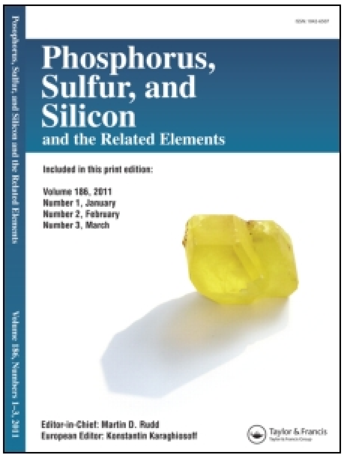

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CRYSTAL STRUCTURE, SOLID-STATE NMR, AND QUANTUM CHEMICAL MODEL CALCULATIONS OF BIS-(DIETHOXYTHIOPHOSPHORYL)-TRISULFANE

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CRYSTAL STRUCTURE, SOLID-STATE NMR, AND QUANTUM CHEMICAL MODEL CALCULATIONS OF BIS-(DIETHOXYTHIOPHOSPHORYL)-TRISULFANE

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Crystals of $(EtO)_2P(S)SSSP(S)(OEt)_2$ are triclinic, $P\bar{1}$, with a = 8.388(1), b = 11.128(2), c = 12.518(1) Å, α = 62.34(6), β = 71.93(2), γ = 84.97(5)°, V = 981.6(6) Å^3, Z = 2, and D_c = 1.36 g/cm^3. The final refinement using 3681 observed reflections for 252 variables gives R = 0.057. The two molecules in the elementar cell are conformation enantiomers.

The ^{31}P CP MAS spectra show two spinning sideband systems, because the two phosphorus atoms of one molecule are chemically nonequivalent in the crystal. The resolution in the ^{13}C CP MAS spectrum allows to distinguish four lines for the methyl groups and three lines for the methylene groups.

NDDO and INDO calculations show, that the conformations with dihedral angles PSSS of ca. 90° have the lowest energies and those with 180 or 0° have considerably higher energies. The relatively high coupling constants $^4J_{PP}$ of bis-(dialkoxythiophosphoryl)-trisulfanes in solution are not caused by conformations with W-like or other plane positions of the PSSSP nuclei.

Key words: Crystal structure; CP MAS NMR; chemical shift anisotropy; quantum chemical calculations; dithiophosphoric; thiophosphoryl trisulfane.

INTRODUCTION

NMR investigations[1,2] of solutions of bis-(dialkoxythiophosphoryl)-trisulfanes show relatively large coupling constants $^4J_{PP}$ ranging from +10 to +13 Hz. It was assumed that a conformation with W-like or an other plane structure of the PSSSP nuclei plays an important role in solution.

For trisulfane analogous compounds with a PSXSP chain (X = Se, Te) it is possible to calculate torsion angles applying the data published by Refaat, Maartmann-Moe und Husebye.[3,4] The torsion angles P1-S1-Se-S2 and P2-S2-Se-S1 are 88.0° and 88.78°, respectively. In case of the tellurium analogous compound these torsion angles are 82.9° and 91.1°. We have investigated the crystal and molecular

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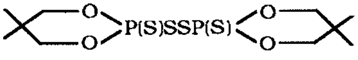
structure of bis-(diethoxythiophosphoryl)-trisulfane (**1**) representing a compound with a PSSSP chain.

In crystalline bis-(dialkoxythiophosphoryl)-disulfanes, $(RO)_2P(S)SSP(S)(OR)_2$, different PSSP torsion angles occur. For R = *i*Pr and *neo*Pe angles[5,6] of 180° were obtained, while for R = Me 105.7° is published[7] and for



89.7° was obtained.[8]

Solid-state CP MAS NMR spectra should show the non-equivalence of the two phosphorus atoms and the four ethyl groups in one molecule of **1** as it was obtained by crystal structure investigation. Additionally the ^{31}P spectra provide some information concerning the chemical shift anisotropy.

Semiempirical quantum chemical calculations were performed to find out if other conformers than those determined in the crystalline state, especially conformers with plane structure of the PSSSP chain, probably exist in solution. Model compound of our calculations was an isolated molecule $(MeO)_2P(S)SSSP(S)(OMe)_2$ **2**. This approximation is permitted since the same value of $^4J_{PP}$ (10.5 Hz)[1] has been measured for **1** and **2** in $CDCl_3$. Using a model geometry for **2** on the base of the crystal structure of **1** conformation energies and coupling constants $^4J_{PP}$ for **2** were calculated by means of NDDO[9] and INDO[10] methods.

RESULTS AND DISCUSSION

Molecular and Crystal Structure

The molecular structure and the atomic numbering of the compound **1** is shown in Figure 1. Bond distances and bond angles are given in Table I, torsion angles in Table II.

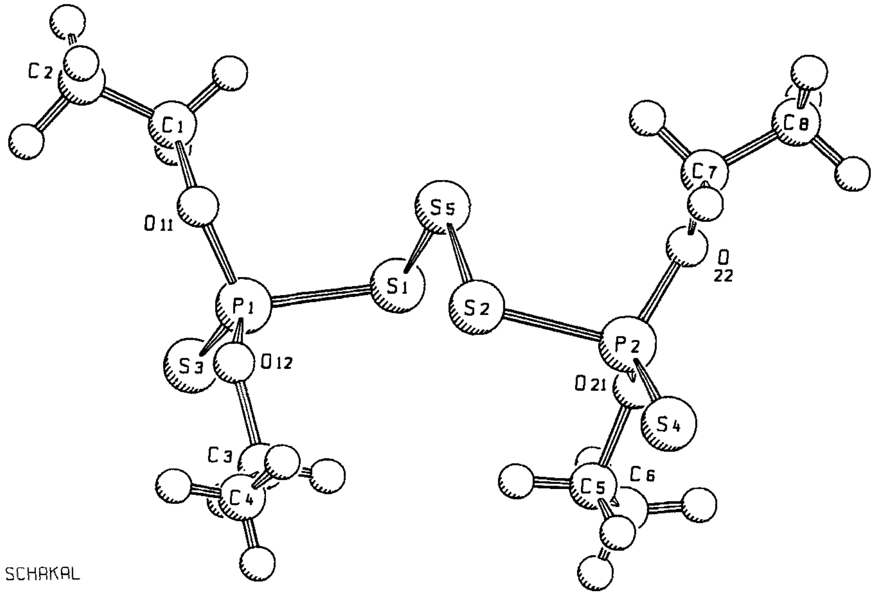


FIGURE 1 Molecular structure of bis-(diethoxythiophosphoryl)-trisulfane **1**

TABLE I
Bond lengths (Å) and bond angles (deg.)

Atoms	Distance	Atoms row	Angle
S(1)–P(1)	2.098(2)	S(1)–S(5)–S(2)	107.4(1)
S(2)–P(2)	2.100(2)	P(1)–S(1)–S(5)	103.2(1)
S(3)–P(1)	1.906(2)	P(2)–S(2)–S(5)	103.8(1)
S(4)–P(2)	1.912(2)	S(1)–P(1)–S(3)	106.4(1)
S(1)–S(5)	2.060(1)	S(2)–P(2)–S(4)	105.7(1)
S(2)–S(5)	2.059(1)	S(1)–P(1)–O(11)	108.6(1)
P(1)–O(11)	1.561(2)	S(1)–P(1)–O(12)	106.2(1)
P(1)–O(12)	1.579(2)	S(2)–P(2)–O(21)	107.5(1)
P(2)–O(21)	1.565(2)	S(2)–P(2)–O(22)	108.6(1)
P(2)–O(22)	1.557(2)	S(3)–P(1)–O(11)	119.2(1)
O(11)–C(1)	1.449(4)	S(3)–P(1)–O(12)	119.1(1)
O(12)–C(3)	1.455(4)	S(4)–P(2)–O(21)	119.0(1)
O(21)–C(5)	1.468(4)	S(4)–P(2)–O(22)	118.8(1)
O(22)–C(7)	1.453(4)	P(1)–O(11)–C(1)	123.7(3)
C(1)–C(2)	1.397(6)	P(1)–O(12)–C(3)	121.4(3)
C(3)–C(4)	1.466(6)	P(2)–O(21)–C(5)	121.2(3)
C(5)–C(6)	1.470(6)	P(2)–O(22)–C(7)	122.3(3)
C(7)–C(8)	1.418(6)	O(11)–C(1)–C(2)	111.8(4)
		O(12)–C(3)–C(4)	108.2(4)
		O(21)–C(5)–C(6)	107.2(4)
		O(22)–C(7)–C(8)	111.1(4)

The P1-S1-S5-S2-P2 chain can be described as trans form with the two phosphorus atoms on opposite sides of the central S_3 plane. The torsion angles P1-S1-S5-S2 and P2-S2-S5-S1 are 86.5° and 86.9°, respectively. These values are in good agreement with the analogous selenium and tellurium compound.

In each diethydithiophosphate group a P—S single bond and a P═S double bond are present. For the double bonds lengths of 1.906(2) Å (P1-S3) and 1.912(2) Å (P2-S4) are found. The sum of the covalent radii[11] $P(sp^3)$—$S(sp^2)$ gives a value of 1.85 Å. The mean value for the P—S-single bonds is 2.099 Å and in a good agreement with the expected value for a $P(sp^3)$—$S(sp^3)$ bond of 2.02 Å. The average P—O, C—O, and C—C bond lengths are 1.556 Å, 1.456 Å and 1.438 Å, respectively, within in close to the corresponding values found in the analogous selenium and tellurium compounds.[3,4]

The central S5 atom is weakly bonded to two sulfur atoms in two neighbouring molecules. The molecules are related to another by a center of symmetry, they are conformational enantiomeres. The distances S5. . . S1 are 3.611 Å (S1: $1 - x$, $-y$,

TABLE II

Torsion angles (deg.)

Nr.	Atoms row	Angle	Nr.	Atoms row	Angle
1	P(1)–S(1)–S(5)–S(2)	86.5(1)	13	P(1)–O(11)–C(1)–C(2)	138.1(8)
2	S(1)–S(5)–S(2)–P(2)	86.9(1)	14	P(1)–O(12)–C(3)–C(4)	- 178.2(7)
3	S(5)–S(1)–P(1)–S(3)	- 173.6(1)	15	P(2)–O(21)–C(5)–C(6)	- 172.0(8)
4	S(5)–S(2)–P(2)–S(4)	- 172.7(1)	16	P(2)–O(22)–C(7)–C(8)	149.9(8)
5	S(3)–P(1)–O(11)–C(1)	-42.7(4)	17	O(11)–P(1)–O(12)–C(3)	176.3(4)
6	S(3)–P(1)–O(12)–C(3)	47.8(4)	18	O(12)–P(1)–O(11)–C(1)	- 171.1(5)
7	S(4)–P(2)–O(21)–C(5)	48.9(4)	19	O(21)–P(2)–O(22)–C(7)	179.3(5)
8	S(4)–P(2)–O(22)–C(7)	-52.4(4)	20	O(22)–P(2)–O(21)–C(5)	177.1(5)
9	S(1)–P(1)–O(11)–C(1)	79.4(4)	21	O(11)–P(1)–S(1)–S(5)	-44.1(2)
10	S(1)–P(1)–O(12)–C(3)	-72.2(4)	22	O(12)–P(1)–S(1)–S(5)	58.5(5)
11	S(2)–P(2)–O(21)–C(5)	-71.0(4)	23	O(21)–P(2)–S(2)–S(5)	59.3(2)
12	S(2)–P(2)–O(22)–C(7)	68.3(4)	24	O(22)–P(2)–S(2)–S(5)	-44.2(2)

$-z$) and S5. . .S2, 3.701 Å (S2: $-x$, $-y$, $-z$), respectively. It is remarkable, that in the analogous compounds with selenium and tellurium these intermolecular distances are significantly shorter. The values for the selenium containing compound are 3.342 and 3.523 Å and for the tellurium containing 3.20 and 3.54 Å.

In solution the two molecules of **1** being different in the crystal lattice are related by conformational motions around the S1-S5 and the S5-S2 bonds.

CP MAS NMR

The ^{31}P CP MAS spectrum of **1** shows two spinning sideband systems with central lines at 83.2 and 85.3 ppm (Figure 2). This two isotropic chemical shifts are expected, because the crystallografic data show the chemical nonequivalence of the two phosphorus atoms in one molecule. This fact will be quite evident by comparison of torsion angles 5 and 8, 9 and 12 as well as 13 and 16, which would possess in pairs the same value in the case of chemical equivalence. The mean value of the both isotropic chemical shifts agree very well with the chemical shift (84.1 ppm) measured in solution.[1]

Consideration of the side band intensities allows the determination of the tensor principal values of the chemical shift anisotropy. The anisotropy data were computed according to Herzfeld and Berger[12] by the MASNMR[13] program for IBM PC/AT, which is applicable for spectra of format of the BRUKER program WIN-NMR. By means of the absolute chemical shift of PH_3 determined by Jameson *et al.*[14] the absolute nuclear magnetic shielding can be calculated according to $\sigma_i = 328 - \delta_i$. In this scale the principal values of the shielding tensors are

for P1 with $\delta_{iso} = 83.2$ ppm: $\sigma_{11} = 136$ $\sigma_{22} = 233$ $\sigma_{33} = 365$ ppm and
for P2 with $\delta_{iso} = 85.3$ ppm: $\sigma_{11} = 138$ $\sigma_{22} = 238$ $\sigma_{33} = 352$ ppm.

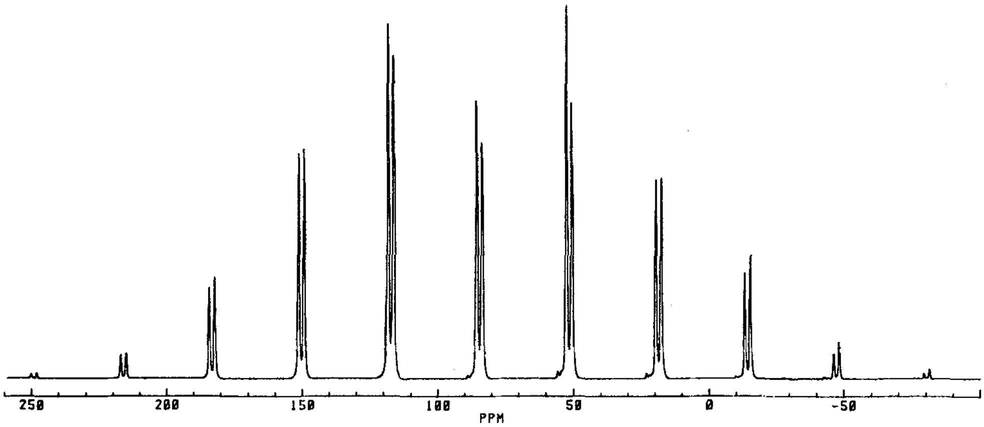


FIGURE 2 Solid-state ^{31}P CP MAS spectrum of bis-(diethoxythiophosphoryl)-trisulfane **1** at a spinning rate of 4.0 kHz

The assignment of these values to P1 and P2 is not possible. The coupling constant $^4J_{PP}$ = 10.5 Hz[1] determined in solution cannot be observed in the solid state because of line widths of 70 Hz.

Comparing the tensor principal values with the values of other P=S compounds[15] the conclusion may be drawn that principal axis 3 almost coincides with the P=S bond axis. For more information concerning the position of the principal axes in the molecular frame can be achieved by quantum chemical calculations of the nuclear magnetic shielding or by single crystal NMR investigations.

A ^{13}C CP MAS spectrum shows the following isotropic chemical shifts δ_{iso}:

OCH_2	64.9,	65.5,	and 65.9 ppm (with double intensity) and
CH_3	16.6,	16.8,	17.0 and 17.5 ppm.

Thereby the chemical nonequivalence of four ethyl groups of one molecule determined by crystal structure analysis is also reflected by ^{13}C solid-state NMR data.

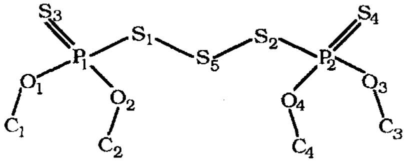
Semiempirical Quantum Chemical Calculations

For the NDDO and INDO calculations a program system by Nieke and Reinhold[16] was used. Concerning the parametrization different sets have been tested:

1. sp basis set with CNDO standard parameters,[9,17,18] labeled NDDO-SP or INDO-SP
2. spd′ basis set for phosphorus and sulfur with modified parameters[19] and optimized orbital exponents,[20–22] labeled NDDO-SPD′.

The calculation of $^4J_{PP}$ was performed on the INDO level using a simple approximation of Pople and Santry.[22] This sum over states method has been shown to be useful in getting trend statements for the values of coupling constants. Examples may be found in papers published by Kowalewski.[24,25] For the determination of the required exitation energies Coulomb and exchange integrals were taken into consideration. Due to former investigations[26,27] the calculation of P—P coupling constants was restricted to the sp basis set. Bond lengths and bond angles for molecule **2** have been taken from the molecular structure analysis of **1**. Instead of the experimental measured dihedral angles S═P—S—S of 172.7° and 173.6° for **1**, after some test calculations a dihedral angle of 180° was used. The methyl protons were fixed in ideally staggered partial conformation.

Six torsion angles were varied during the calculations:



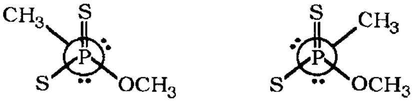
$\varphi_1 = \angle P_1S_1S_5S_2$ $\quad\varphi_3 = \angle S_4P_2O_3C_3$ $\quad\varphi_5 = \angle S_3P_1O_1C_1$

$\varphi_2 = \angle S_1S_5S_2P_2$ $\quad\varphi_4 = \angle S_4P_2O_4C_4$ $\quad\varphi_6 = \angle S_3P_1O_2C_2$.

For the partial conformation of the PSSSP main chain torsion angles φ_1 and φ_2 of 0°, 90° and 180° have been selected. The various combinations of these angles have been used in the calculations. According to the experimental results for the S═P—O—C dihedral angles from 43° to 52° in **1**, ideal gauche arrangements of the methyl groups to $S_{3(4)}$ were used as starting point. Two different gauche arrangements have been taken into account:

—The methyl group has trans position with respect to the second methoxy group on the P atom (**gO**), torsion angles S═P—O—C are 51,7 or −51,7° or

—the methyl group has trans position with respect to S1 or S2 (**gS**), torsion angles S═P—O—C are 59,4° or −59,4°.



gO **gS**

Four different combinations of these arrangements may occur on one phosphorus atom

gS/gS = A **gO/gS** = C
gO/gO = B **gS/gO** = D.

The torsion angles for some of the conformations X/Y with X, Y = *A*, *B*, *C* or *D* being taken into account in the calculations, will be given below:

B/B with $\varphi_3 = 51.7°$, $\varphi_4 = -51.7°$, $\varphi_5 = -51.7°$ and $\varphi_6 = 51.7°$,
D/D with $\varphi_3 = 59.4°$, $\varphi_4 = 51.7°$, $\varphi_5 = 51.7°$ and $\varphi_6 = 59.4°$,
C/B with $\varphi_3 = -59.4°$, $\varphi_4 = -51.7°$, $\varphi_5 = -51.7°$ and $\varphi_6 = 51.7°$,
C/D with $\varphi_3 = -59.4°$, $\varphi_4 = -51.7°$, $\varphi_5 = 51.7°$ and $\varphi_6 = 59.4°$.

The energies of more than 20 selected conformations φ_1/φ_2; X/Y were calculated, in further cases other combinations of φ_1 bis φ_6 were used too. In special cases the energy was minimized as a function of molecular geometry.

For the following partial conformations the calculations lead to especially high total energies:

—φ_1 or φ_2 are equal to 0° and
—φ_3 to φ_6 were so selected, that at least one partial conformation A occurs.

Concerning the sequence of the total energy within a group of favourable conformations the different approximation levels of the calculation methods lead to different results. In Table III the relative energies are summarized for some of the selected conformations, which have been chosen from the 19 most favourable conformations.

In the NDDO-SP calculations mainly the arrangement of the methoxy groups governs this sequence, the arrangement of the main chain has only less influence. The conformation, which is comparable to the molecular structure of **1** (NP18), is higher in total energy than the most favourable of the selected conformations (NP1). By optimization of molecular geometry (see Table IV) a global minimum of the total energy E_{tot}(NDDO-SP) was probably found for the conformation NPO1, which is nearly adequate to the partial conformation NP1.

In contrast to the results above, NDDO-SPD′ calculations show an essential influence of the arrangement of the main chain in the relative energy sequence of the conformations. With constant position of the methoxy groups we have found:

$$E_{90/90^\circ} < E_{180/90^\circ} < E_{180/180^\circ} < E_{180/0^\circ}.$$

Planar arrangements of the PSSSP main chain seem to be clearly unfavourable. Therefore we assume, that these arrangements also in solutions of **1** and **2** or of other trisulfanes have no importance and that relatively high coupling constants $^4J_{\text{PP}}$ are not caused by such conformations. Concerning the position of the methoxy groups with constant arrangement of the main chain the following sequence has been observed:

$$E_{\text{B/B}} < E_{\text{B/D}} = E_{\text{D/B}} < E_{\text{B/C}} = E_{\text{C/B}} < E_{\text{D/D}} < E_{\text{C/D}} = E_{\text{D/C}} < E_{\text{C/C}}$$

The conformation ND1, which adequates the molecular structure of **1**, has been found to have the lowest total energy in this calculations. We assume, that NDDO-SPD′ calculations because of the greater basis set are more useful to reflect the reality. But the energetic splitting of the conformations will be clearly overestimated. Using optimization of molecular geometry we have found a minimum of total energy for the conformation NDO1, which nearly adequates the partial conformation ND1. To prove the global minimum in NDO1, much more time consuming calculations with other starting parameter have to be considered.

According to the INDO-SP calculations the same conclusions as in the NDDO-SPD′ calculations may be drawn concerning the arrangement of the PSSSP main chain (see Table III). For the position of the methoxy groups with constant arrangement of the main chain the following sequence in total energy is obtained:

$$E_{\text{D/D}} < E_{\text{C/D}} = E_{\text{D/C}} < E_{\text{C/C}} < E_{\text{B/C}} = E_{\text{C/B}} < E_{\text{B/D}} = E_{\text{D/B}} < E_{\text{B/B}}$$

However the conformation IP8, which is comparable to the crystal structure **1**, is found to be 8.5 kJ/mol higher in energy than the conformation IP1.

Within the main chain conformations 90/90 and 180/180° the calculated coupling constant $^4J_{\text{PP}}$ strongly depends on the position of the methoxy groups. Considerably

TABLE III

Calculated energies ΔE[a] (kJ/mol) and coupling constants $^4J_{PP}$ (Hz) of selected conformations for **2**

NDDO-SP			NDDO-SPD'			INDO-SP			
Nr.	Conformation	ΔE	Nr.	Conformation	ΔE	Nr.	Conformation	ΔE	$^4J_{PP}$
NP1	90/90; C/C	0.0	ND1	90/90; B/B	0.0	IP1	90/90; D/D	0.0	5.3
NP2	180/90; C/D	0.9	ND2	180/90; B/B	20.2	IP2	90/90; C/D or D/C	1.3	6.8
NP4	90/90; C/D or D/C	1.9	ND3	90/90;D/B or B/D	21.5	IP3	90/90; C/C	1.5	2.1
NP7	180/180; C/C or D/D	4.8	ND4	90/90; C/B or B/C	23.5	IP4	90/90; C/B or B/C	4.0	0.9
NP8	180/180; C/D or D/C	6.1	ND5	90/90; D/D	37.3	IP5	90/90; D/B or B/D	4.3	2.9
NP9	90/90; D/D	6.3	ND8	90/90; C/D or D/C	41.7	IP6	180/90; D/D	5.3	4.3
NP13	90/90; C/B or B/C	13.8	ND11	90/90; C/C	48.7	IP8	90/90; B/B	6.9	8.5
NP15	180/180; C/B or B/C or D/B or B/D	17.5	ND12	180/180; B/B	50.6	IP16	180/180; C/C or D/D	13.6	7.6
NP16	90/90; D/B or B/D	17.9	ND17	180/180; C/B or B/C or D/B or B/D	71.4	IP17	180/180; C/D or D/C	14.6	0.7
NP18	90/90; B/B	29.5	ND18	180/180; C/C or D/D	90.7	IP18	180/180; C/B or B/C or D/B or B/D	17.2	2.4
NP19	180/180; B/B	30.2	ND19	180/180; C/D or D/C	92.7	IP19	180/180; B/B	20.8	8.0

[a] $\Delta E = E_i - E_{min}$ where E_{min} is the lowest energy of the calculated conformations, i.e. NP1, ND1 or IP1, respectively.

TABLE IV

Optimization of torsion angles φ_1 to φ_6 for **2**

Nr.	Starting conformation	Optimized conformation φ_1	φ_2	φ_3	φ_4	φ_5	φ_6	ΔE^a kJ/mol	$^4J_{PP}$ Hz
NPO1	180/180/0/0/0/0[b]	115.9	115.9	− 67.0	− 24.8	− 24.8	− 67.0	− 12.9	-
NPO2	- 90/0/0/0/0/0	− 85.3	−6.8	−7.5	− 82.9	28.3	108.9	9.6	-
NDO1	ND1	84.6	84.6	74.5	− 43.6	− 43.6	74.5	− 15.0	-
IPO1	IP1	93.3	93.3	40.2	130.0	130.0	40.2	− 1.2	6.1
IPO2	IP2 and IP4	88.0	96.3	− 54.0	− 35.6	54.3	41.5	−0.4	7.6
IPO3	IP3	91.5	91.5	− 52.6	− 34.8	− 34.8	− 52.6	0.4	3.3
IPO4	IP8	95.0	95.0	39.6	− 26.8	- 26.8	39.6	3.1	8.4

[a] $\Delta E = E_{opt} - E_{min}$ where E_{min} is the lowest energy of the calculated conformations, i.e. NP1, ND1 or IP1, respectively.

[b] Following starting conformations practically result in the same optimized conformation: 180/90/0/0/0/0; 180/0/0/0/0/0; 90/90/0/0/0/0 and 90/0/0/0/0/0.

TABLE V

Summary of the crystal structure determination for $(H_5C_2O)_2P(S)S_3P(S)(OC_2H_5)_2$

Crystallographic section		
empirical formula	$C_6H_{20}O_4P_2S_5$	
molecular mass	387.5	
lattice constants	a = 8.388(1) Å	α = 62.34(6) °
	b = 11.128(2) Å	β = 71.93(2) °
	c = 12.518(1) Å	γ = 84.97(5) °
V (Å^3)	981.6(6)	
Z	2	
d_{calc} (gcm^{-3})	1.28	
crystal system	triclinic	
space group	$P\bar{1}$	
Data collection		
diffractometer	CAD4	
radiation	MoK_α	
monochromator	graphite	
crystal size (mm)	0.2 x 0.2 x 0.15	
data collection mode	ω / 2θ - scan	
theta range (deg)	3 - 28	
recip. latt. segment	h = −11 → 0	
	k = −10 → 12	
	l = −13 → 14	
no. refl.measd.	6395	
no. unique refl.	4993	
no. refl. F > 3σ(F)	3316	
lin. abs. coeff. (cm^{-1})	7.64	
Structural analysis and refinement		
solution by	Direct phase determination Full-Matrix LSQ. Hydrogen positions of riding model with fixed isotropic U	
data-to-parameter ratio	17.3	
R ; R_w	0.045 ; 0.057	
weighting scheme	$\omega = 1/\sigma^2(F)$	
largest difference peak	0.72 eÅ^3	
largest difference hole	0.57 eÅ^3	
programs used[29,30]	SHELXS86, SHELX76	

high values of the coupling constant have been calculated for some of the conformations with $\varphi_1 = \varphi_2 = 90°$ (IP1, IP2 and IP8). These conformations are essentially more favourable in energy than the conformations IP16 and IP19, which are characterized by a planar W-arrangement of the PSSSP chain. Optimization of molecular geometry (see Table IV) in every case leads to values for φ_1 and φ_2 of about 90°. Apart from the value of the conformation IPO3 the calculated coupling constants of the other conformations are with 6 to 8 Hz close to the experimental value of 10.5 Hz.

Although the semiempirical quantum chemical calculations performed here are not suitable to reflect the energies and coupling constants of the conformers quantitatively, the following conclusions may be drawn at the basis of the described results:

1. In solutions of bis-(dialkoxythiophosphoryl)-trisulfanes no conformations with planar PSSSP arrangements are of importance.
2. The measured relatively high coupling constant ${}^4J_{PP}$ in such solutions is caused by conformations with PSSS dihedral angles of about 90°, and not by planar PSSSP arrangements.

EXPERIMENTAL

The synthesis of bis-(diethoxythiophosphoryl)-trisulfane was done according to Malatesta and Laverone[28] by the reaction of dithiophosphoric acid O,O-diethyl ester with SCl_2 in dried n-Hexane at −20°C. Dithiophosphoric acid ester was synthesized as described by Kabachnik and Mastrjukova.[31]

TABLE VI

Fractional coordinates of the title compound
(Estimated standard deviations are given in parentheses)

Atom	x	y	z	Atom	x	y	z
S(1)	.4003(1)	.1248(1)	.0672(1)	H1A	.503(5)	−.198(4)	.297(3)
S(2)	.0342(2)	.1730(1)	.0082(1)	H1B	.427(5)	−.242(4)	.218(4)
S(3)	.4671(2)	.0526(2)	.3288(2)	H3A	.119(5)	.247(4)	.220(4)
S(4)	−.0900(2)	.4431(2)	−.1851(2)	H3B	.134(5)	.192(4)	.348(3)
S(5)	.2397(2)	.0573(1)	.0080(1)	H5A	.233(5)	.418(4)	−.016(4)
P(1)	.3108(2)	.0125(1)	.2651(1)	H5B	.167(5)	.550(4)	−.121(4)
P(2)	.1065(2)	.3433(1)	−.1713(1)	H7A	−.014(5)	.239(4)	−.287(4)
O(11)	.2725(4)	−.1384(3)	.3006(3)	H7B	.105(5)	.110(4)	−.247(4)
O(12)	.1217(4)	.0467(3)	.3056(3)	H2A	.437(5)	−.429(4)	.402(3)
O(21)	.2682(4)	.4145(3)	−.1828(3)	H2B	.244(5)	−.394(4)	.412(4)
O(22)	.1927(4)	.2938(3)	−.2720(3)	H2C	.320(5)	−.345(4)	.490(3)
C(1)	.4004(8)	−.2349(6)	.3014(8)	H4A	−.133(5)	.260(4)	.346(3)
C(2)	.3485(12)	−.3625(8)	.4063(9)	H4B	−.151(5)	.104(4)	.431(4)
C(3)	.0779(9)	.1784(6)	.3003(6)	H4C	−.164(5)	.164(4)	.295(3)
C(4)	−.1056(10)	.1767(8)	.3474(8)	H6A	.426(5)	.605(4)	−.107(3)
C(5)	.2605(9)	.4881(6)	−.1099(7)	H6B	.450(5)	.616(4)	−.249(4)
C(6)	.4269(12)	.5582(10)	−.1560(11)	H6C	.519(5)	.492(4)	−.137(4)
C(7)	.1004(9)	.2162(8)	−.3030(6)	H8A	.105(5)	.191(4)	−.452(3)
C(8)	.1725(12)	.2419(11)	−.4308(7)	H8B	.296(5)	.236(4)	−.455(4)
				H8C	.167(5)	.344(4)	−.486(4)

The details for the crystal structure determination are listed in Table V, the final atomic coordinates are given in Table VI. A list of structure factors and the thermal parameters are available from the authors on request (J. Sieler).

The high-resolution solid-state NMR spectra were recorded on a BRUKER MSL 300 instrument with cross-polarization, magic angle spinning (2.5–4.0 kHz) and high-power decoupling. The length of the 90 degree pulses was 5 μs, the contact time was 1 ms and the repetition time 5 s. The ^{31}P chemical shift values are referred to brushite, $CaHPO_4.2H_2O$, (1.2 ppm) and ^{13}C chemical shifts to the adamantane CH_2 peak (29.5 ppm).

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