

# Structural Implications of C–H···S Contacts in Organophosphorus Compounds. Studies of 1,6-Anhydro-2-*O*-tosyl-4-*S*-(5,5-dimethyl-2-thioxa-1,3,2-dioxaphosphorinan-2-yl)- $\beta$ -D-glucopyranose by X-ray and Solid-State NMR Methods

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1,6-Anhydro-2-*O*-tosyl-4-*S*-(5,5-dimethyl-2-thioxa-1,3,2-dioxaphosphorinan-2-yl)- $\beta$ -D-glucopyranose (**1**, C<sub>18</sub>H<sub>25</sub>O<sub>8</sub>PS<sub>3</sub>), crystallized from polar and/or nonpolar solvents, forms different modifications in the solid phase. Crystal structures of **1** (obtained from a methanol solution) and its 2-propanol solvate (**1a**) were established by X-ray structure analysis at low temperature. One-component crystal **1** is orthorhombic, space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, with *a* = 7.483(4) Å, *b* = 11.156 (6) Å, *c* = 27.11(2) Å, *V* = 2263 (2) Å<sup>3</sup>, *Z* = 4, and *D*<sub>c</sub> = 1.457 g cm<sup>-3</sup>. Refinement of 275 parameters using 2661 observed reflections (*I* > 2σ(*I*)) converged at *R*(*F*) = 0.0372. The crystal of **1a** is an inclusion structure containing molecules of **1** and 2-propanol in the ratio 1/1; crystals are triclinic, space group *P*1, with *a* = 9.637(6) Å, *b* = 9.709(6) Å, *c* = 8.865(8) Å, α = 110.27(5)°, β = 106.33(5)°, γ = 108.70(6)°, *V* = 661.3(8) Å<sup>3</sup>, *Z* = 1, and *D*<sub>c</sub> = 1.398 g cm<sup>-3</sup>. Full-matrix least-squares refinement of 307 parameters using 2478 observed reflections gave final *R*(*F*) = 0.0349. Intermolecular hydrogen bonds (O–H···O, C–H···O in **1**; O–H···O, O–H···S in **1a**) are present along with the C–H···S=P intermolecular interactions. A search of Cambridge Structural Database shows that such contacts are not unusual for organothio-phosphoryl compounds. The solid-state structures were studied by the NMR spectroscopy. The analysis of the <sup>31</sup>P chemical shift parameters enabled the correlation of the δ<sub>33</sub> principal element of chemical shift tensor and span (Ω) with C–H···S=P contact. The presence of toluene-*d*<sub>8</sub> in the crystal lattice of inclusion complex **1b** was confirmed by <sup>2</sup>H NMR spectroscopy.

## Introduction

Weak hydrogen bonds play an important role in crystal engineering, supramolecular chemistry, molecular recognition, and self-organization of biomolecules.<sup>1,2</sup> Different types of intermolecular interactions including C–H···O, C–H···N, O–H···π, N–H···π, C–H···π were reported very recently.<sup>3–10</sup> The knowledge about the nature of weak interactions combined with known geometry of supramolecular synthons now allows construc-

tion of the supramolecular motifs in the solid phase.<sup>11</sup> Much attention has been paid to C–H···O hydrogen bonds as a factor affecting the structure of organic compounds and natural products.<sup>12,13</sup> After many years of controversy, the role of this type of interaction is no longer a matter of debate. Taylor and Kennard<sup>14</sup> showed that C–H···O contacts are electrostatic by nature and occur for C···O distances between 3.0 and 4.0 Å, assuming that the C–H···O angle is in the range 90–180°. The geometry of C–H···O in carbohydrate crystals was reported by Steiner and Saenger.<sup>15</sup> Its significance in crystal engineering was recently discussed by Desiraju.<sup>16,17</sup> Auffinger et al. have shown the importance of C–H···O hydrogen bonds in the molecular dynamics of anticodon hairpin of t-RNA.<sup>18</sup> To date less attention has been paid to C–H···S hydrogen bonds; however, the significance of this type of interactions in the self-organization of crystals was discussed by Novoa et al.<sup>19</sup>

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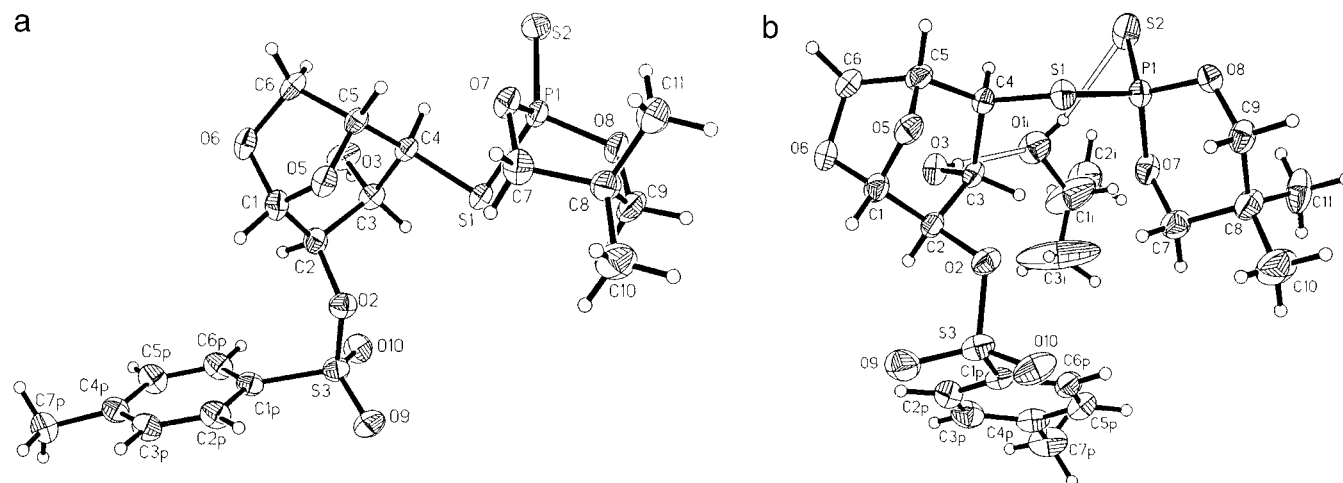
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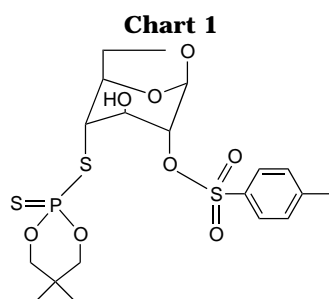
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**Figure 1.** ORTEP plot of molecules with atom numbering and displacement ellipsoids (at 50% probability level): (a) conformation of **1** in homomolecular crystal and (b) conformation of **1a** in its 2-propanol solvate.



**Table 1.** Crystal Data for **1** and the 2-Propanol Solvate **1a**

	<b>1</b>	<b>1a</b>	<b>1a</b>	<b>1a</b>
formula	C <sub>18</sub> H <sub>25</sub> O <sub>8</sub> PS <sub>3</sub>	C <sub>18</sub> H <sub>25</sub> O <sub>8</sub> PS <sub>3</sub> ·C <sub>3</sub> H <sub>8</sub> O		
mol wt	496.53	556.62		
temp, K	150(1)	150(1)	85(2)	298(1)
space group	orthorhombic, P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	triclinic, P1	triclinic, P1	triclinic, P1
<i>a</i> , Å	7.483(4)	9.659(7)	8.865(6)	9.782(6)
<i>b</i> , Å	11.156(6)	9.764(8)	9.709(6)	9.899(7)
<i>c</i> , Å	27.11(2)	8.860(7)	16.390(8)	8.912(6)
$\alpha$ , deg	90	110.27(5)	91.60(5)	111.60(6)
$\beta$ , deg	90	106.33(5)	90.29(5)	106.41(6)
$\gamma$ , deg	90	108.70(6)	110.27(6)	107.45(6)
<i>V</i> , Å <sup>3</sup>	2263(2)	665.5(9)	1322.6(14)	686.3(8)
<i>Z</i>	4	1	2	1
<i>d</i> (calcd), g cm <sup>-3</sup>	1.457	1.389	1.398	
radiatn	Mo K $\alpha$	Mo K $\alpha$		
( $\lambda$ , Å)	(0.71069)	(0.71069)		
$\mu$ , mm <sup>-1</sup>	0.44	0.387		

This work shows that C–H··S and C–H··O hydrogen bonds are one of the factors affecting the molecular

packing of 1,6-anhydro-2-*O*-(tosyl)-4-*S*-(5,5-dimethyl-2-thioa-1,3,2-dioxaphosphorinan-2-yl)- $\beta$ -D-glucopyranose (Chart 1) molecules in the solid phase, whereas the O–H··S interaction is responsible for inclusion of a 2-propanol molecule into the solvate structure.

The structure of different crystals formed by **1** was studied by X-ray crystallography and solid-state NMR techniques. The changes of molecular packing related to hydrogen bonding are apparent from a <sup>31</sup>P CP/MAS experiment and crystallographic data. The <sup>31</sup>P chemical shift parameters, span ( $\Omega$ ), and skew ( $\kappa$ ) as well as principal elements of the chemical shift tensors ( $\delta_{ij}$ ) reflect the changes of local environment of phosphorus. The <sup>2</sup>H and <sup>1</sup>H–<sup>2</sup>H CP/MAS experiments were employed to study the dynamics of toluene-*d*<sub>8</sub> occluded in the crystal lattice of **1b**.

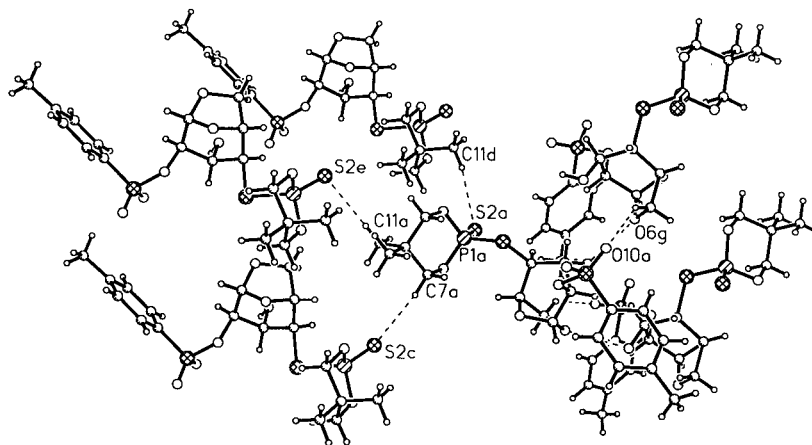
## Results and Discussion

**X-ray Crystal Structure Analysis.** Crystallographic data for **1** and its 2-propanol solvate (**1a**) are given in Table 1. The unit cell parameters of **1a** were determined at room temperature, and two sets of diffraction data were collected at 150 and 85 K. The solvate crystal **1a** undergoes a phase transition below 90 K. Both phases crystallize in the triclinic space group *P1* with a different number of molecules in the unit cell. Selected geometrical parameters for **1** and **1a** at 150 K are presented in Table 2.

**Molecular Structure.** The perspective drawing of molecules with atom numbering scheme is presented in Figure 1. The phosphorus centers covering the phospho-

**Table 2.** Selected Bond Lengths (Å) and Angles (deg)

	<b>1</b>	<b>1a</b> (150 K)	<b>1</b>	<b>1a</b> (150 K)
P(1)–O(7)	1.579(2)	1.582(3)	C(4)–C(5)	1.535(4)
P(1)–O(8)	1.583(2)	1.572(3)	S(3)–O(2)	1.588(3)
P(1)–S(2)	1.916(2)	1.914(2)	O(2)–C(2)	1.453(4)
P(1)–S(1)	2.075(2)	2.070(2)	O(3)–C(3)	1.418(4)
S(1)–C(4)	1.835(3)	1.832(5)	O(5)–C(1)	1.402(4)
C(1)–C(2)	1.531(5)	1.529(5)	O(5)–C(5)	1.439(4)
C(2)–C(3)	1.544(4)	1.531(5)	O(6)–C(1)	1.428(4)
C(3)–C(4)	1.541(5)	1.535(5)	O(6)–C(6)	1.448(5)
O(7)–P(1)–O(8)	105.3(1)	105.8(2)	C(4)–S(1)–P(1)	100.7(1)
O(7)–P(1)–S(2)	111.6(1)	110.9(1)	C(2)–O(2)–S(3)	116.4(2)
O(8)–P(1)–S(2)	113.6(1)	114.0(1)	O(2)–C(2)–C(3)	110.6(2)
O(7)–P(1)–S(1)	107.8(1)	107.7(1)	O(3)–C(3)–C(4)	107.7(3)
O(8)–P(1)–S(1)	102.2(1)	100.3(1)	O(3)–C(3)–C(2)	108.6(3)
S(2)–P(1)–S(1)	115.5(5)	117.1(1)	C(2)–C(3)–C(4)	112.0(2)
			C(4)–C(5)	1.536(5)
			S(3)–O(2)	1.584(3)
			O(2)–C(2)	1.469(4)
			O(3)–C(3)	1.419(4)
			O(5)–C(1)	1.399(5)
			O(5)–C(5)	1.437(4)
			O(6)–C(1)	1.428(5)
			O(6)–C(6)	1.438(5)
			C(4)–S(1)–P(1)	101.6(1)
			C(2)–O(2)–S(3)	117.5(2)
			O(2)–C(2)–C(3)	107.0(3)
			O(3)–C(3)–C(4)	110.1(3)
			O(3)–C(3)–C(2)	107.3(3)
			C(2)–C(3)–C(4)	112.6(3)



**Figure 2.** Packing of molecules in the crystal structure of **1**. Hydrogen-bond geometry: O3···O6, 2.751(3) Å; H···O6, 1.87 Å; O3–H···O6, 172°; and C6···O10, 3.330(4) Å; H···O10, 2.52 Å; C6–H···O10, 119°. The intermolecular S···C distances are 3.764 and 3.885 Å.

**Table 3.** Selected Torsion Angles (deg) and Respective Conformations

	<b>1</b>	<b>1a</b> (150 K)
S2–P1–S1–C4	–39.6(1) ( <i>-sc</i> )	49.6(2) ( <i>sc</i> )
P1–S1–C4–C3	168.3(2) ( <i>ap</i> )	76.9(3) ( <i>sc</i> )
S1–C4–C3–C2	90.3(3) ( <i>ac</i> )	84.0(3) ( <i>sc</i> )
C4–C3–C2–O2	–86.6(3) ( <i>-sc</i> )	–87.4(3) ( <i>-sc</i> )
C3–C2–O2–S3	–99.4(3) ( <i>-ac</i> )	–137.2(2) ( <i>-ac</i> )
C2–O2–S3–C1p	–67.1(2) ( <i>-sc</i> )	70.7(3) ( <i>sc</i> )
O2–S3–C1p–C2p	–73.0(3) ( <i>-sc</i> )	–98.6(3) ( <i>-ac</i> )

rus–oxygen and phosphorus–sulfur bond lengths are very similar (Table 2). For both modifications the P=S bond lengths are comparable: 1.916(2) Å for **1** and 1.920(2) Å for **1a**. Molecular conformations observed in **1** and **1a** are different due to the rotation of axial substituents, i.e. tosyl and 5,5-dimethyl-2-thioxa-1,3,2-dioxaphosphorinan-2-yl groups, at the glucopyranose ring. Rigid fragments of the molecule rotate about the C(2)–O(2), O(2)–S(3), C(4)–S(1), and S(1)–P(1) bonds (Table 3), causing differences in the torsion angle of values up to 157.8° (C2–O2–S3–C1p). The extended conformation of the molecule found in the crystal **1** (homomolecular) changes to the bent one in the presence of 2-propanol (**1a**).

**Crystal Structure.** Figure 2 shows the molecular packing of orthorhombic **1** and Figure 3 presents the arrangement of molecules in the solvate **1a** structure.

For structure **1** three different types of intermolecular contacts are seen: (i) the intermolecular O3–H···O6 bond between hydroxyl and ether oxygen atoms, (ii) the sugar residue bonded by the weak C6–H···O10 hydrogen bond, (iii) the thiophosphoryl group participating in intermolecular P=S···H–C contacts with the hydrophobic part—the methyl and methylene groups—of neighboring molecules.

The solvate crystal **1a** is built up of the molecular complex formed by two intermolecular hydrogen bonds. The 2-propanol hydroxyl group is involved both as a donor and acceptor in the sequence of hydrogen bonds O3–H···O–H···S=P (Figure 4). Additional interactions stabilizing the crystal structure are three contacts of the S(2) atom to the phenyl and methine C–H groups. The S···C distances are shorter than 3.7 Å, while respective S···H distances are in the range 2.90–3.20 Å.

**Cambridge Structural Database (CSD) Search.** The structural implications of C–H···O hydrogen bonds

**Table 4.** Statistical Values Based on the Analysis of the CSD for Intermolecular C–H···X Contacts

parameter	(II) CHSOP <sup>a</sup>		(I) CHOP <sup>a</sup>
	X = S	X = O	X = O
min. C···X (Å)	3.556	3.194	3.152
min. H···X (Å)	2.76	2.49	2.16
mean < C–H···X (deg) <sup>b</sup>	158	157	160
mean < H···X–P (deg)	124	118	129
no. contacts/ crystal structures	50/24	24/15	401/123

<sup>a</sup> For the definition of the group of compounds, see the text.

<sup>b</sup> Geometrical conic correction was applied for the histogram (see ref 24)

in crystals were recently exhaustively discussed by Desiraju<sup>16,17</sup> and Steiner et al.<sup>4,6,7,20,21</sup> The geometrical analysis has been carried out mainly for the carbon-bonded oxygen atoms being a part of the carbonyl C=O, ether C–O–C, or hydroxyl C–OH group. The P–O and P=S acceptors were not considered. Moreover, there are only few reports showing the influence of C–H···S contacts on molecular packing.<sup>19</sup> So, we retrieved structural data for two groups of tetracoordinated phosphorus derivatives: (I) organophosphorus compounds containing the P(O)X<sub>3</sub> fragment (with C, H, O, and P only), where X = O or C; and (II) organothiophosphorus compounds with the S=P(O)X<sub>2</sub> fragment (with C, H, S, O, P), where X = S, O, or C.

The CSD<sup>22</sup> entries refined to the discrepancy factor *R* < 0.07 were considered, and the assumed range of the angle involving hydrogen atom [i.e. C–H···O(–P) or C–H···S(=P)] was 90–180°. The distances applied for analysis of intermolecular contacts were van der Waals radii given by Bondi:<sup>23</sup> *r*(H) = 1.2, *r*(O) = 1.5, *r*(S) = 1.8, and *r*(C) = 1.75 Å. Resulting limits of geometrical parameters for the C–H···O and C–H···S contacts are summarized in Figure 5.<sup>24</sup> The values of characteristic parameters obtained from CSD (Figure 6 and Table 4) clearly indicated that weak electrostatic interactions

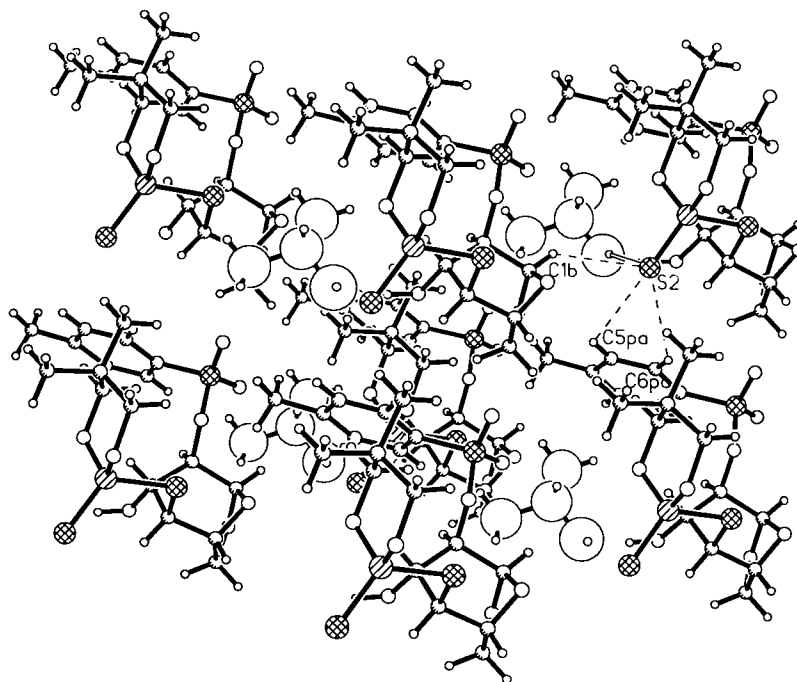
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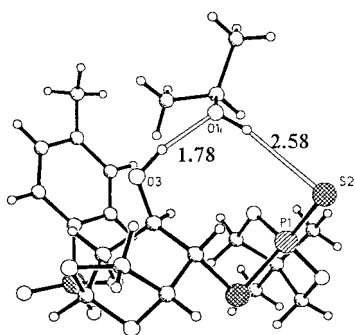
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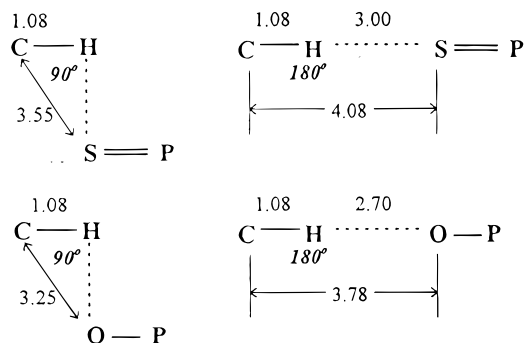
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**Figure 3.** Molecular packing in **1a**. The intermolecular S...C contacts: S2...C1, 3.658(3) Å; S2...C5p, 3.690(3) Å; and S2...C6p, 3.578(3) Å.



**Figure 4.** Geometry of hydrogen bonds linking the molecules **1** and 2-propanol. The H...acceptor distances are given in Å. Donor...acceptor distances: O3...O1i, 2.706(4); and O1i...S2, 3.443(3) Å. Bond angles: O3-H3O...O1i, 166°; and O1i-H10i...S2, 161°.



**Figure 5.** Geometry limiting the CSD search for intermolecular contacts

between hydrophobic fragments of molecules and the P–O or P=S group play an important role in the crystal lattice.

The minimal C...O distance is shorter than the sum of van der Waals radii (3.15 vs 3.25 Å). The geometrical criteria for these contacts are discussed in detail else-

where.<sup>1,7,14,25,26</sup> We found also 50 contacts of the thiophosphoryl S(=P) atom within the range of the C...S distance 3.55–4.01 Å. The C–H...X angle values confirm the nonlinear character of such interactions, and the H...X–P angles, close to 120°, indicate that both for oxygen and sulfur atom the directionality of the lone pair is a very important factor. The C–H...S=P contacts observed in **1** and **1a**, where the C...S distances are in the range 3.578–3.885 Å, have an influence on molecular packing.

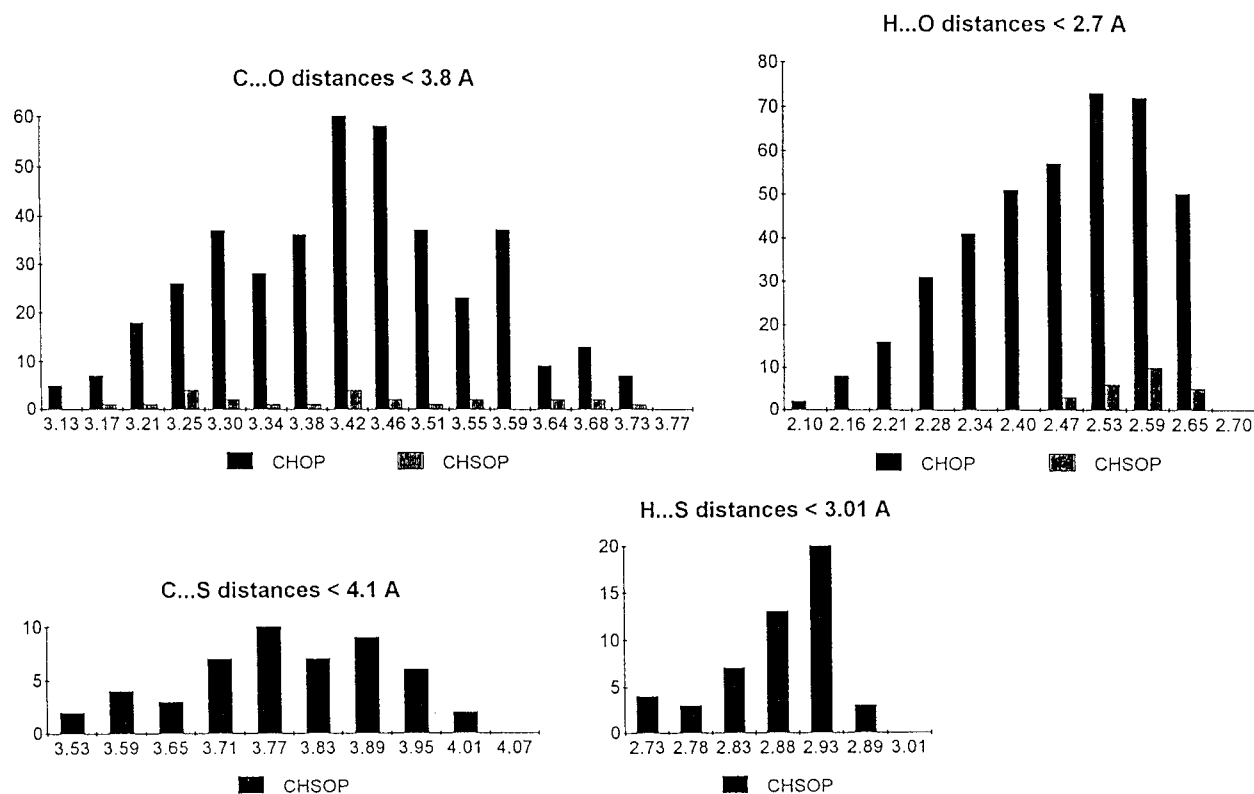
**<sup>31</sup>P CP/MAS and <sup>2</sup>H Solid-State NMR Studies.** The room-temperature <sup>31</sup>P CP/MAS spectra of 1,6-anhydro-2-*O*-tosyl-4-*S*-(5,5-dimethyl-2-thioxa-1,3,2-dioxaphosphorinan-2-yl)-β-D-glucopyranose crystallized from methanol **1** and 2-propanol **1a** are displayed in parts a and b of Figure 7, respectively. Both spectra show a set of spinning sidebands from the large chemical shielding anisotropy (CSA). The phosphorus can be considered as an isolated nucleus, because adjacent atoms in a tetrahedral arrangement are zero spin nuclei. The interactions with active isotopes of sulfur, carbon, and oxygen at natural abundance are below the detectable limit. The dipolar coupling from the protons of glucopyranoses was eliminated by proton decoupling during data acquisition. The principal components of the <sup>31</sup>P chemical shift tensors  $\delta_{ij}$  were calculated from spinning sidebands intensities employing the WINMAS program that is based on the Berger–Herzfeld algorithm.<sup>27,28</sup> The calculated values of principal tensors elements  $\delta_{ij}$  and shielding parameters are given in Table 5. The accuracy of calculations was confirmed by comparison with theoretical spectra shown in Figure 7, parts c and d. The

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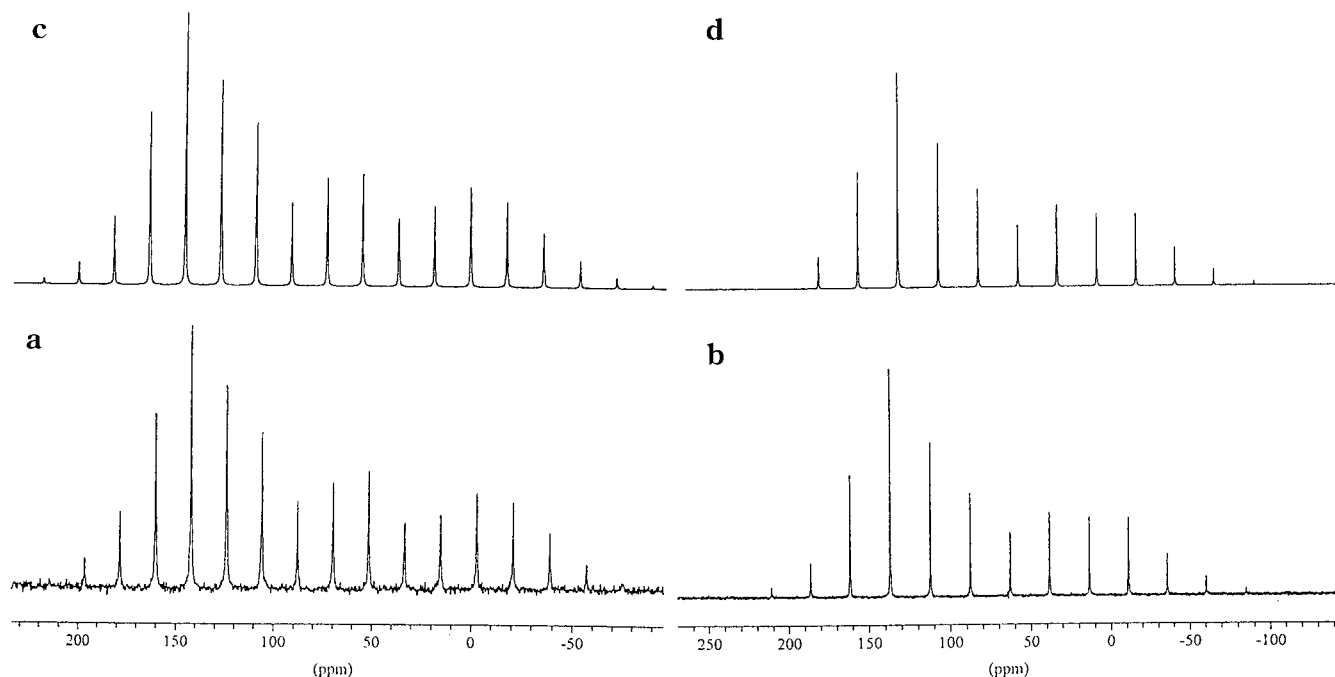
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**Figure 6.** Distribution of the donor...acceptor and H...acceptor distances found for the C–H···O–P and the C–H···S=P contacts.



**Figure 7.** (a)  $^1\text{H}$ - $^{31}\text{P}$  CP/MAS experimental spectrum of **1**,  $\gamma_{\text{rot}} = 2.2$  kHz. (b)  $^1\text{H}$ - $^{31}\text{P}$  CP/MAS experimental spectrum of **1a**,  $\gamma_{\text{rot}} = 2.8$  kHz. (c) Theoretic spectrum of **1**. (d) Theoretic spectrum of **1a**. The experimental spectra have 8K data points, with a contact time 5 ms and 100 scans. Theoretic spectra were calculated employing the program WINMAS, version 940108, Bruker-Franzen Analytik GMBH, Bremen 1994.

resemblance between the two spectra is apparent. The observed single lines in the isotropic part of the spectra are consistent with the X-ray data.

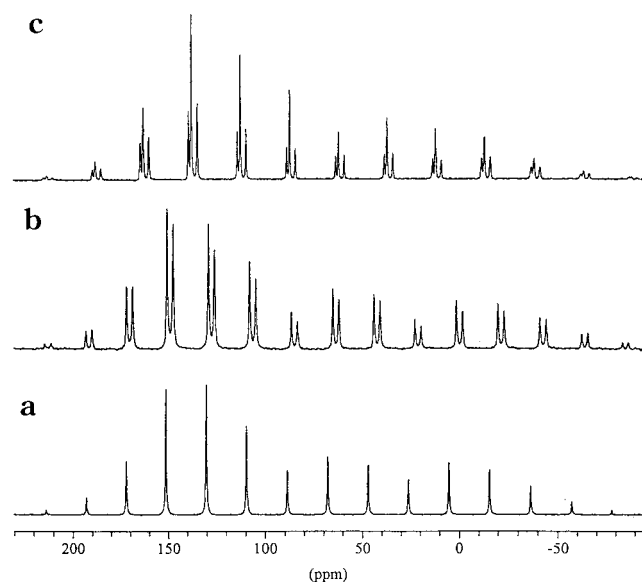
Figure 8a displays **1c** (tritirated from benzene employing hexane) while Figure 8b presents **1b** (crystallized from toluene), and Figure 8c shows **1** crystallized from a

mixture of benzene/petrol ether (vol/vol 1/1) (**1d**). Moreover, we found that a sample crystallized from benzene (**1e**) shows a pattern similar to that observed for **1b** modification. Each sample shows a different number of resonances in the isotropic part due to differences in packing of molecules in the crystal. The variable tem-

**Table 5.**  $^{31}\text{P}$  Chemical Shift Parameters for Different Crystallographic Modifications of 1,6-Anhydro-2-O-tosyl-4-S-(5,5-dimethyl-2-thioxa-1,3,2-dioxaphosphorinan-2-yl)- $\beta$ -D-allopyranose **1**<sup>a</sup>

compd (cryst solvent)	$\delta_{\text{iso}}$ (ppm)	$\delta_{11}$ (ppm)	$\delta_{22}$ (ppm)	$\delta_{33}$ (ppm)	$ \text{gD}\delta $ (ppm)	$\Omega$ (ppm)	$\eta$	$\kappa$
<b>1</b> (methanol)	87.5	185	140	-63	225	248	0.30	0.64
<b>1a</b> (2-propanol)	87.8	184	140	-61	223	245	0.30	0.64
<b>1b</b> (toluene, 298 K) 353 K	86.7	187	148	-75	243	262	0.24	0.70
	83.6	188	148	-85	253	273	0.23	0.71
	87.1	184	141	-64	226	248	0.29	0.65
<b>1c</b> (trituated from toluene with hexane)	87.7	183	141	-63	226	246	0.29	0.65
<b>1d</b> (benzene/petrol ether, vol/vol 1/1)	89.1	193	145	-72	241	265	0.30	0.63
	87.5	186	141	-65	228	228	0.30	0.64
	84.6	186	146	-80	246	246	0.24	0.69
<b>1d'</b> (benzene/petrol ether after few months)	87.2	183	141	-63	226	246	0.28	0.66
<b>1e</b> (benzene)	89.2	190	148	-71	240	261	0.30	0.68
	84.7	185	148	-78	244	263	0.24	0.72

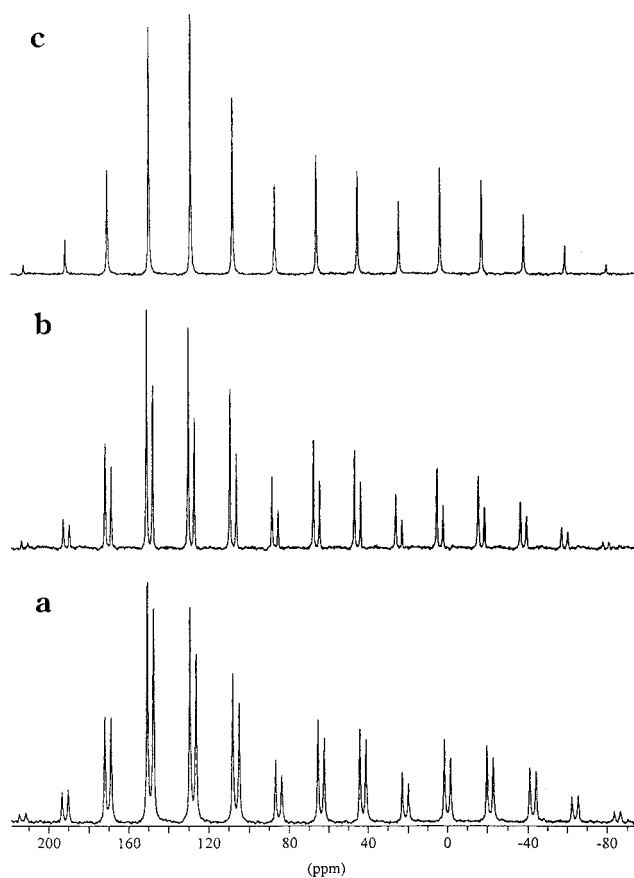
<sup>a</sup> Estimated errors in  $\delta_{11}$ ,  $\delta_{22}$ ,  $\delta_{33}$  are  $\pm 2$  ppm. Errors in  $\delta_{\text{iso}}$  are  $\pm 0.2$  ppm. Principal components of the chemical shift tensor are defined as  $\delta_{11} > \delta_{22} > \delta_{33}$ . Isotropic chemical shift is given by  $\delta_{\text{iso}} = (\delta_{11} + \delta_{22} + \delta_{33})/3$ .



**Figure 8.**  $^1\text{H}$ - $^{31}\text{P}$  CP/MAS experimental spectra of **1**: (a) trituated from toluene with hexane, **1c**; (b) crystallized from toluene, **1b**; (c) crystallized from the mixture benzene/petrol ether (vol/vol 1/1), **1d**. All spectra have 8K data points, with a contact time of 5 ms and 100 scans.

perature (VT)  $^{31}\text{P}$  CP/MAS experiment (Figure 9) revealed that **1b** undergoes a phase transition below the melting point (mp 384 K).

Conclusions regarding the changes of geometry of the thiophosphoric systems may be drawn from analysis of shielding parameters and  $^{31}\text{P}$  principal components of chemical shift tensor,  $\delta_{ii}$ .<sup>29,30</sup> Potrzebowski using a series of bis(organothiophosphoryl) disulfides as well as Grossmann and co-workers employing ab initio IGLO calculations have shown that for dithiophosphoroorganic compounds the  $\delta_{33}$  parameter is oriented along the P=S bond, whereas  $\delta_{22}$  bisects the S=P-S plane.<sup>31,32</sup> Thus, the analysis of  $\delta_{33}$  and  $\delta_{22}$  parameters reflects the changes of the environment of phosphorus. The very detailed analysis of data collected in Table 5 shows several structural features of **1**. For all modifications only small



**Figure 9.** VT  $^{31}\text{P}$  CP/MAS experimental spectra of **1b**. All spectra have 8K data points, with a contact time of 5 ms and 100 scans: (a) at 298 K, (b) at 338 K, and (c) at 378 K.

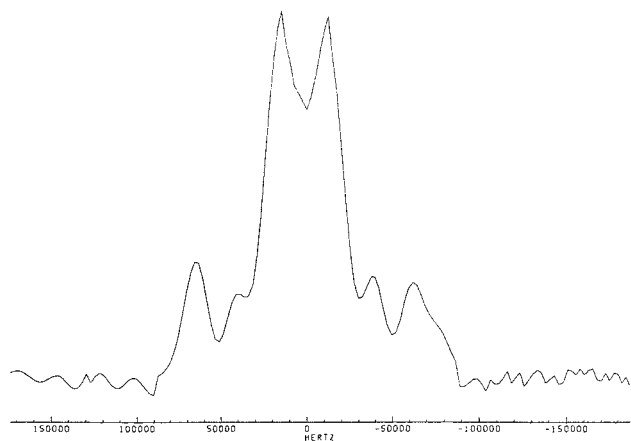
changes of the  $\delta_{11}$  and  $\delta_{22}$  parameters (in the range of a few ppm) are seen. More significant differences are established for  $\delta_{33}$  parameters and cover a range up to 20 ppm. For **1** and **1a**, the  $\delta_{33}$  are upfield compared to modifications crystallized from benzene or toluene. Since for **1** the P=S...H-C contacts are seen and for **1a** the solvent is hydrogen bonded to the P=S unit, we assume that differences between  $\delta_{33}$  values for **1**, **1a**, and **1b** as well as other complexes are due to hydrogen bonding. The origin of this effect is related to the decrease in electronic shielding of the phosphorus as the thiophosphoryl group becomes more polarized during bond formation. The orientation of the  $\delta_{ii}$  with respect to the molecular frame of the thiophosphoryl group concerning the hydrogen bond is shown in Scheme 1.

(29) Potrzebowski, M. J.; Michalski, J. In *Phosphorus-31 NMR Spectral Properties in Compound Characterization and Structural Analysis*; Quin, L. D., Verkade, J. G., Eds.; VCH: 1994; pp 413-426.

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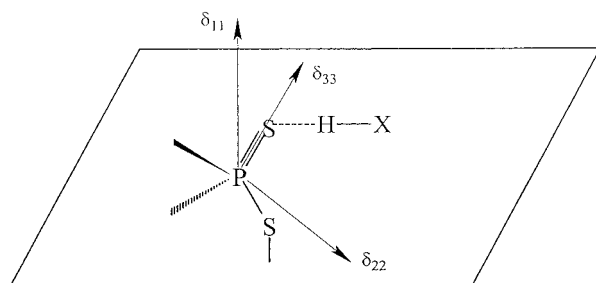
(31) Potrzebowski, M. J. *J. Chem. Soc., Perkin Trans. 2*, **1993**, 63.

(32) Krüger, K.; Grossmann, G.; Fleischer U.; Franke, R.; Kutzelnigg, W. *Magn. Reson. Chem.* **1995**, 33.



**Figure 10.**  $^2\text{H}$  static quadrupolar echo experimental spectrum of toluene- $d_8$  occluded in the crystal lattice of **1b**. The spectrum has 1K data points, with a repetition time of 40 s and 2000 scans.

**Scheme 1**

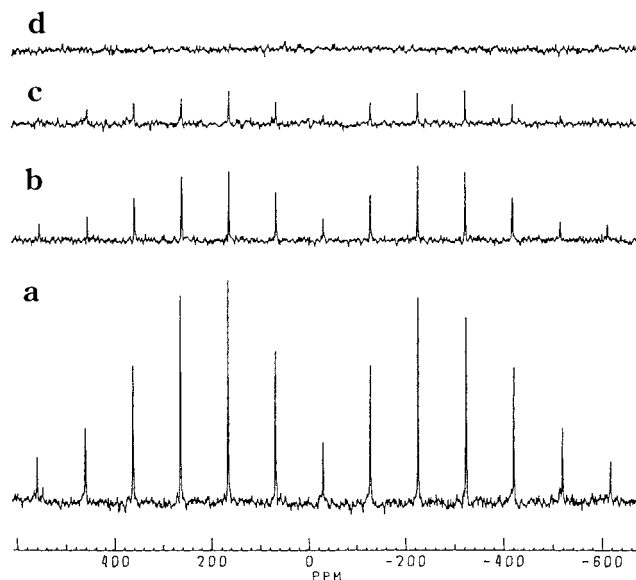


Further information about the nature of interaction was obtained from inspection of the  $\Omega$  parameter, which is expressed by the difference between  $\delta_{11}$  and  $\delta_{33}$ . The smaller values of  $\Omega$  correspond to modifications with hydrogen bonds. The challenging question is whether those complexes which show two resonance lines in the isotropic part of spectra are crystals with two molecules in the asymmetric unit of the crystallographic unit cell or represent different phases. The answer is obtained from the analysis of the VT  $^{31}\text{P}$  CP/MAS experiment. Different rates of resonances decay with increase of temperature (e.g. **1b** modification) and unambiguously show that **1b** consists of two different polymorphic phases.

The presence of toluene in the lattice of **1b** was confirmed by means of a  $^2\text{H}$  NMR experiment for a sample crystallized from toluene- $d_8$ . Figure 10 shows the quadrupolar echo deuterium NMR spectrum recorded at ambient temperatures.

Due to the overlapping of subspectra of aromatic and aliphatic groups with different mobility, the spectrum presents a rather complex pattern. The line shape analysis of the Pake doublets reveals signals from static aromatic groups with quadrupolar splitting of 120 kHz and from aromatic resonances of molecules which undergo small vibrations in lattice of **1b** (quadrupolar splitting of 80 kHz) and signals from  $\text{CD}_3$  group under fast motion regime ( $C_{3v}$  jump, quadrupolar splitting of 30 kHz).<sup>33</sup> Unfortunately, this experiment requires a long time accumulation in order to achieve a sufficient

(33) Jelinski, L. W. In *High Resolution NMR Spectroscopy of Synthetic Polymers in Bulk*; Komoroski, R. A., Ed.; VCH Publishers: 1986; Chapter 10, pp 335–364.



**Figure 11.** VT  $^1\text{H}$ – $^2\text{H}$  CP/MAS experimental spectra of toluene- $d_8$  occluded in the crystal lattice of **1b**. All spectra have 8K data points, a contact time 7 ms and 100 scans: (a) at 298 K, (b) at 338K, (c) at 358 K, and (d) 378 K.

signal-to-noise ratio (2K scans). The optimal relaxation delay was found to be 40 s. Much attention has been paid recently to deuterium high-resolution NMR spectroscopy as an alternative technique to the quadrupolar echo experiment.<sup>34–37</sup> Figure 11a displays the  $^1\text{H}$ – $^2\text{H}$  CP/MAS spectrum of **1c** unexpectedly, with signal only from the  $\text{CD}_3$  group.

Even with experimental conditions (relaxation delay, contact time) varied over a broad range it was not possible to record signals from phenyl- $d_5$ . This rather unexpected result is explained by considering the cross-polarization effect. It is known that efficient cross-polarization requires the close proximity of the  $^1\text{H}$  and  $^2\text{H}$  nuclei<sup>38</sup> and this condition probably is not fulfilled in the case of the phenyl residue.

The VT  $^1\text{H}$ – $^2\text{H}$  CP/MAS experiment in the range 300–353 K (Figure 11a–d) shows the gradual decrease of the amount of toluene in the lattice with the increase of temperature. At 353 K the toluene evaporates from the lattice. Note that at this temperature the phase transition was also observed by means of differential scanning calorimetry (deposited as Supporting Information) and a  $^{31}\text{P}$  CP/MAS experiment.

## Conclusions

There is a great deal of interest in C–H···X (X = O, S, Se) intermolecular contacts. As shown in the Introduction, the literature regarding C–H···O interactions is very extensive. In contrast, there are only a few papers describing C–H···S<sup>19</sup> and C–H···Se hydrogen bonding.<sup>39</sup>

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(36) Potrzebowski, M. J.; Wasiak J.; Ciesielski, W.; Klinowski, J. *J. Magn. Reson.* **1995**, *A114*, 70.

(37) Marks, D.; Zumbulyadis, N.; Vega, S. *J. Magn. Reson.* **1996**, *A122*, 16.

(38) Zumbulyadis, N.; O'Reily, J. M. *J. Am. Chem. Soc.* **1993**, *115*, 4407.

(39) Iwaoka, M.; Tomoda, S. *J. Am. Chem. Soc.* **1994**, *116*, 4463.

A search of the CSD reveals that C–H⋯S intermolecular contacts are not unusual for thiophosphoryl compounds. We have found more examples of C–H⋯S=P contact than for the analogous C–H⋯O=P interactions. This fact can be explained in term of hard and soft hydrogen bonds. The S=P, as a softer acceptor compared to the O=P unit, prefers to hydrogen bond with the soft donor C–H. Such explanation is consistent with ideas of Carrol and Bader,<sup>40</sup> who found a link between the softness of an acceptor and the character of hydrogen bonds, and the recent results of Braga et al., who surveyed the hydrogen bonding in organometallic crystals.<sup>26</sup>

The detailed analysis of the <sup>31</sup>P  $\delta_{ii}$  principal elements of the chemical shift tensor suggests that distinction in values of  $\delta_{33}$  parameters is due to C–H⋯S=P interactions. From inspection of  $\delta_{33}$ , the character of changes in the solid phase related to solvent migration can be deduced. <sup>2</sup>H NMR spectroscopy is another source of useful information about the nature of solvates (inclusion complexes) for **1**. This experiment not only confirms the presence of deuterated solvent molecule in the crystal lattice but also provides information about the molecular motions.

### Experimental Section

**Single-Crystal X-ray Analysis of 1 and 1a.** The diffraction data were collected on a KM4 diffractometer with graphite-monochromated Mo K $\alpha$  radiation. Colorless crystals of **1** (C<sub>18</sub>H<sub>25</sub>O<sub>8</sub>PS<sub>3</sub>) were obtained from a methanol solution. Data were collected at 150(2) K using a crystal with dimensions 0.5 × 0.5 × 0.7 mm. Reflections were measured up to  $\theta_{\max} = 30.1^\circ$ ; 3423 independent reflections ( $0 \leq h \leq 10$ ,  $0 \leq k \leq 15$ ,  $0 \leq l \leq 38$ ) were recorded and 2661 were observed ( $I > 2\sigma(I)$ ). The structure was solved by direct methods (the SHELXS-86 program)<sup>41</sup> and refined by full-matrix least-squares on  $F^2$  (SHELXL-93).<sup>42</sup> Final  $R$  indices  $\{wR(F^2) = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ ;  $R(F) = \sum(|F_o| - |F_c|) / \sum |F_o|\}$  were  $R(F) = 0.0372$  and  $wR(F^2) = 0.1018$  for the 275 parameters refined, i.e. anisotropic non-hydrogen atoms. Positions of hydrogen atoms on carbon atoms were calculated assuming ideal geometry; the hydrogen atom of the hydroxyl group was located in a difference electron density map. Isotropic temperature factors of hydrogen atoms have values of  $1.2U_{eq}$  for bonded non-hydrogen atoms.

Solvate crystals (C<sub>18</sub>H<sub>25</sub>O<sub>8</sub>PS<sub>3</sub>·C<sub>3</sub>H<sub>8</sub>O) were obtained from a 2-propanol solution by very slow evaporation (3 weeks) of the solvent at about 285 K. A crystal of dimensions 0.2 × 0.25 × 0.27 mm selected for data collection was sealed in a glass capillary. Intensities were measured at 85(2) K. Within the  $\theta$  range 2.5–26.0° and the  $hkl$  index ranges  $-11 \leq h \leq 11$ ,  $-11 \leq k \leq 11$ ,  $0 \leq l \leq 10$ , 2648 reflections were collected, of which 2515 were independent. The structure was solved by direct methods and the full-matrix least-squares refinement (on  $F^2$ ) of 307 parameters using 2478 observed reflections, which converged at final  $R$  indices of  $R(F) = 0.0349$ ,  $wR(F^2) = 0.0915$ .

At 85(2) K, 5309 reflections were collected. Within the  $\theta$  range 2.5–26.0° and the  $hkl$  index ranges  $0 \leq h \leq 10$ ,  $-11 \leq k \leq 11$ ,  $-20 \leq l \leq 20$ , 5040 reflections were independent. The structure was solved by direct methods and full-matrix least-squares refinement (on  $F^2$ ) of 610 parameters using 4359 observed reflections, which converged at final  $R$  indices of  $R(F) = 0.0427$ ,  $wR(F^2) = 0.1067$ . The non-hydrogen atoms were refined with anisotropic thermal parameters. The C-bonded hydrogen atoms were positioned from the geometry of the

molecules while the hydroxyl group H-atoms were found in a difference electron density map. The isotropic thermal factors of hydrogen atoms were  $U_{iso} = 1.2U_{eq}$  of the atom to which they are bonded.

**NMR Measurements.** Cross-polarization magic angle spinning (CP/MAS) solid-state <sup>2</sup>H and <sup>31</sup>P NMR spectra were recorded on a Bruker 300 MSL instrument with high-power proton decoupling at 46.07 MHz for <sup>2</sup>H and 121.46 MHz for <sup>31</sup>P. For the <sup>1</sup>H–<sup>2</sup>H CP/MAS, experiment the powdered samples of **1** were placed in a cylindrical rotor and spun at 2.0–4.5 kHz, the field strength for <sup>1</sup>H decoupling was 1.05 mT, a contact time of 7 ms, a repetition time of 6 s, and a spectral width of 250 kHz were used, and 8K data points represented the FID. For <sup>2</sup>H static spectra, recorded on Bruker 300 MSL instrument, the quadrupolar echo ( $\pi/2 - \tau_1 - \pi/2 - \tau_2 - \text{acquire}$ ) pulse sequence was employed with  $\pi/2 = 3.2$  ms,  $\tau_1 = 32$  ms, and  $\tau_2 = 30$  ms, a repetition time of 40 s and a spectral width of 2 MHz were used, and 1K data points represented the FID.

The <sup>31</sup>P CP/MAS NMR spectra were recorded in the presence of high-power proton decoupling. Powder samples of **1** were placed in a cylindrical rotor and spun at 2.0–4.5 kHz. The field strength for <sup>1</sup>H decoupling was 1.05 mT, a contact time of 5 ms, a repetition of 6 s, and a spectral width of 50 kHz were used, and 8K data points represented the FID. Spectra were accumulated 100 times, which gave a reasonable signal-to-noise ratio. <sup>31</sup>P chemical shifts were calibrated indirectly through bis(dineopentoxythiophosphoryl) disulfide set at 84.0 ppm.

The principal elements of the <sup>31</sup>P chemical shift tensor and shielding parameters were calculated employing the program WINMAS. The details describing the method and accuracy of calculations are exhaustively discussed elsewhere.<sup>27,28</sup>

The principal components ( $\delta_{ii}$ ) were used for calculation of the shielding parameters anisotropy ( $\Delta\delta$ ), asymmetry ( $\eta$ ), span ( $\Omega$ ), and skew ( $\kappa$ ).<sup>43</sup>

If

$$|\delta_{11} - \delta_{iso}| > |\delta_{33} - \delta_{iso}|$$

and

$$\delta_{11} > \delta_{22} > \delta_{33}$$

then

$$\Delta\delta = \delta_{11} - (\delta_{22} + \delta_{33}) \quad (1)$$

$$\eta = (\delta_{22} - \delta_{33}) / (\delta_{11} - \delta_{iso}) \quad (2)$$

If

$$|\delta_{11} - \delta_{iso}| < |\delta_{33} - \delta_{iso}|$$

and

$$\delta_{11} > \delta_{22} > \delta_{33}$$

then

$$\Delta\delta = \delta_{33} - (\delta_{11} + \delta_{22}) \quad (3)$$

$$\eta = (\delta_{22} - \delta_{11}) / (\delta_{33} - \delta_{iso}) \quad (4)$$

Moreover,

$$\Omega = \delta_{11} - \delta_{33} \quad (5)$$

$$\kappa = 3(\delta_{22} - \delta_{iso}) / \Omega \quad (6)$$

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(43) Mason, J. *Solid State Nucl. Magn. Reson.* **1993**, *2*, 285.



**Synthesis of 1.** The method of synthesis of **1** was published in ref 44.

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**Supporting Information Available:** Tables of atomic coordinates and thermal parameters, bond lengths and angles, an ORTEP view of  $C_{18}H_{25}O_8PS_3$  and  $C_{18}H_{25}O_8PS_3 \cdot C_3H_8O$ , Refcodes from CSD searches, and differential scanning calorimetry data (28 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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