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Synthesis, Crystal Structure, and NMR Spectroscopy of a 1,3,2λ⁵,4λ⁵-Oxathiadiphosphetane

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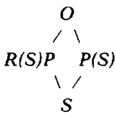
ABSTRACT

From the crude product of the synthesis of the dithiadiphosphetane $[RP(S)S]_2$ *(with* $R = 2,4,6\text{-}iPr_3C_6H_2$*), the trans-oxathiadiphosphetane*  $\begin{array}{ccc} & \mathrm{O} & \\ & / \ \backslash & \\ \mathrm{R(S)P} & & \mathrm{P(S)R} \\ & \backslash \ / & \\ & \mathrm{S} & \end{array}$ *has been isolated,* $C_{30}H_{46}OP_2S_3$*. X-ray structure analysis and mass spectroscopic investigations give unequivocal evidence for this structure: monoclinic, C2/c (no. 15),* $a = 13.066(8)$*,* $b = 21.726(8)$*,* $c = 12.070(6)$ *Å,* $\beta = 103.54(10)°$*,* $V = 3331$ *Å*^{3}*,* $Z = 4$*, and* $D_c = 1.158$ *g/cm*^{3}*. The asymmetric unit consists of half the formula unit. Solid-state* ^{31}P *NMR spectra give information about the chemical shift anisotropy. Results of IGLO calculations of the* ^{31}P *nuclear magnetic shielding tensor agree satisfactorily with the experimental data. Monitoring the reaction of several dithiadiphosphetanes with benzophenone in solution by* ^{31}P *NMR spectroscopy indicates that additional oxathiadiphosphetanes as well as thiotrimetaphosphonates are present.*

INTRODUCTION

^{31}P NMR solution spectra of dithiadiphosphetanes 1 show, besides the signals of *trans* and *cis* isomers at $\delta = 14–61$, almost constantly signals of low intensity at $\delta > 65$ [1]. For compounds with substituted aromatic groups R, often only one signal between $\delta = 66$ and 75 is observed. In some earlier articles [2,3], one signal in this range was erroneously assigned to the dithiadiphosphetane. The correct values for several dithiadiphosphetanes were given in a later publication [4].

In view of the chemical shift values, oligomeric perthiophosphonic acid anhydrides $(RPS_2)_n$, $n > 2$, and oxygen-containing phosphorus compounds can be supposed to be the origin of these signals. Such compounds are also discussed in connection with dithiadiphosphetanes in the literature. Based on results of kinetic investigations, Hahn et al. [5] assumed that a perthiophosphonic acid anhydride with $n = 4$ is involved in the *cis/trans* isomerization of dithiadiphosphetanes in solutions. A cyclic compound of the composition $(EtPOS)_n$ should be formed according to Kinnear and Perren [6] on treatment of $[EtP(S)S]_2$ with warm water. The attempt of Roesky and Bormann to prepare $(MePOS)_n$ according to this procedure failed. But the corresponding ethyl compound $[EtP(S)O]_3$ obtained by

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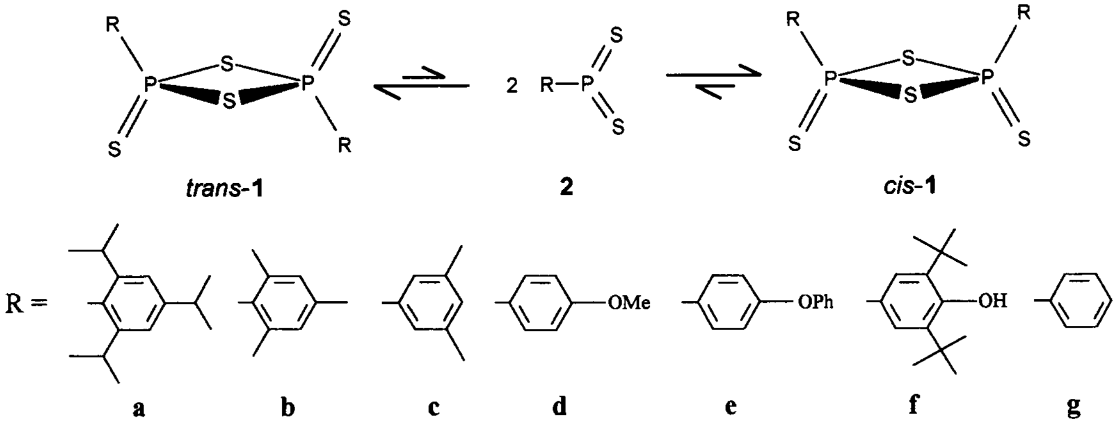


SCHEME 1

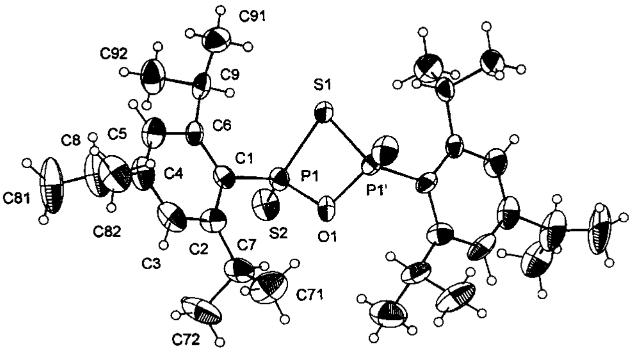


FIGURE 1 Molecular structure of 2,4-bis(2,4,6-tri-*iso*-propylphenyl)-2,4-dithioxo-1,3,2,4-oxathiadiphosphetane **3a**.

treating $EtP(O)Cl_2$ with H_2S [7] had the same melting point as the compound described in [6]. Scheibye et al. [8] and Pedersen and Lawesson [9] isolated and identified a 6-membered ring compound $[RP(S)O]_3$ from the reactions of β-ketoesters and β-ketoamides with $[RP(S)S]_2$ (R = *p*-$MeOC_6H_4$). The $^{31}P\{^1H\}$ NMR spectrum of this compound was of the AB_2 type and does not explain the observed singlet above 65 ppm.

In a previous article, we reported an investigation of the *cis*/*trans* isomerization reaction of dithiadiphosphetanes 1 via a dithioxophosphorane 2 [10] (see Scheme 1) on the example $(2,4,6\text{-}i\text{Pr}_3C_6H_2PS_2)_2$. Now our experiments have been focused on the side-product having $\delta = 66–75$ in reaction solutions of the dithiadiphosphetane synthesis and its separation for the structure elucidation. In the case of R = 2,4,6-$i\text{Pr}_3C_6H_2$ (a), the structure of this side-product 3 has been determined using different spectroscopic methods and X-ray diffraction analysis.

For other substituents R (b, c, d, e, f, g), the side-product 3 has been characterized by its ^{31}P chemical shift and the molar mass. In some cases, the reaction of 1 with benzophenone has been investigated by ^{31}P NMR spectroscopy in the NMR tube.

RESULTS AND DISCUSSION

Purification of the crude product obtained in the reaction of the organylphosphane RPH_2 (R = 2,4,6-$i\text{Pr}_3C_6H_2$) with sulfur yielded, in addition to *cis*- and *trans*-1a, a small quantity of an unknown compound (δ_P = 75.4, $CDCl_3$). In the $^{31}P\{^1H\}$-^{13}C satellite spectrum, the four outer lines of the AB part of an ABX spin system with the difference $\nu_A - \nu_B$ being very small were observed (J_{PP} = 14.2 Hz). The ^{13}C NMR spectrum run at ambient temperature showed broadened signals for all ^{13}C atoms not being situated on the C_1–C_4 axis of the phenyl ring. If the solution was cooled to 263 K, the rotation of the 2,4,6-$i\text{Pr}_3C_6H_2$ group around the P–C bond was frozen, and the formerly broad signals were split into two signals.

By high-resolution mass spectrometry, the molar mass of compound 3a was found to be in agreement with the molecular formula $C_{30}H_{46}OP_2S_3$ (Table 3) and with an oxathiadiphosphetane structure 3a [11]. Recently, Yoshifuji et al. described a similar oxathiadiphosphetane with R = 2,4-di-*tert*-butyl-6-methoxyphenyl [12].

X-Ray Structure Analysis

The oxathiadiphosphetane 3a crystallizes in the monoclinic centrosymmetric space group C2/c (no. 15) with four molecules per unit cell. The asymmetric unit consists of half the formula unit. Molecular structure and atomic labeling are shown in Figure 1. The molecule consists of a PSPO ring with the bulky organyl groups in the *trans* configuration. Thus, the isolated compound is a *trans*-2,4-dithioxo-1,3,2,4-oxathiadiphosphetane. There is a twofold rotation axis running through the atoms O1 and S1. Therefore, the second part of the molecule P'(S2')R' is generated by symmetry.

As in *trans*-dithiadiphosphetanes 1 (R = Ph,

TABLE 1 Selected Atomic Distances (Å), Bond Angles (°), and Torsion Angles (°) for **3a**

Distance		*Bond Angle*		*Torsion Angle*	
P1–O1	1.677(5)	P1–S1–P1′	78.4(2)	S2–P1–C1–C2	86.7
P1–S1	2.108(4)	P1–O1–P1′	105.3(5)	S2–P1–C1–C6	−92.4
P1–S2	1.893(4)	S1–P1–O1	88.2(3)	S1–P1–C1–C2	−136.6
P1–C1	1.818(9)	S2–P1–C1	115.1(3)	S1–P1–C1–C6	44.3
P1···P1′	2.666(5)	S1–P1–C1	111.8(3)	O1–P1–C1–C2	−42.2
		S1–P1–S2	117.0(2)	O1–P1–C1–C6	138.7
		S2–P1–O1	115.6(2)	S2–P1–O1–P1′	119.2
		O1–P1–C1	105.7(3)	S2–P1–S1–P1′	−118.0

Symmetry transformations for equivalent atoms: $-x, y, -z + 1/2$.

TABLE 2 Solid-State ^{31}P NMR Data of **3a** and Results of IGLO Calculations for **3a′**, R = 2,6-iPr$_2$C$_6$H$_3$[a] (Chemical Shifts and Shieldings in ppm)

	Chemical Shift or Shielding				*Angles between Principal Axes and the Dipolar Vector* **P···P** *[°]*	
Compound	δ_{iso}	σ_{11}	σ_{22}	σ_{33}	***3-P···P***	ϕ[b]
3a (CP MAS)	75.8	61	220	475		
3a (CP ECHO)	75.1	60	221	477	70–75	29–32
3a′ (DIGLO)	64.4	81	230	481	69.4	22.3
trans-**1a** (CP MAS)[c]	27.8	116	237	548		

[a] Experimental geometry of **3a** has been used.

[b] ϕ is the angle between the projection of the dipolar vector **P···P** on the plane of the principal axes *1* and *2* and the axis *1*.

[c] Data in Ref. [10] are similar.

2,4,6-Me$_3$C$_6$H$_2$, p-MeOC$_6$H$_4$) [13], the four-membered ring is planar. The endocyclic bond angles differ considerably from those in *trans*-1. Substitution of one ring sulfur atom by oxygen causes a decrease of the bond angle P1–S1–P1′ by nearly 10° while the S1–P1–O1 angle is about 5° smaller than S1–P1–S1′. The shorter P–O bond length leads furthermore to a shortening of the endocyclic and exocyclic P–S bonds. The tetrahedral surroundings of the P atom are strongly disturbed (see Table 1). Similar to *trans*-1 (R = 2,4,6-Me$_3$C$_6$H$_2$) [13b] and *cis*-1a [10], the phenyl ring is almost perpendicular to the S=P–C plane due to the bulky substituents in the *ortho*-position. The corresponding dihedral angle is 87.15°. Furthermore, the oxathiadiphosphetane is characterized by a short atomic P···P distance of 2.666 Å.

Solid-State NMR and IGLO Calculations

The ^{31}P CP MAS spectrum of the investigated crystalline product shows two sideband systems, a major system for the oxathiadiphosphetane 3a (80%) and a minor system for the *trans*-dithiadiphosphetane 1a (20%). The observed spinning frequency-dependent splitting of the sideband system of 3a is caused by dipolar interaction of the two P atoms. The chemical shift tensors of both P nuclei have different orientations since the molecule has no inversion center.

The static solid-state spectrum of the mixture of the two compounds is difficult to analyze. For that reason, the principal values of the ^{31}P shielding tensors in Table 2 must be characterized as estimated values.

IGLO calculations [14] of a model compound for 3a (where R = 2,6-iPr$_2$C$_6$H$_3$) using the experimental geometry of 3a show a good agreement between calculated principal values of the chemical shift tensor and experimental data (see Table 2). This allows the utilization of another result of these calculations, namely, the orientation of the principal axes *1*, *2*, and *3* in the molecular framework (see Figure 2). The angle *3*–P=S has a value of 17.1°, and therefore, the most shielded component is directed almost along the P=S bond. Hence, the basic orientation of the principal axes system of the nuclear magnetic shielding tensor of 3a is quite similar to those of the *trans*-dithiadiphosphetanes [MeP(S)S]$_2$ [15] and [MeSP(S)S]$_2$ [16], where the angle *3*–P=S amounts to 21.2° and 26.3°, respectively. While the two dithiadiphosphetanes possess a mirror plane (the S=P–C plane) with the principal axis *2* perpendicular to this plane, in the oxathiadiphosphetane 3a, the axis *2* deviates from the normal on the S=P–C plane by 9.7°.

The angles estimated from the static CP spec-

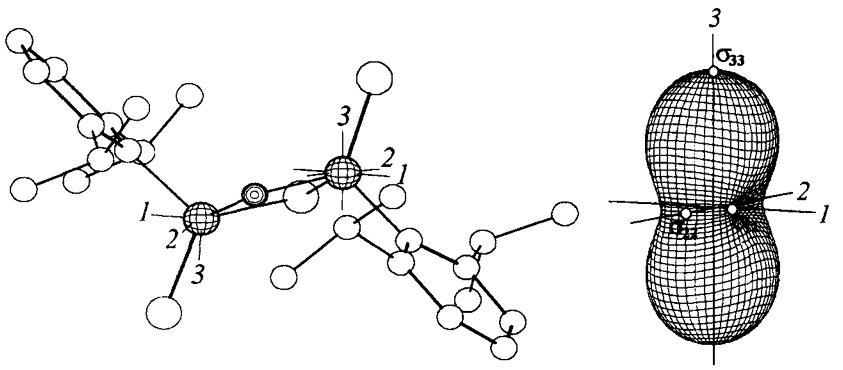
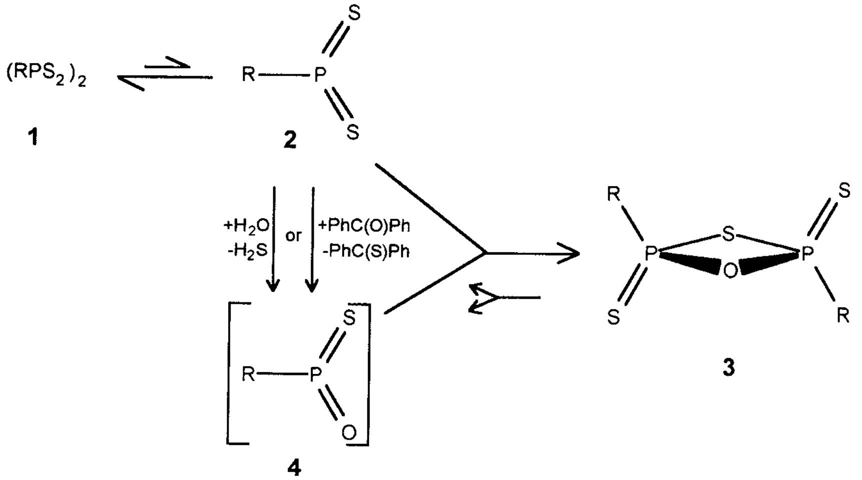


FIGURE 2 Orientation of the principal axes *1*, *2*, and *3* in the molecular framework calculated by the IGLO method and pictorial representation of the nuclear magnetic shielding tensor for the right P atom of the model compound *trans*-2,4-bis(2,6-di-*iso*-propylphenyl)-2,4-dithioxo-1,3,2,4-oxathiadiphosphetane.

SCHEME 2



trum (see Table 2) that describe the orientation of the dipolar vector P · · · P with respect to the principal axes system satisfactorily agree with the calculated values. On comparison of the principal values σ_{ii} of 3a and *trans*-1a, it becomes obvious that the substitution of one ring sulfur atom by oxygen causes a deshielding of σ_{11} and σ_{33}.

In Figure 2, furthermore, a pictorial representation of the nuclear magnetic shielding tensor as proposed by Radeglia [17] is given. This ovaloid describes the dependence of the nuclear shielding on the external magnetic field direction. The distance between the origin of the coordinate system (investigated nucleus) and any point on the ovaloid surface corresponds to the value of the measurable nuclear magnetic shielding in the chosen direction. If this direction coincides with one of the principal axes *1*, *2*, or *3*, then the shielding is equal to the principal value σ_{ii} of the tensor (marked by circles in Figure 2).

Formation of Oxathiadiphosphetanes

Monitoring of the reaction of dithiadiphosphetanes 1 with benzophenone by means of 1D ^{31}P NMR spectroscopy indicated the formation of oxathiadiphosphetanes, especially if dithiadiphosphetanes with bulky aryl substituents were used and benzophenone was applied in an amount lower than the stoichiometric ratio.

If a solution of *cis*-1a in *o*-dichlorobenzene was heated to about 353 K for 10 to 15 minutes, the other isomer *trans*-1a and the monomer 2a were formed. By cooling this solution to room temperature, the equilibrium between *cis*-1a and *trans*-1a and the monomer 2a was frozen, and the ratio of the three components was about 2:1:1. Furthermore, a signal of low intensity for the oxathiadiphosphetane 3a was observed due to a side reaction of 2a with water adsorbed on the surface of the glass devices (see Scheme 2).

If a few crystals of benzophenone were added and the solution was refluxed for 2 minutes, its color changed from yellow (due to the monomer) via green to blue (thiobenzophenone). In the ^{31}P NMR spectrum, the intensity of the monomer peak decreased, whereas the signal of the oxathiadiphosphetane increased significantly. We assume, in agreement with Yoshifuji et al. [12], that benzophenone reacts with the monomer 2a yielding thiobenzophenone and an intermediate oxothioxophosphorane R–P(S)(O) 4a that forms in a consecutive reaction with another molecule of 2a, the oxathiadiphosphetane 3a.

The existence of an equilibrium between the *cis* and *trans* dithiadiphosphetanes 1a and the dithioxophosphorane 2a was directly proved by 2D exchange ^{31}P NMR spectroscopy at 393 K, as described in a previous article [10]. While in this 2D spectrum, no exchange cross peaks of the oxathiadiphosphetane 3a were observed, in the 2D exchange ^{31}P NMR spectrum of a sample with R = mesityl measured at 393 K cross peaks between *cis* and *trans* dithiadiphosphetane 1b and the oxathiadiphosphetane 3b were present (δ = 71.7, *o*-dichlorobenzene) (see Figure 3). This can presumably be explained by a distinct dissociation of the oxathiadiphosphetane 3b, in comparison to 3a, giving the dithioxophosphorane 2b and the oxothioxophosphorane 4b (see Scheme 2). The reaction of two molecules of 2b yields either *cis*-1b or *trans*-1b. The equilibrium on the right in Scheme 2 should be almost completely changed to the side of the oxathiadiphosphetane 3b since it is not possible to prove the existence of such an oxothioxophosphorane 4b by ^{31}P solution NMR (δ is expected to be larger than 200) [18]. In the case of dithiadiphosphetane 1b, the cross peaks to 2b cannot

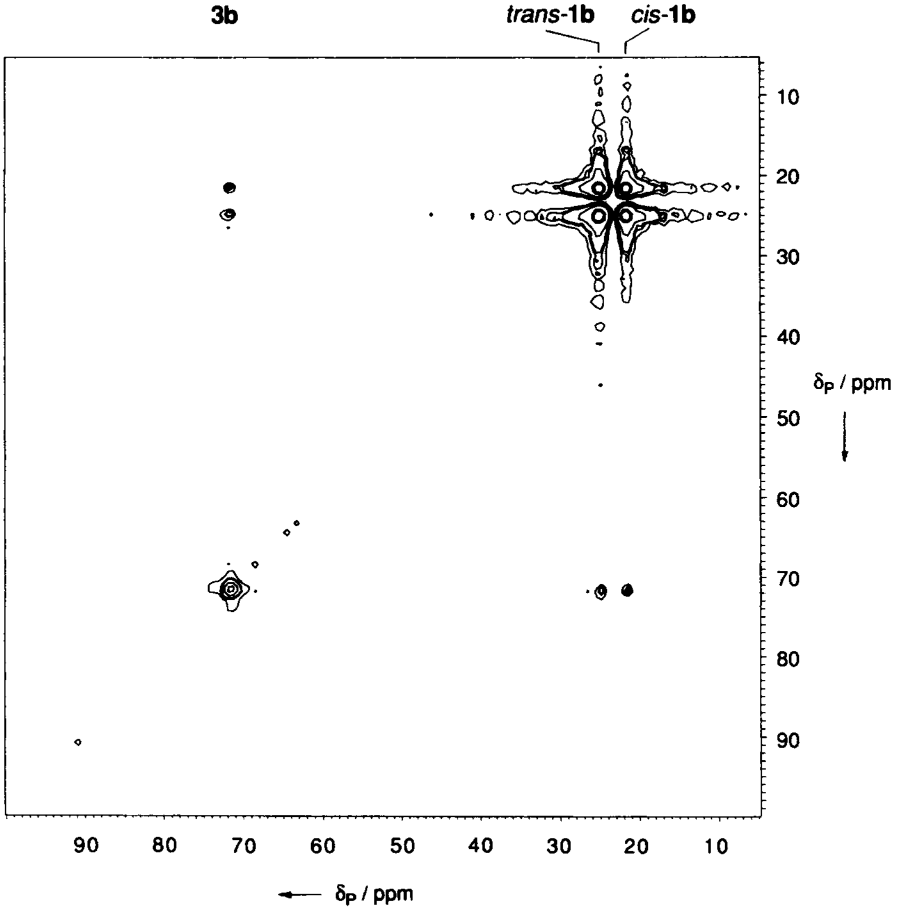
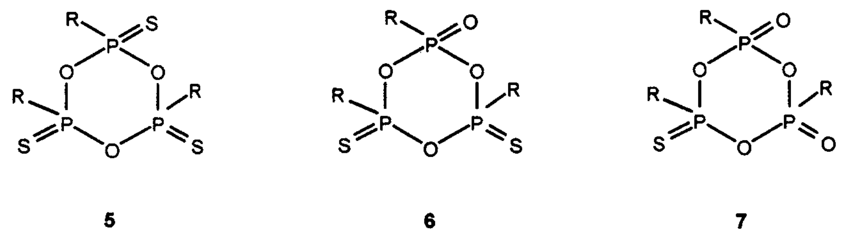


FIGURE 3 ^{31}P 2D exchange NMR spectrum of $(2,4,6\text{-}Me_3C_6H_2PS_2)_2$ **1b** in *o*-dichlorobenzene at 393 K. NOESY pulse sequence, τ_m = 500 ms, SI2 = 1 K, SI1 = 0.5 K spectrum, 70 Hz/pt, 1 hour. The final matrix was symmetrized prior to plotting.



SCHEME 31

TABLE 3 ^{31}P NMR and MS Data of Oxathiadiphosphetanes $[RP(S)]_2SO$ **3**

Comp.	*R*	*δp [ppm]*	*M [g mol⁻¹]* *exp.*	*calc.*
3a	$2,4,6\text{-}^i Pr_3C_6H_2$	75.4^a	580.223	580.2186
3b	$2,4,6\text{-}Me_3C_6H_2$	73.0 and 71.2^a	412.031	412.0308
3c	$3,5\text{-}Me_2C_6H_3$	66.1^b	384.002	383.9995
3d	$p\text{-}MeOC_6H_4$	68.9^a	387.959	387.9580
3e	$p\text{-}PhOC_6H_4$	68.1^a	511.991	511.9893
3f	$3,5\text{-}^t Bu_2\text{-}4\text{-}HOC_6H_2$	71.6^a	584.180	584.1771
	$2,4\text{-}^t Bu_2\text{-}6\text{-}MeOC_6H_2$^{c}	74.8^a		

[a] Solution in $CDCl_3$.
[b] Solution in *o*-dichlorobenzene.
[c] Ref. [12].

be observed since, at this temperature, the concentration of **2b** is too low, leading to a broad signal.

By reaction of other dithiadiphosphetanes with benzophenone, some oxathiadiphosphetanes can be assigned (Table 3). In general, only one isomer is observed; because of the short distance between the phosphorus atoms the *trans* arrangement of the organyl groups is more likely. However, in the case of the mesityl compound, a second signal is observed, probably arising from the *cis* isomer.

On increasing the quantity of benzophenone added, further signals besides that of the oxathiadiphosphetane become obvious. They are caused by the presence of different linear and cyclic compounds with two or more P atoms where either two or three oxygen atoms are attached to each P atom. For some of the cyclic compounds (see Table 4), the structures can be assigned by consideration of ^{31}P chemical shift values and P–P coupling constants. Different spin systems arising from compounds 5, 6, and 7 are observed (Scheme 3).

Dithiadiphosphetanes 1 with sterically less demanding substituents such as phenyl, *p*-methoxyphenyl and *m*-xylyl give these products even after addition of small amounts of benzophenone, whereas products of the constitution **5a** and **6a** have not been observed. In the case of alkyldithiadiphosphetanes, we were not able to confirm the formation of the corresponding oxathiadiphosphetanes.

Oxathiadiphosphetanes were also detected as impurities in the mass spectra of several dithiadiphosphetanes (see Table 3). The origin of peaks at M-16 (intensity less than 3% of M) in the mass spectra of dithiadiphosphetanes with the molar mass M is still unknown, although their chemical composition is quite clear. Van der Knaap and Bickelhaupt [19] have described such peaks, and they assigned them to ions of the composition [M–S + O]. We believe that such a quasi-trimolecular reaction is not very probable in the ion source of a mass spectrometer, especially under the CI conditions (high excess of CH_5^+ ions in the positive ion mode or of CH_4 molecules and low-energy electrons in the negative ion mode) chosen in our experiments. It is more likely that the oxathiadiphosphetanes are formed in a reaction of dithiadiphosphetanes with traces of water, as already described by Moedritzer [20]. The formation of oxathiadiphosphetanes when dissolving dithiadiphosphetanes in (not extremely) dry solvents supports this assumption.

EXPERIMENTAL

Reaction of 2,4,6-tri-iso-Propylphenylphosphane with Sulfur. To a suspension of 6.18 g (24.1 mmol) S_8 in 200 mL toluene, 15.0 g (64.4 mmol) of 2,4,6-$iPr_3C_6H_2PH_2$ in 100 mL toluene was added slowly. After 2 hours of refluxing, the solution was cooled, and the solvent was partially removed under vacuum. To the residue, 150 mL of acetonitrile was added, and the microcrystalline white precipitate that had formed was separated by filtration, washed with acetonitrile, and dried under vacuum (13.0 g crude product). Repeated extraction of the crude product with toluene gave pure *trans*-**1a**, whereas a crystalline product containing 80% **3a** and 20% *trans*-**1a** was obtained from the toluene extract after addition of acetonitrile.

3a, $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 75.2, $^2J_{PP}$ = 14.2 Hz; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 263 K) δ 134.0 ($^1J_{PC}$ = 114.5 Hz, $^3J_{PC}$ = 4.2 Hz, C1), 149.0, 148.5 (C2, 6), 122.9, 122.6 (C3, 5), 153.1 (C4), 33.6, 31.6 (C7, 9), 34.2 (C8), 24.8, 24.0, 23.7, 23.7, 23.6, 23.1 (6 CH_3).

A single crystal of **3a** suitable for X-ray work was obtained by recrystallization from benzene/acetonitrile.

Preparation of the Dithiadiphosphetanes. All compounds were synthesized according to known procedures. The reaction of 2,4,6-$Me_3C_6H_2PH_2$ with S_8 yielded **1b** [10]. Reactions of 3,5-$Me_2C_6H_3P(S)Cl_2$ and $PhP(S)Cl_2$ with H_2S gave **1c** and **1g**, respectively [21]. The other dithiadiphosphetanes were obtained from reactions of P_4S_{10} with the corresponding aromatic compounds: **1d**, $MeOC_6H_5$ [22]; **1e**, $PhOC_6H_5$ [23]; and **1f**, 2,6-$t$$Bu_2$-$HOC_6H_3$ [24].

NMR Experiments. ^{31}P and ^{13}C NMR spectra were measured at spectrometer frequencies of 121.5 and 75.5 MHz, respectively, using a Bruker MSL 300

TABLE 4 ^{31}P NMR Data of Thiotrimetaphosphonates **5–7** (Solvent *o*-Dichlorobenzene)

Comp.	Spin System	R	*δ [ppm]*				*J [Hz]*				
			P_A	P_B	P_X	P_Y	P_AP_B	P_AP_X	P_BP_X	P_AP_Y	P_XP_Y
5b	AB_2	2,4,6-$Me_3C_6H_2$	64.2	63.0			52.2				
5c		3,5-$Me_2C_6H_3$	73.8	70.8			52.9				
5d		*p*-$MeOC_6H_4$[a]	73.3	71.1			49.3				
5g		Ph	72.6	70.0			51.3				
6b	A_2X	2,4,6-$Me_3C_6H_2$	67.2		0.2			40.7			
6d		*p*-$MeOC_6H_4$	71.1		3.1			43.8			
6g		Ph	70.2		1.8			44.4			
6b	ABX	2,4,6-$Me_3C_6H_2$	65.0	63.7	−1.5		62.0	44.5	37.8		
6c		3,5-$Me_2C_6H_3$	74.1	71.7	1.4		53.7	46.4	37.8		
6d		*p*-$MeOC_6H_4$	73.7	71.9	2.6		50.7	44.2	32.2		
6g		Ph	73.0	70.9	1.4		51.3	45.2	32.9		
7b	AX_2	2,4,6-$Me_3C_6H_2$	66.1		−1.9			50.9			
7b	AXY	2,4,6-$Me_3C_6H_2$	67.4		1.0	−0.1		38.2		48.4	35.5

[a] Ref. [9].

TABLE 5 Crystal Data and Structure Refinement for **3a**

Formula	$C_{30}H_{46}OP_2S_3$
Formula weight	580.8
Radiation	MoKα (λ = 0.71073 Å)
Crystal system	monoclinic
Space group	C2/c (no. 15)
Unit cell dimensions a α	13.066(8) Å 90.00°
b β	21.726(8) Å 103.54(10)°
c γ	12.070(6) Å 90.00°
Volume	3331 Å^3
Z	4
Density (calc.)	1.158 g/cm^3
Absorption coefficient	0.34 mm^{-1}
Crystal size	0.25 × 0.2 × 0.1 mm
Scan type	ω-scan 4.0 + 0.35 tgθ
θ-range	$1 < \theta < 32°$
Index range	$-10 \leq h \leq 5$; $0 \leq k \leq 20$; $-5 \leq l \leq 10$
Reflections collected	5374
Independent reflections	2011
Observed reflections $F_0 > 4\sigma(F_0)$	871
Number of parameters refined	165
Final R indices	R1 = 0.0818; wR2 = 0.2161
Largest difference peak and hole	0.22 e/Å^3; −0.29 e/Å^3

spectrometer. For temperature-controlled measurements, the temperature control unit B-VT 1000 was used. Solid-state ^{31}P NMR spectra were acquired by the cross polarization (CP) technique and magic angle spinning (MAS) of the sample at frequencies between 2.5 and 4 kHz. The MAS spectra were analyzed using the programs MASNMR and WINMAS [25]. Static CP ^{31}P NMR spectra were acquired by a Hahn spin-echo experiment. The spectra were evaluated according to the dipolar splitting ratio method [26] (the different orientations of the principal axes systems of both P nuclei have been neglected; due to overlap of the spectra of 3a and *trans*-1a, the exact analysis is not useful). The principal values of the chemical shift tensor were obtained with a standard deviation of 5 ppm. The ^{31}P chemical shifts were converted to shieldings using the data of Jameson et al. [27], $\sigma(^{31}P) = 328$ ppm $-\delta(^{31}P)$. The data are reported following the convention $\sigma_{33} \geq \sigma_{22} \geq \sigma_{11}$. The isotropic chemical shift is given by $\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$.

Mass Spectrometry. Electron impact (EI) and direct chemical ionization (DCI) mass spectra were recorded on a Finnigan MAT 95 mass spectrometer. The DCI mass spectra were obtained using methane in the positive as well as in the negative ionization mode. The DCI wire was heated linearly from 25 to 1500°C over a 3-minute period. Spectra were taken every 5 seconds. In the case of the high-resolution EI spectra, the resolution power was about 5000. For the determination of the exact masses by peak matching, perfluorokerosene was used as the mass standard.

IGLO Calculation. The calculations were performed using the experimentally determined atomic coordinates of 3a and replacing the *iso*-propyl group in the *para* position by a hydrogen atom. First, the electronic ground state was calculated with the TURBOMOLE package [28]. The ^{31}P shielding tensors were calculated with the direct IGLO program (DIGLO) [29] using the following Huzinaga basis sets [30]: [3s]/(2s) for H, [7s 3p]/(4s 2p) for C, [9s 5p 1d]/(5s 4p 1d) for O, [11s 7p 2d]/(7s 6p 2d) for P and S (with the d exponents 1.0 for O, 1.40; 0.35 for P, and 1.60; 0.40 for S).

X-ray Diffraction Analysis. A single crystal of 3a suitable for X-ray diffraction was selected using a polarization microscope, placed in a glass capillary and measured on an Enraf-Nonius four-circle CAD4 diffractometer with graphite-monochromated MoKα radiation at ambient temperature (294 K). The monoclinic lattice constants were determined using the automatic search routine of the CAD4 diffractometer (centering and indexing nine reflections in the range 2θ = 13°–26°). Despite the high quality of the crystal, the reflections showed very broad and asymmetric profiles independent of the crystallographic orientation. Two data sets in the $\omega/2\theta$ and the ω mode were measured. However, only one set (ω mode) gave elucidative intensity data. The experimental data were Lp corrected using XCAD4 [31]. The space group was determined by reflection conditions. For two space groups, the structure could be solved and refined (noncentrosymmetric space group Cc: R1 = 0.066; centrosymmetric space group C2/c: R1 = 0.082). Despite the better R value for the acentric space group Cc (no. 9) especially, the geometric arrangement of the phenyl rings shows large deviations from the usual one. Standard deviations of bond lengths and bond angles are larger, and furthermore, it is not possible to determine the absolute configuration for the noncentrosymmetric structure. Despite the unusual broad scan angle (4.0 + 0.35 tgθ), the structure solution by direct methods with SHELXS86 [32] gave appropriate atomic coordinates for the whole molecule. Atomic coordinates and anisotropic temperature factors of the nonhydrogen atoms were refined using SHELXL93 [33]. The hydrogen atoms have been calculated in idealized positions. Details of data collection and refine-

TABLE 6 Fractional Atomic Coordinates and Equivalent Isotropic Temperature Factors for Nonhydrogen Atoms of **3a**. Atoms S1 and O1 on Special Positions **4e**

Atom	x	y	z	U_{eq} [Å^2]
P1	0.07425(18)	0.33834(11)	0.19079(21)	0.054(1)
S1	0	0.26316(15)	1/4	0.071(1)
S2	0.05581(22)	0.34593(14)	0.03105(23)	0.086(1)
O1	0	0.38520(37)	1/4	0.059(2)
C1	0.2085(7)	0.3488(4)	0.2735(7)	0.054(3)
C2	0.2420(8)	0.4089(4)	0.3050(8)	0.066(3)
C3	0.3441(9)	0.4149(5)	0.3730(9)	0.086(4)
C4	0.4099(9)	0.3657(7)	0.4083(9)	0.084(4)
C5	0.3754(8)	0.3086(6)	0.3706(9)	0.080(3)
C6	0.2742(7)	0.2983(4)	0.3020(7)	0.051(3)
C7	0.1793(9)	0.4656(5)	0.2615(10)	0.088(4)
C71	0.1496(10)	0.5027(5)	0.3578(12)	0.135(5)
C72	0.2366(10)	0.5071(5)	0.1935(12)	0.146(6)
C8	0.5204(10)	0.3774(8)	0.4807(13)	0.137(6)
C81	0.5985(10)	0.3842(9)	0.4280(14)	0.186(9)
C82	0.5205(9)	0.3957(6)	0.5962(10)	0.117(5)
C9	0.2467(7)	0.2325(4)	0.2630(9)	0.062(3)
C91	0.2443(8)	0.1900(5)	0.3634(10)	0.093(4)
C92	0.3221(8)	0.2097(5)	0.1929(11)	0.110(4)

ment are given in Table 5, final atomic coordinates in Table 6.

Supplementary material is available by referring to CSD-No. 401815, names of the authors, and citation of the article at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Federal Republic of Germany.

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