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A Phosphorus–Tin Cage Molecule with an Extremely Shielded ^{31}P Nucleus: $P_4[Sn(C_6H_5)_2]_3$

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ABSTRACT: The structure of the compound $P_4[Sn(C_6H_5)_2]_3$ was deduced from the ^{119}Sn and ^{31}P NMR spectra and it was shown to be a structural analogue of the hetero-nortricyclene P_4S_3. The apical phosphorus atom exhibits an extremely negative ^{31}P chemical shift of -554.65 ppm, and the basal phosphorus atoms also resonate at high field strengths. The ^{31}P spectrum includes all tin satellite signals of the [mono-$^{117/119}$Sn] isotopomers. The spectra are analyzed as $A_2A'MX$ spin systems (A, M = ^{31}P; X = $^{117/119}$Sn). The ^{31}P data for analogous tricyclic cage molecules are presented and discussed. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: NMR; ^{31}P NMR; ^{119}Sn NMR; tristannatetraphosphanortricyclene; $A_2A'MX$ spin system; highly shielded ^{31}P nucleus

INTRODUCTION

Fully heterosubstituted nortricyclenes with a P_4E_3 framework, which contains bridging elements E of group 14, 15 or 16 of the Periodic Table, have already been investigated by NMR spectroscopy. The NMR data have been correlated with structure parameters of these cage molecules,[1] the satellite spectra of [mono-Se] and [bis-Se] isotopomers interpreted,[2] stereoisomers established[3,4] and unusual solvent effects reported.[5] All chemical shifts of the nortricyclene derivatives lie in the range from $+67$ to -370 ppm, i.e. clearly within the known ^{31}P chemical shift range of about 2000 ppm for dissolved or gaseous diamagnetic phosphorus compounds. The phosphinidene complex $(t\text{-}C_4H_9)P[Cr(CO)_5]_2$ with $\delta\,^{31}P = +1362$ ppm is at the low field end,[6] and the most shielded value occurs for gaseous white phosphorus ($\delta\,^{31}P = -553.1$ ppm).[7] The paramagnetic osmium(IV) complex $OsCl_4P[(n\text{-}C_4H_9)_2C_6H_5]_2$ extends the range on the high-field side to -1219 ppm.[8] For the phosphorus tin cluster $[Sn_6(PR)_6]$, $R = Si[CH(CH_3)_2]_3$ with phosphorus atoms of coordination number 4 an unusual high-field shift of -472.2 ppm has been observed.[9] Reported here are the NMR parameters of the nortricyclene derivative $P_4[Sn(C_6H_5)_2]_3$ with bridging tin atoms.

EXPERIMENTAL

The synthesis of the hexaphenyltristannatetraphosphanortricyclene will be described elsewhere.[10] All sample concentrations were approximately 0.03 M. Because of photosensitivity, samples were protected against daylight.

The ^{31}P and ^{119}Sn spectra were measured in C_6D_6 at 300 K on a Bruker AM 200 FT spectrometer at 81.015 and 74.631 MHz, respectively, using 10 mm sample tubes. One ^{119}Sn spectrum was recorded on a Bruker AM 400 FT spectrometer in a 5 mm sample tube. ^{31}P chemical shifts are given relative to external aqueous 85% H_3PO_4; $\delta\,^{119}$Sn is referenced to external $(CH_3)_4Sn$. As usual, low-frequency shifts are taken to be negative. In each case, excitation pulses of 40° were used and the digital resolution was about 0.2 Hz per point ($^{117/119}$Sn satellite line width: 1.0–1.5 Hz). The maximum value of the recording time for all co-added transients was 4.7 days for ^{31}P (91 500 scans) and 15.0 days for ^{119}Sn (257 350 scans). The simulation and iteration of the $A_2A'MX$ spin systems were performed on an Aspect 3000 computer applying Bruker software (PANIC program). Chemical shifts are considered to be accurate to ±0.01 ppm; standard deviations of the coupling constants range of the [mono-^{119}Sn] isotopomer is 0.07 [$^1J(P_AP_{A'})$]–0.17 [$^1J(^{119}SnP_M)$].

RESULTS AND DISCUSSION

The $^{31}P\{^1H\}$ NMR spectrum of $P_4[Sn(C_6H_5)_2]_3$ consists of an A_3X system lying upfield, whose quartet and doublet lines have a 10.0 Hz splitting, are separated by 270 ppm and each is flanked by $^{117/119}$Sn satellites. The ^{119}Sn satellites create an $A_2A'MX$ spin system together with the signals of the $^{119}Sn\{^1H\}$ spectrum which could be fully analyzed by simulation and verified by measurements at different field strengths (see Table 1; atomic numbering is given). The central quartet of the

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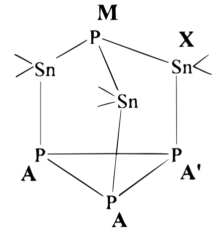
Table 1. Chemical shifts and coupling constants of the $A_2A'MX$ spin system of the [mono-^{119}Sn] isotopomer of hexaphenyltristannatetraphosphanortricyclene, $P_4[Sn(C_6H_5)_2]_3$, in C_6D_6 at 300 K



δ (ppm)		^1J (Hz)		02^2J (Hz)	
$^{31}P_A$	−285.01	$P_AP_{A'}$	−252.8	$P_{A,A'}P_M$	±10.0
$^{31}P_M$	−554.65	$^{119}SnP_{A'}$	+1294.5	$^{119}SnP_A$	+17.5
^{119}Sn	+235.70	$^{119}SnP_M$	+1069.6		

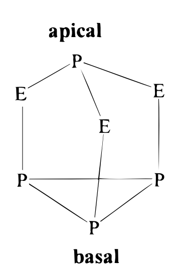
apical phosphorus atom at $\delta\,^{31}P = -554.65$ ppm lies at an unusually high magnetic field. According to our knowledge, this is the most negative $\delta\,^{31}P$ value that has been observed so far for a dissolved diamagnetic phosphorus compound. The $^{117/119}$Sn satellites of this quartet can be considered as overlapping M parts of two $A_2A'MX$ spin systems, which create quartets on their own; since no $^{117}Sn^{119}Sn$ NMR isotope effects on $\delta\,^{31}P$ appear, the geminal P_AP_M and $P_{A'}P_M$ coupling constants can be assumed to have the same absolute value (see Fig. 1).

All theoretically expected 64 $^{117/119}$Sn satellite signals of both overlapping A_2A' parts of the central doublet at −285.01 ppm of the basal phosphorus atoms could be resolved (see Fig. 2).[11] With $^1J(P_AP_{A'}) = -252.8$ Hz the simulation yields a ^1J(PP) value which lies within the range for *cis*-substituted triphosphacyclophosphanes.[12] The ^{31}P signals from the three possible [bis-Sn] isotopomers could be detected only partially with low intensity in the region of the apical phosphorus quartet because of the large number of lines of the corresponding higher order six-spin systems and the low natural abundance of the individual $P_4(Sn<)_3$ isotopomers (approximately 10% of [mono-^{119}Sn] isotopomers).

The $^{119}Sn\{^1H\}$ X part of the $A_2A'MX$ spin system of $P_4[Sn(C_6H_5)_2]_3$ consists of two $a_2a'x$ subspectra; the four small peaks of each subspectrum indicate the higher order character of the $^{119}Sn\{^1H\}$ spectrum (see Fig. 3). At shorter measuring times, such as over a weekend (number of transients 50 000; cf. experimental section), no detection of these peaks is possible and the remaining 16 signals could be misinterpreted as first-order splittings of four different tin coupling constants in place of only three. Nevertheless, the absolute values of both $^1J(^{119}SnP)$ coupling constants and of $^2J(^{119}SnP_A)$ can be taken directly from this higher order spectrum;[11] the corresponding signs are obtained from the X part simulation (see Fig. 3). With +235.7 ppm the chemical shift $\delta\,^{119}$Sn lies within the ^{119}Sn shift range of five-membered P_4Sn heterocycles with phenyl- or alkyl-substituted tin atoms.[13]

The $\delta\,^{31}P$ values of P_4E_3 cage compounds given in Table 2 show the expected variations. Relative to E = P, the sulfur and selenium bridging atoms cause a

Table 2. ^{31}P chemical shifts and geminal PP coupling constant of $P_4[Sn(C_6H_5)_2]_3$ in comparison with analogous hetero-nortricyclene cage molecules P_4E_3



E	$\delta\,^{31}P_{apical}$ (ppm)	$\delta\,^{31}P_{basal}$ (ppm)	^2J(PP) (Hz)	Ref.
S[a]	+67	−121	71	5
Se[b]	+37.40	−104.50	71.3	2
PH[c]	−122.4	−170.7	+58.47	3
PCH_3 [d]	−91.9	−154.4	+38.3	4
Si $(CH_3)_2$ [e]	−361.1	−245.9	15.8	14
Sn $(C_6H_5)_2$	−554.65	−285.01	10.0	This work

[a] In CS_2; both chemical shifts are solvent dependent up to 34.5 ppm.[5]
[b] In CS_2.
[c] Symmetrical isomer in 1-methylnaphthalene.
[d] Symmetrical isomer in tetrahydrofuran.
[e] In C_6H_6.

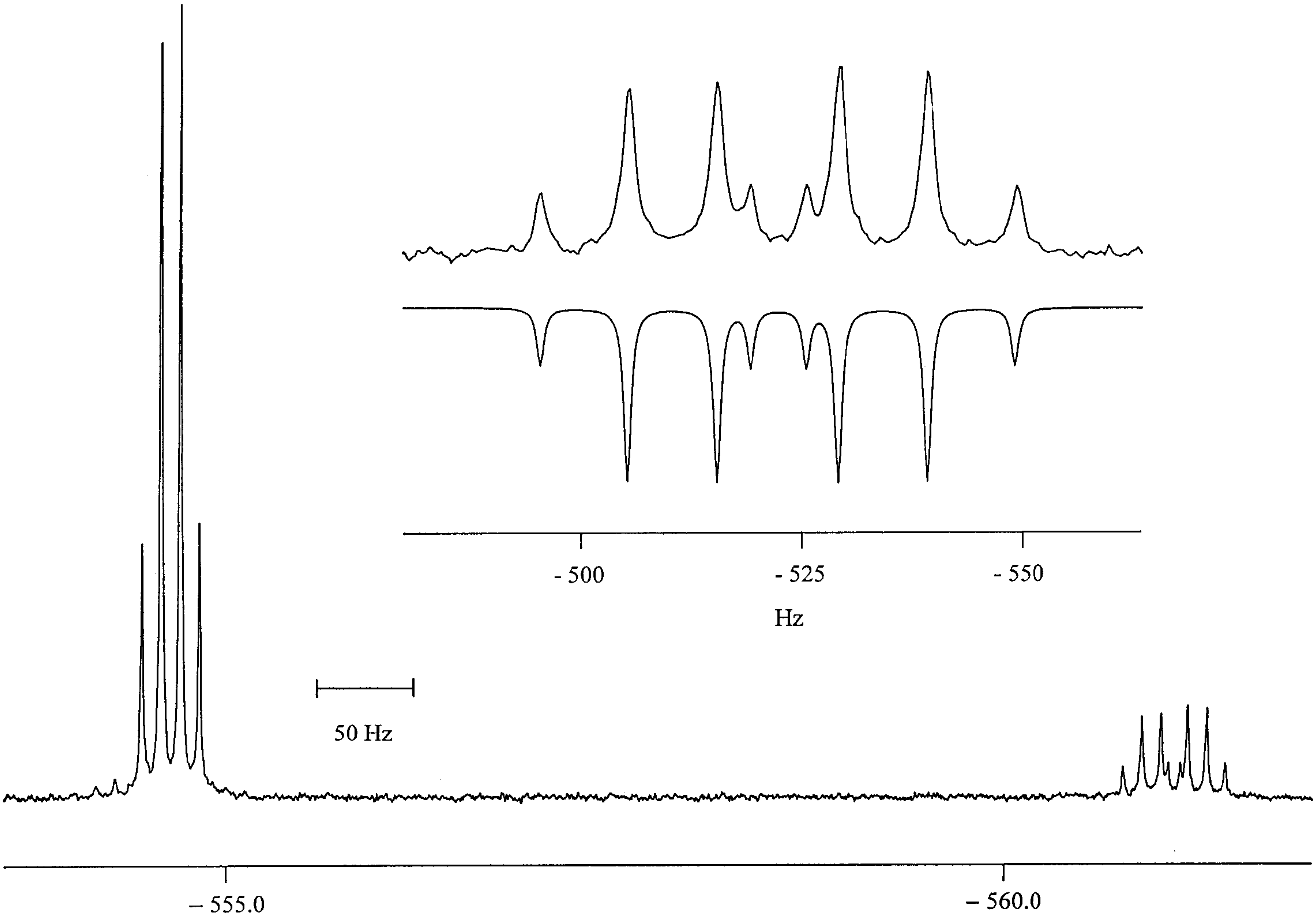


Figure 1. High-field quartet with high-field $^{117/119}$Sn satellites in the 81.015 MHz $^{31}P\{^1H\}$ NMR spectrum of the apical phosphorus atom of the $P_4(Sn<)_3$ cage in C_6D_6 at 300 K (91 500 scans; total experimental time 4.7 days). The overlapping first-order satellite quartets [$^2J(PP) = 10$ Hz] are simulated as M parts of the $A_2A'MX$spin systems of the [mono-^{117}Sn] and [mono-^{119}Sn] isotopomers and co-added (top). The origin of the Hz scale (see text) is the center of the main quartet. The remaining $^{117/119}$Sn satellite signals are symmetrical to the main quartet (for atomic numbering, see Table 1) and separated from the corresponding high-field satellites by $^1J(^{117}SnP_M)$ and $^1J(^{119}SnP_M)$, respectively. The frequency marking holds for the main spectrum.

deshielding of the phosphorus atoms as expected because of the positive partial charge at these atoms, whereas with E = Si or Sn the phosphide character causes a noticeable shielding effect. The maximum ^{31}P shift difference appearing in these tricyclic cage molecules occurs with about 600 ppm at the apical phosphorus atoms, more than three times the value at the basal phosphorus atoms of nearly 180 ppm (see Table 2). This can be connected with the fact that the apical P atom has three neighboring bridge atoms and the basal P atoms only one. The linear dependence of all the tabulated values of $\delta\,^{31}P_{basal}$ and $\delta\,^{31}P_{apical}$, which can be correlated to a good approximation through $\delta\,^{31}P_{basal} = 0.29\ \delta\,^{31}P_{apical} - 130$ (least squares refinement parameters: 0.29 ± 0.02; -130 ± 6), with a gradient of 0.29, confirms this presumption.

The values of the geminal PP coupling constants via the bridging atoms differ considerably. With E = S or Se they are approximately 70 Hz, whereas the silicon and tin bridged phosphidic cages show noticeably smaller values of about 10 Hz.

The extraordinary shielding ability of the apical phosphorus atom of $P_4[Sn(C_6H_5)_2]_3$ ($\delta\,^{31}P = -554.65$ ppm) can be interpreted phenomenologically with the so-called 'heavy atom effect.' In the series of haloalkanes $C(Hal)_4$, Hal = F, Cl, Br, I,[15] or in the series C_6H_5—X—CH_3, X = O, S, Se, Te,[16] this effect leads to an increasing ^{13}C upfield shift and can be described with the aid of a diamagnetic correlation term.[17] The tetrahaloborate ions $B(Hal)_4^-$, Hal = Cl, Br, I, also show a remarkably increasing shielding of the boron nucleus in this order (Cl → I: −135 ppm).[18] In this context, the $\delta\,^{31}$P values of tertiary phosphanes of type $P(R)_3$ with substituents R, which contain the bridging atoms E of the P_4E_3 cage, are of interest (see Table 3).

The ^{31}P signals of these compounds show the same marked tendency for higher field strengths as the lines of $^{31}P_{apical}$ of the tricyclic P_4E_3 cages, which exhibit for the individual apical phosphorus atom an upfield shift relative to $\delta\,^{31}$P of the phosphane with suitable substituents (with the exception of R = PH_2). Similarly, the shielding maximum of these phosphanes is observed

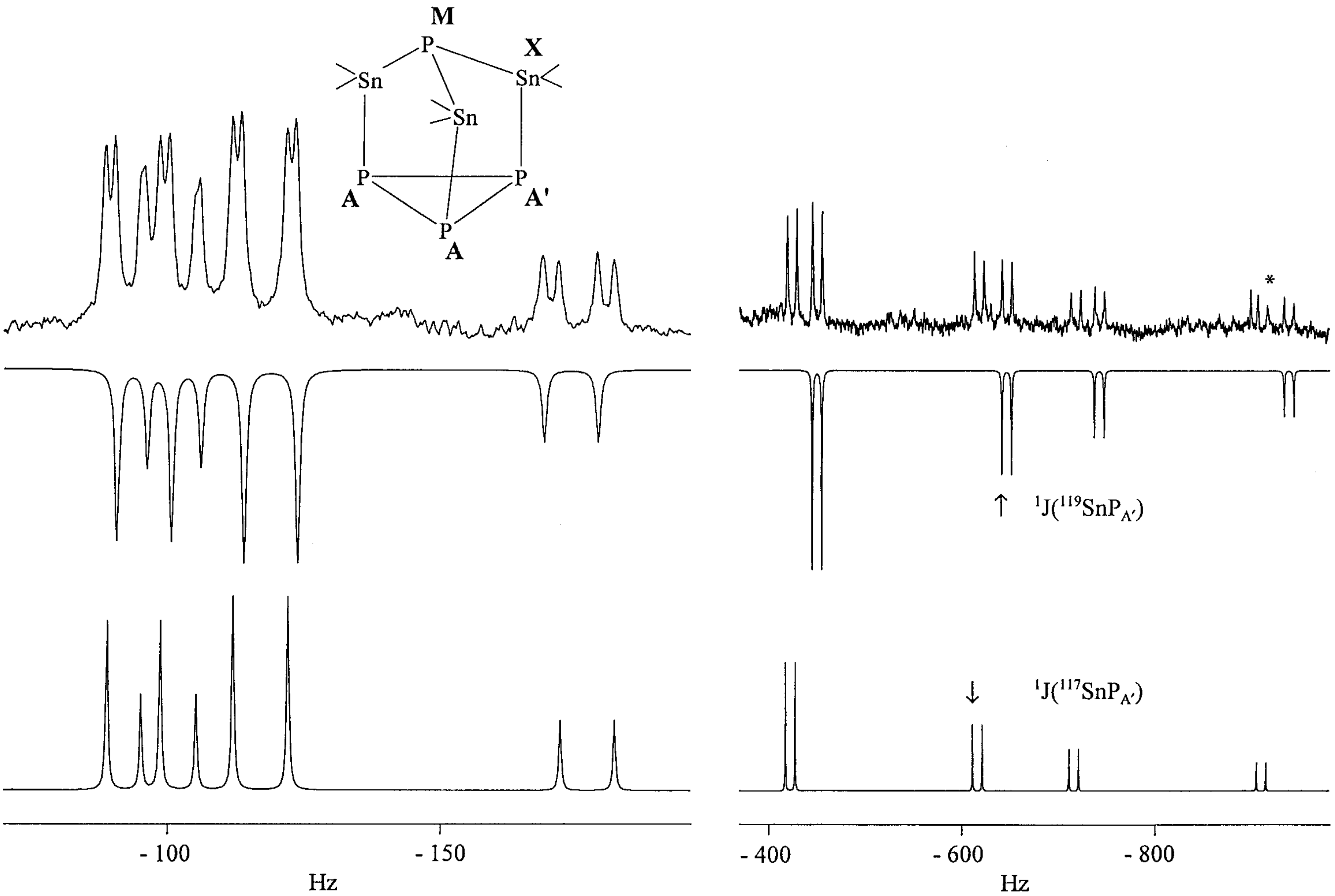


Figure 2. High-field $^{117/119}Sn$ satellites of the basal phosphorus atoms of the title compound in the 81.015 MHz $^{31}P\{^1H\}$ NMR spectrum (for recording conditions, see Fig. 1; the asterisk indicates an impurity). The residual $^{117/119}Sn$ satellite signals are symmetric to the main doublet [$^2J(PP) = 10$ Hz] at −285.01 ppm. The origin of the Hz scale (see text) is the center of this doublet (top). The lines marked with arrows and the corresponding downfield lines in the simulated A_2A' part of the $A_2A'MX$ spin system of the [mono-^{119}Sn] isotopomer (middle) and of the [mono-^{117}Sn] isotopomer (bottom) are separated by $^1J(^{119}SnP_{A'})$ and $^1J(^{117}SnP_{A'})$, respectively.

with substituents R containing the heaviest metal atom, i.e. tin. Therefore, one can assume a similar bonding situation and substituent dependence of the P—E bonds of the apical phosphorus atom of the nortricyclene derivatives and the corresponding P—element bonds of the listed tertiary phosphanes.

For better clarification of the results and their phenomenological interpretations, *ab initio* NMR calculations (SOS-DFPT/BII)[22] were performed for the parent compound $P_4(SnH_2)_3$. The extraordinary ^{31}P chemical shifts of $P_4[Sn(C_6H_5)_2]_3$ were confirmed.[10]

Table 3. ^{31}P chemical shifts of tertiary phosphanes of type $P(R)_3$

R	$\delta\,^{31}P$ (ppm)	Ref.
SCH_3	+124.5	19
$SeCH_3$	+107.0	19
PH_2	−147.6	20
Si $(CH_3)_3$	−251.2	21
Sn $(C_6H_5)_3$	−323	21
Sn $(CH_3)_3$	−330	21

Further calculations show the connection between the extreme $\delta\,^{31}P$ values of the $P_4(Sn<)_3$ cage and experimentally less accessible molecules such as tetrahedral $(SnH)_nP_{4-n}$, $n = 0$–4, cluster compounds or $P(SnH_3)_3$.[10]

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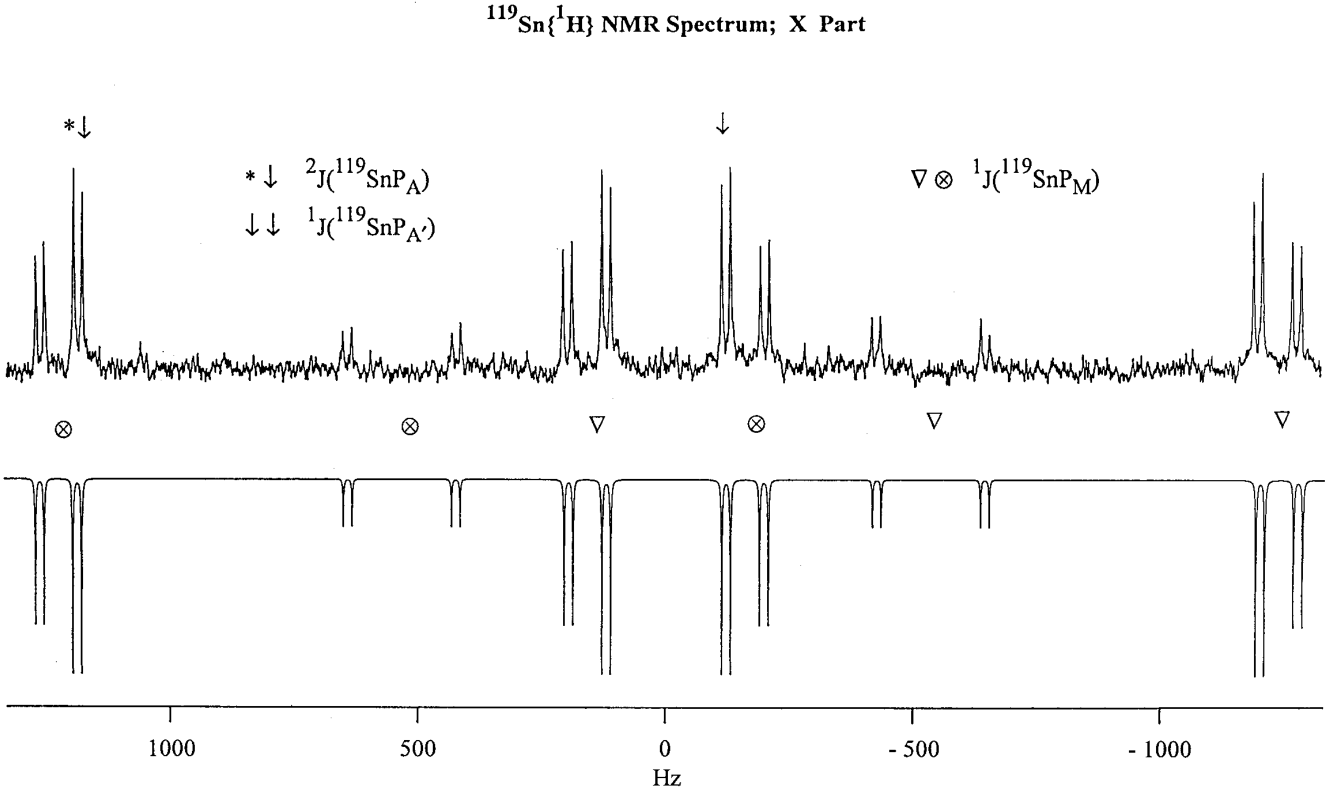

Figure 3. 74.631 MHz ^{119}Sn{^{1}H} NMR spectrum of $P_4[Sn(C_6H_5)_2]_3$ in C_6D_6 at 300 K (total experimental time 15.0 days; 257 350 scans). The Hz scale (see text) is centered at $\delta\,^{119}Sn = +235.70$ ppm. The lines marked with crossed circles and triangles form in each case an $a_2a'x$ subspectrum of the X part of the $A_2A'MX$ system; the centers of these two subspectra will be displaced by $^1J(^{119}SnP_M)$. The X part of the complete $A_2A'MX$ simulation is given below.

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