ELSEVIER

Journal of Organometallic Chemistry 486 (1995) 51–56

Journal of Organometallic Chemistry

Organotin esters of 3-(2-furanyl)-2-propenoic acid: their characterization and biological activity

Muhammad Danish [a], Helmut G. Alt [a,*], Amin Badshah [b], Saqib Ali [b], Muhammad Mazhar [b], Nazar-ul-Islam [c]

[a] *Laboratorium für Anorganische Chemie, Universitätsstrasse 30, D-95440 Bayreuth, Germany*
[b] *Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan*
[c] *Department of Pharmacy, Peshawar University, Peshawar, Pakistan*

Received 14 March 1994; in revised form 17 June 1994

Abstract

Multinuclear NMR and Mössbauer spectroscopy have been carried out for di- and triorganotin carboxylates derived from 3-(-2-furanyl)-2-propenoic acid. Their spectroscopic characterization showed that triorganotin carboxylates are either 4-coordinate monomers or 5-coordinate polymers with bridging carboxylate groups. Although a polymeric structure is favoured for most compounds in the solid state, the solution studies indicated that they exist as monomeric 4-coordinate species in non-coordinating solvents. Diorganotin carboxylates of the general formula $R_2Sn(OOCCHCHC_4H_3O)_2$ and dimeric $[(R_2SnOOCCHCHC_4H_3O)_2O]_2$ are penta-coordinate in noncoordinating solvents while in the solid phase intra- or intermolecular interactions are possible. Moreover, we report the fluxional behaviour of carboxylate anions in dimeric distannoxanes. The biological activity of these organotin carboxylates proved them to be powerful biocides.

Keywords: Organotin; NMR; Biological activity; 3-(2-furanyl)-2-propenoic acid; Esters

1. Introduction

Organotin compounds being biologically active are extensively used as fungicides, pesticides, antifouling coating materials, polymer stabilizers and preservatives of wood [1–6]. In order to develop new kinds of organotin biocides we have synthesized a series of new organotin carboxylates and tested their antibacterial and antifungal activity. The screening test showed that some of these compounds are powerful biocides. Moreover their structures have been investigated by multinuclear NMR and Mössbauer spectroscopy and correlated with their biological activity.

2. Experimental section

The new compounds were prepared according to our earlier report [7] and the literature method [8]. Triorganotin carboxylates (compounds I–V) were prepared by refluxing the appropriate chloride and silver salt of 3-(2-furanyl)-2-propenoic acid in a 1:1 molar ratio in anhydrous chloroform under inert atmosphere

$$R_3SnCl + AgOOCCHCHC_4H_3O \longrightarrow R_3SnOOCCHCHC_4H_3O + AgCl$$

R = Me, Et, n-Bu, Ph, Cyhex

Diorganotin carboxylates (compounds VIa and VIIa) were prepared by the condensation of carboxylic acid and diorganotin oxide in a 2:1 molar ratio

$$R_2SnO + 2HOOCCHCHC_4H_3O \longrightarrow R_2Sn(OOCCHCHC_4H_3O)_2 + H_2O$$

R = Me, n-Bu (type "a")

whereas dimeric distannoxanes (compounds VIb and VIIb) were obtained by the condensation of the carboxylic acid and the diorganotin oxide in a 1:1 molar ratio

$$4R_2SnO + 4HOOCCHCHC_4H_3O \longrightarrow \{(R_2SnOOCCHCHC_4H_3O)_2]_2\} + 2H_2O$$

R = Me, n-Bu (type "b")

* Corresponding author.

SSDI 0022-328X(94)05050-L

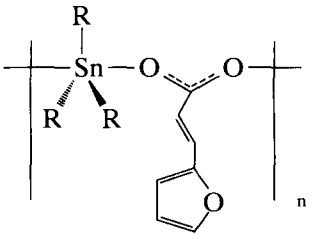
Water formed during the condensation reaction was continuously removed by the use of a Dean and Stark trap.

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM 500 MHz spectrometer using $CDCl_3$ as internal reference. ^{119}Sn NMR spectra were obtained on a Jeol FX 90Q instrument with Me_4Sn as external reference. ^{119m}Sn Mössbauer spectra were obtained with a constant acceleration microprocessor-controlled spectrometer (Cryophysics Ltd., Oxford, UK); a barium stannate source was used at room temperature, and samples were packed in Perspex discs and cooled to 80 K. Isomer shift data are relative to SnO_2.

3. Results and discussion

3.1. Spectral studies of triorganotin carboxylates

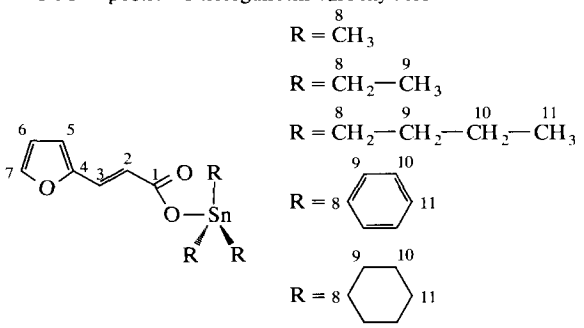
The ^{1}H, ^{13}C and ^{119}Sn NMR data of the tri-organotin carboxylates are given in Tables 1, 2 and 5. The expected resonance signals were assigned by their multiplicity and intensity pattern, and their coupling constants. The solution NMR spectral data for compounds I–V are consistent with a 4-coordinate monomeric species as suggested for comparable systems [9,10]. The Mössbauer spectra (Table 3) of compounds I and III show a quadrupole splitting value of 3.48 and 3.50 respectively. Holmes et al. [10] reported that the quadrupole splitting parameters for monomeric tri-organotin esters fall in the range of 2.30–2.55 mm s^{-1} while those having a five coordinate chain structure formed by bridging carboxylate groups give quadrupole splitting values in the range of 3.59–3.70 mm s^{-1}. The quadrupole splitting values of 3.48 and 3.50 mm s^{-1} are in close agreement with 5-coordinated tin with bridging carboxylate groups (structure I). A similar explanation is given for compound II.



(I)

R = Me, Et, n-Bu, Ph

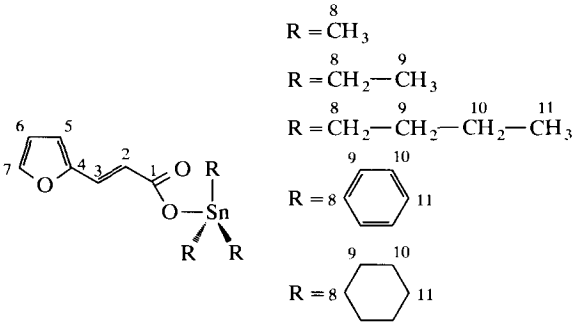
Table 1
^{1}H NMR spectra of triorganotin carboxylates [a]



Proton	I R = methyl	II R = ethyl	III R = n-butyl	IV R = phenyl	V R = cyclohexyl
2	6.33 (d, 16.0)	6.32 (d, 16.0)	6.32 (d, 15.7)	6.43 (d, 16.0)	6.33 (d, 15.5)
3	7.35 (d, 16.0)	7.36 (d, 16.0)	7.32 (d, 15.7)	7.50 (d, 16.0)	7.32 (d, 15.5)
5	6.55 (d, 4.5)	6.55 (d, 3.5)	6.50 (d, 3.3)	6.58 (d, 3.4)	6.53 (d, 2.5)
6	6.45 (dd, 2.4,4.5)	6.43 (dd, 3.5,1.7)	6.41 (dd, 1.7,1.5)	6.46 (dd, 1.8,1.8)	6.43 (dd, 1.4,1.5)
7	7.45 (d, 3.4)	7.44 (d, 1.0)	7.4 (d, 1.0)	7.47 (d, 2.0)	7.44 (d, 1.0)
8	0.58 ^{2}J[58]	1.36 ^{2}J[56]	1.57–1.63	– –	1.10–2.00
9		1.19 ^{3}J[87.5]	(m)	7.8 (dd, 2,2.1)	(m)
10			1.23–1.54 (m)	7.48 (ddd,1,1.8,3.1)	
11			0.88 (t, 7.0)	7.78 (ddd,2,3,1)	

a = chemical shifts in ppm ^{3}J (H–H) in Hz, $^{n}J[^{119}Sn–H]$ in Hz, d = doublet, dd = doublet of doublet, ddd = double doublet of doublets, t = triplet, m = multiplet.

Table 2
^{13}C NMR data of triorganotin carboxylates [a]

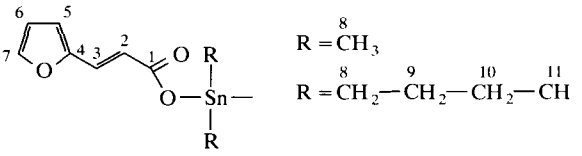


Carbon	I R = methyl	II R = ethyl	III R = n-butyl	IV R = phenyl	V R = cyclohexyl
1	172.0	175.1	172.0	172.0	171.8
2	113.7	113.47	113.5	112.1	113.3
3	130.7	130.5	130.5	132.1	130.2
4	151.2	151.3	151.4	151.1	151.5
5	117.6	117.6	117.9	116.0	118.2
6	112.0	111.9	112.0	112.2	112.0
7	144.0	144.2	144.2	144.7	144.1
8	2.3	7.9	16.5	137.2	33.7
	^{1}J[400.0]	^{1}J[369.0]	^{1}J[358.0]	^{1}J[648.0]	^{1}J[340.6]
9		9.93	27.8	136.9	31.18
		^{2}J[25.4]	^{2}J[20.7]	^{2}J[48.8]	^{2}J[13.8]
10			27.0	128.9	29.4
			^{3}J[64.9]	^{3}J[62.2]	^{3}J[64]
11			13.6	130.1	26.9
				^{4}J[13.3]	

a = chemical shifts in ppm, $^{n}J[^{119}Sn-^{13}C]$ in Hz.

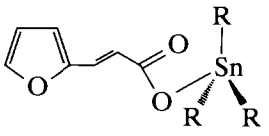
On the basis of Mössbauer and ^{119}Sn NMR parameters compound IV is suggested to possess a trigonal bipyramidal geometry in the solid state and a tetrahedral geometry in noncoordinating solvents. This leads to a slight contradiction with Sharma [11], who found a ^{119}Sn chemical shift at −116 ppm and a quadrupole splitting value of 2.44 mm s^{-1} for $[(C_6H_5)_3Sn(O_2CCH{=}CHC_6H_4OCH_3\text{-}p)]$. In the present case a ^{119}Sn chemical shift at −114 ppm is consistent with the above mentioned report but a large quadrupole splitting value (3.39 mm s^{-1}) strongly recommends a penta-coordinate environment around tin in the solid phase (structure I). Multinuclear NMR data for these compounds in $CDCl_3$ thus reflect a breakdown of a polymer into its monomeric components which is a common behavior of triorganotin carboxylates. Hence compounds I–IV adopt the structure (I). Mössbauer and multinuclear NMR data confirm that compound V remains in a tetrahedral geometry as a solid as well as in solution (II).

Table 4
^{1}H NMR spectra of diorganotin carboxylates "a" and "b" [a]



Proton	VIa R = methyl	VIb R = methyl	VIIa R = n-butyl	VIIb R = n-butyl
2	6.35	6.24	6.40	6.28
	(d, 15.6)	(d, 16.0)	(d, 15.8)	(d, 15.5)
3	7.52	7.33	7.55	7.32
	(d, 15.6)	(d, 16.0)	(d, 15.8)	(d, 15.5)
5	6.65	6.59	6.64	6.58
	(d, 3.4)	(d, 3.4)	(d, 3.4)	(d, 3.5)
6	6.45	6.44	6.45	6.45
	(dd, 1.8, 1.8)	(dd, 3.4, 1.7)	(dd, 2, 3.4)	(dd, 3.4, 1.7)
7	7.50	7.46	7.50	7.45
	(d, 1.7)	(d, 1.7)	(d, 1.0)	(d, 1.5)
8	1.12	0.898		
	^{2}J[78.0]	^{2}J[89.0]		
		0.85	1.75–1.74	1.60–1.70
		^{2}J[86.0]	(m)	(m)
9				
10			1.42–1.40	1.56, 1.37
			(m)	(tq, 6,9), (tq, 7,7)
11			0.92	0.87, 0.85
			(t, 7.0)	(t, 7.0), (t, 7.0)

a = chemical shifts in ppm, ^{3}J(H–H) in Hz, $^{n}J[^{119}Sn-H]$ in Hz
d = double, dd = doublet of doublet, t = triplet, m = multiplet.

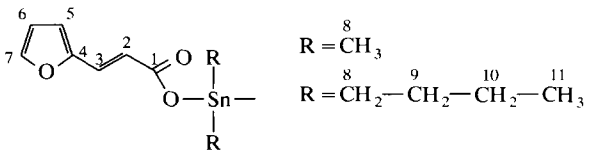


(II)
R = Cyhex

Table 3
Mössbauer and ^{119}Sn NMR data of tri- and diorganotin carboxylates

Mössbauer parameters						
Compound	IS (mm s^{-1})	QS (mm s^{-1})	Γ_1 (mm s^{-1})	Γ_2 (mm s^{-1})	ρ	^{119}Sn NMR δ (ppm)
I	1.2	3.48	0.88	0.89	2.9	133.0
II	–	–	–	–	–	106.0
III	1.38	3.5	0.92	0.91	2.54	104.0
IV	1.26	3.39	1.01	1.00	2.69	−114.0
V	1.46	2.80	0.96	0.98	1.92	12.0
VIa	1.16	3.35	0.88	1.00	2.89	−123.0
VIb	–	–	–	–	–	−175.0, −189.0
VIIa	1.33	3.21	0.92	0.94	2.42	−152.0
VIIb	–	–	–	–	–	−205.0, −214.0

Table 5
^{13}C NMR data of diorganotin caboxylates "a" and "b" [a]

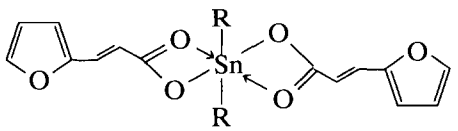


Carbon	VIa R = methyl	VIb R = methyl	VIIa R = n-butyl	VIIb R = n-butyl
1	175.1	173.0	175.7	172.4
2	115.0	114.0	114.8	113.7
3	132.9	130.6	132.2	130.2
4	150.7	151.2	150.6	151.4
5	115.4	119.1	115.1	119.3
6	111.9	112.2	112.0	112.1
7	144.1	144.4	144.7	144.2
8	4.52 ^1J[655.0]	9.43, 6.34 ^1J[810.0], ^1J[758.0]	25.00 ^1J[592.0]	28.96, 27.34 ^1J[724.5], ^1J[693.0]
9			26.4 ^2J[35.0]	27.6, 27.3 ^2J[35.4], ^2J[32.5]
10			26.0 ^3J[99.5]	26.9, 26.8 ^3J[133.4], ^3J[120.0]
11			13.3	13.6

a = chemical shifts in ppm, $^n J[^{119}Sn-^{13}C]$ in Hz.

3.2. Spectral studies of compounds VIa and VIIa

The NMR spectra for compounds of the type "a", (Table 3–5) show well resolved signals for the methyl groups of the methyltin and butyltin substituents thus indicating one tin site. Di-organotin carboxylates having a five-coordinate tin centre show tin chemical shifts in the range of −110 to −161 ppm [12]. The ^{119}Sn NMR spectra of compounds VIa and VIIa show sharp signals at −123 and −152 ppm respectively which are assignable to a five-coordinate tin atom. At the same time from quadrupole splitting values (Table 3), using the Sham and Bancraft model [13], C–Sn–C angles for compounds VIa and VIIa are found to be 138° and 134° respectively; they are very close to the calculated equivalent angles 140° in $Me_3Sn(O_2CCH_3)_2$ [14] and 137° in $Bu_2Sn(O_2CCH{=}CHC_6H_4OCH_3\text{-}p)_2$ [11], and $Bu_2Sn(OCOC_6H_5)_2$ [12]. Recently Sandhu [16] reported that di-organotin carboxylates exhibiting ρ value greater than 2.1 possess a *trans* octahedral geometry around the tin atom. Hence ρ values of 2.88 and 2.41 support a similar structure (III) as that described by Sandhu [16], Tiekink [17], and Gielen et al. [8].

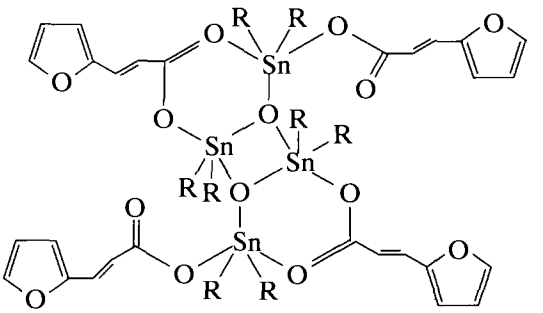


(III)

R = Me, n-Bu

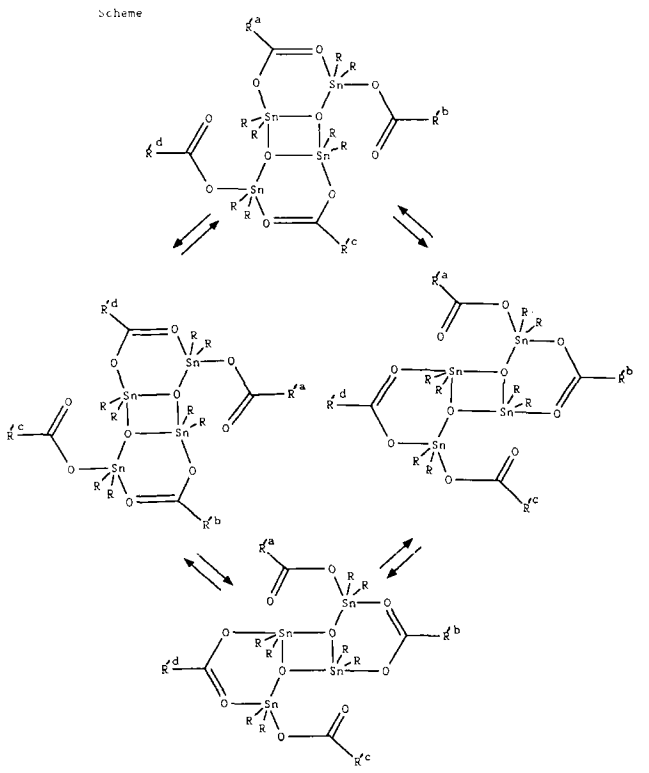
3.3. Spectral studies of compounds VIb and VIIb

In contrast to the type "a" the ^1H NMR spectra of compounds "b", (Table 4) show two unresolved sets of signals: one for the alkyl groups linked to the endocyclic tin and the other one for the exocyclic tin respectively. Similarly the ^{13}C NMR spectra (Table 5) also show "pairs" of signals deriving from two different environments around the alkyl groups. The ^{119}Sn NMR spectra show two signals at −175 and −189 ppm and −204 and −214 ppm for compounds VIb and VIIb due to two non-equivalent penta-coordinate tin sites [8,11]. These compounds adopt the common dicarboxylato tetraorganodistannoxane structural mode [18]. Each tin atom from the two pairs of exo- and endocyclic tins is linked by a bidentate, bridging carboxylate ligand while the remaining carboxylate groups behave as monodentate ligands with exocyclic tin atoms as shown in structure (IV).



(IV)

R = Me, n-Bu



Scheme 1.

Table 6
Antibacterial activity [a]

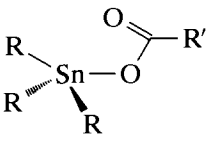
Bacterium	Organotin carboxylates				
Gram positive	I	III	IV	V	VIa
B. anthracis	+ +	+ + + +	+ + +	+ +	+
S. aureus	+ +	+ + + +	+	+	+ +
S. facealis	+ +	+ + + +	+ +	+ +	+
C. pseudodiphtherium	+ +	+ + +	+	+	+
C. diphtheriae	+ +	+ + + +	+	+	+
Gram negative					
E. coli	+	+	+	+	+
P. pseudomaliae	+	+	+	+	+
A. sobriae	+ + +	+	+ +	+	+
S. boydii	+	+	+	+	+
V. cholera	+ +	+	+	+	+ +

a = 200 mg ml^{-1}, b = 250 mg ml^{-1}
+ + + + = highly active, + + + = moderately active, + + = slightly active, + = not active

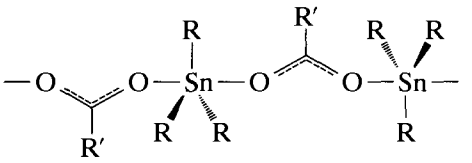
The carboxylates linked with exo- and endocyclic tin atoms should produce different R′ signals; however, in the NMR spectra there is only one set of signals obviously due to a very similar environment. To date there is no report dealing with the non-equality of carboxylate groups in such compounds. There may be a fast exchange in the coordination behaviour of carboxylate groups attached to endo- and exocyclic tin as reflected by different alkyl signals in NMR spectra. A possible mechanism to explain this fluxional behaviour is given in Scheme 1.

3.4. Biological testing

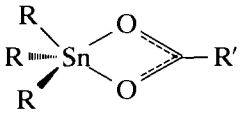
Biological activity tests for some of these compounds were carried out against various bacteria and fungi by the "agar well diffusion" method [19]. The results are given in Tables 6 and 7 respectively. The screening tests show that tributyltin carboxylate is the most potent candidate against gram positive bacteria, with decreasing activity for derivatives in which the R groups have more or fewer carbon atoms. However, enhanced antifungal activity is associated with trimethyl-, tributyl- and triphenyltin carboxylates. It is well established that triorganotin compounds (R_3SnL) are significantly more biocidally active than other classes with either more or less hydrocarbon groups bonded to tin [4]. It has been noticed that fairly high concentrations of R_2SnL_2 are required to inhibit mycobacterium phlei than corresponding R_3SnL species. Moreover any biological activity associated with R_4Sn compounds arises from their rapid in vivo or in vitro dealkylation to triorganotin species whereas monoorganotin compounds have no noticeable activity. Within the R_3SnL unit, the nature of the R group determines the species specificity of the biocide. Apparently the function of L is to support the transport of the active organotin moiety to the site of the action, where it is released by hydrolysis. Hence anionic ligands L play a secondary role in determining the degree of activity of R_3SnL compounds. Among organotin compounds, carboxylate derivatives are used as anticancer and antitumour agents in vivo or in vitro as well as fungicides or bactericides [20–26]. Not all the triorganotin carboxylates are essentially active biocides. Biocidal activity of triorganotin carboxylates is related to their structure by the fact that the species generating a tetrahedral structure in solution are more active [4]. Triorganotin carboxylates adopt three structural types in the solid phase.



(V)



(VI)



(VII)

A monomeric structure (V), can be 4-coordinate, whereas a polymeric structure (VI) generally contains 5-coordinate tin atoms. Five coordinate compounds which adopt structural type (VII) inevitably occur when the carboxylate group acts as a chelating ligand [15]. Both the monomeric 4-coordinate and the polymeric 5-coordinate carboxylates are more active than the 5-coordinate chelated monomer as the former generated tetrahedral species in solution where the polymeric arrangements are rapidly converted into

Table 7
Antifungal activity [b]

Fungus	Organotin carboxylates				
	I	III	IV	V	Via
Aspergillus niger	+ + +	+ + + +	+ + +	+ +	+
Ascomycetes	+ + +	+ + +	+ + +	+ +	+ + +
Dutarium rotatum	+ + +	+ + + +	+ + +	+ +	+ + +
Fusarium solani	+ + +	+ + +	+ +	+ +	+ + +
Candida albicans	+ +	+ + + +	+ + +	+ +	+
Candida tropicalis	+ +	+ + + +	+ + +	+ +	+ +
Alterneria solani	+ + +	+ + +	+ + +	+ + +	+ +
Penicillium notatum	+	+ +	+ +	+ +	+

See footnote to Table 6.

monomeric forms by intermolecular fragmentation. On the other hand, the chelated monomers retain their 5-coordinate structure even in solution which is evident from their NMR spectra in non-coordinating solvents [4,27]. It has been reported that within a series the tributyltin derivative is highly active against gram positive bacteria while tributyl and triphenyl derivatives are active against fungi [4,22,28–31]. Our screening tests are quite consistent with earlier reports except that the trimethyltin derivative is also found to be an active fungicide. This can be best explained on the basis of a triorganotin-ligand relationship which dictates that the function of an anionic group or groups is to aid the transport of the active organotin moiety to the site of the action. It seems almost certain that the anionic ligand is displaced from tin when the organometallic unit is bonded to the active site of a biological system [4]. Alternatively the anionic ligand may remain bonded to tin until it reaches its receptor site, where it is displaced by a suitable donor atom. Under such circumstances, an anionic ligand may well influence the ease with which an R_3SnL molecule is transported [4]. Thus the increased fungicidal activity of trimethyltin derivatives is probably due to the furanylacrylate group which could act as a carrier in this series.

Acknowledgment

M. Danish is grateful to the Deutscher Akademischer Austauschdienst (DAAD) for the award of a fellowship and to Gabriele von Massow for her assistance in obtaining NMR spectra. Sincere thanks are due to Prof. Dr. M. Gielen for his valuable advice and Dr. K.C. Molloy for recording the Mössbauer spectra.

References

[1] B. Jousseaume, V. Guillou, N. Noiret, M. Pereyre and J.M. France, *J. Organomet. Chem., 450* (1993) 97.
[2] Xie Qing-Lan, Y. Zhi-Qiang, Z. Zu-Xin and Z. Dian-Kun, *Appl. Organomet. Chem., 6* (1992) 193.
[3] S. Ali, M. Mazhar, A. Kalsoom and A. Qadeer, *Pak. J. Sci. Ind. Res., 34* (1991) 114.
[4] K.C. Molloy, Bioorganotin Compounds. In F.R. Hartley, (ed.) *The Chemistry of Metal–Carbon Bond*, Vol. 5, Wiley, New York, 1989.
[5] T. Horiguchi, H. Shiraishi, M. Shimizu, S. Yamazaki and M. Morita, *Main Group Met. Chem., 17* (1994) 81.
[6] A. Kumari, I. Singh and J.P. Tandon, *Main Group Met. Chem., 17* (1994) 347.
[7] S. Ali, M. Danish, A. Badshah, M. Mazhar, Atta-ur-Rehman and N.U. Islam, *J. Chem. Soc., Pak., 15* (1993) 154.
[8] M. Gielen, A. El Khloufi, M. Biesemans, F. Kayser and R. Willem, *Appl. Organomet. Chem., 7* (1993) 201.
[9] M. Nadvornik, J. Holecek, K. Handlir, and A. Lycka, *J. Organomet. Chem., 275* (1984) 43.
[10] P.J. Smith, R.O. Day, V. Chandrasekhar, J.M. Holmes and R.R. Holmes, *Inorg. Chem., 25* (1986) 2495.
[11] H.K. Sharma, S. Lata, K.K. Sharma, K.C. Molloy and P.C. Waterfield, *J. Organomet. Chem., 353* (1988) 9.
[12] J. Holecek, M. Nadvornik, K. Handlir and A. Lycka, *J. Organomet. Chem., 315* (1986) 299.
[13] T.K. Sham and G.M. Bancroft, *Inorg. Chem., 14* (1975) 2281.
[14] T.P. Lockhart, W.F. Manders and E.M. Holt, *J. Amer. Chem. Soc., 108* (1986) 6611.
[15] K.C. Molloy, K. Quill and I.W. Nowell, *J. Chem. Soc., Dalton Trans.*, (1987) 101.
[16] G.K. Sandhu and G. Kaur, *Main Group Met. Chem., 13* (1990) 149.
[17] E.R.T. Tiekink, *J. Organomet. Chem., 408* (1991) 323.
[18] C. Vatsa, V.K. Jain, T. Kesavadas and E.R.T. Tiekink, *J. Organomet. Chem., 408* (1991) 157.
[19] S.U. Kazmi, S.N. Ali, S.A. Jamal and Atta-ur-Rehman, *J. Phar. Sci., 4* (1991) 113.
[20] N.F. Cardarelli, *Tin as Vital Nutrient*, (ed.) 1st., CRC Press Inc. Boca Raton, Florida, 1986.
[21] I. Omae, *Organotin Chemistry. J. Organomet. Chem. Lib., 21* Elsevier, New York, 1989.
[22] A.G. Davis and P.J. Smith, in G. Wilkinson (ed.), *Comprehensive Organometallic Chemistry. The Synthetis Reactions and Structures of Organometallic Compounds.*, Vol. 2, Pergamon., New York, 1982.
[23] M.T. Musmeci, G. Madonia, M.T.L. Guidice, A. Silvestri, G. Ruisi and R. Barbieri, *Appl. Organomet. Chem., 6* (1992) 127.
[24] M. Baulam, M. Biesemans, J.M. Piret, R. Willem and M. Gielen, *Appl. Organomet. Chem., 6* (1992) 197.
[25] M. Gielen, *Main Group Met. Chem., 17* (1994) 1.
[26] J.M. Hook, B.M. Linahan, R.L. Taylor, E.R.T. Tiekink, L. van Gorkom and L.K. Webster, *Main Group Met. Chem., 17* (1994) 293.
[27] K.C. Molloy, K. Quill, S.J. Blunden and R. Hill, *Polyhedron, 5* (1986) 959.
[28] S.W. Ng, A.J. Kuthubutheen, V.G.K. Das, A. Lindens and E.R.T. Tiekink, *Appl. Organomet. Chem., 8* (1994) 37.
[29] R. Willem, M. Biesemans, M. Baulam, A. Delmotte, A. El Khloufi and M. Gielen, *Appl. Organomet. Chem., 7* (1993) 11.
[30] K.C. Molloy, T.G. Purcell, E. Hahn, H. Schumann and J.J. Zuckerman, *Organometallics, 5* (1986) 85.
[31] A.J. Crowe, *Met. Complexes Cancer Chemother.*, in B.K. Keppler (ed), VCH, Weinheim, Germany, 369.