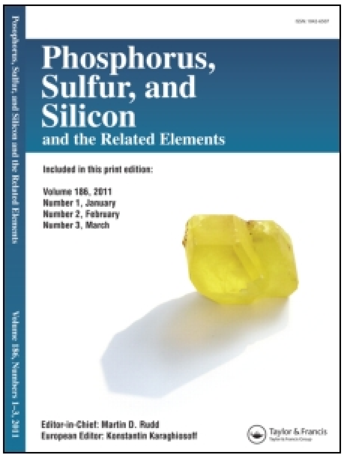

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2,4-BIS(METHYLTHIO)-2,4-DITHIOXO-1,3,2,4-DIAZADIPHOSPHETIDINES-NMR CHARACTERIZATION AND CRYSTAL STRUCTURE

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2,4-BIS(METHYLTHIO)-2,4-DITHIOXO-1,3,2,4-DIAZADIPHOSPHETIDINES-NMR CHARACTERIZATION AND CRYSTAL STRUCTURE

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Dedicated to Prof. G. Großmann on the occasion of his 65th birthday.

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New diazadiphosphetidines of the composition $[MeSP(S)NR]_2$ have been investigated by ^{31}P, ^{13}C and ^1H NMR spectroscopy and the configuration of the ring compound has been assigned. Structures of the 1,3-diphenyl compound **1g** and the 1,3-di(*ortho*-tolyl) compound **1h** have been determined by X-ray single-crystal analysis. Crystals of **1g** and **1h** grown from chloroform are colourless prisms of *trans* configuration. Single crystals of **1h** obtained from dichloromethane are colourless plates of *cis* configuration. Crystal data: **1g** (*trans*) monoclinic, C2/c, Z = 4, a = 9.373(2), b = 16.145(3), c = 11.705(2) Å, β = 92.11(3)°; **1h** (*trans*) monoclinic, $P2_1/c$, Z = 2, a = 7.083(1), b = 18.275(4), c = 8.257(2) Å, β = 110.13(3)°; **1h** (*cis*) monoclinic, $P2_1/n$, Z = 4, a = 9.994(2), b = 15.702(2), c = 13.668(5) Å, β = 105.14(2)°.

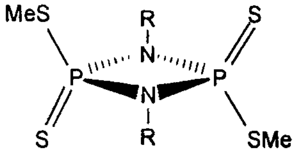
Key words: Diazadiphosphetidines, crystal structure, NMR.

INTRODUCTION

Syntheses of diazadiphosphetidines often yield *cis/trans* isomer mixtures.[1–3] The configuration assignment of the products is usually done by X-ray diffraction methods and in some favourable cases by combination of IR and Raman spectroscopic investigations. NMR spectroscopy can be applied provided that characteristic coupling patterns occur or information on the vicinity of atoms or atomic groups can be gained by special experiments. Although many papers on diazadiphosphetidines have been published systematic NMR investigations of compounds of the composition $[R^1P(S)NR^2]_2$ are rare and only some P-P coupling constants are known.[4–12]

This paper deals with the NMR spectroscopic characterization of diazadiphosphetidines $[MeSP(S)NR]_2$ **1** which have been prepared according to Donath and Meisel.[13] It is to answer the question if for a certain group of diazadiphosphetidines the magnitude of chemical shifts and coupling constants can be used for the configuration assignment. Bis(methylthio)-diazadiphosphetidines have been chosen as model compounds because the P-P coupling constant can be easily obtained from ^1H NMR spectra. To evaluate the results structures of compounds **1g** and **1h** have been determined by X-ray single-crystal analysis. Furthermore, the results are compared with some data of $[EtSP(S)NR]_2$ **2**.

The following compounds have been investigated:



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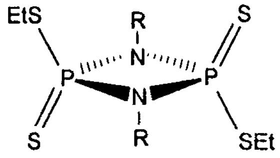

2

R	Me	Bu	c-C_6H_{11}	c-$C_{12}H_{23}$	$PhCH_2$	Allyl	Ph
1	**a**	**b**	**c**	**d**	**e**	**f**	**g**
2		**b**			**e**		**g**

R	o-MeC_6H_4	α-Naphthyl	o-$CF_3C_6H_4$
1	**h**	**i**	**j**

Scheme 1

RESULTS AND DISCUSSION

NMR Spectroscopy

Analysis of ^1H NMR spectra of 2,4-bis(methylthio)-diazadiphosphetidines **1** provides the P-P coupling constant (MeS signal realizes the X-part of an $(AX_3)_2$ spin system). For a detailed description of the analysis of $(AX_n)_2$ spin systems see Reference 14. If the P-P coupling constant is large enough, it is directly observable in the X-part (see Figure 1). If $^2J_{PP}$ was smaller than 2 Hz a spectrum simulation was carried out. Fitting of the simulated ^1H and ^{13}C signals of the MeS group and the experimental spectra allows the determination of $^2J_{PP}$ with an error less than 0.5 Hz.

The configurations of **1c**, **d**, **e** and **f** can be easily elucidated using NMR spectroscopy because these compounds possess prochiral centers at the α-C atoms of the

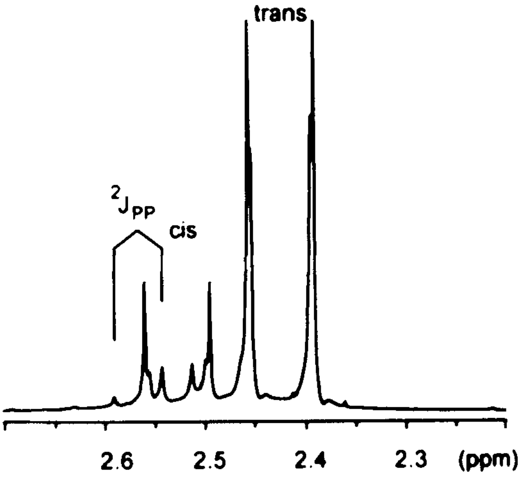

FIGURE 1 ^1H-NMR spectrum of *cis*- and *trans*-$[MeSP(S)NPh]_2$ (part).

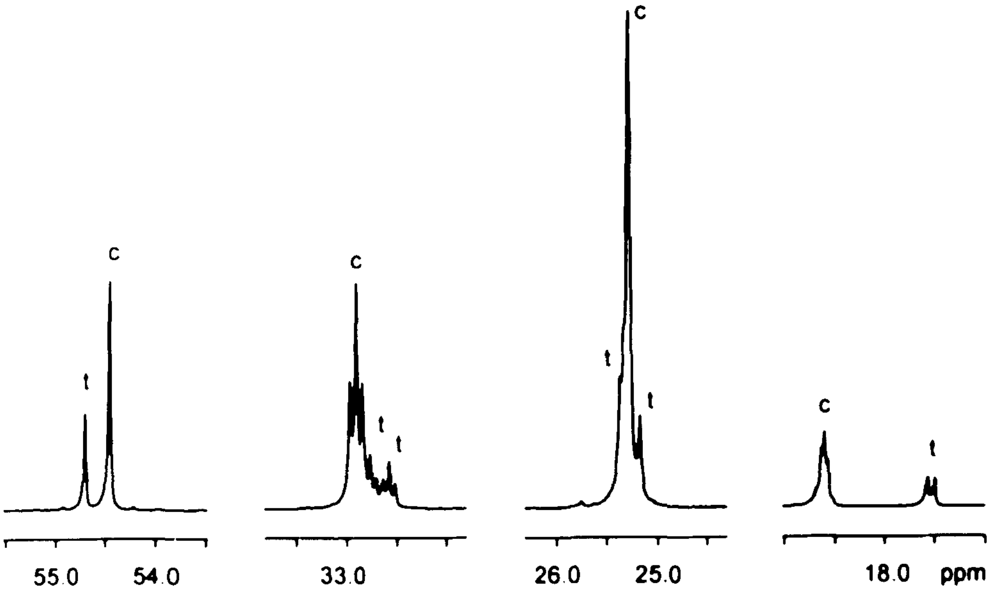

FIGURE 2 ^{13}C-NMR spectrum of a mixture of *cis*- (70%) and *trans*-[MeSP(S)Nc-C$_6$H$_{11}$]$_2$ (30%).

exocyclic N substituents. Only in the *trans* isomer of the benzyl compound the CH$_2$ protons are diastereotopic. Together with the two coupling P atoms they form an AA'XY-spin system. Thus, the CH$_2$ signal of *trans*-**1e** is of higher order, the same signal of *cis*-**1e** is a triplet.

^{13}C NMR spectra of the cyclohexyl compound **1c** show a different number of signals for the both isomers (see Figure 2). Due to diastereotopic β-C and γ-C atoms the cyclohexyl substituent of *trans*-**1c** gives six signals whereas in *cis*-**1c** these C atoms are enantiotopic giving only four signals. Furthermore, the splitting of the MeS signal is very different. Since the P-P coupling constant of *cis*-**1c** is about 6 Hz and of the same magnitude as $^2J_{PC}$ a triplet-like signal is observed. The P-P coupling constant of *trans*-**1c** is only 2 Hz and hence, a doublet-like MeS-signal results.

Comparing the NMR spectra of compounds **1c** and **1e** the following conclusions may be drawn which are confirmed by the NMR data of *cis*- and *trans*-**1d**:

$$\delta(P)\text{: } cis > trans \quad |^2J_{PP}|\text{: } cis > trans \quad \delta(S\underline{C}H_3)\text{: } cis > trans$$

These relations were used to assign the configuration of the compounds compiled in Table I. The assignment is in good agreement with our experimental results that: i) the *trans* isomer is formed in a higher yield during the methylation and ii) the *trans* isomer shows better crystallization properties. The configuration assignment of **1g** could be confirmed by X-ray diffraction analysis of a single crystal as will be shown below.

Comparing the NMR data of the phenyl compound with those of *ortho*-substituted aryl compounds large deviations are found. Usually, the difference of the ^{31}P chemical shift values of *cis* and *trans* isomer is about 3 ppm whereas *ortho*-tolyl and α-naphthyl compound show very small differences of about 0.5 ppm. In reverse to other investigated compounds *ortho*-tolyl, α-naphthyl and *ortho*-trifluoromethyl-

TABLE I

^{31}P and ^{1}H chemical shifts and P-P and P-H coupling constants of 2,4-bis(methylthio)-diazadiphosphetidines $[MeSP(S)NR]_2$ **1** and 2,4-bis(ethylthio)-diazadiphosphetidines $[EtSP(S)NR]_2$ **2** in $CDCl_3$

compd	R	*trans*					*cis*				
		δ(P)	$\delta(SCH_n)$	$^{2}J_{PP}$	$^{3}J_{PH}$	$^{5}J_{PH}$	δ(P)	$\delta(SCH_n)$	$^{2}J_{PP}$	$^{3}J_{PH}$	$^{5}J_{PH}$
1a	Me	81.3	2.35	1.7	+17.6	+0.7	84.6	2.40	4.4	+18.0	+0.7
1b	Bu	80.3	2.37	1.3	+17.4	+0.8	83.3	2.41	5.4	+18.3	+0.5
1c	$c\text{-}C_6H_{11}$	72.2	2.47	0.7	+18.0	+0.3	75.1	2.43	5.9	+18.2	+0.5
1d	$c\text{-}C_{12}H_{23}$	74.6	2.48	1.8	+17.3	+0.9	75.8	2.44	9.1	+18.4	+0.5
1e	$PhCH_2$	81.1	2.04	0.6	+18.2	+0.3	84.7	2.10	5.0	+18.8	+0.4
1f	Allyl	79.2	2.38	1.2	+17.9	+0.6					
1g	Ph	67.3	2.44	0.9	+19.1	+0.4	71.2	2.54	14.6	+19.3	+0.3
1h	$o\text{-}MeC_6H_4$	81.8	2.38	36.5	+19.0	+0.5	81.2	2.35	37.8	+19.2	+0.4
1i	α-Naphthyl[a]	83.7	2.30	37.4	+19.1	+0.6	84.0	2.28	37.6	+19.8	+0.2
1j	$o\text{-}CF_3C_6H_4$[a]	90.8	2.40	22.0	+20.4	+0.6					
2b	Bu	79.4		0.5			81.6	2.94	4.4		
2e	$PhCH_2$						83.5	2.70	4.2	Σ 18.6	
2g	Ph	65.7	3.02	1	Σ 17.3		70.3	3.05	15		

[a] *Cis*- and *trans*-isomer cannot be unambiguously assigned.

phenyl compounds are characterized by large P-P coupling constants which are almost similar for both isomers.

^{31}P NMR spectra of the *ortho*-tolyl compound run at variable temperatures between 300 K and 423 K show two separate ^{31}P signals at all temperatures. Line broadening has not been detected. Thus, a restricted rotation of the tolyl group does not account for the two ^{31}P signals.

Since both isomers of **1h** and **1i** are formed in similar yields and furthermore, ^{31}P chemical shifts and P-P coupling constants differ only slightly an unambiguous configuration assignment cannot be done by NMR. Probably, the very small differences are caused by the bulkiness of the substituents (*ortho*-tolyl, α-naphthyl), especially in the vicinity of the P-substituents. This prevents a coplanar arrangement of the phenyl (naphthyl) ring and the PN_2P ring. Due to sterical hindrance the phenyl (naphthyl) ring is turned out of this plane almost perpendicular to the PN_2P ring. This assumption is supported by the results of ^{13}C NMR spectroscopy. As well known, vicinal P-C coupling constants show a characteristic dependence on the dihedral angle.[15] Although the coupling constants $^3J_{PNCC}$ of diazadiphosphetidines **1** and **2** are rather small (2–7 Hz) differences between phenyl and *ortho*-substituted aryl compounds are obvious. In the phenyl compound the vicinal coupling constant is larger (see Table II). Thus, a conformation with P—N—C—C dihedral angles close to 0° and 180°, respectively, should predominate in solution whereas for the *o*-tolyl compound a conformation with values close to 90° and −90° should be the preferred one. Differences in the preference of conformations are also reflected by the chemical shifts of the *ortho*-C atoms (see Table II; Ph: $C_{2,6}$; *o*-MeC_6H_4: C_6). In the *ortho*-tolyl compound $\delta(C_6)$ is ca. 10–12 ppm shifted to higher frequencies.

Further, it is interesting that in *ortho*-substituted aryl compounds long range couplings $^4J_{PC}$ and $^5J_{PC}$ are visible. The assignment of the ^{13}C resonances of **1h** has been confirmed by selective ^1H decoupling experiments, that of **1j** by considering the ^{19}F-^{13}C couplings.

The configuration assignment of the bis(ethylthio)-diazadiphosphetidines **2** is based on analogeous relations like for the bis(methylthio)-diazadiphosphetidines **1**. It is also valid that $\delta(P)$, $|^2J_{PP}|$ and $\delta(S\underline{C}H_2)$ of the *cis* isomer are larger for compounds with N substituents like *n*-alkyl and phenyl.

Crystal Structure Analysis

Some crystal structures of diazadiphosphetidines with four-coordinate phosphorus atoms $[R^1P(S)NR^2]_2$ are known from the literature.[5,12,13,16–23] Accordingly, it can be summarized that in *trans* isomers the PN_2P ring is planar (C_{2h} symmetry) whereas in *cis* isomers this ring is either folded or planar (C_{2v} symmetry). The magnitude of the ring puckering depends on the bulkiness of the substituents attached to phosphorus and nitrogen. Furthermore, the nitrogen substituent mainly affects the geometry at the ring nitrogen. Depending on its bulkiness it is turned out of the ring plane and causes variations of the bond angles within the four-membered ring.

Recrystallization of a pure isomer of **1g** from chloroform yielded single crystals of X-ray structure analysis quality (Figure 3). Single crystals of **1h** were obtained by slow crystallization either from chloroform (*trans* isomer) or dichloromethane (*cis* isomer) of a sample containing the isomer mixture (see Figues 4 and 5).

TABLE II

^{13}C Chemical shifts and P-C coupling constants of 2,4-bis(methylthio)-diazadiphosphetidines $[MeSP(S)NR]_2$ **1** and 2,4-bis(ethylthio)-diazadiphosphetidines $[EtSP(S)NR]_2$ **2** in $CDCl_3$

compd	R	$\delta(SCH_n)$ $(^2J_{PC}; ^4J_{PC})$	$\delta(CH_3)$ $(^3J_{PC}; ^5J_{PC})$	$\delta(C_1)$ $(^2J_{PC})$	$\delta(C_2)$ $(^3J_{PC})$	$\delta(C_3)$ $(^4J_{PC})$	$\delta(C_4)$ $(^5J_{PC})$	$\delta(C_5)$	$\delta(C_6)$	$\delta(C_7)$
trans-**1a**	Me	16.89 (±5.4; ±0.6)		24.48						
cis-**1a**		18.25 (±4.9; ±1.2)		24.72						
trans-**1b**	Bu	16.84 (±5.6; ±0.3)		40.42	31.97 (2.5)	20.40	13.55			
cis-**1b**		18.13 (±3.8; ±1.2)		40.44	31.93 (3.0)	20.30	13.60			
trans-**1c**	c-C_6H_{11}	17.48 (±5.2; ±0.4)		54.59	32.68 (4.2)	25.30	25.09	25.27	32.49 (4.7)	
cis-**1c**		18.60 (±4.3; ±0.8)		54.45	32.91 (4.9)	25.28	25.28	25.28	32.91 (4.9)	
trans-**1e**	$PhCH_2$	16.59 (Σ 5.8)		44.14	135.92 (2.1)	129.09	128.60	128.03	128.60	129.09
cis-**1e**		17.80 (±4.9; ±0.2)		44.32	136.21 (3.3)	128.83	128.56	127.84	128.56	128.83
trans-**1f**	Allyl	17.01 (±5.2; ±0.5)		42.73	132.44 (2.9)	119.07				
trans-**1g**	Ph	17.31 (±5.3; ±0.5)		134.46 (1.2)	119.31 (7.1)	129.81	125.11 (< 1)	129.81	119.31 (7.1)	

cis-**1g**		18.95 (Σ 5.3)		133.90 (0.8)	121.70 (6.5)	129.61	125.71 (1.2)	129.61	121.70 (6.5)	
trans-**1h**	*o*-MeC$_6$H$_4$	18.85 (Σ 5.3)		130.86 (1.6)	139.23 (4.1)	131.48 (2.2)	128.95 (2.6)	126.54 (2.4)	131.56 (3.2)	19.68 (1.0)
cis-**1h**		18.82 (Σ 5.0)		130.78 (1.6)	139.64 (4.0)	131.42 (2.1)	129.05 (2.7)	126.48 (2.5)	131.58 (3.2)	19.58 (1.1)
1j	*o*-CF$_3$C$_6$H$_4$	18.23 broad		130.26	130.14 (4.4)	127.26	132.32	129.16 (2.4)	136.01 (3.9)	123.04
trans-**2b**	Bu	29.58 (±5.1; ±0.2)	15.16 (±7.1; 0)	40.60	31.93 (2.6)	20.41	13.58			
cis-**2b**		31.10 (±4.7; ±0.1)	16.00 (Σ 6.0)	40.50	31.85 (3.0)	20.31	13.60			
cis-**2e** [a]	PhCH$_2$	31.04	15.37 (Σ 4.4)	44.66	136.68 (3.3)	128.92	128.50	127.69	128.50	128.92
trans-**2g**	Ph	29.96 (±6.7; ∓0.8)	14.83 (±7.5; ∓0.2)	134.78	119.50 (7.2)	129.73	124.94	129.73	119.50 (7.2)	
cis-**2g**		31.89 (Σ 4.9)	15.62 (Σ 6.4)	133.96	122.40 (6.2)	129.51	125.84	129.51	122.40 (6.2)	

[a] *Solvent used* C$_6$D$_6$.

Further data: *trans*-**1d**: δ(^{13}C): 17.95 (SCH$_3$), 52.41 (C$_1$), 30.23 (C$_2$, $^3J_{PC}$ = 3.4 Hz), 30.16 (C$_{12}$, $^3J_{PC}$ = 3.4 Hz); *cis*-**1d**: 18.72 (SCH$_3$), 51.85 (C$_1$), 29.63 (C$_2$, $^3J_{PC}$ = 4.3 Hz), 29.63 (C$_{12}$, $^3J_{PC}$ = 4.3 Hz).

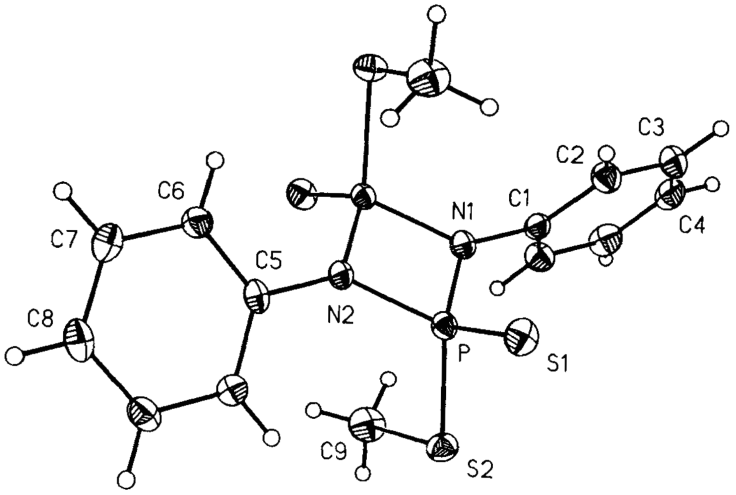

FIGURE 3 Molecular structure of *trans*-[MeSP(S)NPh]$_2$.

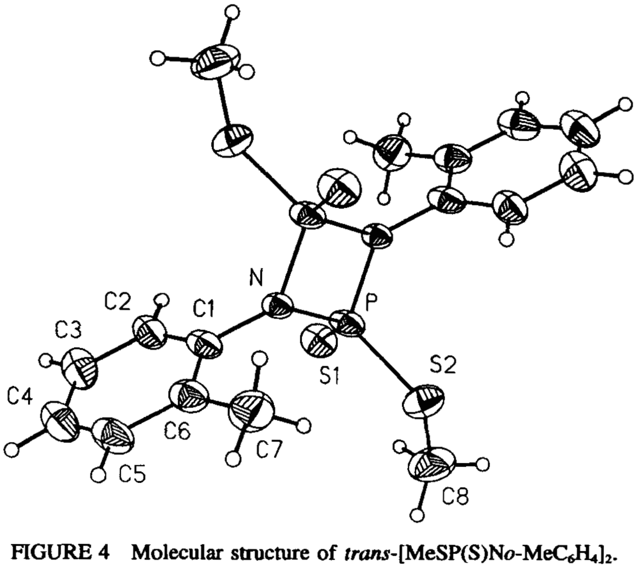

FIGURE 4 Molecular structure of *trans*-[MeSP(S)N*o*-MeC$_6$H$_4$]$_2$.

As expected the PN$_2$P ring of *trans*-**1g** and *trans*-**1h** is planar. In *cis*-**1h** this ring is folded. The molecule of **1g** is characterized by a twofold axis given by N(1) ··· N(2). The molecule of *trans*-**1h** is associated with a crystallographic inversion centre while the molecule of *cis*-**1h** has no symmetry element.

Comparing the bond lengths and bond angles of the three molecules it becomes obvious that some of these values are very similar for both isomers of **1h** but differ considerably from those of **1g** (see Tables III–V). The bond angles of the PN$_2$P ring of the *o*-tolyl compounds are shifted by ca. 1.5° towards right angles compared to those of the phenyl compound. This is reflected by remarkable differences of the

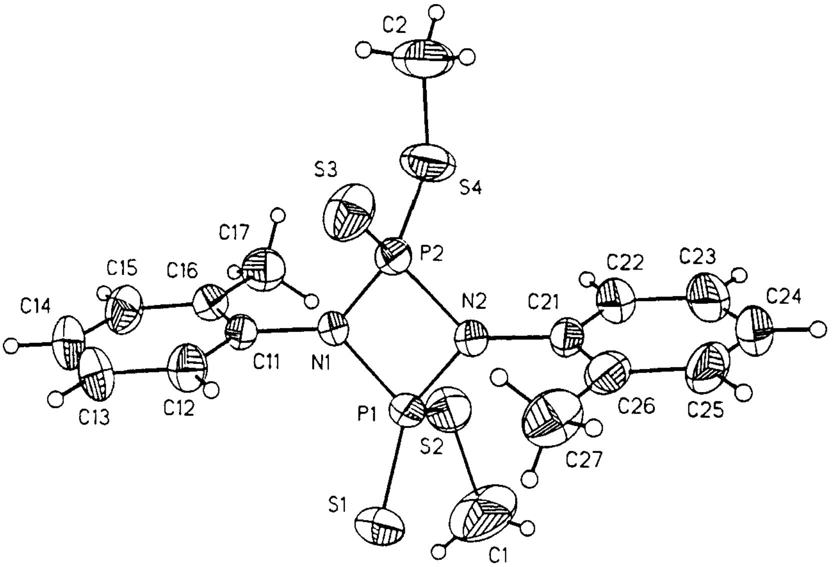

FIGURE 5 Molecular structure of *cis*-[MeSP(S)N*o*-MeC$_6$H$_4$]$_2$.

TABLE III
Selected atomic distances [Å], bond angles and torsion angles [°] for compound *trans*-**1g**

P–N(1)	1.690(2)	P–N(2)	1.697(2)
P–S(1)	1.9160(9)	P–S(2)	2.0574(10)
P···P#	2.5562(13)	S(2)–C(9)	1.813(2)
N(1)–C(1)	1.440(4)		
N(1)–P–N(2)	81.97(10)	S(1)–P–S(2)	108.51(4)
S(1)–P···P#1	132.57(5)	C(1)–N(1)–P	130.84(6)
P–N(1)–P#1	98.31(12)	C(5)–N(2)–P	131.13(6)
P#1–N(2)–P	97.75(12)		
P–N(1)–C(1)–C(2)	-81.65	P-N(1)-C(1)-C(2)#1	98.35
P–N(2)–C(5)–C(6)	142.73	P-N(2)-C(5)-C(6)#1	-37.27
S(1)–P–S(2)–C(9)	173.5		

Symmetry transformations for equivalent atoms: # -x, y, -z+3/2

atomic distances P···P being 2.556 Å (*trans*-**1g**), 2.521 Å (*trans*-**1h**) and 2.532 Å (*cis*-**1h**), respectively.

In the phenyl compound the C atom attached to the ring nitrogen is situated in the PN$_2$P plane leading to a trigonal planar N surroundings. In the *trans-ortho*-tolyl compound the N atom is trigonal pyramidal with the attached C atom 0.3025 Å off plane. In the corresponding *cis* isomer both N atoms have different trigonal pyramidal surroundings (sum of the bond angles: N(1) 354.75°, N(2) 358.38°). Comparing the dihedral angles between selected planes the following conclusions may be drawn: i) **1g**: the two phenyl substituents are rotated by different angles (37.1° and 81.6° with

TABLE IV

Selected atomic distances [Å], bond angles [°] and torsion angles [°] for compound *trans*-**1h**

P–N	1.688(3)	P–N#1	1.686(3)
P–S(1)	1.922(2)	P–S(2)	2.059(2)
P···P#1	2.521(2)	S(2)–C(8)	1.805(6)
N(1)–C(1)	1.434(5)		
N–P–N#1	83.3(2)	S(1)–P–S(2)	115.13(7)
S(1)–P···P#1	130.11(10)	C(1)–N–P	129.7(3)
C(1)–N–P#1	131.4(3)	P–N–P#1	96.7(2)
P–N–C(1)–C(2)	-72.4	P–N–C(1)–C(6)	106.8
P–N#1–C(1)#1–C(2)#1	-86.35	P–N#1–C(1)#1–C(6)#1	94.4
S(1)–P–S(2)–C(8)	-2.5		

Symmetry transformations for equivalent atoms: # -x+2, -y+1, -z

TABLE V

Selected atomic distances [Å], bond angles [°] and torsion angles [°] for compound *cis*-**1h**

P(1)–N(1)	1.686(3)	P(1)–N(2)	1.688(3)
P(1)–S(1)	1.919(2)	P(1)–S(2)	2.067(2)
P(1)···P(2)	2.532(2)	S(2)–C(1)	1.792(6)
N(1)–C(11)	1.452(4)	N(1)–P(2)	1.697(3)
P(2)–N(2)	1.699(3)	P(2)–S(3)	1.914(2)
P(2)–S(4)	2.067(2)	S(4)–C(2)	1.803(5)
N(2)–C(21)	1.443(4)		
N(1)–P(1)–N(2)	83.41(14)	S(1)–P(1)–S(2)	115.60(8)
S(1)–P(1)···P(2)	130.69(8)	C(11)–N(1)–P(1)	129.3(2)
C(11)–N(1)–P(2)	128.5(3)	P(1)–N(1)–P(2)	96.95(14)
N(1)–P(2)–N(2)	82.75(14)	S(3)–P(2)–S(4)	115.24(8)
S(3)–P(2)···P(1)	129.23(8)	C(21)–N(2)–P(1)	130.3(3)
C(21)–N(2)–P(2)	131.1(2)	P(1)–N(2)–P(2)	96.78(14)
P(1)–N(1)–C(11)–C(12)	71.0	P(1)–N(1)–C(11)–C(16)	-108.0
P(1)–N(2)–C(21)–C(22)	85.4	P(1)–N(2)–C(21)–C(26)	-96.75
P(2)–N(1)–C(11)–C(12)	-77.4	P(2)–N(1)–C(11)–C(16)	103.6
P(2)–N(2)–C(21)–C(22)	-75.6	P(2)–N(2)–C(21)–C(26)	102.2
S(1)–P(1)–S(2)–C(1)	-20.1	S(3)–P(2)–S(4)–C(2)	7.3

respect to the PN_2P ring plane); between the phenyl substituents of one molecule an angle of 118.7° is realized (anti-clinal position); ii) **1h**: both tolyl substituents are rotated in such a way that the substituents are approximately perpendicular to the PN_2P plane (angle between phenyl ring and PN_2P ring plane 96.8° for *trans*-**1h**, 87.6 and 86.2° for *cis*-**1h**). The corresponding torsion angles P—N—C—C (Tables IV and V) confirm the preferable perpendicular position of the *ortho*-tolyl substituent with respect to the PN_2P ring. Besides, the bulkiness of the nitrogen substituent

TABLE VI

Summary of crystal data, data collection and structure refinement for *trans*-**1g**, *trans*-**1h** and *cis*-**1h**

	trans-**1g**	*trans*-**1h**	*cis*-**1h**
formula	$C_{14}H_{16}N_2P_2S_4$	$C_{16}H_{20}N_2P_2S_4$	$C_{16}H_{20}N_2P_2S_4$
M_r	402.47	430.52	430.52
crystal system	monoclinic	monoclinic	monoclinic
space group	C2/c	$P2_1/c$	$P2_1/n$
a, Å	9.373(2)	7.083(1)	9.994(2)
b, Å	16.145(3)	18.275(4)	15.702(2)
c, Å	11.705(2)	8.257(2)	13.668(5)
β, deg	92.11(3)	110.13(3)	105.14(2)
V, Å^3	1770.1(6)	1003.5(4)	2070.4(9)
Z	4	2	4
D_x, g/cm^3	1.510	1.425	1.381
μ, cm^{-1}	7.14	6.35	6.15
T, K	293 (2)	153 (2)	293 (2)
λ(MoKα), Å	0.71073	0.71073	0.71073
diffractometer	Siemens	Stoe-Siemens AED	KUMA KM-4
scan mode	ω–2θ	ω–2θ	ω–2θ
max 2θ, deg	45	50.2	53.3
hkl ranges	h = -10 to 10	h = -8 to 8	h = -11 to 11
	k = -17 to 17	k = -21 to 15	k = -18 to 12
	l = -12 to 12	l = -9 to 9	l = -16 to 12
reflections collected	2298	3298	4136
independent	1149	1781	2822
observed [$I_0 > 2\sigma(I_0)$]	1147	1777	2818
refinement method	Full-matrix least-squares on F^2		
no. of parameters refined	104	111	221
R1	0.0281	0.0507	0.0527
wR2	0.0760	0.1246	0.1376

affects the position of the MeS group. In the phenyl compound *trans*-**1g** both exocyclic P substituents are anti-periplanar with the torsion angle φ (S═P—S—C) being 173.6°. In the *ortho*-tolyl compounds these substituents are syn-periplanar with φ being 2.5° (*trans*) and −20.1° and 7.3° (*cis*), which causes a larger endocyclic S—P═S bond angle.

The C—C bond lengths of the phenyl group are very similar (1.38 to 1.387 Å) whereas these values alternate and vary from 1.365 to 1.407 Å for the *o*-tolyl group. The conformation differences of both *trans* isomers as well as the similar bond and torsion angles of the *cis* and *trans* isomer of **1h** are well reflected by the corresponding NMR data.

The investigations have shown that differences of $\delta(P)$, J_{PP} and $\delta(S\underline{C}H_3)$ in the solution NMR spectra of diazadiphosphetidines $[MeSP(S)NR]_2$ can be used for the configuration assignment of the ring compound. The assignment is not unambiguous

TABLE VII

Fractional atomic coordinates and equivalent isotropic temperature factors [Å^2] for *trans*-**1g**

atom	x	y	z	U_{eq}
P	0.1351(1)	0.3805(1)	0.7388(1)	0.016(1)
S(1)	0.2512(1)	0.3811(1)	0.6075(1)	0.024(1)
S(2)	0.2670(1)	0.3768(1)	0.8832(1)	0.022(1)
N(1)	0	0.3120(1)	0.7500	0.018(1)
N(2)	0	0.4496(1)	0.7500	0.017(1)
C(1)	0	0.2228(2)	0.7500	0.019(1)
C(2)	0.0008(2)	0.1803(1)	0.6473(2)	0.023(1)
C(3)	0.0010(2)	0.0945(1)	0.6479(2)	0.028(1)
C(4)	0	0.0519(2)	0.7500	0.028(1)
C(5)	0	0.5387(2)	0.7500	0.016(1)
C(6)	-0.1121(2)	0.5811(1)	0.6964(2)	0.020(1)
C(7)	-0.1118(2)	0.6670(1)	0.6972(2)	0.023(1)
C(8)	0	0.7098(2)	0.7500	0.024(1)
C(9)	0.1427(3)	0.3889(2)	0.9971(2)	0.031(1)

TABLE VIII

Fractional atomic coordinates and equivalent isotropic temperature factors [Å^2] for *trans*-**1h**

atom	x	y	z	U_{eq}
P	1.0114(2)	0.5320(1)	0.1383(1)	0.035(1)
S(1)	1.2405(2)	0.5724(1)	0.3163(1)	0.041(1)
S(2)	0.7418(2)	0.5427(1)	0.1792(2)	0.044(1)
N	1.0308(5)	0.4462(2)	0.0697(4)	0.026(1)
C(1)	1.1140(8)	0.3818(2)	0.1674(5)	0.035(1)
C(2)	1.3248(7)	0.3765(2)	0.2466(5)	0.037(1)
C(3)	1.4064(8)	0.3155(3)	0.3424(6)	0.047(1)
C(4)	1.2814(8)	0.2604(3)	0.3627(6)	0.048(1)
C(5)	1.0772(9)	0.2661(2)	0.2839(6)	0.047(1)
C(6)	0.9874(8)	0.3266(2)	0.1842(6)	0.039(1)
C(7)	0.7660(8)	0.3321(3)	0.0981(7)	0.051(1)
C(8)	0.8145(10)	0.5862(3)	0.3880(7)	0.066(2)

if an *ortho*-substituted aryl group is attached to the ring nitrogen since in this case these data are too similar for both isomers.

The P-P coupling constant covers a wide range although only the N-substituent was changed. A variation of this substituent causes both changes of the geometry of the compound and of the electronic situation at the P and N atoms.

X-ray diffraction analysis of single crystals of **1g** and **1h** confirm the configuration assignment for **1g** based on NMR data and support the interpretation of conformational effects.

TABLE IX

Fractional atomic coordinates and equivalent isotropic temperature factors [Å^2] for *cis*-**1h**

atom	x	y	z	U_{eq}
P(1)	-0.3141(1)	0.2001(1)	-0.2421(1)	0.037(1)
S(1)	-0.1715(1)	0.2845(1)	-0.2011(1)	0.066(1)
S(2)	-0.4556(1)	0.2217(1)	-0.3799(1)	0.057(1)
N(1)	-0.2737(3)	0.0960(2)	-0.2445(2)	0.032(1)
C(1)	-0.4391(9)	0.3335(4)	-0.4002(6)	0.112(3)
C(11)	-0.1586(4)	0.0562(2)	-0.2735(3)	0.032(1)
C(12)	-0.0279(4)	0.0653(3)	-0.2106(3)	0.045(1)
C(13)	0.0869(5)	0.0286(3)	-0.2353(4)	0.051(1)
C(14)	0.0636(5)	-0.0160(3)	-0.3252(4)	0.056(1)
C(15)	-0.0665(5)	-0.0240(3)	-0.3881(4)	0.052(1)
C(16)	-0.1842(4)	0.0113(3)	-0.3648(3)	0.037(1)
C(17)	-0.3258(5)	0.0016(3)	-0.4369(4)	0.053(1)
P(2)	-0.3557(1)	0.0629(1)	-0.1572(1)	0.039(1)
S(3)	-0.2507(2)	0.0139(1)	-0.0325(1)	0.061(1)
S(4)	-0.5243(1)	-0.0079(1)	-0.2352(1)	0.063(1)
N(2)	-0.4023(3)	0.1671(2)	-0.1593(2)	0.034(1)
C(2)	-0.5348(7)	-0.0933(3)	-0.1493(5)	0.088(2)
C(21)	-0.5097(4)	0.2089(2)	-0.1242(3)	0.036(1)
C(22)	-0.6455(5)	0.2008(3)	-0.1819(4)	0.051(1)
C(23)	-0.7527(6)	0.2401(3)	-0.1500(5)	0.067(2)
C(24)	-0.7186(7)	0.2850(3)	-0.0598(6)	0.078(2)
C(25)	-0.5859(7)	0.2914(3)	-0.0037(4)	0.068(2)
C(26)	-0.4736(5)	0.2530(3)	-0.0326(3)	0.048(1)
C(27)	-0.3284(6)	0.2623(4)	0.0301(4)	0.066(2)

EXPERIMENTAL

Syntheses: 2,4-Bis(methylthio)-diazadiphosphetidines **1** and 2,4-bis(ethylthio)-diazadiphosphetidines **2** were prepared from py.PS_2Cl (py = pyridine)[24] and the corresponding primary amine according to Donath *et al.*[13]

A mixture of primary amine (0.05 mol), triethylamine (9.9 g, 0.1 mol) and benzene (20 ml) was added dropwise to a suspension of py.PS_2Cl (10.5 g, 0.05 mol) in benzene (40 ml). The reaction mixture was boiled under reflux for two hours. After the mixture has been cooled the precipitate was filtered off and washed with MeOH to remove the amine hydrochloride. The precipitate (0.01 mol) was suspended in benzene (50 ml) and freshly distilled alkyl iodide (0.05 mol) was added. The mixture was slightly refluxed for 0.5 h (MeI) or 4 h (EtI), respectively. After cooling the amine hydroiodide was filtered off. Removal of the solvent *in vacuo* yielded crude **1** and **2**, respectively. Repeating the crystallization from cyclohexane allowed either isolation or enrichment of one isomer.

The 1,3-dicyclohexyl-diazadiphosphetidine **1c** (compare References 25 and 26) was obtained when modifying the above procedure as follows. The mixture of primary amine, triethylamine and py.PS_2Cl in benzene was refluxed for 2 1/2 h. After cooling the solution the precipitate, which was completely soluble in MeOH, was filtered off. The solvent was partially removed *in vacuo* and MeI (20 ml) and benzene (30 ml) were added to the residue. This mixture was refluxed for 1 h. After cooling the precipitate was filtered off and washed with benzene. Removal of the solvent *in vacuo* yielded a brown viscous crude product. The crude product was washed several times with hot cyclohexane. Crystalline **1c** was obtained from the cyclohexane extract after removal of the solvent.

NMR measurements: Solution NMR spectra were recorded on Bruker spectrometers WH 90DS (^1H at 90.0 MHz) and MSL 300 (^{31}P at 121.5 MHz, ^{13}C at 75.5 MHz). A digital resolution of 0.1 Hz for ^1H spectra and 0.4 Hz for ^{13}C spectra was achieved. The compounds were dissolved in $CDCl_3$. ^{31}P chemical shifts are referenced to 85% phosphoric acid (0 ppm); ^1H and ^{13}C chemical shifts to TMS (0 ppm).

Crystal structure determination: Single crystals of **1g** and **1h** suitable for X-ray work were obtained by recrystallization from chloroform (*trans* isomers) and dichloromethane (*cis*-**1h**). The crystals were attached to glass fibers using either epoxy resin or silicon grease. For the low temperature measurement (*trans*-**1h**) the goniometer head with the crystal was mounted on the diffractometer in the cold nitrogen stream of the Cryosystems low temperature device. Crystal data and details of data collection, structure determination and refinement are summarized in Table VI. The lattice parameters of **1g** were refined by a least-squares fit to 42 reflections with $\theta = 25.1-30.1°$, those of *trans*-**1h** by a fit to 44 reflections with $\theta = 7.6-26.9°$ and of *cis*-**1h** by a fit of 31 reflections with $\theta = 11.0-29.9°$. The structures were solved by direct methods and the E-maps revealed all non-hydrogen atoms. The hydrogen atoms of the phenyl rings were inserted in the idealized positions, the positions of the hydrogens of the methyl groups were found by a circular electron density calculation around the appropriate carbon atoms. The non-hydrogen atoms were refined anisotropically, hydrogen atoms were refined on the assumption of a "ride-on" model with U values fixed to 1.2 U_{eq} (phenyl rings) or 1.5 U_{eq} (methyl groups) of the carbon atoms to which they were attached. Final atomic coordinates are given in Tables VII–IX.

The programs employed were SHELXS-86[27] for structure solution, SHELXL-93[28] for structure refinement, and the figures were drawn using the XP program of the Siemens SHELXTL system.[29]

Full details of the structure determination will be deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein- Leopoldshafen, Germany and can be obtained from there on quoting the full literature citation and the reference numbers.

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