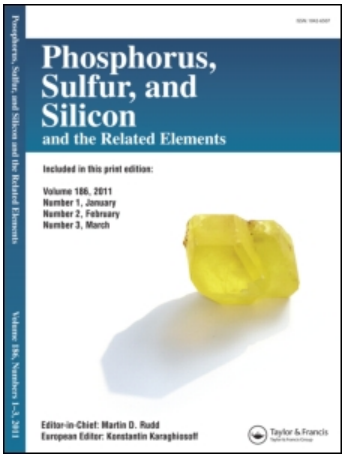

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^{31}P SOLID STATE NUCLEAR MAGNETIC RESONANCE INVESTIGATIONS ON SUBSTITUTED ETHYLMERCAPTOCYCLOTETRAPHOSPHAZENES

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^{31}P SOLID STATE NUCLEAR MAGNETIC RESONANCE INVESTIGATIONS ON SUBSTITUTED ETHYLMERCAPTO-CYCLOTETRAPHOSPHAZENES

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The present study deals with ^{31}P magic angle spinning solid state nuclear magnetic resonance (NMR) investigations on various substituted ethylmercaptocyclotetraphosphazenes. Through analyses of spinning side band intensities the isotropic chemical shifts, the principal values of the magnetic shielding tensor, the span and skew could be determined and interpreted with regard to the different substituents of the compounds. In addition, the crystal structural parameters of $N_4P_4Cl_4(SC_2H_5)_4$ were determined by X-ray structural analysis. Using these parameters ^{31}P NMR chemical shifts and the principal values of the magnetic shielding tensor were calculated by the individual gauged of localized orbitals (IGLO) method.

Keywords: Cyclophosphazenes; Crystal structure; Solid state nuclear magnetic resonance; Quantum chemical calculations

1. INTRODUCTION

In previous papers we have described ^{31}P solid state NMR investigations on chlorocyclophosphazenes[1] and dimethylamidoderivatives of hexachlorocyclo- triphosphazene[2]. These studies on substituted cyclophosphazenes were continued in the search for further relations between NMR and structural parameters of the phosphazenes.

Figure 1 shows the substituted ethylmercaptocyclotetraphosphazenes investigated including octachlorocyclotetraphosphazene $N_4P_4Cl_8$ from

which cyclote- traphosphazenes with four different substituent groups (-PCl_2, -$P(SC_2H_5)_2$, -$P(NH_2)_2$, -$P(OCH_3)_2$) were prepared and used for NMR measurements.

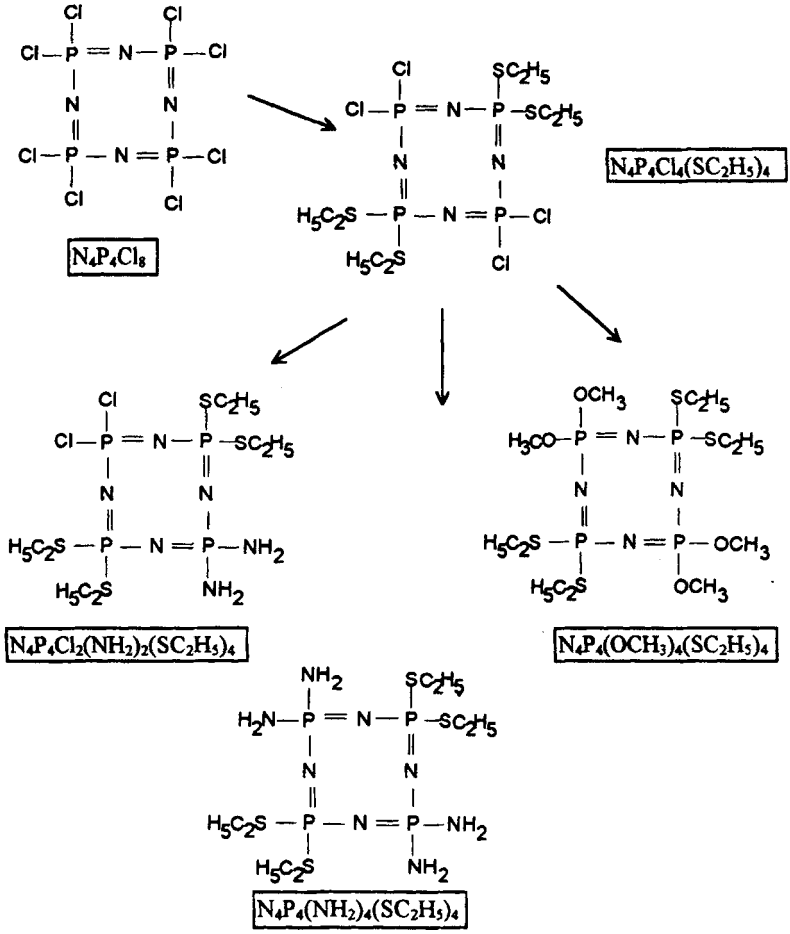

FIGURE 1 Investigated ethylmercaptocyclotetraphosphazenes

Because there are no crystal structural data available of these substituted compounds we determined them for $N_4P_4Cl_4(SC_2H_5)_4$ by X-ray structural analysis. Hence it was possible to calculate the NMR parameters (principal

values of the shielding tensor, span, skew) and compare them with the experimentally obtained values.

2. THEORY

The structure of the phosphazenes and the NMR properties of their ^{31}P nuclei permit the application of ^{31}P NMR spectroscopy for structural investigations. It is known that the structure of dissolved molecules can differ from the solid state structure because of the flexibility of the P-N bonds. Therefore liquid and solid state NMR measurements are necessary to compare the chemical shifts in liquids and the isotropic chemical shifts in solids.

The pattern of a ^{31}P solid state NMR spectrum is mainly caused by the aniso- tropy of the ^{31}P chemical shift. The sideband spectra recorded by using the method of magic angle spinning (MAS) can be interpreted with regard to the principal values of the chemical shift tensor δ_{ii}, from which it is possible to determine the NMR parameters:

isotropic chemical shift	δ_{iso}
span	Ω
skew	k [3]

To explain the experimental values we applied the *ab initio* IGLO method to calculate the principal values of the shielding tensor σ_{ii}. The principal values of the ^{31}P shielding tensor are connected with those of the chemical shift tensor in the following way:

$\sigma_{ii} = 328 \text{ ppm} - \delta_{ii}$ [4].

3. EXPERIMENTAL

Octachlorocyclotetraphosphazene $N_4P_4Cl_8$ was formed from PCl_5 and NH_4Cl by a procedure described already by Schenck and Römer[5].

$N_4P_4Cl_4(SC_2H_5)_4$was prepared according to the method of Carroll and Shaw[6] using $N_4P_4Cl_8$ and $NaSC_2H_5$. The solid product was the precursor for further reactions with nucleophilic reagents (Table I).

TABLE I Preparation of the substituted ethylmercaptocyclotetraphosphazenes[7]

product	*reagent*	*solvent*	*temperature*	*purification*
geminal	NH_3 in 25%	ether	room temp.	
$N_4P_4Cl_2(NH_2)_2(SC_2H_5)_4$	aqueous solution			recrystallization
$N_4P_4(NH_2)_4(SC_2H_5)_4$	NH_3 (liquid)	ether	-50°C	recrystallization
$N_4P_4(OCH_3)_4(SC_2H_5)_4$	$NaOCH_3$	benzene	0°C/room temp.	recrystallization

NMR spectroscopy

^{31}P NMR spectra were recorded using a Bruker MSL 300 spectrometer at a resonance frequency of 121.496 MHz.

The solid state measurements were carried out under the following conditions:

pulse program:	cpcycl (Bruker software)
MAS frequency:	2 – 8 kHz (dependent on the optimal conditions for the interpretation of the sideband spectra)
number of scans:	300 (except $N_4P_4(OCH_3)_4(SC_2H_5)_4$: 16)
pulse repetition time:	5 s
external standard:	Na_3PO_4 (δ = 6.39 ppm)
temperature:	room temperature (except $N_4P_4(OCH_3)_4(SC_2H_5)_4$: –60°C)

The principal values of the chemical shift tensor were determined from the sideband spectra in accordance with Herzfeld/Berger[8] with the program WINMAS (Bruker). To verify the obtained results we simulated spectra using the principal values of the tensor, line width and Lorentz/Gauss ratio as input para- meters and compared the results with the experimental spectra.

IGLO calculations

The IGLO calculations were carried out on the basis of the crystal structure. Because of an efficient management of the disturbance integrals the DIGLO implementation of Meier et al.[9] was employed. Huzinaga's basis sets[10] used and augmented by a polarization function are shown in Table II.

TABLE II Basis sets for the IGLO calculations

atom	*basis sets*	*functions*
C	basis II	(9s 5p 1d)/[5s 4p 1d] with μ(d) = 1,0
	DZ-IGLO	(7s 3p) /[4s 2p]
Cl	basis II	(11s 7p 2d)/[7s 6p 2d] with μ(d1) = 0,4, μ(d2) = 1,6
	DZ-IGLO	(10s 6p) /[6s 4p]
H	DZ-IGLO	(3s) /[2s]
O	DZ-IGLO	(3s 7p) /[4s 2p]
P	basis II	(11s 7p 2d)/[7s 6p 2d] with μ(d1) = 0,35, μ(d2) = 1,4
S	DZ-IGLO	(10s 6p) /[6s 4p]

Experimental Procedure for X-ray Crystallography

Colorless crystals, suitable for X-ray diffraction, were obtained from a chloroform n-hexane solution.

Single crystals of $N_4P_4Cl_4(SC_2H_5)_4$ were mounted on a glass fiber and transfered to the diffractometer. Diffraction measurements were made with an Enraf-Nonius CAD-4 diffractometer at room temperature using graphite-monochromated Cu-Kα radiation (λ = 1.5418 Å) with ϖ-2θ scans. The structure was solved by direct methods, non-hydrogen atoms were located from difference Fourier synthesis and refined by full matrix least squares on F^2 with anisotropic thermal parameters. Hydrogen atoms were calculated and allowed to ride on their corresponding carbon atoms. An empirical absorption correction was performed using psiscans. Crystallographic data and the results of refinements are summarized in Table III.

Further details of the X-ray analyses were deposited with the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D 76344 EggensteinLeopoldshafen, Germany*.

* Requests should contain the deposition number CSD 407151, names of authors, and citation of this article.

TABLE III Crystal data and structure refinement for $N_4P_4Cl_4(SC_2H_5)_4$

Empirical formula	C4 H10 C12 N2 P2 S2
Formula weight	283.10
Temperature	293(2) K
Wavelength	1.54180 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 18.350(3) Å alpha = 90°
	b = 9.7970(10) Å beta = 117.170(10)°
	c = 15.160 (3) Å gamma = 90°
Volume	2424.7(6) $Å^3$
	Z=4
Density (calculated)	1.551 Mg/m^3
Absorption coefficient	10.193 mm^{-1}
F(000)	1152
Crystal size	0.4 × 0.3 × 0.3 mm
Theta range for data collection	5.27 to 74.60°
Index ranges	-22<=h<=20, 0<=k<=12, 0<=1<=18
Reflections collected	2473
Independent reflections	2473
Absorption correction	Semi-empirical from psi-scans
Max. and min. transmission	1.0 and 0.6
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2473 /0/119
Goodness-of-fit on F^2	1.074
Final R indices [I>2sigma(I)]	R1 = 0.0455, wR2 = 0.1187
R indices (all data)	R1 = 0.0493, wR2 = 0.1220
Largest diff. peak and hole	0.448 and –0.388 $e.A^{-3}$

4. RESULTS

^{31}P liquid state NMR spectra

In the proton decoupled ^{31}P liquid state NMR spectra of the ethylmercaptocyclotetraphosphazenes in $CDCl_3$ solution one signal appears for each differently substituted P atom. Table IV shows the chemical shifts of the investigated compounds.

TABLE IV ^{31}P chemical shifts of ethylmercaptocyclotetraphosphazenes (including $N_4P_4Cl_8$) in liquid state ($CDCl_3$)

compound	*group*	*chemical shift [ppm]*
$N_4P_4Cl_8$	PCl_2	-5,5
$N_4P_4Cl_4(SC_2H_5)_4$	PCl_2	-8,1
	$P(SC_2H_5)_2$	30,1
$N_4P_4Cl_2(NH_2)_2(SC_2H_5)_4$	PCl_2	-7,9
	$P(NH_2)_2$	2,7
	$P(SC_2H_5)_2$	28,2
$N_4P_4(NH_2)_4(SC_2H_5)_4$	$P(NH_2)_2$	3,7
	$P(SC_2H_5)_2$	27,8
$N_4P_4(OCH_3)_4(SC_2H_5)_4$	$P(OCH_3)_2$	-0,9
	$P(SC_2H_5)_2$	29,7

^{31}P solid state NMR spectra

Figure 2 shows, respectively the 8 and 3 kHz MAS spectra of $N_4P_4Cl_4(SC_2H_5)_4$. In the former spectrum the individual signals are separated, the narrow lines are due to the $P(SC_2H_5)_2$ groups. For the PCl_2 groups a fivefold splitting appears caused by residual dipolar coupling of phosphorus with the neighbouring chlorine nuclei[1,2]. Despite the good separation of the signals the 8 kHz spectrum is unsuitable to determine the principal values of the chemical shift tensor because of too small a number of sidebands and considerable differences in the intensities of the sideband 0 and 1. Therefore the 3 kHz spectrum was used for the further investigations. The overlapping signals of the PCl_2 and $P(SC_2H_5)_2$ groups were separated by means of the program WINFIT considering the known pattern of the PCl_2 groups. In this way we also obtained the sideband intensities of $N_4P_4(NH_2)_4(SC_2H_5)_4$ from the 2 kHz spectrum (Figure 3a). In the spectrum of $N_4P_4Cl_2(NH_2)_2(SC_2H_5)_4$ (Figure 3b) three isotropic signals appear due to the PCl_2, $P(NH_2)_2$ and $P(SC_2H_5)_2$ groups. Because of the broad lines, particulary of the PCl_2 group, the signals overlap even at a MAS frequency of 6 kHz.

The methoxy compound $N_4P_4(OCH_3)_4(SC_2H_5)_4$ is crystalline at room temperature. However, with NMR measurements at this temperature liquid state spectra were obtained because of strong motions in the molecule.

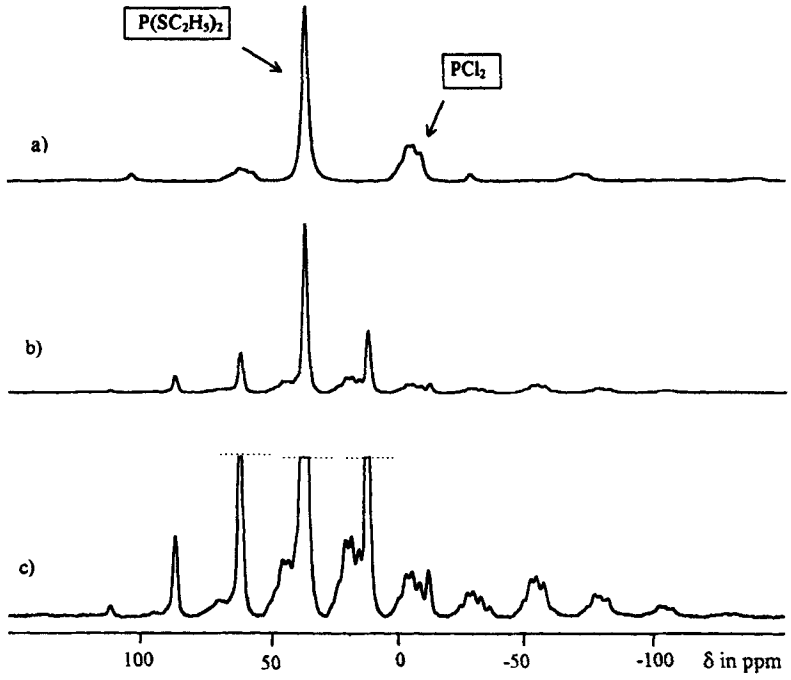

FIGURE 2 ^{31}P solid state NMR spectra of $N_4P_4Cl_4(SC_2H_5)_4$ a) 8 kHz spectrum b) and c) 3 kHz spectra

This phenomenon could also be observed on other phosphazenes containing methoxy groups, e.g. $N_3P_3(OCH_3)_6$. In order to freeze these motions NMR experiments were carried out at a temperature of –60°C. The 2.5 kHz spectrum obtained (Figure 4a) shows a strong overlap of the signals. The sideband intensities could be determined by a simulation using the program LINESIM (Figure 4b).

The results of the Herzfeld/Berger sideband analyses (principal values of the shielding tensor, span, skew, isotropic chemical shift) are shown in Table V and Figure 5.

The comparison between the isotropic chemical shift δ_{iso} of the solid compound and the chemical shift of the dissolved molecules yields information about possible structural changes. Of the investigated ethylmercaptocyclotetraphosphazenes only the PCl_2 groups in $N_4P_4Cl_4(SC_2H_5)_4$ and

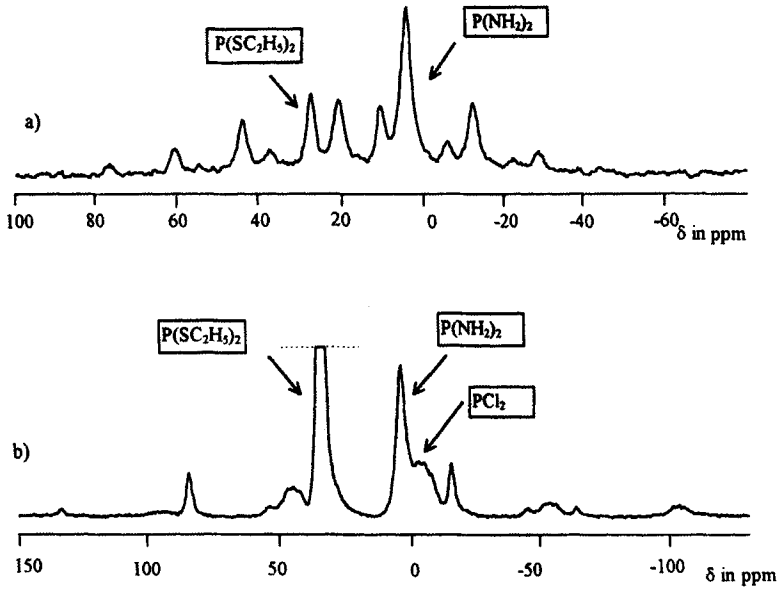

FIGURE 3 ^{31}P-solid state NMR spectra a) $N_4P_4(NH_2)_4(SC_2H_5)_4$(2 kHz) b) $N_4P_4Cl_2(NH_2)_2(SC_2H_5)_4$ (6 kHz)

$N_4P_4Cl_2(NH_2)_2(SC_2H_5)_4$ show significant differences (ca. 7 ppm) and thus indicate a considerable change of the structure. All other substituent groups show only slight differences between δ_{iso} in solids and the chemical shift in liquids since presumbly only negligible structural changes occur during the dissolution process.

The solid state NMR parameters obtained show that span and skew reflect the influence of the various substituents. Thus, the span significantly increases in the order

$$P(OCH_3)_2 \leq P(NH_2)_2 \leq P(SC_2H_5)_2 << PCl_2.$$

In comparison to $N_4P_4Cl_8$ which is completely substituted by chlorine atoms, the span of PCl_2 groups in ethylmercaptocyclotetraphosphazenes is essentially larger:

$N_4P_4Cl_8$	$\Omega_{PCl_2} = 135$ ppm
$N_4P_4Cl_4(SC_2H_5)_4$	$\Omega_{PCl_2} = 191$ ppm
$N_4P_4Cl_2(NH_2)_2(SC_2H_5)_4$	$\Omega_{PCl_2} = 177$ ppm.

TABLE V ^{31}P solid state NMR parameters of ethylmercaptocyclotetraphosphazenes (including $N_4P_4Cl_8$)

compound	*group*	δ_{iso} *[ppm]*	*principal values of the shielding tensor*			*span [ppm]*	*skew*
			σ_{11}	σ_{22} *[ppm]*	σ_{33}		
$N_4P_4Cl_8$ T form	PCl_2	-5,0	272,3	319,5	407,2	134,9	0,3
		-6,7	274,0	321,2	408,9	134,9	0,3
		11	294	299	358	64	0,8
		9	270	328	360	90	-0,3
$N_4P_4Cl_4(SC_2H_5)_4$	PCl_2	-5,8	253,1	304,1	444,2	191,1	0,5
	$P(SC_2H_5)_2$	37	244,1	304,0	324,9	80,8	-0,5
	PCl_2	15	266	276	397	131	0,8
	$P(SC_2H_5)_2$	32	253	313	321	68	-0,8
$N_4P_4Cl_2(NH_2)_2(SC_2H_5)_4$	PCl_2	-4,0	269,0	281,2	446,0	177,0	0,9
	$P(SC_2H_5)_2$	34,7	242,8	300,5	336,7	93,9	-0,2
	$P(NH_2)_2$	4,6	284,0	320,8	365,5	81,5	0,1
$N_4P_4(NH_2)_4(SC_2H_5)_4$	$P(SC_2H_5)_2$	27,8	255,4	303,1	342,2	86,8	-0,1
	$P(NH_2)_2$	4,7	290,7	322,8	356,4	65,7	0
$N_4P_4(OCH_3)_4(SC_2H_5)_4$	$P(SC_2H_5)_2$	31,8	267,9	292,0	328,7	60,8	0,2
	$P(OCH_3)_2$	-0,4	305,4	311,2	368,6	63,6	0,8

IGLO results

For the compounds investigated the span of the $P(SC_2H_5)_2$ groups ranges between 81 and 94 ppm, except for $N_4P_4(OCH_3)_4(SC_2H_5)_4$ with a noticably small span of 61 ppm.

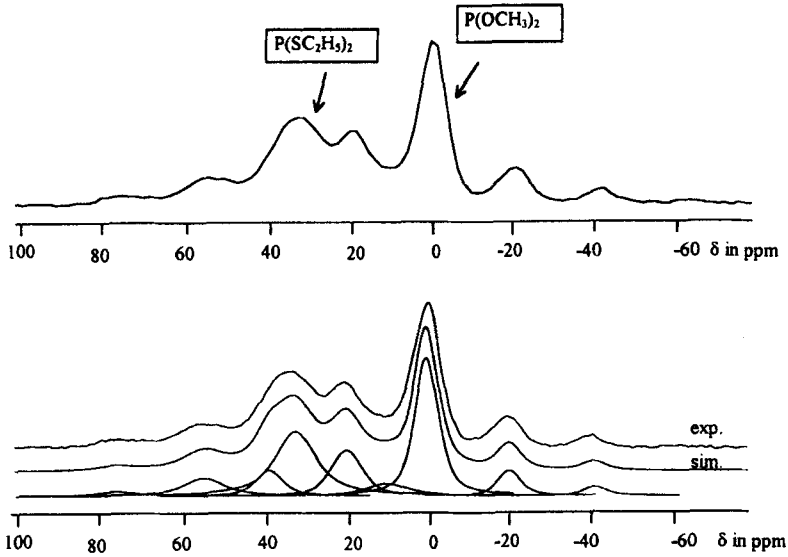

FIGURE 4 ^{31}P solid state NMR spectrum of $N_4P_4(OCH_3)_4(SC_2H_5)_4$(2.5 kHz) a) measured spectrum (-60°C) b) simulated spectrum

The skew of PCl_2, $P(OCH_3)_2$ and $P(NH_2)_2$ groups is positive in all cases whereas within the $P(SC_2H_5)_2$ groups the sign changes:
$N_4P_4Cl_4(SC_2H_5)_4$: k = – 0,5
$N_4P_4(OCH_3)_4(SC_2H_5)_4$: k = + 0,2.

IGLO calculations

With X-ray structural analysis the structural parameters of $N_4P_4Cl_4(SC_2H_5)_4$ could be determined:

Results of X-ray crystal structure analysis

The X-ray crystal structure analysis of $N_4P_4Cl_4(SC_2H_5)_4$ yields the molecule structures shown in Figure 6 and 7. Crystal data, details of the structure refinement, atomic coordinates and anisotropic displacement

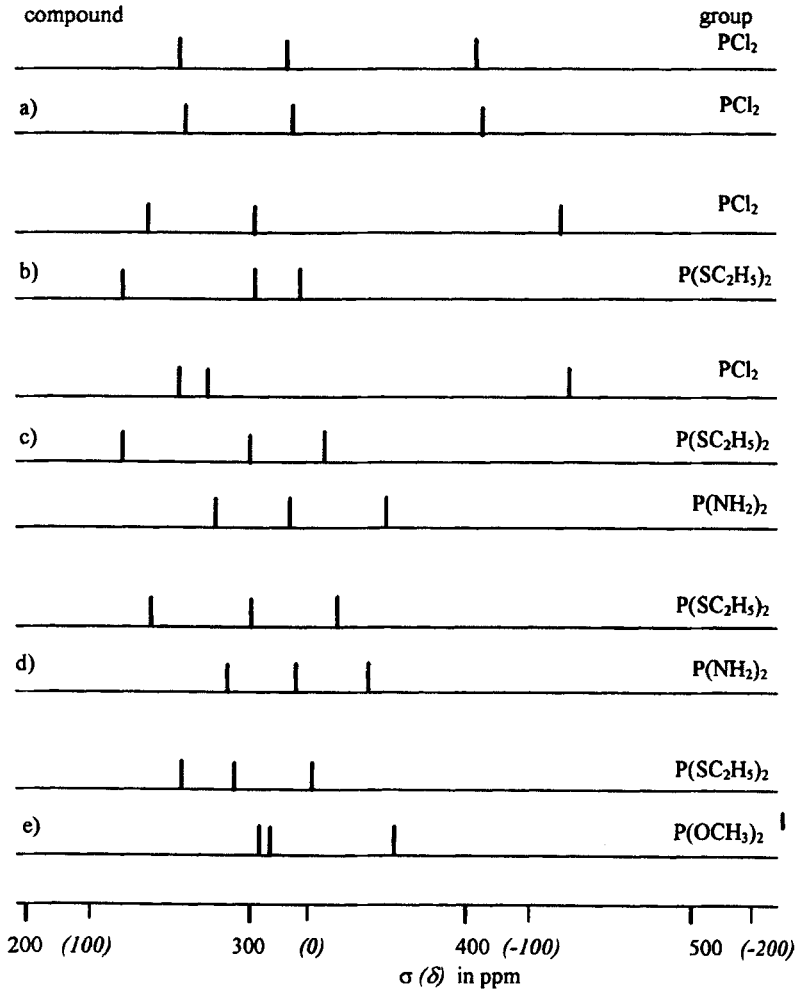

FIGURE 5 Principal values of the shielding (chemical shift) tensor of ethylmercaptocyclotetraphosphazenes (including $N_4P_4Cl_8$) a) $N_4P_4Cl_8$ (T form) b) $N_4P_4Cl_4(SC_2H_5)_4$ c) $N_4P_4Cl_2(NH_2)_2(SC_2H_5)_4$ d) $N_4P_4(NH_2)_4(SC_2H_5)_4$ e) $N_4P_4(OCH_3)_4(SC_2H_5)_4$

parameters of the non-hydrogen atoms are given in Tables 3, 6, 7. $N_4P_4Cl_4(SC_2H_5)_4$ crystallizes in the space group C2/c. The four molecules in the unit cell occupy a fourfold special position (Wyckoff notation *e*) with symmetry 2.

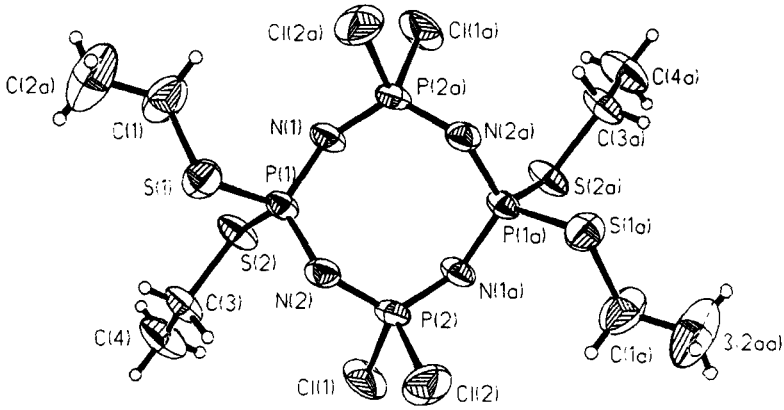

FIGURE 6 Molecular structure of $N_4P_4Cl_4(SC_2H_5)_4$ (ORTEP 50% thermal ellipsoids)

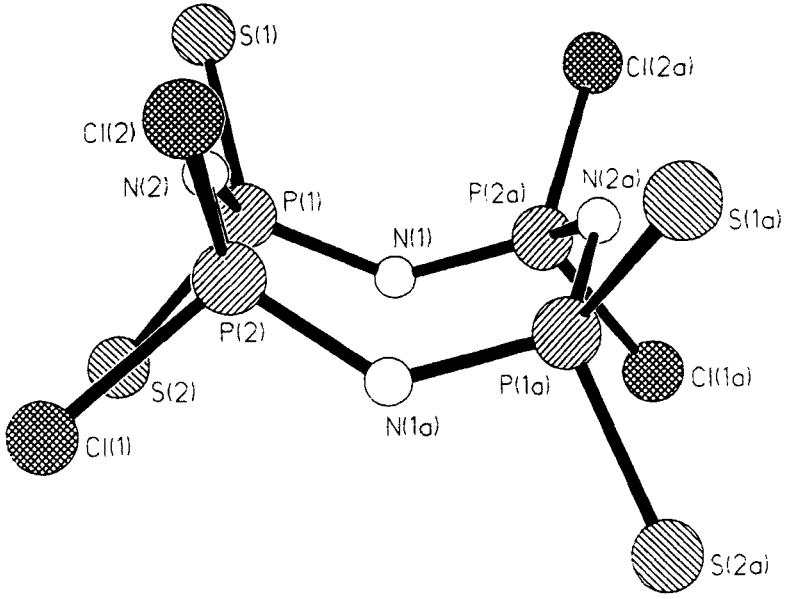

FIGURE 7 Conformation of the eight membered ring in $N_4P_4Cl_4(SC_2H_5)_4$. The ethyl groups are omitted for clarity

The N_4P_4 ring is saddle-shaped with all four phosphorous atoms lying in one plane. The nitrogen atoms are alternately above and below the plane of the phosphorous atoms (Figure 7). The conformation of the eight membered ring is reflected by torsion angles between 39 and 49°. The parent compound $N_4P_4Cl_8$ crystallizes in two modifications denoted as K- and T-form, which have been characterized by X-ray diffraction[11]. The conformation of both forms is different from that in $N_4P_4Cl_4(SC_2H_5)_4$. The intramolecular distances and angles of $N_4P_4Cl_4(SC_2H_5)_4$ are given in Table VIII. The molecule has four independent P-N bonds. The P-N bonds from P(1) are somewhat longer than those from P(2), due to the different substituents at the two phosphorous atoms. The observed values between 1.558 and 1.599 Å are considerably shorter than P-N single bonds. The sum of covalent radii of P and N is 1.8 Å, typical P-N single bond lengths have been reported to be 1.77 Å[12]. Short P-N bonds are characteristic for phosphornitriles because of the double bond character between P and N[11]. The P-Cl distance is similiar to that in $N_4P_4Cl_8$. The observed distances P-S and S-C are equal to distances found in other compounds with P-S-C structural units[13].

TABLE VI Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for $N_4P_4Cl_4(SC_2H_5)_4$. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

	x	*y*	*z*	*U(eq)*
P(1)	690(1)	1616(1)	4004(1)	35(1)
P(2)	1024(1)	1748(1)	2349(1)	38(1)
S(1)	901(1)	3124(1)	5033(1)	54(1)
S(2)	1293(1)	-145(1)	4702(1)	53(1)
Cl(1)	1914(1)	367(1)	2633(1)	79(1)
Cl(2)	1427(1)	3306(1)	1821(1)	78(1)
N(1)	-238(1)	1101(3)	3493(2)	40(1)
N(2)	1060(2)	2297(3)	3336(2)	38(1)
C(1)	427(4)	2323(6)	5740(4)	82(2)
C(2A)	670(20)	2975(27)	6689(14)	120(7)
C(2B)	265(46)	3294(37)	6291(57)	112(16)
C(3)	2346(2)	488(4)	5349(3)	58(1)
C(4)	2920(3)	-680(5)	5718(4)	82(1)

TABLE VII Anisotropic displacement parameters ($A^2 \times 10^3$) for $N_4P_4Cl_4(SC_2H_5)_4$. The anisotropic displacement factor exponent takes the form: $-2\ pi^2\ [h^2a^{*2}U11 + \ldots + 2\ h\ k\ a^*b^*U12\ ]$

	U11	*U22*	*U33*	*U23*	*U13*	*U12*
P(1)	24(1)	35(1)	41(1)	2(1)	12(1)	-7(1)
P(2)	22(1)	45(1)	48(1)	–3(1)	16(1)	-1(1)
S(1)	59(1)	54(1)	58(1)	-14(1)	35(1)	-24(1)
S(2)	28(1)	43(1)	71(1)	15(1)	8(1)	-7(1)
Cl(1)	33(1)	110(1)	79(1)	-17(1)	13(1)	29(1)
Cl(2)	82(1)	95(1)	73(1)	-6(1)	49(1)	-42(1)
N(1)	23(1)	45(1)	47(1)	6(1)	12(1)	-6(1)
N(2)	29(1)	40(1)	45(1)	-3(1)	18(1)	–9(1)
C(1)	108(4)	88(3)	79(3)	-13(3)	67(3)	-33(3)
C(2A)	195(17)	110(13)	86(9)	-23(7)	91(11)	-44(11)
C(2B)	175(38)	95(17)	151(35)	25(20)	150(34)	24(21)
C(3)	28(2)	59(2)	66(2)	11(2)	4(1)	-10(2)
C(4)	39(2)	73(3)	107(4)	26(3)	11(2)	4(2)

TABLE VIII Bond lengths [Å], angles [°] and selected torsion angles [°] for $N_4P_4Cl_4(SC_2H_5)_4$

P(1)-N(1)	1.596(2)	N(1)-P(1)-N(2)	119.4(2)
P(1)-N(2)	1.599(2)	N(1)#1-P(2)-N(2)	122.8(1)
P(2)-N(2)	1.564(3)	P(2)#1-N(1)-P(1)	130.7(2)
P(2)-N(1)# 1	1.558(2)	P(2)-N(2)-P(1)	128.1(2)
		N(1)-P(1)-S(1)	112.7(1)
P(2)-Cl(1)	2.010(1)	N(2)-P(1)-S(1)	101.1(1)
P(2)-Cl(2)	2.014(1)	N(1)-P(1)-S(2)	100.8(2)
		N(2)-P(1)-S(2)	113.0(1)
P(1)-S(1)	2.053(1)	S(1)-P(1)-S(2)	109.93(5)
P(1)-S(2)	2.062(1)	Cl(1)-P(2)-Cl(2)	100.70(7)
S(1)-C(1)	1.836(4)	N(1)#1-P(2)-Cl(1)	105.0(2)
S(2)-C(3)	1.831(3)	N(2)-P(2)-Cl(1)	110.6(1)
C(1)-C(2B)	1.39(4)	N(1)#1-P(2)-Cl(2)	110.7(1)
C(1)-C(2A)	1.44(2)	N(2)-P(2)-Cl(2)	104.9(1)

C(3)-C(4)	1.481(6)	C(1)-S(1)-P(1)	99.3(2)
		C(3)-S(2)-P(1)	100.3(1)
N1#1 – P2 – N2 – P1	42.4 (3)	C(2B)-C(1)-S(1)	110.0(9)
N1 – P1 – N2 – P2	-49.4 (3)	C(2A)-C(1)-S(1)	112.2(7)
N2 – P1 – N1 – P2#1	-39.9 (3)	C(4)-C(3)-S(2)	109.6(3)

Symmetry transformations used to generate equivalent atoms: # 1 -x,y,-z+1/2

The angles N-P-N are, respectively 119.4 and 122.8 °, the angles P-N-P 128. and 130.7°. These values agree well with endocyclic angles observed in other phosphonitrilic molecules[11]. The angle S-P-S is 109.93°, in a normal range for a tetrahedrally coordinated atom. The angles N-P-S are about 100° and 113°. The large difference between these two values is caused by the conformation of the eight membered ring, with the nitrogen atoms placed above and below the plane of the phosphorous atoms. There is a disorder at one of the methyl groups (C2), which was resolved with site occupation factors 0.5 / 0.5.

The structural parameters were the input values for the IGLO calculation.

The calculated principal values of the shielding tensor, span and skew are represented in Table V. Despite of small deviations the IGLO results are in a good agreement with the experimentally obtained values.

In either case the span of PCl_2 group is twice as large as that of the $P(SC_2H_5)_2$ group. In absolute terms the calculated spans are smaller than the experimentally obtained values. This can also be observed for the span of the PCl_2 group in $N_4P_4Cl_8$ additionally shown in Table 5. For both compounds the ratio calculated span / experimental span is approximately the same.

The isotropic chemical shift of the $(SC_2H_5)_2$ group is very well described using the IGLO method. However, for the PCl_2 groups of $N_4P_4Cl_4(SC_2H_5)_4$ and $N_4P_4Cl_8$ there is a decrease of up to 20 ppm shielding compared with the experimental data.

Comparing the values of skew we found a good agreement between the experimental and calculated results, in particular related to the sign which is positive for the PCl_2 and negative for the $P(SC_2H_5)_2$ groups.

Pictorial representation of the shielding tensor

By way of illustration of the results we endeavor to make a pictorial representation of the shielding tensor as an ovaloid[14] using $N_4P_4Cl_4(SC_2H_5)_4$

as an example. Figure 8 shows that the value of span determines the shape of the tensor. Thus, the large span of the PCl_2 group (Ω=191 ppm) leads to a significant stretching of the ovaloid in the direction of the z axis, whereas a small span (Ω= 81 ppm for the $P(SC_2H_5)_2$ group) leads to more spherically shaped tensor.

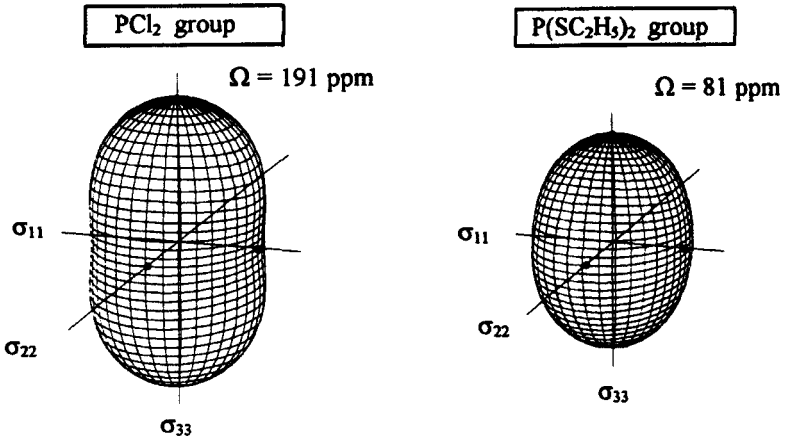

FIGURE 8 Pictorial representation of the shielding tensors of $N_4P_4Cl_4(SC_2H_5)_4$

5. CONCLUSIONS

Variously substituted ethylmercaptocyclotetraphosphazenes were investigated using ^{31}P solid state NMR spectroscopy.

By comparing the isotropic chemical shift and the chemical shift in the liquid state it was observed that most of the phosphazenes maintain their structure in solution. Only the PCl_2 groups in $N_4P_4Cl_4(SC_2H_5)_4$ and $N_4P_4Cl_2(NH_2)_2$ $(SC_2H_5)_4$ show significant differences (ca. 7 ppm) and hence indicate a considerable change of the structure.

It could be shown that particularly the parameters span and skew describe the influence of the different substituents. The span increases in the sequence: $P(OCH_3)_2$ – $P(NH_2)_2$ – $P(SC_2H_5)_2PCl_2$; the skew of PCl_2, $P(OCH_3)_2$ and $P(NH_2)_2$ groups is positive in all cases, while the $P(SC_2H_5)_2$ groups display positive and negative skews. The causes of the change of sign should be further investigated.

The results of the IGLO calculations correspond well with the experimental data. Although in this study only the NMR parameters of one compound were calculated, judging from the results of previous investigations it can be concluded that the IGLO method is excellently suitable for the calculation of the principal values of the magnetic shielding tensor of cyclophosphazenes.

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