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MÖSSBAUER, MULTINUCLEAR MAGNETIC RESONANCE AND MASS SPECTROMETRIC STUDIES OF ORGANOTIN CARBOXYLATES OF *m*-METHYL *TRANS*-CINNAMIC ACID

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Abstract—The synthesis and spectroscopic characterization (^{1}H, ^{13}C, ^{119}Sn NMR, ^{119m}Sn Mössbauer and mass spectrometry) of a series of organotin carboxylates of *m*-methyl *trans*-cinnamic acid are described. Different literature methods have been successfully applied for the qualitative structural characterization of these compounds. Triorganotin carboxylates are essentially penta-coordinate in the solid state with R_3SnO_2 geometry, while tetra-coordinate in non-coordinating solvents. Diorganotin carboxylates with a 1 : 2 molar ratio ($R_2SnO : 2HOCOR'$) are hexa-coordinate as solids, while there is an equilibrium between hexa- and penta-coordinated states in solution. Moreover, compounds with a 1 : 1 molar ratio ($R_2SnO : HOCOR'$), adopt a characteristic tetraorganodicarboxylato distannoxane structural mode. Interesting results have been observed for tricyclohexyltin derivatives and stannoxanes. 2D NMR has been employed for the assignments of protons of high-spin systems.

There are many reports dealing with the impact of organotin chemistry in the biosphere.[1-6] Our contribution in this regard relates to the synthesis and characterization of organotin derivatives of donor ligands containing chalcogens, with special reference to their biological applications.[7-11] The exploration of structure–activity relationships of such systems has led to numerous reports in recent years.[12-20] Recent literature shows that organotin

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derivatives of substituted benzoic acid and cinnamic acid are potent candidates against cancer and tumours in mammals.[21–24] In order to extend the structural chemistry and biological applications of such systems we have prepared a new series of organotin carboxylates derived from *m*-methyl *trans*-cinnamic acid. Qualitative structural characterization of these compounds is based on C—Sn—C angles which have been calculated from NMR and Mössbauer data.

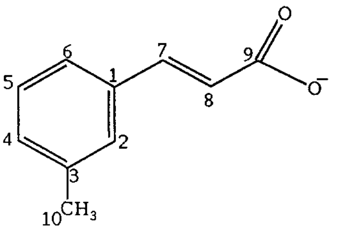

Fig. 1. The *m*-methyl *trans*-cinnamate anion.

EXPERIMENTAL

Organotin carboxylates were synthesized by the condensation of an appropriate carboxylic acid and corresponding organotin oxides at reflux temperature in toluene using a conventional Dean and Stark separator.

Physical properties and spectroscopic data are given in Tables 1–8.

$$(R_3Sn)_2O + 2HOOCR' \longrightarrow 2R_3SnOOCR' + H_2O$$

R = Me, Bu^n, Cyhex, Ph(**I**, **IV**, **VII** and **VIII**)

$$R_2SnO + 2HOOCR' \longrightarrow R_2Sn(OOCR')_2 + H_2O$$

R = Me, Bu^n(**II** and **V**)

$$4R_2SnO + 4HOOCR' \longrightarrow \{[(R_2SnOOCR')_2O]_2\} + 2H_2O$$

R = Me, Bu^n(**III** and **VI**)

In all cases $R' = m\text{-}CH_3C_6H_4CH{=}CH{-}$ (see Fig. 1).

Instrumentation

^{119m}Sn Mössbauer spectra were obtained with a constant acceleration microprocessor-controlled spectrometer (Cryoscopic Ltd, Oxford U.K.); the barium stannate source was used at room temperature and samples were packed in perspex discs and cooled to −193°C. Isomer shift data are relative to SnO_2. The ^{1}H and ^{13}C NMR were recorded on Bruker AM 500 spectrometer using $CDCl_3$ as an internal reference [δ $^1H(CDCl_3) = 7.24$: δ $^{13}C(CDCl_3) = 77.0$]. ^{119}Sn NMR spectra were obtained on a Jeol FX 90Q instrument with Me_4Sn [$\Xi(^{119}Sn) = 37.290665$ MHz] as an external reference. Mass spectral data were measured on a MAT 8500 Finnigan, Germany. Solid-state ^{119}Sn CP/MAS NMR were measured at 25°C on a Bruker MSL 300 spectrometer. The compounds were placed in air-tight inserts,[25] fitting into the commercial ZrO_2 rotors of the double-bearing probehead. All ^{119}Sn CP/MAS were run at two different spinning speeds for assignment of the isotropic δ^{119}Sn values.

RESULTS AND DISCUSSION

Multinuclear NMR and Mössbauer parameters (Tables 2–7) have been used to calculate C—Sn—C angles for the structural characterization of these carboxylates. In ambiguous cases, 2D heteronuclear shift correlation (HETCOR) of the type $^{13}C/^1H$ [based on $^1J(^{13}C–^1H)$] were used to confirm the assignments. ^{13}C NMR together with the HETCOR experiment proved extremely valuable for the structural assignments because ^{1}H NMR

Table 1. Physical parameters

Compound	Recrystallizing solvent	Yield (%)	Physical state	Mp (°C)
I	Dichloromethane	92	Colourless, crystalline	154
II	Dichloromethane	83	White, amorphous	165–167
III	Chloroform/ether	85	White, amorphous	101–102
IV	Chloroform	78	White, crystalline	57
V	Dichloromethane	78	Colourless, crystalline	87–88
VI	Dichloromethane	88	Colourless, oily	—
VII	Dichloromethane	75	White, crystalline	128
VIII	Dichloromethane	80	White, crystalline	63–65

Table 2. ^{1}H NMR data of triorganotin derivatives[a,b]

Proton	**I** R = methyl	**IV** R = n-butyl	**VII** R = phenyl	**VIII** R = cyclohexyl
2	7.16 (d, 7.43)	7.15 (d, 7.34)	7.26 (d, 7.47)	7.13 (d, 7.55)
4/6	7.25 (t, 7.49, 7.49)	7.25 (t, 8.10, 8.10)	7.35 (t, 7.96, 7.96)	7.22 (t, 7.50, 7.50)
5	7.31 (d, 4.35)	7.33 (d, 6.56)	7.43 (d, 7.44)	7.32 (d, 8.74)
7	7.59 (d, 16.00)	7.59 (d, 15.90)	7.90 (d, 16.00)	7.58 (15.90)
8	6.46 (d, 16.00)	6.48 (d, 15.90)	6.77 (d, 16.00)	6.48 (d, 15.90)
10	2.35 (s)	2.35 (s)	2.23 (s)	2.32 (s)
α	0.60 [58.80]	1.30 [53.90]	— —	1.92 [45.20]
β		1.65 [68.00]	7.97 [61.50]	1.92, 1.67 [36.80], [28.60]
γ		1.35 [3.40]	7.61 [15.70]	1.67, 1.33 [23.20], [n.o.]
δ		0.92 (t, 7.00)	7.59 (m)	1.67, 1.33 (m)

[a] Chemical shift (δ) in ppm, ^3J(H–H) in Hz, ^nJ[^{119}Sn–H] in Hz.

[b] In the case of n-butyl, phenyl and cyclohexyl derivatives ^nJ[^{119}Sn–H] has been measured using 2D heteronuclear correlation.

s = singlet, d = doublet, t = triplet, n.o. = not observed.

Table 3. ^{1}H NMR data of diorganotin derivatives[a]

Proton	**II** R = methyl	**III** R = methyl	**V** R = n-butyl	**VI** R = n-butyl
2	7.12 (d, 7.30)	7.20 (d, 7.40)	7.18 (d, 7.53)	7.18 (d, 7.48)
4/6	7.19 (t, 7.70, 7.70)	7.28 (t, 7.52, 7.52)	7.27 (t, 8.00, 8.00)	7.28 (t, 7.50, 7.50)
5	7.26 (d, 7.90)	7.36 (d, 8.10)	7.33 (d, 6.17)	7.37 (d, 8.17)
7	7.68 (d, 16.00)	7.57 (d, 15.80)	7.76 (d, 16.00)	7.60 (d, 15.85)
8	6.42 (d, 16.00)	6.41 (d, 15.80)	6.48 (d, 16.00)	6.45 (d, 15.85)
10	2.29 (s)	2.38 (s)	2.36 (s)	2.39 (s)
α	1.10 [78.50]	0.98, 0.90 [90.86], [86.50]	1.82 [69.10]	1.84-1.78 (m)
β			1.45 [106.80]	1.69-1.58 (m)
γ			1.30 [2.30]	1.48–1.45 (m)
δ			0.90 (t, 7.33)	0.94, 0.92 (t, 7.30, 7.30)

[a] See footnotes to Table 1.

Table 4. ^{13}C NMR data of triorganotin derivatives[a]

Carbon	I R = methyl	IV R = n-butyl	VII R = phenyl	VIII R = cyclohexyl
1	134.67	134.99	134.49	135.19
2	130.55	130.44	130.82	130.33
3	138.31	138.27	138.25	138.23
4	128.60	128.58	128.59	128.55
5	128.50	128.51	128.36	128.51
6	125.00	125.04	125.10	125.05
7	119.65	119.00	117.95	120.23
8	144.18	143.06	145.77	143.56
9	172.06	172.00	173.20	171.86
	—	—	—	[11.70]
10	21.20	21.25	21.16	21.22
α	−2.20	16.49	138.42	33.96
	[402.00]	[362.00]	[659.00]	[340.00]
β		27.82	136.70	31.10
		[21.80]	[49.00]	[14.52]
γ		27.00	128.79	28.96
		[68.00]	[69.00]	[65.21]
δ		13.59	130.00	26.96
			[13.30]	[7.20]

[a] Chemical shifts (δ) in ppm, $^{n}J(^{119}\text{Sn}-^{13}\text{C})$ in Hz.

Table 5. ^{13}C NMR data of diorganotin derivatives[a]

Carbon	II R = methyl	III R = methyl	V R = n-butyl	VI R = n-butyl
1	134.30	134.00	134.40	135.10
2	131.50	130.00	131.20	130.54
3	138.50	138.00	138.50	138.39
4	128.80	128.69	128.80	128.79
5	128.50	128.67	128.74	128.56
6	125.40	125.16	125.63	125.09
7	117.10	121.19	117.37	121.52
8	147.00	144.00	146.62	143.59
9	176.00	173.00	175.69	172.59
10	21.23	21.30	21.20	21.60
α	5.20	9.80, 6.60	25.42	29.49, 27.55
	[633.00]	[815.00], [756.00]	[569.00]	[732.00], [697.90]
β			26.64	27.76, 27.41
			[34.00]	[35.95], [32.50]
γ			26.24	26.89, 26.77
			[93.00]	[136.00], [123.00]
δ			13.42	13.60

[a] See footnote to Table 3.

Table 6. Mössbauer and ^{119}Sn NMR data[a]

Compound	Mössbauer parameters				^{119}Sn NMR
	δ (mm s^{-1})	Δ (mm s^{-1})	Γ_1 (mm s^{-1})	Γ_2 (mm s^{-1})	δ (ppm)
I	1.27	3.55	0.92	0.89	129
II	1.18	3.41	1.01	1.08	−140
III	1.13	3.14	0.83	0.91	−175.07, −191.39
	1.30	3.65	—	—	— —
IV	1.28	3.50	0.91	0.97	107.98
V	1.28	3.35	0.90	0.97	−153
VI	—	—	—	—	−204.40, −217.20
VII	1.24	3.41	1.01	1.08	−114.32
VIII	1.41	2.63	0.96	0.87	12

[a] $\delta \pm 0.02$, $\Delta \pm 0.04$, $\Gamma \pm 0.02$ mm s^{-1}.

spectra, even at 500 MHz, were very complex in some cases. Solid-state ^{119}Sn NMR spectra for only representative compounds have been recorded for comparison with that of the solution phase. Using Lockhart's equation[26] the C—Sn—C angles (Table 7) for the trimethyltin derivative (**I**) based on $^2J(^{119}\text{Sn–C–}^1\text{H})$ (Fig. 2) and $^1J(^{119}\text{Sn–}^{13}\text{C})$ (Fig. 3) are found to be 111.44° and 112°, respectively.

These values are typically in the range for a tetrahedral environment of the tin atom. However, the ^{119}Sn chemical shifts (Table 6) in solution (129 ppm) and in the solid phase (−40 ppm) show a remarkable difference. This difference of 169 ppm strongly suggests that this compound is monomeric tetra-coordinated in solution and polymeric penta-coordinated in the solid state. The polymeric nature in the solid state is further strengthened from Mössbauer data, i.e. quadrupole splitting (Δ) 3.55 mm s^{-1} and isomer shift (δ) 1.27 mm s^{-1}. Similarly, tributyltin and triphenyltin derivatives show C—Sn—C angles of 112° and 116°,[27,28] providing evidence for tetrahedral geometry in non-coordinating solvents, whereas Δ 3.53 and 3.35 mm s^{-1}, respectively, are in accordance with a R_3SnO_2 moiety. Thus, triorganotin derivatives are polymeric due to strong intermolecular interactions, with the tricyclohexyltin derivative (**VIII**) as an exception, which is being considered as a monomer.

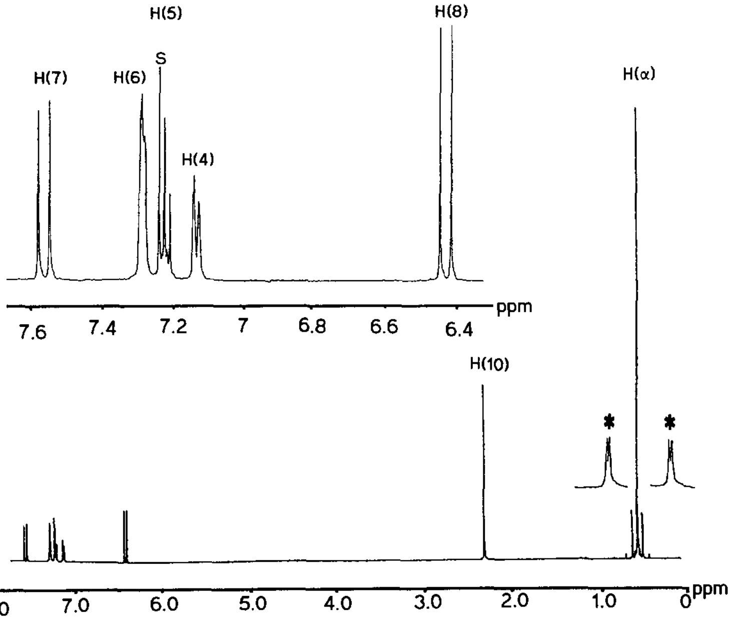

Fig. 2. 500.13 MHz ^{1}H NMR of $[m\text{-CH}_3\text{C}_6\text{H}_4\text{CHCHCOOSn(CH}_3)_3]$ in $CDCl_3$ at 25°C. The range of olefinic protons is expanded. The AB spin-system of the alkenyl group and protons of the ring are clearly visible. The expanded $^{119/117}$Sn satellites are marked by asterisks and solvent by s.

Table 7. C—Sn—C angles based on NMR parameters

Compound	$^1J(^{119}Sn–^{13}C)$	$^2J(^{119}Sn–C–^1H)$	Θ (°)	
			^1J	^2J
I	402	58.79	112	111.44
II	633	78.50	132.28	128.99
III	815	90.86	148.25	146.38
	756	86.50	143.07	139.68
IV	359	—	112.4	—
V	569	—	131.99	—
VI	732	—	147	—
	697	—	143	—
VII	659	—	117	—

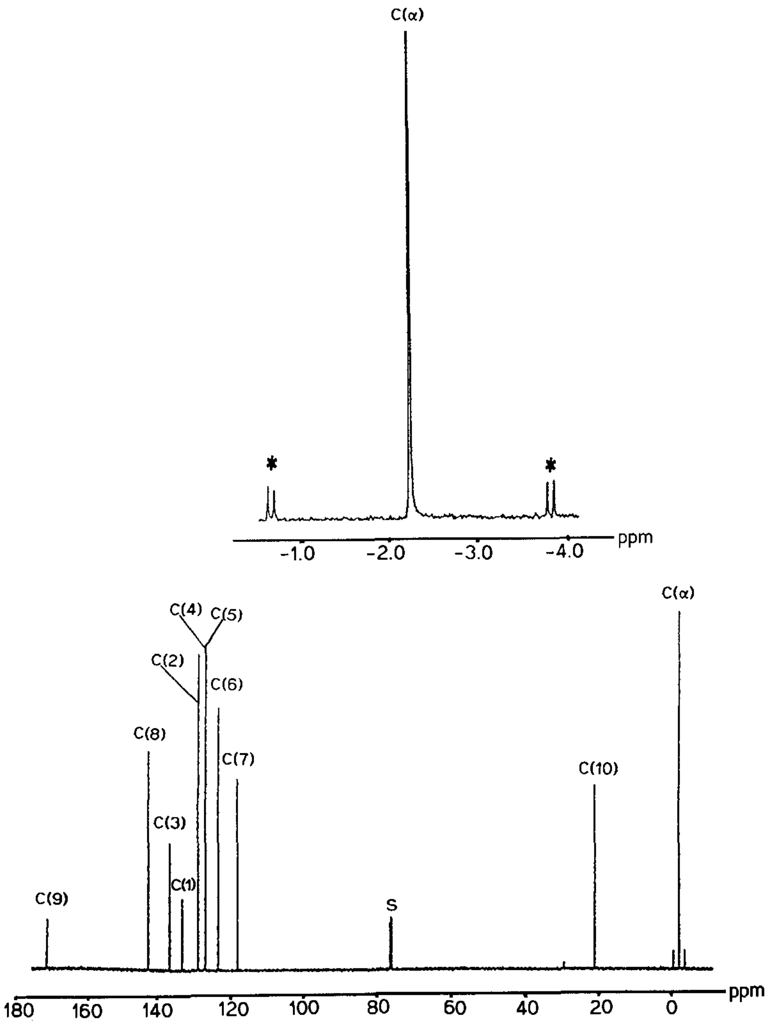

Fig. 3. 500.13 MHz ^{13}C NMR of $[m\text{-}CH_3C_6H_4CHCHCOOSn(CH_3)_3]$ in $CDCl_3$ at 25°C. The range of $^1J(^{119/117}Sn—^{13}C)$ is expanded. The $^{119/117}Sn$ satellites are marked by asterisks and solvent by s.

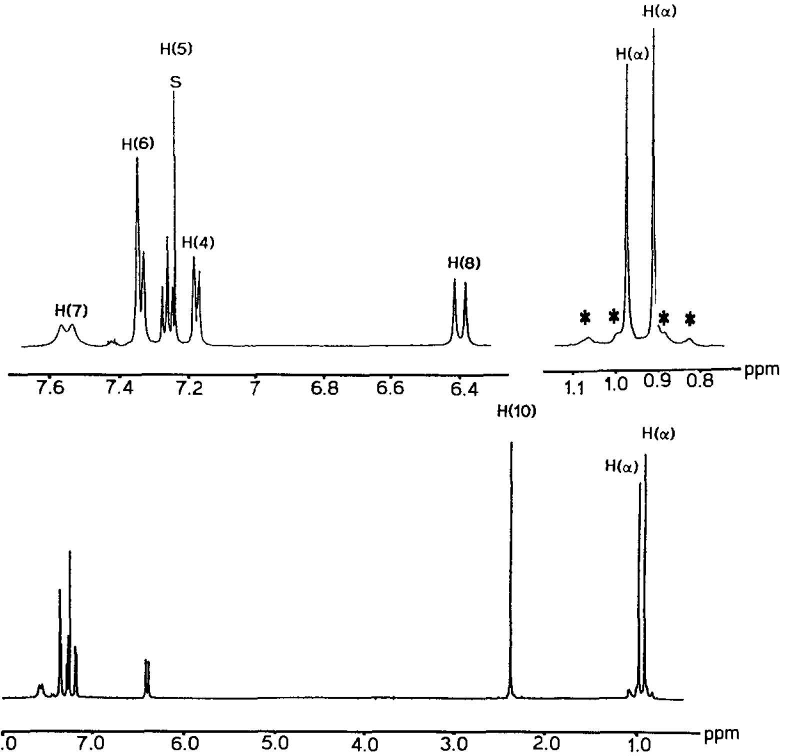

Fig. 4. 500.13 MHz ^{1}H NMR of [{*m*-$CH_3C_6H_4CHCHCOOSn(CH_3)_2$}$_2$O]$_2$ in $CDCl_3$ at 25°C. The range of olefinic as well as alkyl protons is expanded. The broad nature of the AB spin-system of the olefinic protons is due to dynamic equilibrium between penta- and hexa-coordinate states around tin atoms. The unresolved $^{119/117}$Sn satellites are marked by asterisks and solvent by s.

It is interesting to note that $^2J(^{119}Sn—O—^{13}C)$ coupling, which is rare in the literature, is observed only for this compound, the reason for which is not fully understood. δ ^{119}Sn NMR in solution as well as in the solid state (12 ppm) clearly indicates that this compound has the same geometry in both phases. The quadrupole splitting value (Δ 2.63 mm s^{-1}) is at the limits between the tetra- and penta-coordinated state.[29] X-ray reports show that there is no significant inter- or intramolecular interaction

Table 8. Monoisotopic (80 eV) mass spectral data

	Intensity (%)							
Ionic species	I	II	III	IV	V	VI	VII	VIII
$[M-R]^+$	100	8	5	100	100	100	100	100
$[M-LR]^+$	35	—	—	11	—	15	—	—
$[M-SnR_3]^+$	36	—	—	38	—	—	3	10
$[M-RCO_2]^+$	55	5	3	3	10	—	30	—
$[M-R_2CO_2]^+$	—	—	—	—	5	—	9	4
$[M-R_3CO_2]^+$	15	—	—	—	—	—	6	13
$[M-L]^+$	27	100	100	7	7	—	—	—
$[M-LRCO_2]^+$	—	6	3	—	—	10	—	—
$[M-LR_2CO_2]^+$	—	5	7	—	18	5	—	—
$[M-SnR_3CO_2]^+$	51	—	—	40	—	—	11	—
$[M-SnLR_2CO_2]^+$	—	51	51	—	12	20	—	—
$[M-SnLR_2C_2H_2CO_2]^+$	—	62	62	—	6	10	—	—
$[M-SnR_3C_2H_2CO_2]^+$	31	—	—	37	—	—	8	10

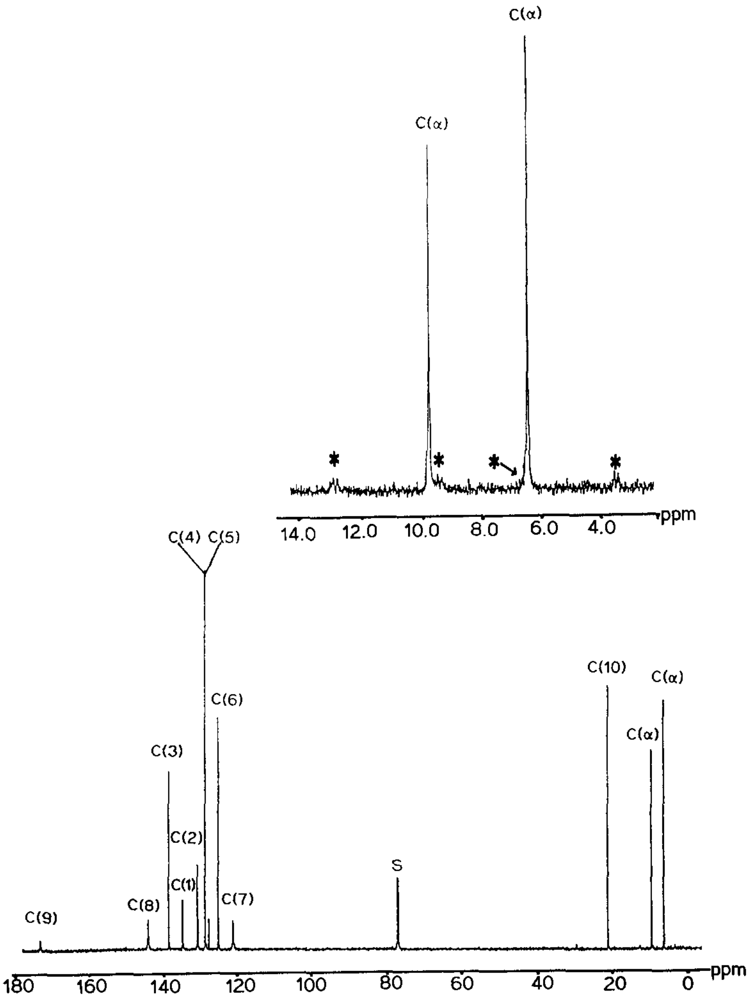

Fig. 5. 500.13 MHz ^{13}C NMR of [{*m*-CH$_3$C$_6$H$_4$CHCHCOOSn(CH$_3$)$_2$}$_2$O]$_2$ in CDCl$_3$ at 25°C. The range of tin-methyl carbons is expanded. The broad nature of carbonyl carbon is due to the same dynamic effect as reflected by the proton spectrum (Fig. 4). The $^{119/117}$Sn satellites are marked by asterisks and solvent by s.

in tricyclohexyltin carboxylates.[30–32] Hence, tin in **VIII** has an essentially tetrahedral environment.

In diorganotin derivatives, R$_2$SnL$_2$, where R = Me, the C—Sn—C angles[26] calculated by ^1J and are ^2J 132° and 129°. The ^{119}Sn peak (−140 ppm) is very broad at room temperature; however, it becomes very sharp at −30°C. This shows that at room temperature there is an equilibrium between penta- and hexa-coordinate states. When R = Bu^n, this angle by the Lycka relation[27] is 132°. These angles are in the range for a six-coordinated tin environment describing skew-trapezoidal geometry. It has been observed that δ ^{119}Sn NMR for the butyl derivative in CDCl$_3$ and in the solid phase (−154 and −161 ppm, respectively) are rather similar. A difference of 10 ppm in solution and the slightly broad nature of the ^{119}Sn peak is due to the reason described for the methyl derivative.

The difference in characterization of diorganotindicarboxylates (R$_2$SnL$_2$) and tetraorganodicarboxylato distannoxanes {[(R$_2$SnL)$_2$O]$_2$} is now well established. In ^{1}H NMR (Table 3) only one singlet due to methyl groups is seen for **II**, whereas two unresolved singlets for **III** were observed. A similar dichotomy was shown by ^{13}C (Table 4) and ^{119}Sn NMR spectra (Table 6) (Figs 4 and 5). We have observed that the Mössbauer spectra of **III** show a pair of doublets with Δ 3.14 and 3.65 mm s^{-1}. Such a pair of doublets is not usually observed in stannoxanes,[22] which is probably due to the low range of the Mössbauer scale. The pair of doublets clearly indicates the presence of two tin sites. The difference in Δ values for these two pairs (3.65–3.14 = 0.51 mm s^{-1}) strongly suggests that the tin atoms have different coordination numbers, although multinuclear NMR in non-coordinating solvents advocates a very similar environment for both the tin atoms. The broad nature of the olefinic protons and carbonyl carbon (compared with trialkyltin derivatives) shows a dynamic equilibrium between penta- and hexa-coordinate states. However, in the solid phase intra- or intermolecular interactions are possible which may result in hexa- or even hepta-coordinate geometry around the tin atoms. A similar explanation holds true for **VI**.

The 80 eV monoisotopic mass spectral fragmentations of the compounds are given in Table 8. Their fragmentation patterns obey the established routes described in earlier reports.[21,24]

A very weak molecular ion peak (8%) was observed only for the phenyl derivative. The most frequent fragmentation route is the elimination of an R group, and to a lesser extent through tin–oxygen cleavage. However, secondary fragmentation is a consequence of loss of CO_2 molecules or the R group; the former being the most probable and frequent pathway. Peaks for R_3Sn^+ and R_2Sn^+ are either absent or very weak, which indicates that the fragmentation route through these species is not favourable.

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