGLO LMO Contributions[a] to the Principal Values σ_{ii} of **1**, **4**, **5A** and **5B**

	σ_{11}(LMO)				σ_{22}(LMO)				σ_{33}(LMO)			
LMO	**1**	**4**	**5A**	**5B**	**1**	**4**	**5A**	**5B**	**1**	**4**	**5A**	**5B**
Core P[b]	771	772	777	777	775	778	774	778	786	791	792	793
P=S	−260	−292	−267	−271	−230	−230	−235	−237	5	9	10	10
P−C$_{hy}$	−122	−123	−117	−112	−48	−14	−14	−20	−120	−116	−123	−121
P−C$_{Me}$	−23	−74	−95	−88	−126	−115	−89	−88	−152	−159	−156	−164
P−C$_{Me}$	−90	−43	−23	−34	−70	−113	−132	−139	−156	−165	−169	−160
3 lp S=[c]	−16	−18	−13	−9	−13	−10	−10	−9	60	69	69	69
$\sum$[d]	260	222	262	263	288	296	294	292	423	429	423	427
total[e]	252	214	257	258	281	290	289	288	397	407	401	406

[a] Data for crystal structure geometry. [b] Core P are the contributions of the K and L shells of the phosphorus atom. [c] 3 lp S= denotes the sum of contributions of the three lone-pair LMOs of the sulfur atom. [d] $\sum$ is the sum of the considered LMO contributions. [e] Total is the sum of all LMO contributions.

P=S bond (O1 = 3.00 Å) than in compounds **1**−**3** and **5** (O1 or C 3.11−3.22 Å). Therefore, the special location of the β atom O1 to phosphorus is the reason for the higher deshielding value σ_{11} in **4**.

Conclusion

The complex study of a series of (1-hydroxyalkyl)dimethylphosphine sulfides by X-ray diffraction, ^{31}P solid-state MAS NMR, and IGLO calculations allows a better understanding of correlations between molecular structure and nuclear magnetic shielding anisotropy and also of influences of intermolecular interactions on the shielding properties in the solid state. According to the crystal structure data in all five compounds, intermolecular O−H···S hydrogen bonds are present and, additionally, intermolecular and intramolecular O−H···O hydrogen bonds in **5**. Comparison of the principal values σ_{11}, σ_{22}, and σ_{33} of the experimental shielding tensors of these structurally similar compounds and IGLO calculations shows a qualitative agreement of the results concerning the orientation of the principal axes: (i) the axis *3* lies nearly along the P=S bond; (ii) the slight deviations (a few degrees) of the axis 1 from the normal to the S=P−C$_{hy}$ plane show that the principal value σ_{11} is determined by the P=S bond, the P−C$_{hy}$ bond, and additionally by the substituents R[1] and R[2]; (iii) the plane perpendicular to the axis 2 lies far away from the substituents

R[1] and R[2]. Short intermolecular O−H···S interactions between molecules of **5A** lead to a larger deshielding and allow the assignment of the two sets of experimental principal values to the molecules **5A** and **5B**. The lowest σ_{11} value found for compound **4** can be explained by the high deshielding contribution of the P=S LMO, which is caused by the shortest distance between the P=S bond and an atom in a position β to the phosphorus. By the pictorial representation of the absolute nuclear magnetic shielding tensors as ovaloids, a correct image of the shielding anisotropy is obtained.

Supporting Information Available: Listings of crystallographic data, atomic coordinates, bond distances and angles, anisotropic displacement parameters, hydrogen coordinates, ellipsoid plots, and stereoscopic pairs of packing diagrams and listings of IGLO calculations including the coordinates used and the phosphorus nuclear shielding data (45 pages). Ordering information is given on any current masthead page.

IC960469O