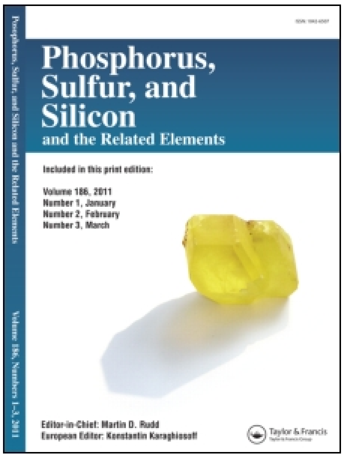

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

NMR INVESTIGATIONS ON DIASTEREOMERIC MIXTURES OF BIS(DIALKOXYTHIOPHOSPHORYL) SULFANES AND -POLYSULFANES CONTAINING *sec.* BUTOXY GROUPS. ASSIGNMENT OF ^{31}P, ^{13}C AND ^{1}H NMR SIGNALS IN A MIXTURE OF SEVEN DIASTEREOMERS USING SHIFT-CORRELATED 2D NMR SPECTRA

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To cite this Article Großmann, Gisbert and Kober, Hartmut(1991) 'NMR INVESTIGATIONS ON DIASTEREOMERIC MIXTURES OF BIS(DIALKOXYTHIOPHOSPHORYL) SULFANES AND -POLYSULFANES CONTAINING *sec.* BUTOXY GROUPS. ASSIGNMENT OF ^{31}P, ^{13}C AND ^{1}H NMR SIGNALS IN A MIXTURE OF SEVEN DIASTEREOMERS USING SHIFT-CORRELATED 2D NMR SPECTRA', Phosphorus, Sulfur, and Silicon and the Related Elements, 61: 3, 269 — 281

To link to this Article: DOI: 10.1080/10426509108036808

URL: http://dx.doi.org/10.1080/10426509108036808

Phosphorus, Sulfur, and Silicon, 1991, Vol. 61, pp. 269–281
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NMR INVESTIGATIONS ON DIASTEREOMERIC MIXTURES OF BIS(DIALKOXYTHIOPHOSPHORYL) SULFANES AND -POLYSULFANES CONTAINING *sec.* BUTOXY GROUPS. ASSIGNMENT OF ^{31}P, ^{13}C AND ^{1}H NMR SIGNALS IN A MIXTURE OF SEVEN DIASTEREOMERS USING SHIFT-CORRELATED 2D NMR SPECTRA

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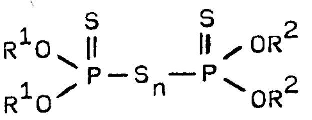
(Received November 12, 1990; in final form February 7, 1991)

Synthesizing compounds of the structure



n = 1 - 4
R^1 = sBu
R^2 = Me, Et, iPr, iBu, sBu

diastereomeric mixtures were obtained. If possible, the ^{31}P chemical shifts and P—P coupling constants of the individual diastereomers were determined from the ^{31}P NMR spectra of these diastereomeric mixtures.

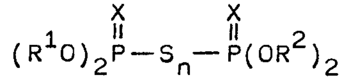
In addition, the mixture of the seven diastereomers of bis(di-*sec.* butoxythiophosphoryl)disulfane was analyzed using shift-correlated ^{31}P–^{31}P {^{1}H}, ^{13}C–^{31}P {^{1}H}, ^{13}C–^{1}H {^{31}P} and ^{1}H–^{1}H {^{31}P} 2D NMR spectra. In this way, the ^{31}P, ^{13}C and ^{1}H chemical shifts and the corresponding coupling constants were assigned to the diastereomers.

The appearance of regions of similar chemical shift into which the ^{1}H, ^{13}C and ^{31}P signals of identical atoms or atom groups can be classified is characteristic of all the diastereomeric mixtures investigated. These regions can be explained mainly by the symmetry relations of a molecule moiety $(sBuO)_2P(S)S$—.

Key words: ^{31}P NMR; 2D NMR; organophosphorus sulfanes; diastereomers; P—P coupling constants.

INTRODUCTION

In a previous paper[1] we reported on NMR spectroscopical characterization of bis(dialkoxyphosphoryl)- and -(dialkoxythiophosphoryl)sulfanes and -polysulfanes of the following structure:



$$(R^1O)_2\overset{X}{\overset{\|}{P}}—S_n—\overset{X}{\overset{\|}{P}}(OR^2)_2$$

n = 1 - 4
X = O, S
R^1, R^2 = Me, Et, iPr, iBu

Continuing these studies in this paper, we present results of NMR spectroscopical investigations on the following compounds:

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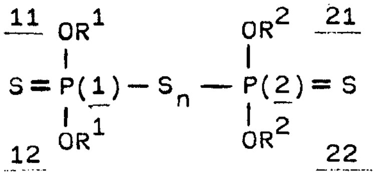


$$S{=}P(1)(OR^1)_2{-}S_n{-}P(2)(OR^2)_2{=}S$$

n	1	2	3	4
	1	**2**	**3**	**4**

$R^1 = CH_3CH_2(CH_3)CH$ (**e**)

$R^2 = CH_3$ (**a**), CH_3CH_2 (**b**), $(CH_3)_2CH$ (**c**), $(CH_3)_2CHCH_2$ (**d**), $CH_3CH_2(CH_3)CH$ (**e**)

It is characteristic of these sulfanes and polysulfanes that at least one molecule moiety contains two chiral *sec.* butoxy groups (**e**). Their chirality and also the pseudoasymmetry of phosphorus atoms which appears in some cases results in the fact that these compounds exist in several diastereomeric forms. These diastereomers were characterized referring to the chirality of ester groups and to pseudoasymmetry of phosphorus atoms. Thereby, both phosphorus atoms were characterized by *1* and *2*, respectively, and the four ester groups by *11*, *12*, *21* and *22*, respectively, as indicated in the formula.

The investigation's aim is the ^{31}P NMR spectroscopical characterization of these diastereomers. Furthermore, the ^1H and ^{13}C NMR signals of the individual diastereomers of bis(di-*sec.* butoxythiophosphoryl)disulfane (**2ee**) were assigned by using different 2D NMR techniques.

Unfortunately, only conjectures can be made concerning the absolute configuration of the pseudoasymmetric phosphorus atoms.

RESULTS AND DISCUSSION

1. *Stereochemical Description of the Diastereomers*

O,O-di-*sec.* butoxydithiophosphoric acid $(sBuO)_2PS_2H$ (**5**), used for synthesizing the compounds **1**–**4**, was prepared using the racemic mixture of (*R*)- and (*S*)-*sec.* butanol. Hence, it contains both the enantiomer pair (*R*,*R*)- and (*S*,*S*)-**5** and the meso form (*R*,*S*)-**5**.

One obtains three diastereomeric compounds **A**, **B**, and **C**, when the mixed compounds of the structures **1**–**4** ($R^1 \neq R^2$) are prepared from this diastereomeric mixture of **5** and achiral O,O-dialkyl dithiophosphoric acids. Their configuration is determined by the stereoisomerism of the molecule moiety formed by **5** (phosphorus *1*), see Table I. The (*R*, *R*)- and (*S*, *S*)-form of **5** results in the formation of the pair of enantiomers B with diastereotopic *sec.* butoxy groups (Figure 1).

TABLE I
Stereochemical description of diastereomers of compounds **1–4**

Diastereomer	Chirality of the ester groups				Pseudoasymmetry of the phosphorus atoms		Relative frequency[a]	Chemically nonequivalent ester groups[b]
	11	*12*	*21*	*22*	*1*	*2*		
A	*R*	*S*	—	—	*r*	—	1	(*11*, *12*)
B	*R*	*R*	—	—	—	—	2	*11*, *12*
	S	*S*	—	—	—	—		
C	*S*	*R*	—	—	*s*	—	1	(*11*, *12*)
I	*R*	*S*	*R*	*S*	*r*	*r*	1	[(*11*, *12*), (*21*, *22*)]
II	*S*	*R*	*S*	*R*	*s*	*s*	1	[(*11*, *12*), (*21*, *22*)]
III	*R*	*S*	*S*	*R*	*r*	*s*	2	(*11*, *12*), (*21*, *22*)
IV	*R*	*S*	*R*	*R*	*r*	—	4	*11*, *12*, *21*, *22*
	R	*S*	*S*	*S*	*r*	—		
V	*S*	*R*	*R*	*R*	*s*	—	4	*11*, *12*, *21*, *22*
	S	*R*	*S*	*S*	*s*	—		
VI	*R*	*R*	*R*	*R*	—	—	2	[*11*, *21*], [*12*, *22*]
	S	*S*	*S*	*S*	—	—		
VII	*R*	*R*	*S*	*S*	—	—	2	[*11*, *22*], [*12*, *21*]

[a] Derived from theory of combinations.

[b] Isochronic groups are summarized: enantiotopic groups in parentheses and in brackets groups whose chemical equivalence is involved by other properties of symmetry.

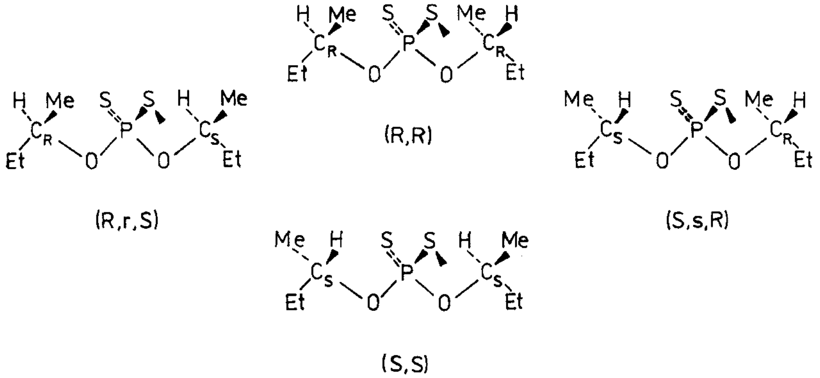


FIGURE 1 Configurations of a molecule moiety $(sBuO)_2P(S)S$-.

The diastereomeric compounds A and C are derived from the meso-form of **5**. In these cases, the different chirality of the *sec.* butoxy groups *11* and *12* in connection with two additional different phosphorus substituents results in pseudoasymmetry of phosphorus *1*.[4] Hence, the diastereomers A and C can be named as the (*R*, *r*, *S*)- and (*S*, *s*, *R*)-form, respectively. Their *sec.* butoxy groups are enantiotopically (Figure 1).

For the compounds **1ee–4ee**, the number of diastereomers increases to seven (I–VII) because a molecule now contains four chiralic *sec.* butoxy groups. In addition, the phosphorus atom is also pseudoasymmetrical when the molecule moiety has (*R*, *S*)-configuration. The diastereomers IV–VI are enantiomeric pairs. Diastereotopy and enantiotopy, resp., of the sec. butoxy groups of the different diastereomers were deduced from molecule symmetry and are stated in Table I.

2. ^{31}P *NMR Spectroscopical Characterization of the Diastereomeric Mixtures*

The signal assignment in the ^{31}P $\{^1H\}$ NMR spectra of the diastereomeric mixtures is done using the relative signal intensities, chemical shifts, value of the P—P coupling constant and, in some cases, shift-correlated ^{31}P–^{31}P $\{^1H\}$ 2D NMR spectra. The ^{31}P chemical shifts and P—P coupling constants are summarized for the diastereomers of compounds **1–4** in the Tables II and III. The P—P coupling constants were determined from AX spin systems.

The group $(sBuO)_2P(S)S$- results in ^{31}P NMR signals between 81.9 and 85.0 ppm for diastereomeric mixtures of polysulfanes **2–4**. The corresponding signals for sulfanes **1** are high-field shifted[1] and are observed between 75.8 and 76.7 ppm.

Three signal groups are found in the ^{31}P NMR spectrum of the diastereomeric mixture of every compound investigated (comp. e.g., Figures 2 and 3). Mostly, they are well separated.

These signal groups are caused by the three diastereomeric configurations of a molecule moiety $(sBuO)_2P(S)S$-, which are illustrated in Figure 1. Based on signal intensities, the central signal group is assigned to the (*R*, *R*)- and (*S*, *S*)-configurations. The outer ones are assigned to the (*R*, *r*, *S*)- and (*S*, *s*, *R*)-configurations, respectively.

TABLE II

^{31}P chemical shifts in ppm and P—P coupling constants in Hz of the diastereomers of $(sBuO)_2P^1(S)$-S_n-$(S)P^2$ with $n = 1$–4

R^2	Diastereomer[a]	Nucleus P^1	**1eR²**		**2eR²**		**3eR²**		**4eR²**	
			δ_P	$^2J_{PP}$	δ_P	$^3J_{PP}$	δ_P	$^4J_{PP}$	δ_P	$^5J_{PP}$
a	A	*1*	76.29	−19.4	84.97	1.5	83.61	+11.8	84.14	0.7
		2	83.35		89.73		90.01		89.65	
	B	*1*	76.16	−19.9	84.20	1.6	82.83	+11.6	83.37	0.7
		2	83.35		89.77		89.95		89.65	
	C	*1*	75.85	−20.3	83.37	1.7	81.95	+11.5	82.48	0.7
		2	83.35		89.80		89.88		89.65	
b	A	*1*	76.58	−18.9	84.72	0.8	83.81	+11.9	84.44	0.7
		2	79.6		84.0		84.65		84.6	
	B	*1*	76.52	−19.6	84.04	1.0	83.02	+11.7	83.37	0.7
		2	79.6		84.0		84.58		84.6	
	C	*1*	76.25	−20.3	83.13	1.0	82.11	+11.5	82.75	0.7
		2	79.6		84.0		84.51		84.6	
c	A	*1*	76.7	−17.4	83.84	0.5	84.25	+12.8	84.45	0.7
		2	76.07[b]		82.35[b]		82.45		82.79[b]	
	B	*1*	76.7	−18.2	83.22	0.5	83.47	+12.7	83.72	0.7
		2	76.01		82.30		82.36		82.58	
	C	*1*	76.7	−18.8	82.52	0.5	82.56	+12.5	82.79	0.8
		2	75.96[b]		82.26[b]		82.30		82.49[b]	
d	A	*1*	76.60	−18.2	84.80	0.3	84.17	+12.2	84.52	0.6
		2	79.8		84.51		85.54		85.4	
	B	*1*	76.57	−19.0	84.06	0.3	83.37	+12.0	83.75	0.6
		2	79.8		84.56		85.47		85.4	
	C	*1*	76.33	−19.5	83.24	0.3	82.48	+11.9	82.89	0.6
		2	79.8		84.63		85.39		85.4	

[a] Stereochemical description of the diastereomers, see Table I.

[b] Signal assignments may be interchanged.

TABLE III

^{31}P chemical shifts in ppm and P—P coupling constants in Hz of the seven diastereomers of $(sBuO)_2P^1(S)\text{-}S_n\text{-}S)P^2(OsBu)_2$ with n = 1–4.

Dia-stereo-mer[a]	Nucleus[a] P_1	1ee		2ee		3ee		4ee	
		δ_P	$^2J^b_{PP}$	δ_P	$^3J_{PP}$	δ_P	$^4J^b_{PP}$	δ_P	$^5J_{PP}$
I	*1/2*	76.47		83.96		84.51		84.55	
II	*1/2*	76.19		82.62		82.74		82.92	
III	*1*	76.40	−18.2	83.85	0.6	84.36	+12.9	84.53	0.6
	2	76.29		82.75		82.88		82.94	
IV	*1*	76.49	−20.1	83.90	0.7	84.43	+13.0	84.54	0.6
	2	76.43		83.40		83.75		83.79	
V	*1*	76.21	−18.2	82.67	0.5	82.81	+12.7	82.93	0.6
	2	76.44		83.27		83.57		83.77	
VI[c]	*1/2*	76.47		83.33		83.67		83.78	
VII[c]	*1/2*	76.43		83.32		83.66		83.78	

[a] Nomenclature, see introduction and Table I.

[b] Sign as determined in Reference 1.

[c] The assignment of VI and VII may be interchanged.

But a simple assignment, which of both signal groups is caused by the (*R*, *r*, *S*)- and (*S*, *s*, *R*)-configuration, resp., cannot be made by NMR spectroscopy.

In the next section, we will present a proposal based on analyzing the 2D NMR spectra, which substantiates the assignment used in the Tables II–IV.

The ^{31}P chemical shifts difference of adjacent signal groups is about 0.8 ppm for tri- and tetrasulfanes. This value characterizes the ^{31}P chemical shift effect caused by changing the configuration of an ester group. This conclusion can be made because only insignificant interactions are expected between the molecule moieties of these compounds. A similar value of about 0.7 ppm is observed for the disulfanes **2**.

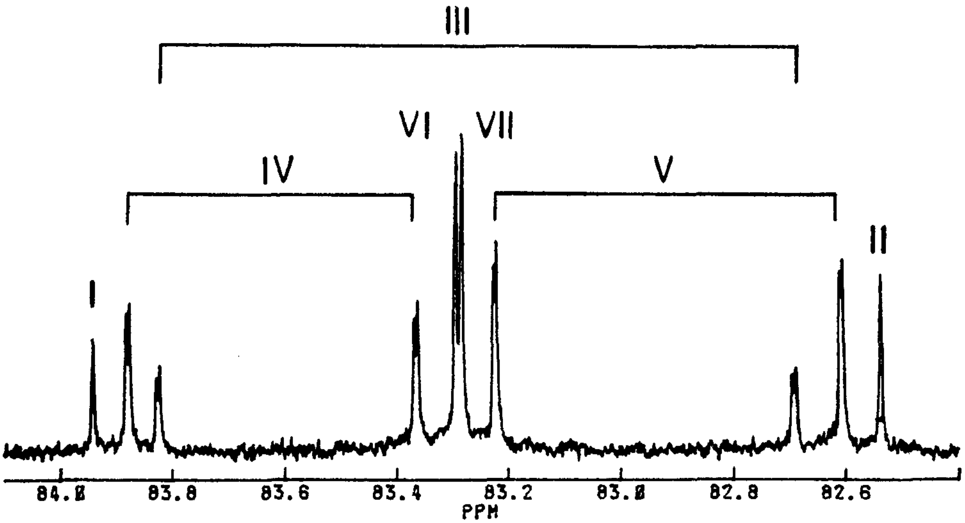


FIGURE 2 ^{31}P {^{1}H} spectrum of the seven diastereomers of $(sBuO)_2P(S)\text{-}S_2\text{-}P(S)(OsBu)_2$ (**2ee**), I–VII.

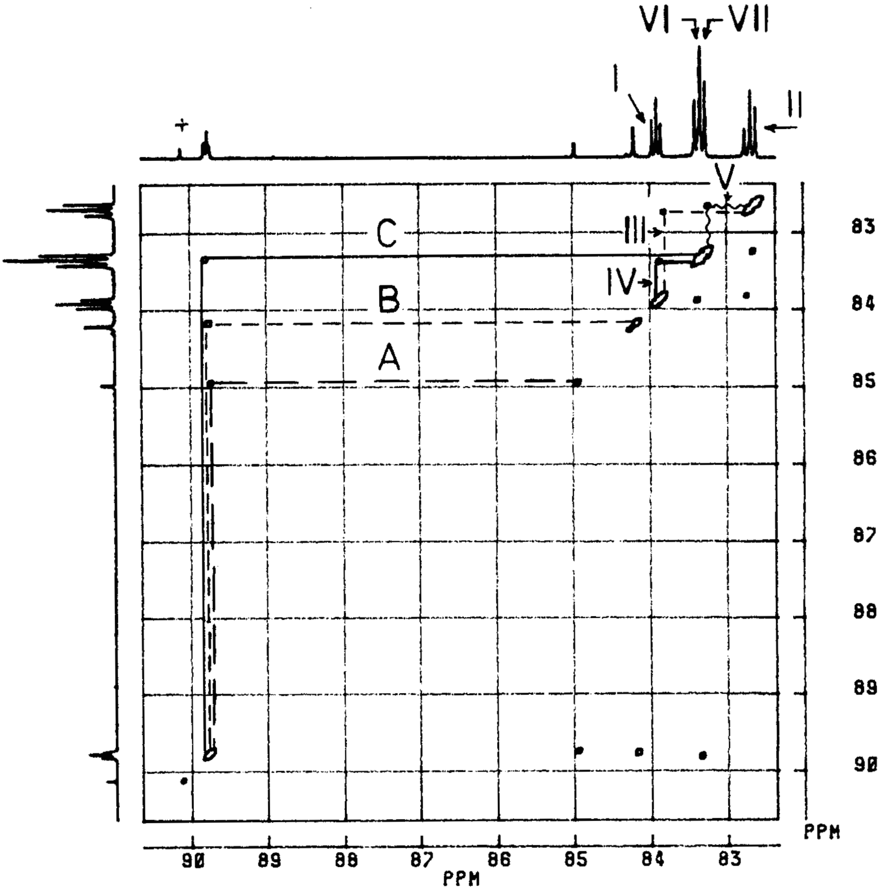


FIGURE 3 ^{31}P COSY spectrum of a disulfanes mixture containing the three diastereomers of $(sBuO)_2P(S)$-S_2-$P(S)(OMe)_2$ (**2ea**), A–C, the seven diastereomers of $(sBuO)_2P(S)$-S_2-$P(S)(OsBu)_2$ (**2ee**), I–VII, and bis(di-methoxythiophosphoryl)disulfane (+). Spectrum was obtained by broad-band ^{1}H decoupling.

Superposition of steric and electronic interactions between both molecule moieties of sulfanes **1** should cause the decrease of this ^{31}P chemical shift effect to 0.3 ppm for these compounds.

Differences in the configuration of a molecule moiety influence the ^{31}P chemical shift of the other molecule moiety, as well. But this effect is mostly smaller than 0.1 ppm. For some mixed compounds investigated, this effect is so insignificant that the signals for phosphorus *2* of the three diastereomers were observed without separation.

The P—P coupling constants can be determined only for diastereomers the phosphorus atoms of which result in a AX (AB) spin system. This is the case for all mixed compounds and the diastereomers III, IV and V of **1ee–4ee** (Table II and III). The connection of the lines was determined by $^{31}P-^{31}P$ $\{^1H\}$ spectroscopy (Figure 3).

Both phosphorus atoms are chemically equivalent in the diastereomers I, II, VI and VII and result in a singlett in the ^{31}P $\{^1H\}$ NMR spectra in each case (Figure

TABLE IV

Chemical shifts in ppm and coupling constants in Hz of the seven diastereomers of bis(di-*sec.* butoxythiophosphoryl) disulfane (**2ee**)

Dia-stereo-meres[a]	*sec.* butoxy groups[a]	CH			H_A—C—H_B				$CH_3(CH)$			$CH_3(CH_2)$	
		δ_C	$^2J_{PC}$	δ_H	δ_C	$^3J_{PC}$	δ_H[b]	δ_H[b]	δ_C	$^3J_{PC}$	δ_H	δ_C	δ_H
I	*11, 12, 21, 22*	78.950	8.0	4.572	29.795	6.7	1.669	1.568	20.590	3.4	1.272	9.215	0.868
II	*11, 12, 21, 22*	78.865	7.5	4.601	30.055	5.8	1.652	1.566	20.500	4.1	1.296	9.250	0.878
III	*11, 12*	78.960	8.0	4.572	29.790	6.2	1.669	1.568	20.605	3.3	1.272	9.200	0.868
	21, 22	78.855	7.8	4.601	30.040	5.8	1.652	1.566	20.510	4.2	1.296	9.250	0.878
IV	*11*	78.955	8.3	4.572	29.795	6.7	1.669	1.568	20.610	3.7	1.272	9.200	0.868
	12	78.955	8.3		29.795	6.7			20.590	3.4		9.215	
	21	78.900	7.8	4.585	29.815	6.6	1.669	1.568	20.625	3.3	1.272	9.175	0.868
	22	78.890	7.8		30,030	5.4	1.652	1.566	20.485	4.2	1.296	9.265	0.878
V	*11*	78.865	7.6	4.601	30.040	5.8	1.652	1.566	20.505	3.9	1.296	9.250	0.878
	12	78.845	7.6		30.055	5.4			20.505	3.9			
	21	78.920	7.7	4.585	29.815	6.6	1.669	1.568	20.640	3.3	1.272	9.150	0.868
	22	78.900	8.1		30.040	5.8	1.652	1.566	20.480	3.8	1.296	9.265	0.878
VI[c]	*11, 21*	78.890	8.1	4.585	30.030	5.8	1.652	1.566	20.480	4.2	1.296	9.265	0.878
	12, 22	78.905	7.8		29.815	6.6	1.669	1.568	20.640	3.3	1.272	9.150	0.868
VII[c]	*11, 22*	78.905	7.8		29.815	6.6	1.669	1.568	20.620	3.7	1.272	9.175	0.868
	12, 21	78.890	8.1	4.585	30.040	5.8	1.652	1.566	20.485	4.1	1.296	9.265	0.878

[a] Nomenclature, see introduction and Table I.

[b] $^2J_{AB} = -14.1$ Hz.

[c] Assignment of VI and VII may be interchanged.

2). Determining ${}^{n}J_{PP}$ (n = 2–5) by analyzing the ${}^{31}P$ coupled ${}^{1}H$ and ${}^{13}C$ NMR spectra, resp., as described in Reference 1, was impossible because of overlapping signal groups of the seven diastereomers.

The ${}^{n}J_{PP}$ values (n = 2–5) determined from AX spin systems are comparable with those of other bis(dialkoxythiophosphoryl) sulfanes and -polysulfanes given in Reference 1. Mostly, significant differences are observed for ${}^{2}J_{PP}$ and ${}^{4}J_{PP}$ values of the diastereomers of sulfanes and trisulfanes, respectively. Generally, an increase in ${}^{31}P$ chemical shift of phosphorus *1* is connected with a positivation of ${}^{2}J_{PP}$ and ${}^{4}J_{PP}$, respectively.

3. 2D NMR Investigations of a **2ee** *Diastereomeric Mixture*

The signals of the individual diastereomers intricately overlap in the 1D ${}^{13}C$ and ${}^{1}H$ spectra of the **2ee** diastereomeric mixture. It is only obvious that they form groups around two or three positions. But the ${}^{13}C$ and ${}^{1}H$ signals can be unambiguously assigned to the signals in the ${}^{31}P$ spectrum using different 2D NMR spectra correlated by hetero- and homonuclear coupling constants. By this method, complete NMR characterization of each diastereomer is possible without the separation of the diastereomers.

Compound **2ee** was used for a demonstration of this method because in this case all signals of the diastereomers are well separated in the ${}^{31}P$ NMR spectra and furthermore, the small P—P coupling constants result in spectra of approximately first order.

The assignment of the ${}^{13}C$ signals is possible for the carbon atoms in β- and γ-position to the phosphorus using ${}^{13}C$–${}^{31}P$ shift-correlated spectra (Figure 4). Furthermore, the P—C coupling constants can be assigned using these spectra. Scheme I presents the strategy for assigning all ${}^{13}C$ and ${}^{1}H$ signals to the ${}^{31}P$ signals. The conclusions from 2D spectra concerning the mutual signal assignment are summarized in Table IV.

Three groups of ${}^{13}C$ signals results from the chiral carbon atoms. They correspond to the three groups of ${}^{31}P$ signals. This means that their ${}^{13}C$ chemical shift is determined by the configuration of a molecule moiety (Figure 1). In other words, the stereochemical arrangement of the other *sec.* butoxy group of the molecule moiety influences the chemical shift of the CH signal.

By comparison, the position of CH_2 and γ-CH_3 signals is determined essentially by the configuration of the *sec.* butoxy group referring to the stereochemical arrangement at the phosphorus atom. Hence, the molecule moieties of *(R, R)*- and *(S, S)*-configuration, resp., characterized by the central ${}^{31}P$ chemical shift region, result in ${}^{13}C$ signals in two shift regions due to the ester group's diastereotopy. On the other hand, the molecule moieties of (*R*, *r*, *S*)- and (*S*, *s*, *R*)-configuration contain enantiotopic CH_2- and γ-CH_3 groups. For this reason, both *sec.* butoxy groups result in the same ${}^{13}C$ chemical shift. These shifts are different for (*R*, *r*, *S*)- and (*S*, *s*, *R*)-configurations.

A comparison of the vicinal coupling constants ${}^{3}J_{PC}$ shows that they are generally larger for the CH_2 group than for the γ-CH_3 group. These values can be used to estimate the preferred conformation.

Following Samitov and Karataeva[5] the coupling constants ${}^{3}J_{PC}^{trans}$ and ${}^{3}J_{PC}^{gauche}$ for

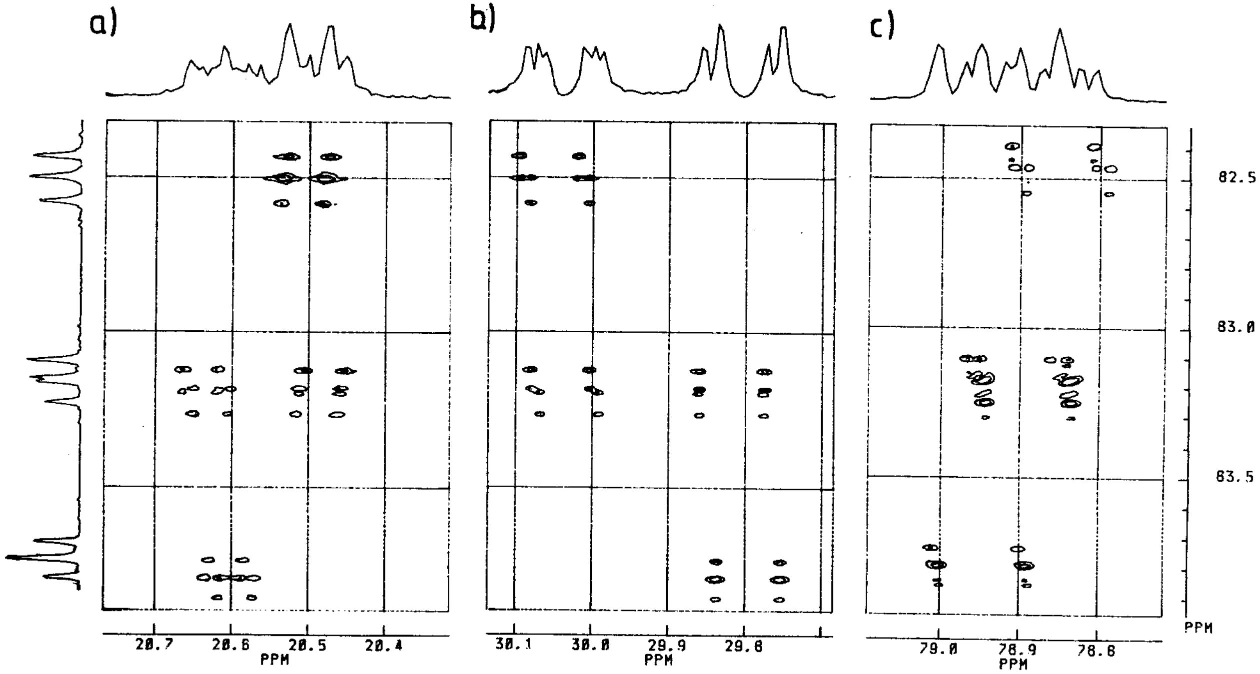
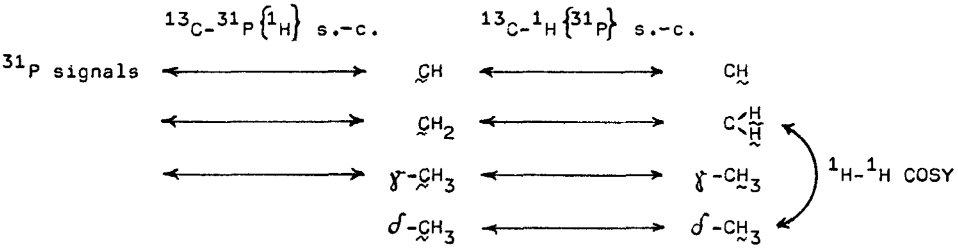


FIGURE 4 2D ^{13}C–^{31}P {^{1}H} shift-correlation for bis(di-*sec*. butoxythiophosphoryl)disulfane (**2ee**): a) γ-methyl group, b) methylene group, c) methine group.

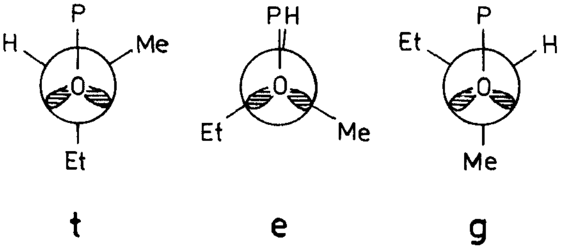


SCHEME I Combination of different 2D techniques for a complete assignment of all ^{13}C and ^1H signals to the ^{31}P signals (s.c.-shift-correlation).

dithiophosphates are 8.8 and 2.2 Hz. A coupling constant $^3J^{120°}_{PC}$ must be taken into consideration if a conformation with a *eclipsed*-position of the proton to the phosphorus is important. Such a conformation was observed for bis(di-isopropoxy-dithiophosphoryl) disulfane in the solid state.[6]

Using the Karplus curve in Reference 5, it can be estimated that it's value is approximately the same as $^3J^{gauche}_{PC}$. The value of $^3J^{trans}_{PC}$ should be somewhat larger because $^3J_{PC}$ values of 8.8 and 8.4 Hz, resp., were determined for bis(di-ethoxy-thiophosphoryl)- and bis(di-isobutoxythiophosphoryl) trisulfane.[1]

To estimate the fraction of the *trans*-conformation (p_t), we have used $J^t = 10$ Hz and $J^g = J^{120°} = 2.5$ Hz. Assuming three conformations



p_t and p_g can be calculated with the following equations:

$$p_t = \frac{\overline{J_{PCH_2}} - J^g_{PC}}{J^t_{PC} - J^g_{PC}} \quad \text{and} \quad p_g = \frac{\overline{J_{PCH_3}} - J^g_{PC}}{J^t_{PC} - J^g_{PC}}.$$

For I, values of 0.54 and 0.12 were calculated for p_t and p_g, respectively. Due to the obviously preferred *trans*-conformation of the ethyl group this conformation was used for the representation of molecule moieties in Figure 1.

It can be seen by a careful inspection of the coupling constants $^3J_{PC}$ in Table IV, that for certain *sec.* butoxy groups, higher CH_2 coupling constants (6.2–6.7 Hz) and lower γ-CH_3 values (3.3–3.7 Hz) and, for other lower CH_2 coupling constants (5.4–5.8 Hz) and higher γ-CH_3 values (3.8–4.2 Hz) are typical. Hence, for II p_t and p_g are 0.42 and 0.21, respectively.

We believe that these differences can be used for a determination of the absolute configuration of the (*R*, *r*, *S*)- and (*S*, *s*, *R*)-molecule moieties. Examining Figure 1 one can see that the methyl groups of the *sec.* butoxy groups in the molecule moieties (*R*, *r*, *S*) and (*S*, *s*, *R*) have a different position with regard to the thion and thiol sulfur, respectively. We assume that the "bisaxial" position of methyl groups and thion sulfur is more unfavourable than that of methyl groups and thiol sulfur. Therefore, the *trans*-conformation of (R, r, S)-molecule moiety shown in Figure 1 will be more probable than that shown for (S, s, R)-molecule moiety. And, vice versa, a *gauche*-conformation with the γ-methyl group in *trans*-position to the phosphorus will be more probable for the (S, s, R)-configuration than for the (R, r, S)-arrangement. That's why we assume that the molecule moiety with the larger coupling constant $^3J_{PC}$ of the CH_2 group is of the configuration (R, r, S) and that with the larger γ-CH_3 coupling constant has the configuration (S, s, R).

If one compares the ^{31}P and ^{13}C NMR data of the arrangement with the preferred "bisaxial" position of methyl group to thion sulfur and that with preferred "bisaxial" position of methyl group to thiol sulfur, the following conclusions can be drawn:

lower $^3J_{PC}$	for	CH_2
higher $^3J_{PC}$	for	γ-CH_3
higher δ_c	for	CH_2
lower δ_c	for	γ-CH_3
lower δ_p.		

These characteristics were used for assigning the NMR data in the Tables II–IV both to the diastereomers A and C and to the diastereomers I–V.

If our considerations are not correct, the assignments have to be changed on the one hand for diastereomers I and II and on the other hand for IV and V. This is valid also for phosphorus *1* of diastereomers A and C.

Starting from the ^{13}C assignments for β- and γ-carbons, the corresponding proton signals were assigned using ^{31}P broad-band decoupled ^{13}C–^1H shift-correlated spectra (Table IV).

The spectra reproduced in Figure 5 show that the configurational influences on the chemical shift observed in the ^{13}C spectra are detectable also for ^1H chemical shifts, but to a smaller extent. Hence, two ^1H chemical shift regions were observed for the protons of the γ-CH_3 group and three for the proton of the methine group. For the CH_2 protons, one has to take into consideration that both protons are diastereotopic due to the prochirality of the methylene carbon. That's why they result in two signals.

The two shift regions observed for the carbon are less pronounced in the ^1H spectrum.

A COSY spectrum was recorded for assigning the ^1H signals of the δ-CH_3 group due to their correlation to the protons of the CH_2 group. A distinct influence of the configuration was not observed for the chemical shift of the ^1H signals of the δ-CH_3 group.

In addition to the dominant influence of the configuration of the molecule moiety observed on the number and position of signals, also the configuration of the other moiety influences both values. But these effects are significantly smaller. They lead to a further differentiation within the shift regions discussed above. But, this dif-

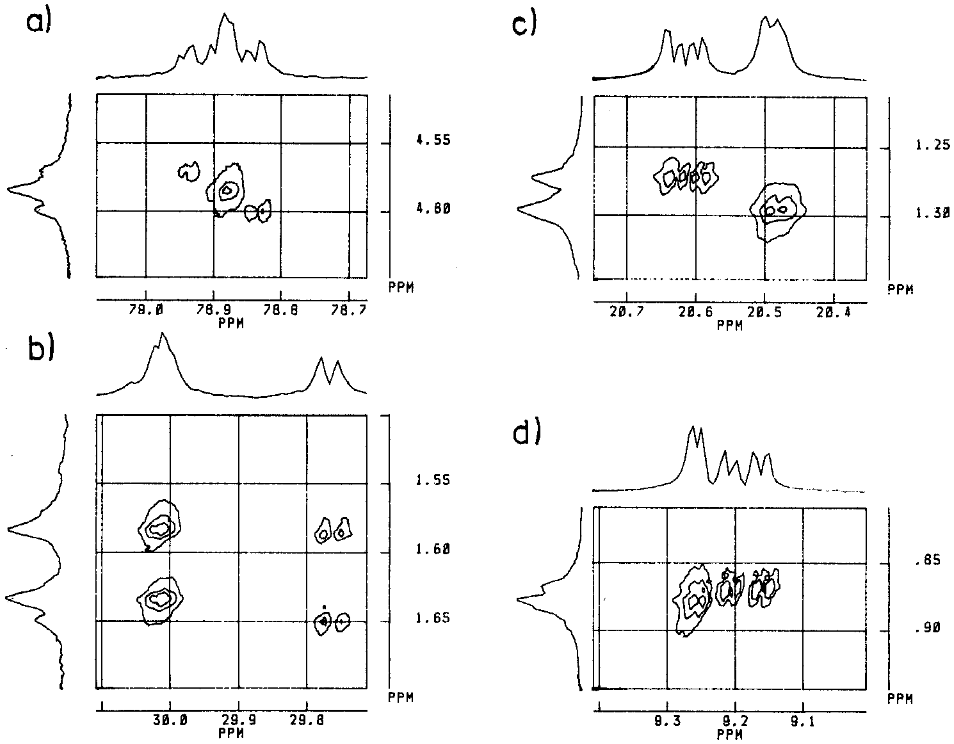


FIGURE 5 2D $^{13}C-^{1}H$ $\{^{31}P\}$ shift-correlation for bis(di-*sec.* butoxythiophosphoryl)disulfane (**2ee**): a) methine group, b) methylene group, c) γ-methyl group, d) δ-methyl group.

ferentiation cannot be interpreted in greater detail.

Finally, it should be pointed out that diastereomeric pairs A and C, I and II as well as IV and V are not exactly formed by synthesizing disulfanes in the mole ratio 1:1 as it should be expected by random formation.

In this connection, it can be shown experimentally that the mixed disulfanes **2ea** are formed also by exchange reactions from disulfanes **2aa** and **2ee**. This fact refers to reactions which are connected with scission and reformation of the S—S bond. They lead to a dynamic equilibrium of the diastereomers both for the mixed disulfane **2ea** and for **2ee**. Under these conditions, the deviation from the statistically expected equipartition of the diastereomeric pairs can be explained by small sterically dependent energy differences. The γ-methyl group is directed to the other molecule moiety in the preferred *trans*-conformation for the diastereomers A, I and IV of (*R*, *r*, *S*)-configuration (see Figure 1). Compared with it, only a methine proton is in this position for the diastereomers C, II and V of (*S*, *s*, *R*)-configuration. Hence, it can be understood that diastereomers C, II and V dominate (Figure 2).

EXPERIMENTAL

Synthesis. O,O-di-*sec.* butyldithiophosphoric acid (**5**) was prepared from P_4S_{10} and the racemic mixture of (*R*)- and (*S*)-*sec.* butanol following.[2] It contains both the enantiomers (*R*, *R*)-**5** and (*S*, *S*)-**5** and the meso-form (*R*, *S*)-**5**. Two signals of the same intensity were observed in the ^{31}P NMR spectrum at 82.23 and 82.14 ppm.[3]

Synthesis of sulfanes and polysulfanes **1–4** was described in Reference 1. Also the "symmetric" compounds ($R^1 = R^2$) are contained in the diastereomeric mixtures of mixed compounds ($R^1 \neq R^2$). These compounds were not separated.

NMR measurements. All compounds were measured as solutions in $CDCl_3$ at ambient temperature.

^{31}P NMR spectra of mixed compounds were obtained on a Bruker WH 90 DS spectrometer operating at 36.44 MHz under conditions described in Reference 1. For recording the ^{31}P NMR spectra of **1ee** and **4ee**, a Bruker MSL 400 spectrometer operating at 162,000 MHz was used.

All other NMR spectra were recorded on a Bruker MSL 300. The spectrometer was operated at a frequency of 300.13 MHz for ^{1}H, 75.475 MHz for ^{13}C and 121.495 MHz for ^{31}P.

For recording the shift-correlated 2D NMR spectra the following pulse programs were used: CPCORD, a modified version of XHCORD[7] for $^{31}P-^{13}C\ \{^{1}H\}$, XHCORD for $^{1}H-^{13}C\ \{^{31}P\}$, COSYN45 for $^{1}H-^{1}H\ \{^{31}P\}$ and $^{31}P-^{31}P\ \{^{1}H\}$.

In all cases, the data matrices were selected in such a manner that the effective digital resolution after transformation was 0.3–0.5 Hz/point in both dimensions. All ^{13}C and ^{1}H chemical shifts were referenced to $CDCl_3$ at 77.00 and 7.28 ppm, respectively.

ACKNOWLEDGEMENT

We thank Dr. W. Storek (Central Institute of Physical Chemistry, Berlin) for recording ^{31}P NMR spectra on a BRUKER MSL 400 spectrometer.

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