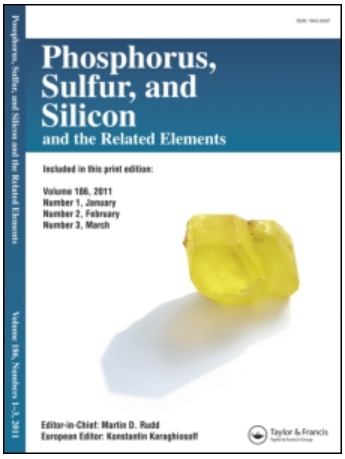

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SYNTHESIS AND MULTINUCLEAR MAGNETIC RESONANCE STUDY (^{1}H, ^{13}C, ^{15}N, ^{29}Si, ^{31}P NMR) OF BIS(AMINO)PHOSPHINYL- AND AMINO(*tert*-BUTYL)PHOSPHINYL SULFUR DIIMIDES

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SYNTHESIS AND MULTINUCLEAR MAGNETIC RESONANCE STUDY (^{1}H, ^{13}C, ^{15}N, ^{29}Si, ^{31}P NMR) OF BIS(AMINO)PHOSPHINYL- AND AMINO(*tert*-BUTYL)PHOSPHINYL SULFUR DIIMIDES

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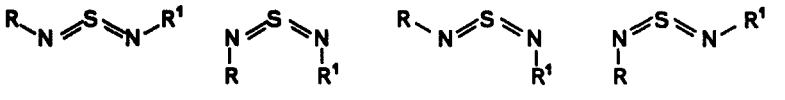
Sulfur diimides bearing either bis(amino)phosphinyl (**1, 4, 5**) or amino(*tert*-butyl)phosphinyl substituents (**2, 3**) were prepared by salt elimination reactions from the potassium sulfur diimides K_2SN_2, KNSNtBu and $KNSNSiMe_3$ and aminophosphinyl chlorides. Bulky amino groups are essential to prevent self-degradation of the sulfur diimides via sulfur abstraction. The compounds were characterized by multinuclear magnetic resonance (^{1}H, ^{13}C, ^{15}N, ^{29}Si and ^{31}P NMR). The configuration of some of the new sulfur diimides could be established by combined information from NMR measurements at low temperature, in particular by ^{15}N and ^{31}P NMR. These results suggest that all sulfur diimides studied are highly fluxional, undergoing fast E/Z ⇄ Z/E rearrangement at room temperature and most of them also at −100°C. The free activation enthalpy, $\Delta G^{\#}$, of this process is at least 10 kJ/mol lower for bis[amino(*tert*-butyl)phosphinyl sulfur diimides (**2**) than for *N*-amino(*tert*-butyl)phosphinyl-*N'*-*tert*-butyl sulfur diimides (**3**). In the absence of the P-*tert*-butyl group, it was not possible at all to observe a distinct configuration at low temperature.

Key words: Sulfur diimides; multinuclear NMR; fluxionality in solution.

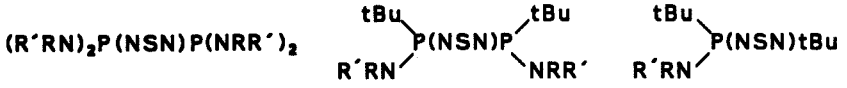
INTRODUCTION

The synthetic potential of the heterocumulene system in sulfur diimides depends on the nature of the substituents and on the preferred structure in solution.[1] Sulfur diimides containing either organometallic substituents or substituents which bear additional functional groups are of particular interest in this respect and are, therefore, extensively studied at the present time.[2–5] Recently, we have reported on the synthesis of the first examples of P-functionally substituted phosphinyl sulfur diimides.[6] However, the question for the preferred configuration (E/E, Z/Z or fast E/Z ⇄ Z/E rearrangement, see Scheme I) had remained open.



SCHEME I Configurations of sulfur diimides

In continuing these studies, we have now prepared a variety of aminophosphinyl sulfur diimides (**1** to **5**) and studied them by multinuclear magnetic resonance (^{1}H, ^{13}C, ^{15}N, ^{29}Si, ^{31}P NMR) in order to obtain information about their structure in solution.



1

	a	b	c
R	iPr	$-(CH_2)_2-$	$-(CH_2)_3-$
R'	iPr	tBu	tBu

2

	a	b	c
R	Me	Me	Me
R'	tBu	Ph	2-biph

3

	d	e	f	g	h
	Et	Bu	Bz	Ph	iPr
	Ph	Ph	tBu	Ph	$SiMe_3$

$(R'RN)_2P(NSN)R^1$

4 (R^1 = tBu), **5** (R^1 = $SiMe_3$)

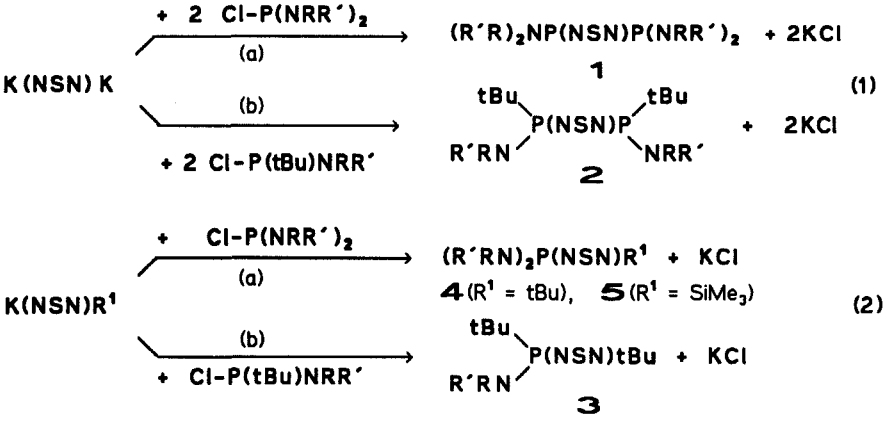
	a	b	c	d	e
R	iPr	$-(CH_2)_2-$	$-(CH_2)_3-$	Bz	$-(SiMe_2)_2-$
R'	iPr	tBu	tBu	tBu	tBu

(R = $-(CH_2)_n-$ and $-(SiMe_2)_2-$ indicate part of the 1,3,2-diazaphosphacyclopentane (n = 2) or -cyclohexane (n = 3) ring; Bz = CH_2-C_6H_5; 2-biph = 2-C_6H_5-C_6H_4).

RESULTS AND DISCUSSION

Synthesis

All compounds **1** to **5** were prepared by salt elimination reactions, using the respective potassium sulfur diimides[7,8] and phosphorus chlorides[9] [Equations (1) and (2)]. If R^1 = $SiMe_3$, the reaction according to Equation (2b) leads to transimidation (exchange of imido groups), and the products **2** are obtained together with bis(trimethylsilyl) sulfur diimide. As reported previously,[6] bulky substituents at the amino nitrogen atoms in **1**, **4**, and **5** and also at the phosphorus atom in **2** and **3** are necessary in order to prevent self-degradation by sulfur abstraction. The adequate choice of substituents is particularly critical in the case of the



bis(amino)phosphinyl sulfur diimides **1**. Thus, compounds **1b, c** with the 1,3,2-diazaphosphacyclopentane- and -cyclohexane ring, respectively, are stable for sev-

TABLE I

^{13}C and ^{31}P NMR data[a] of bis[(bisamino)phosphinyl] sulfur diimides (**1**)

Compound	$\delta^{13}C$		$\delta^{31}P$
Nr	R	R´	
1a	46.2,[b] 24.1, 25.1 [12.8] [12.7] [5.2]		73.8
1b	44.8 [9.4]	52.8,29.6 [13.7] [11.1]	88.4
1c	39.4,[c] 28.7 [4.4] [< 2]	55.7,30.0 [23.4] [15.8]	79.8

[a] In [D_8]-toluene (ca. 10–20% V/V) at 25°C; coupling constants $J(^{31}P^{13}C)$ (in Hz) are given in square brackets.
[b] $\delta^{15}N$ (PNiPr) −296.7, $^1J(^{31}P^{15}N)$ 73.8 Hz.
[c] $\delta^{15}N$ (PNtBu) −305.7, $^1J(^{31}P^{15}N)$ 69.2 Hz.

TABLE II

^{13}C and ^{31}P NMR data[a] of bis[amino(*tert*-butyl)phosphinyl] sulfur diimides (**2**)

Compound	$\delta^{13}C$			$\delta^{31}P$
Nr	R	R´	tBu-P	
2a	31.1,31.2 [7.5] [7.5]	55.8,30.1,30.2 [30.8] [13.1] [13.1]	35.9,36.0,27.5,27.4 [16.4] [16.4] [18.5] [18.5]	91.9,90.4
2b	34.1,34.2 [5.9] [5.9]	150.5,150.6[b] [23.4] [23.4]	36.9,37.0,26.2,26.4 [18.0] [18.0] [18.5] [18.5]	93.7,92.7
2c	38.0,38.3 [6.7] [6.7]	149.1,149.2[c] [22.8] [22.8]	37.6,38.0,27.0,27.2 [20.6] [20.6] [18.5] [18.5]	99.5,98.2
2d	40.9,41.6,13.6,13.9 [< 2] [< 2] [< 2] [< 2]	147.7,147.8[d] [22.2] [22.2]	36.6,36.8,26.3,26.6 [20.5] [20.5] [19.1] [19.1]	98.3,97.3
2e	47.5,31.9,20.4,14.0 [< 2] [< 2] [< 2] [< 2]	148.3,148.4[e] [21.3] [21.3]	36.7,36.9,26.3,26.6 [18.8] [18.8] [19.1] [19.1]	97.8,97.8
2f	49.5, 144.0[f] [8.6] [< 2]	57.5,30.5 [23.1] [13.7]	35.6, 26.3 [18.0] [18.8]	96.0,95.0
2g	148.1,149.3[g] [8.2] [8.2]		37.5,37.6,25.8 [18.1] [18.1] [20.5]	91.5,91.1

[a] See footnote a, Table I.
[b] Other ^{13}C resonances: 117.3 [18.0], 117.4 [18.0] (o); 128.8 (m); 120.0, 120.1 (p).
[c] Other ^{13}C resonances (not assigned): 139.4 [2.2], 137.3, 131.9, 130.0, 127.0, 126.9, 125.5 [2.2], 124.4 [2.2].
[d] Other ^{13}C resonances: 121.5 [14.2] (o); 128.6 (m); 121.2, 121.3 (p).
[e] Other ^{13}C resonances: 124.8 [6.5], 125.2 [6.5] (o); 128.7 (m); 121.5 (p).
[f] Other ^{13}C resonances (not assigned): 127.6, 126.6, 125.7.
[g] Other ^{13}C resonances: 123.9 (o); 128.9 (m), 126.8 (p).

TABLE III

^{13}C and ^{31}P NMR data[a] of *N*-amino(*tert*-butyl)phosphinyl-*N'*-*tert*-butyl sulfur diimides (**3**)

Compound	$\delta^{13}C$				$\delta^{31}P$
Nr	R	R'	tBu-P	tBuN=	
3a	29.9[b]	55.2,29.6 [12.9][13.1]	35.0,27.0 [16.4][18.5]	61.2,29.9	90.2
3b	34.1 [6.0]	151.2[c] [23.4]	36.5,26.5 [17.4][15.7]	61.7,30.5	94.5
3c	37.0 [7.6]	149.1[d] [22.9]	37.3,26.6 [22.3][18.5]	61.6,29.7	97.7
3d	41.5,14.0 [< 2] [< 2]	148.4[e] [22.3]	36.9,26.4 [18.0][18.5]	61.7, 30.5	99.7
3e	48.0,31.1,20.6,14.0 [< 2] [< 2] [< 2] [< 2]	149.1[f] [19.7]	36.9,26.6 [18.8][18.0]	62.0,30.5	95.3
3f	47.8, 143.8[g] [7.7] [3.4]	57.2,30.3 [22.2][12.8]	34.6,25.8 [15.4][18.8]	61.7,29.6	94.0
3g	149.5,126.1,128.7,123.6 [8.2] [7.3] [< 2] [< 2]		35.4,26.5 [13.6][19.1]	61.8,30.7	92.9
3h	46.8,25.7 [2.4][8.6]	4.4[h] [12.7]	35.6,26.6 [22.9][18.6]	61.7,30.0	92.5

[a] See footnote a, Table I.
[b] Detected only by 2D $^{13}C/^{1}H$ heteronuclear shift correlation.
[c] Other ^{13}C resonances: 117.5 [18.0] (o); 128.6 (m); 119.9 [2.2] (p).
[d] Other ^{13}C resonances (not assigned): 141.7, 139.8 [6.5], 137.2, 131.8 [1.1], 129.8 [2.2], 128.3, 128.1, 126.8, 124.5 [2.2].
[e] Other ^{13} resonances: 122.0 [13.6] (o); 128.6 (m); 121.4 [1.8] (p).
[f] Other ^{13} resonances: 122.6 [12.5] (o); 128.7 (m); 121.7 [1.9] (p).
[g] Other ^{13} resonances (without assignment): 127.7, 126.5, 125.6.
[h] $\delta^{29}Si$ 5.9; $^{2}J(^{31}P^{29}Si)$ 30.8 Hz.

eral hours at room temperature, whereas the corresponding sulfur diimide with $(MetBuN)_2P$ groups starts to decompose below 0°C and cannot be obtained under comparable conditions. The P-*tert*-butyl group in **2** and **3** exerts a useful stabilizing effect, allowing to reduce the steric demand of the amino group. The compounds **1** to **5** are isolated as light- to dark-red, air- and moisture-sensitive, oily liquids or solids (**1a**,[6] **2c**). The solids can be purified by recrystallization, whereas the liquids always retain some impurities (<10%). The liquid compounds decompose upon attempts of either distillation or chromatography on silica gel and Al_2O_3.

NMR measurements

The proposed structures of compounds **1** to **5** are deduced conclusively from their ^{1}H (see Experimental Part), ^{13}C and ^{31}P NMR spectra (Tables I–IV). The twin set of ^{1}H, ^{13}C and ^{31}P NMR signals for compounds **2** is caused by the presence of diastereomers, proving that any inter- or intramolecular exchange of phosphinyl substituents must be slow as compared to the NMR time scale. It has been shown[10]

TABLE IV

^{13}C, ^{15}N, ^{29}Si and ^{31}P NMR data[a] of *N*-bis(amino)phosphinyl-*N'*-*tert*-butyl-(**4**) and -*N'*-trimethylsilyl sulfur diimides (**5**)

Compound			$\delta^{13}C$	$\delta^{31}P$	$\delta^{29}Si$	$\delta^{15}N$	
Nr	R	R'	tBuN= /Me_3SiN=			=NtBu	PNRR'
4a	46.0,24.1,24.6 [12.0][11.9][5.2]		61.3, 30.4	75.9	-	-68.1[b] [< 2]	-291.1 [74.1]
5a	46.5,24.1,24.5 [12.8][8.6][5.1]		1.4	71.1	1.0	-	nm
4b	44.5 [9.4]	52.6,29.5 [13.7][10.6]	61.2,30.0	90.9	-	-72.1[b] [< 2]	-301.4 [62.2]
5b	44.7 [8.5]	52.5,29.6 [13.7][11.1]	1.2	88.7	1.4	-	nm
4c	38.9,28.9 [4.3][< 2]	55.4,29.4 [23.4][15.4]	61.2,30.1	82.2	-	nm	-305.5 [69.6]
5c	39.3,29.0 [4.4][< 2]	55.4,29.5 [23.4][15.3]	1.0	78.7	1.1	nm	-306.4 [68.3]
4d	48.7, 141.8[c] [7.7] [1.7]	56.8,30.7 [27.4][15.4]	60.2,29.7	86.2	-	nm	nm
5d	48.0, 143.5[d] [6.8] [1.7]	57.0,30.8 [27.5][13.7]	0.7	81.4	3.0	nm	nm
4e	3.4, 4.6[e] [< 2][< 2]	56.7,33.2 [29.9][13.7]	61.2,30.1	120.7	-	nm	-291.2 [61.3]

[a] See footnote a, Table I; nm = not measured.
[b] Measured at −10°C.
[c] Other ^{13} resonances (not assigned): 127.2, 127.0, 126.2.
[d] Other ^{13} resonances (not assigned): 127.3, 126.7, 125.4.
[e] δ^{29}Si (Si—Si) −4.7; $^2J(^{31}P^{29}Si)$ 10.3 Hz.

that the δ^1H(=NtBu) values indicate the Z- (high frequency resonances: $\delta^1H > 1.40$) and E-position (low frequency resonances: $\delta^1H < 1.10$) of the =NtBu group. In the case of compounds **3**, averaged ^{1}H(=NtBu) NMR signals are observed at room temperature.

At low temperature, the expected two types of ^{1}H(=NtBu) resonance signals are found for all compounds **3**, with slightly greater integral intensity of the signal for the E-position of the =NtBu group. It is therefore possible to assign ^{13}C and ^{31}P resonances at low temperature to the E/Z and Z/E isomers, respectively (see Figure 1). Thus the ^{31}P NMR signal of a phosphinyl group in Z-position is always at higher frequency than that of the phosphinyl group in E-position. Although the Δ^{31}P values (2.5 to 9 ppm; for most examples $\Delta^{31}P > 7$ ppm) are fairly small, the observed influence on ^{31}P nuclear shielding appears to be a general effect. This is supported by the observation of the 30:70 ratio of ^{31}P NMR signals for Z- and E-position of the phosphinyl substituents in **2c**. Since the Z/Z configuration is unlikely for steric reasons, an equilibrium mixture is assumed to be present with E/Z (=Z/E) and E/E isomer in a ratio of 60:40. It is noteworthy that the barrier to

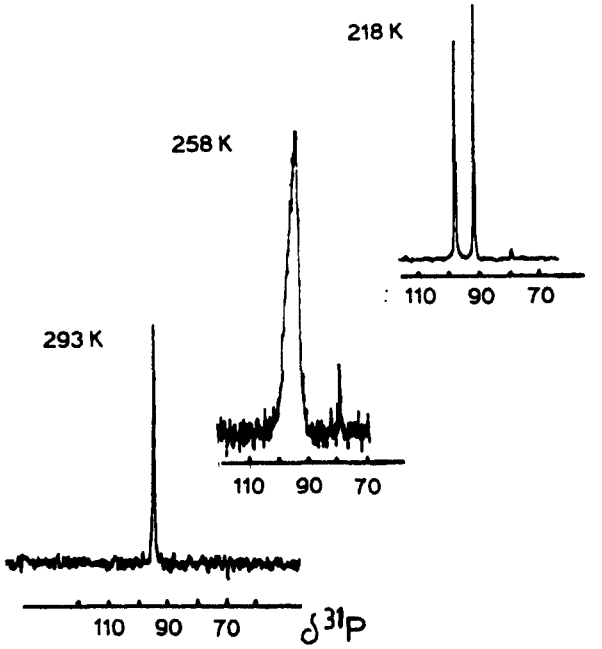


FIGURE 1 36.4 MHz $^{31}P\{^1H\}$ NMR spectra of PhBuN(tBu)P(NSN)tBu (**3e**) at variable temperature, showing the averaged ^{31}P NMR signal for fast E/Z ⇄ Z/E rearrangement at 293 K, the coalescence at 258 K and two signals for the E/Z and Z/E isomers at 218 K.

TABLE V

Results of temperature-dependent multinuclear NMR studies of some *N*-amino(*tert*-butyl)phosphinyl-*N'*-*tert*-butyl sulfur diimides (**3**)[a]

Compound			$\delta^{13}C$ (tBuN=)		$\delta^{31}P$		$\delta^{15}N$ (PN=)		$\delta^{15}N$ (=NtBu)	
Nr	T_c[b]	$\Delta G^{\#}$[c]	Z / E		E / Z		E / Z		Z / E	
3a	253	47.6	62.1,28.8	60.9,31.2	89.0	97.3	-59.1 [68.1]	-139.5 [75.9]	-65.0 [< 2]	+28.4 [11.8]
3d	263	49.5	62.0,28.9	61.0,31.5	95.4	103.8	-58.2 [75.1]	-138.5 [80.0]	-68.0 [< 2]	+26.7 [11.0]
3e	258	48.3	62.1,28.9	61.4,31.2	88.4	97.5	nm	nm	nm	nm
3g	243	48.1	62.2,28.9	61.4,31.2	90.0	92.4	nm	nm	nm	nm

[a] All spectra were measured in [D_8]-toluene, at least 20 K lower than T_c. The E/Z assignment is based on ^1H(=NtBu) resonances, their integral ratio and that of the corresponding ^{31}P resonances; nm = not measured.

[b] Coalescence temperature, [K].

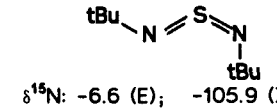
[c] Free activation enthalpy, $\Delta G^{\#}(T_c)$, [kJ/mole].

rotation/inversion of the sulfur diimides is very low for the bis(phosphinyl) sulfur diimides **1** and **2**. Indeed, only in the case of **2c** it was possible to slow down the dynamic process for observing different configurations. In the case of the compounds **3**, the free activation enthalpy, $\Delta G^{\#}$, for the same process is increased by

≈10 kJ/mole, allowing for a more convenient observation by NMR methods (see Table V). Compound **2c** has also been studied by solid-state ^{31}P NMR using cross polarization and magic angle spinning (CP/MAS). Because of the low melting point the spectrum was recorded at −20°C, showing two rather broad and overlapping signals with isotropic $\delta^{31}P$ values similar to those in liquid phase at low temperature.

There are also temperature-dependent changes in the ^{1}H and ^{13}C NMR signals of the substituents R and R′ of the amino group. These are related to hindered rotation about the P—N(amino) bond and correspond closely to the findings reported for the respective phosphorus chlorides which have been reported elsewhere.[9]

The most versatile tool for establishing a definite configuration of sulfur diimides in solution should be ^{15}N NMR due to the sensitivity of ^{15}N nuclear shielding with respect to E- or Z-position of the substituent. The difference in $\delta^{15}N$ values is particularly large for =NtBu groups, as has been shown for di-*tert*-butyl sulfur diimide[10] for which the E/Z configuration dominates at low temperature (−40°C).



$\delta^{15}N$: -6.6 (E); -105.9 (Z)

The measurement of ^{15}N NMR spectra for the NSN fragment of the compounds **1** to **5** is not straightforward owing to the dynamic processes in addition to the inherently low sensitivity of the ^{15}N nuclei to the NMR experiments. The application of polarization transfer (PT) techniques, such as INEPT,[11] is hampered as long as longitudinal and transverse relaxation times $T_1(^1H)$, $T_2(^1H)$ and $T_2(^{15}N)$ are short because of the dynamic nature of the system. In most cases, the magnitude of long range couplings $|\ ^nJ(^{15}N^1H)\ |$ ($n > 3$) proved to be too small (<0.3 Hz) for PT. In general, we found that $\delta^{15}N$ and $^1J(^{31}P^{15}N)$ values of the amino groups were readily detected at room temperature using the refocused INEPT sequence with ^1H decoupling,[11b] and the data were in the expected range.[12] Under these conditions the ^{15}N(=NtBu) resonances were not detected. However, at sufficiently low temperatures (see Table IV), ^{15}N resonances of the =NtBu group could be observed, also using the INEPT sequence, based on $^3J(^{15}N^1H) \approx 2.5$ Hz.

For detection of the other sulfur diimide ^{15}N resonances direct ^{15}N NMR measurements had to be carried out, either without ^1H decoupling or with inverse gated ^1H decoupling (NOE suppression). Since these experiments require larger amounts of sample and much spectrometer time, they were performed only for two examples (**3a, 3d**) for which the dynamic situation had been analyzed by NMR measurements of other nuclei. As shown in Figure 2, the mixture of Z/E and E/Z-isomers gives rise to four ^{15}N resonances of which one appears as singlet and three are split into doublets, two according to $^1J(^{31}P^{15}N)$ and one, at highest frequency, to $^3J(^{31}PNS^{15}N)$. The characteristic high frequency shift of the ^{15}N NMR signal for the =NtBu group in E-position and the splitting owing to $^1J(^{31}P^{15}N)$ allows for the unambiguous assignment of the ^{15}N resonances to the E/Z and Z/E isomer, respectively.

The $\delta^{29}Si$ data of compounds **5** (Table IV) are fairly constant and do not indicate a preferred configuration. Measurements at low temperature (down to −100°C) did not reveal the presence of an isomer with a distinct configuration.

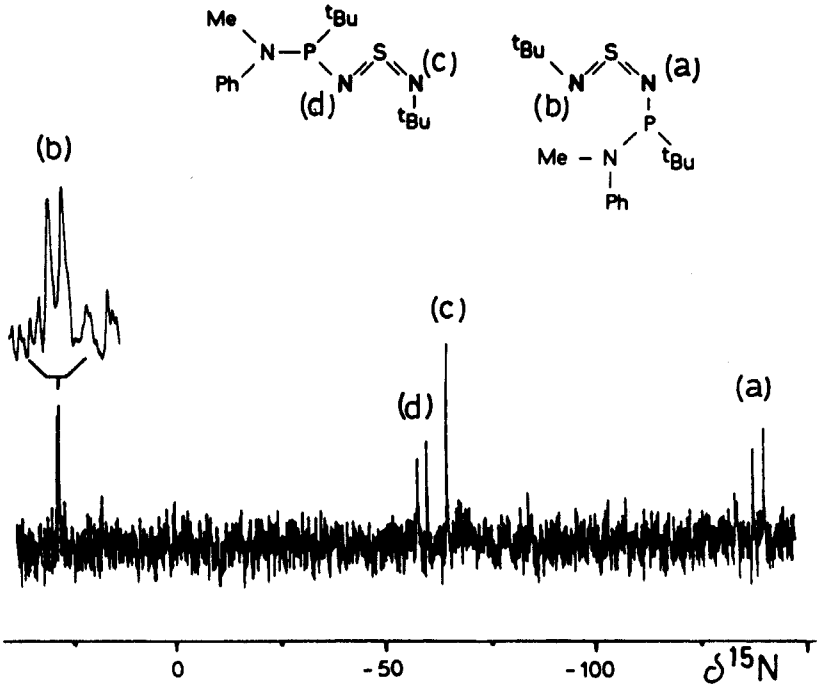


FIGURE 2 30.4 MHz $^{15}N\{^1H\}$ NMR spectrum of tBuMeN(tBu)P(NSN)tBu (**3a**) in toluene at −50°C.

All NMR data obtained for the sulfur diimides **1** to **5** are consistent with a highly dynamic system with regard to the various configurations shown in Scheme 1. Greater steric demand of substituents appears to increase the fluxional character. The presence of E/Z and Z/E isomers has been proved beyond doubt by ^{15}N NMR (**3a, 3d**), and the existence of an E/E isomer (**2c**) in addition to the E/Z isomer is proposed on the basis of low-temperature ^{31}P NMR data. In contrast, no evidence for the Z/Z configuration has been found.

EXPERIMENTAL

All compounds were prepared and handled under inert atmosphere (Ar), and all precautions were taken to exclude traces of moisture. The phosphorus chlorides[9,13] and potassium sulfur diimides[7,8] were prepared according to literature procedures. NMR spectra were recorded using JEOL FX90Q and Bruker AC 300 spectrometers, both equipped with a multinuclear unit and a variable temperature unit. A Bruker MSL 300 spectrometer served for measuring the solid-state ^{31}P CP/MAS NMR spectra of **2c**. The air- and moisture sensitive compound **2c** had to be packed into an air-tight insert[14] which fits into the commercial ZrO_2-rotor of the double bearing probe head. Chemical shifts are given with respect to TMS (δ^1H, referred to the ^1H resonance of the non-deuterated solvent; $\delta^{13}C$, referred to the ^{13}C resonance of the deuterated solvent; $\delta^{29}Si$, referred to $\Xi(^{29}Si)$ = 19.867184 MHz), neat $MeNO_2$ ($\delta^{15}N$, referred to $\Xi(^{15}N)$ = 10.136767 MHz) and 85% aqueous H_3PO_4 ($\Xi(^{31}P)$ = 40.480747 MHz). Mass spectra [EI, 70 eV, data given as m/z (%)] were recorded by a Varian MAT CH-7 instrument. Elemental analyses were carried out by Pascher, Remagen.

Bis[bis(amino)phosphinyl] sulfur diimides (**1a,[6] b, c**). At room temperature, a solution of 10 mmoles of the respective bis(amino)phosphorus chloride is added to a suspension of 0.7 g (5 mmoles) of K_2SN_2 in 30 ml of a mixture of solvents (hexane/dimethoxyethane/acetonitrile: 15/15/1). After stirring for 24 h the red reaction mixture is filtered and the solvents are removed in vacuo. The compounds **1b** and **1c** are isolated as highly viscous red oils in 80 to 90% yield. Compound **1a** is isolated in 90% yield as a microcrystalline powder (mp 55°C).

1b: ^{1}H NMR: $\delta[J(^{31}P^1H)]$ = 2.98 m, 8H, NCH_2; 1.24 [1.0] d, 36H, NtBu.

1c: ^{1}H NMR: 3.32 m, 8H, NCH_2; 2.87 m, 4H, CH_2; 1.27 [1.9] d, 36H, NtBu. MS: 490 (1, M); 276 (6.5, M-214); 215 (100, -BuN$(CH_2)_3$NBuP).

Bis[amino(tert-butyl)phosphinyl] sulfur diimides (**2a, b, c, d, e, f, g**). A solution of 10 mmoles of the respective amino(*tert*-butyl)phosphinyl chloride in 20 ml of acetonitrile is added at room temperature to a freshly prepared suspension of 0.7 g (5 mmoles) of K_2SN_2 in 30 ml of acetonitrile. The color of the reaction mixture changes immediately to red. After stirring for 12 h the acetonitrile is removed in vacuo and the residue is extracted with hexane. The hexane is also removed, leaving the sulfur diimides **2** as red highly viscous liquids, except for **2c** which is a red microcrystalline powder (mp. 52°C). The yields are in the range of 80–90%.

2a: ^{1}H NMR: $\delta[J(^{31}P^1H)]$ = 2.56 [2.6]/2.49 [2.6] d, 6H, NMe; 1.24 [<1] d, 18H, NtBu; 1.12 [14.5]/1.11 [14.5] d, 18H, PtBu. MS: 408 (5, M); 351 (34, M-Bu); 294 (12, M-2 Bu); 208 (78); 86 (25, BuMeN); 57 (100, C_4H_9).

2b: ^{1}H NMR: 7.0–7.4 m, 10H, Ph; 2.58 [1.9]/2.57 [1.9] d, 6H, NMe; 1.02 [14.7]/1.01 [14.7] d, 18H, PtBu. MS: 448 (6, M); 391 (59, M-Bu); 334 (6, M-2Bu); 218 (41); 106 (100, PhMeN).

2c: ^{1}H NMR: 7.0–7.4 m, 18H, 2-Biph; 2.86 [1.9]/2.82 [1.9] d, 6H NMe, 1.03 [14.1] d, 18H, PtBu. MS: 545 (15, M-C_4H_8); 418 (15, M-BiphMeN); 212 (100, Biph-$NPCH_2$); 182 (30, BiphMeN).

$C_{34}H_{42}N_4P_2S$	Calc:	C, 67.98 H, 7.05 N, 9.33%
(600.75)	Found:	C, 66.06 H, 7.21 N, 9.31.

2d: ^{1}H NMR: 7.0–7.3 m, 10H, Ph; 3.31 m, 4H, and 0.85 t, 6H NCH_2CH_3; 0.96 [14.5] d, 18H, PtBu. MS: 476 (0.2, M); 419 (1.2, M-Bu); 356 (0.7, M-NPhEt); 120 (100, PhEtN).

2e: ^{1}H NMR: 6.9–7.3 m, 10H, Ph; 3.50/3.40 m, 4H, NCH_2; 1.03 [14.1] d, 18H, PtBu.

2f: ^{1}H NMR: 7.0–7.3 m, 10H, Ph; 3.40 m, 4H, NCH_2; 1.08 [1.2] d, 18H, NtBu; 1.01 [14.9] d, 18H, PtBu.

2g: ^{1}H NMR: 7.0–7.3 m, 20H, Ph; 0.93 [14.9] d, 18H, PtBu.

N-Amino(tert-butyl)phosphinyl-N'-tert-butyl sulfur diimides (**3a, b, c, d, e, f, g, h**). The synthesis of the sulfur diimides **3** proceeds in the same way as for compounds **1** and **2**, using KNSNtBu and the respective phosphorus chlorides. In the case of **3c** and **3h** a mixture of hexane/THF (6:1) was used for extraction. All compounds **3** were isolated as deep red, viscous liquids in 80–90% yield.

3a: ^{1}H NMR: $\delta[J(^{31}P^1H)]$ = 2.40 [2.6] d, 3H, NMe; 1.42 s, 9H, NSNtBu; 1.17 [1.1] d, 9H, NtBu; 1.00 [14.0] d, 9H, PtBu.

3b: ^{1}H NMR: 7.0–7.2 m, 5H, Ph; 2.69 [1.7] d, 3H, NMe; 1.18 s, 9H, NSNtBu; 1.02 [14.5] d, 9H, PtBu. MS: 311 (21, M); 254 (100, M-Bu); 106 (76, PhMeN).

3c: ^{1}H NMR: 7.0–7.3 m, 9H, 2-biph; 2.81 [1.7] d, 3H, NMe; 1.43 s, 9H, NSNtBu; 0.93 [13.7] d, 9H, PtBu. MS: 387 (15, M); 330 (14, M-Bu); 212 (100, Biph-$NPCH_2$).

3d: ^{1}H NMR: 7.0–7.3 m, 5H, Ph; 3.34 [2.1] m, 2H, and 0.88 t, 3H, NCH_2CH_3; 1.23 s, 9H, NSNtBu; 1.04 [13.9] d, 9H, PtBu. MS: 325 (18, M); 268 (81, M-Bu), 120 (100, PhEtN).

3e: ^{1}H NMR: 7.0–7.3 m, 5H, Ph; 3.40 m, 2H, NCH_2; 1.34 s, 9H, NSNtBu; 1.11 [14.1] d, 9H, PtBu.

3f: ^{1}H NMR: 7.0–7.3 m, 5H, Ph; 3.50 m, 2H, NCH_2; 1.43 s, 9H NSNtBu; 1.09 [1.1] d, 9H, NtBu; 1.00 [14.5] d, 9H, PtBu.

3g: ^{1}H NMR: 7.0–7.4 m, 10H, Ph; 1.24 s, 9H NSNtBu; 0.97 [14.7] d, 9H, PtBu. MS: 373 (18, M), 316 (100, M-Bu), 168 (39, Ph_2N).

3h: ^{1}H NMR: 3.82 m, 1H, 1.12 d, 3H, 1.07 d, 3H, NiPr; 1.43 s, 9H, NSNtBu; 1.01 [13.8] d, 9H, PtBu; 0.23 [2.0] d, 9H, $SiMe_3$. MS: 335 (12, M), 278 (100, M-Bu), 222 (12, $PrSiMe_3N$)PNSNH).

N-Bis(amino)phosphinyl-N'-tert-butyl (**4a,[6] b, c, d, e**) *and -N'-trimethylsilyl sulfur diimides* (**5a,[6] b, c, d**). The same procedure as for compounds **2** is applied, using KNSNtBu and $KNSNSiMe_3$, respectively. The bis(amino)phosphinyl chlorides are added as solutions in 30 ml of hexane, exept of **4e** (acetonitrile). The products are deep red viscous oils which are isolated in 80–90% yield.

4b: ^{1}H NMR: $\delta[J(^{31}P^1H)]$ = 2.81 m, 4H, NCH_2; 1.49 s, 9H, NSNtBu, 1.13 [1.0] d, 18H, NtBu. MS: 318 (84, M), 201 (100, M-NSNBu).

5b: ^{1}H NMR: 2.92 m, 4H, NCH_2; 1.23 [1.2] d, 18H, NtBu; 0.29 s, 9H, $SiMe_3$.

4c: ^{1}H NMR: 3.12 m, 4H, NCH_2; 2.76 m, 2H, CH_2; 1.46 s, 9H, NSNtBu; 1.28 [2.2] d, 18H, NtBu. MS: 332 (11, M), 215 (100, M-NSNBu).

5c: ^{1}H NMR: 3.31 m, 4H, NCH_2; 2.88 m, 2H, CH_2; 1.29 [2.4] d, 18H, NtBu; 0.27 s, 9H, $SiMe_3$. MS: 348 (12, M); 215 (100, M-NSNSiMe_3).

4d: ^{1}H NMR: 7.1–7.4 m, 10H, Ph; 3.02 m, 4H, NCH_2; 1.47 s, 9H, NSNtBu; 1.09 [2.0] d, 18H, NtBu.

5d: ^{1}H NMR: 7.1–7.4 m, 10H, Ph; 3.05 m, 4H, NCH_2; 1.08 [1.9] d, 18H, NtBu, 0.23 s, 9H, $SiMe_3$. MS: 488 (0.5, M); 401 (24, M-$NSiMe_3$); 162 (18, BuBzN); 91 (100, C_7H_7).

4e: ^{1}H NMR: 1.44 s, 9H, NSNtBu; 1.27 [1.5] d, 18H, NtBu, 0.34 s, 6H, 0.24 s, 6H, $SiMe_2$-$SiMe_2$.

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