X-Ray and NMR study of tetra- and penta-coordinated stanoxanes derived from *trans*-cinnamic acid

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Contribution to Professor Rosalinda Contreras on the occasion of her 60th anniversary

Abstract

We report a new stanoxano polymer structure **1**, derived from *trans*-cinnamic acid and triphenyltin chloride. X-ray structure shows a carboxylated bridge between two tin groups in a linear rearrangement, the pack in the unit cell is conformed by non-classical interactions (D-H···A), because the presence of aromatic rings were observed C-H···π interacting in a supramolecular structure. In solution the compound **1** was compared with tributhyltin-*trans*-cinnamete **2**, the NMR data shown penta- and tetra-coordinated compounds respectively, both compounds were dissolved in DMSO-d_6 and the tin geometry goes from penta- to hexa-coordinated for **1** and from tretracoordinated to pentacoordinated for **2**.

Keywords: *trans*-Cinnamic acid, X-ray polymer structure, tin compounds

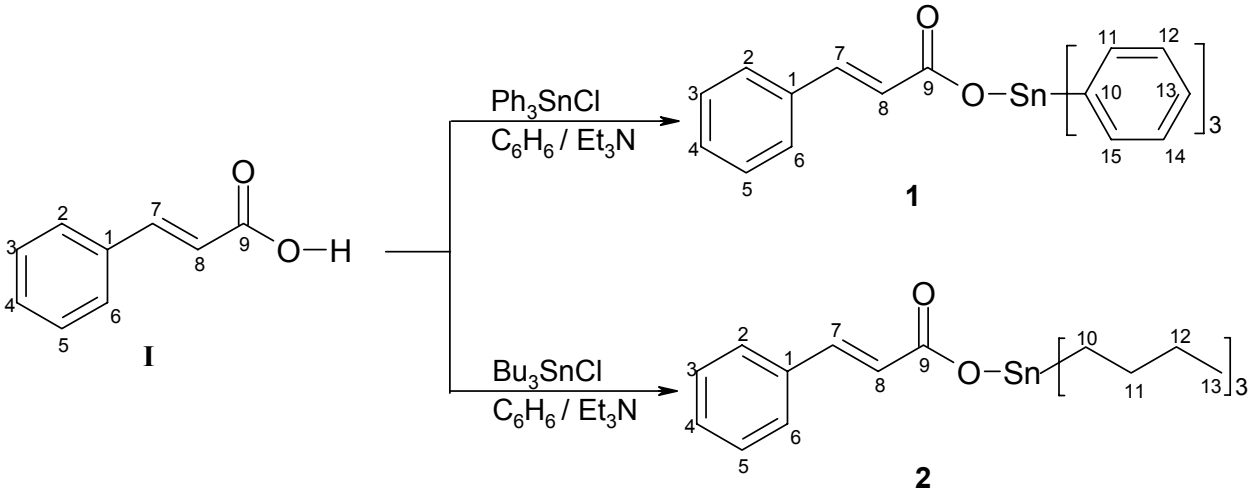
Introduction

trans-Cinnamic acid is found as structural unit in anti-oxidant compounds, in some drugs and balsams.[1] It is a cinnamaldehyde derivative that comes from cinnamon, in the last ten years the cinnamic acid and its derivatives were found to be anti-bacterials, anti-fungals, and are important in the synthesis of cumarinic derivatives.[2] The interest in organotin compounds is because their biological activity,[3] so the understanding of the structural base needs special attention of the

electronic effects and coordination number. It is well known the potential activity of tin compounds as anti-cancer and anti-tumor agents[4] and the relationship between the organic fragment and organometallic tin plays an important role in some biological aspects, for example as nematicidal and insecticidal.[5] The spectroscopic study of tetra- and pentacoordinated stanoxanes derived from *trans*-cinnamic acid; base their importance on their organic structure, because they are models of NMR and X-ray diffraction and biological assays.

Results and Discussions

Compounds **1** and **2** were obtained following the procedure shown in the Scheme 1, this is a variation of the Gielen[6] method (see experimental section), and we use benzene as solvent because we need to avoid solvent coordination. Both compounds which are white solids, were obtained in good yields and they are stable to air and moisture. Then the compounds **1** and **2** were dissolved in DMSO-d_6 to get compounds **3** and **4** also were analysed spectroscopically.

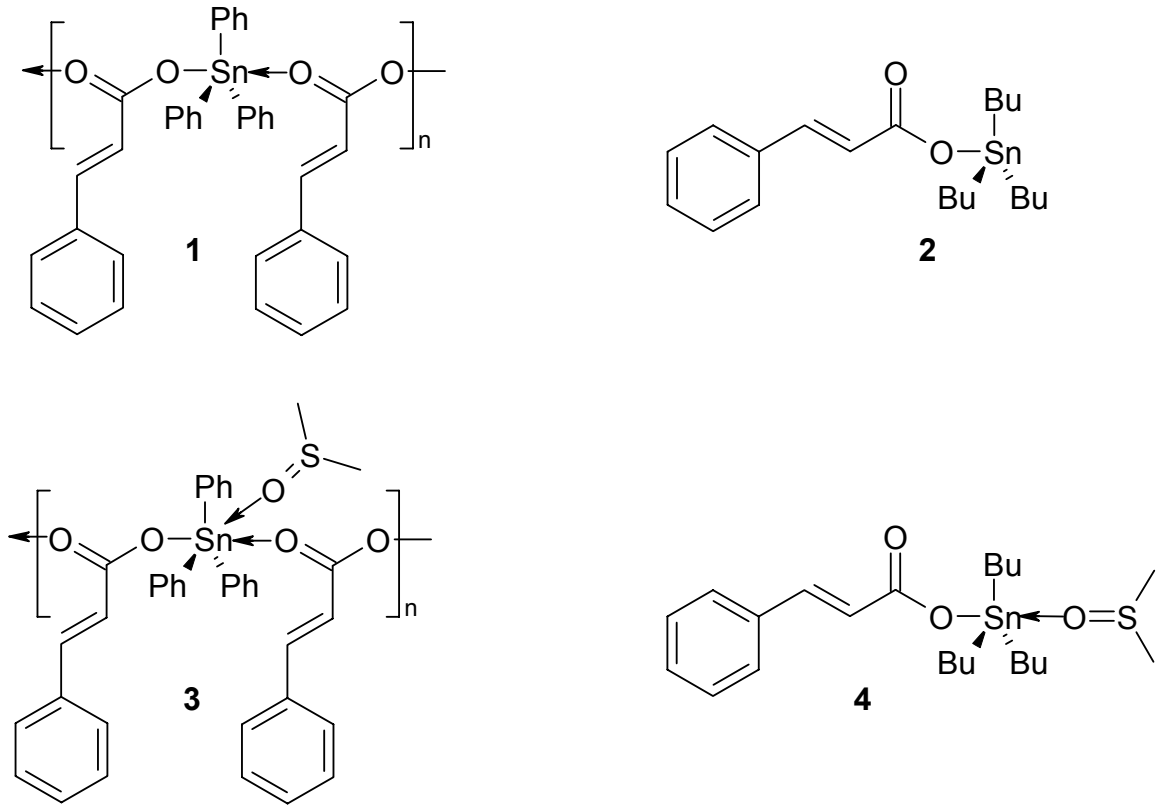


Scheme 1. Syntheses of complexes **1** and **2**, and numerbering system used to analyse the spectrum.

NMR Analyses

All compounds have good spectra; and were corroborated with COSY and HETCOR experiments, tables 1 and 2, chemical shifts are characteristics of the respective coordination number in solution.[7] The ^{119}Sn values in -112.0 for compound **1** with a $\Delta\delta$ = - 64 ppm with respect to the starting material Ph_3SnCl[8] and in +110.9 for compound **2** with a $\Delta\delta$ = - 30 ppm with respect to the starting material Ph_3SnCl,[9] are indicative of penta- and tetra-coordinated compounds, respectively. Danutsh[10] *et al.* reported the ^{119}Sn chemical shift of Me_3Sn-*m*-Me-*trans*-cinnamate with ^{119}Sn = + 129 ppm, that is close in value to compound **2**. A related

carboxylic triphenyltin compound was reported by Holeček[11] *et al.* $Ph_3SnOC(O)Ph$ with ^{119}Sn = -110 ppm and tributyltin compound by Davies[8] *et al.* of $Bu_3SnOC(O)C_6H_4OCOMe$-2 with ^{119}Sn = + 115 ppm, both compounds corroborate the assignment of compounds **1** and **2**. The acidity of **1** and **2** were evident when we added DMSO-d_6 to obtain compounds **3** and **4**, the chemical shifts change their value at lower frequency, -260.2 ($\Delta\delta$(**1-3**) = 148 ppm) for **3** and -20.0 for **4** ($\Delta\delta$(**2-4**) = 131 ppm), it changes the geometry around the tin atom, so tin goes from pentacoordinated (compound **1**) $\rightarrow$ hexacoordinated (compound **3)** and from tetracoordinated (compound **2**) $\rightarrow$ pentacoordinated (compound **4)**. (Scheme 2) When we analyzed the ^{119}Sn values of Ph_3SnCl and Ph_3SnCl(DMSO-d_6), the $\Delta\delta$ = 181 ppm, we found the same behaviour, but different magnitude, that was found in compounds **1-4**.[11,12]



Scheme 2. Structure proposes of tetra-, penta- and hexa-coordinated compounds.

Because the *trans*-cinnamic acid and phenyl nuclei are not modified, the ^{13}C chemical shifts have not meaningful changes. The C7 position goes at lower frequency from starting material **I** to **1** ($\Delta\delta$=2.4), **2** ($\Delta\delta$=3.4), **3** ($\Delta\delta$=5.5) and **4** ($\Delta\delta$=6.0), the same behaviour was observed for C9 position but the $\Delta\delta$ values are smaller (0.6, 0.6, 2.4, 2.3, respectively) than C7. The C8 signal is shifted to higher frequency from that in the starting material **I** to **1** ($\Delta\delta$=2.3), **2** ($\Delta\delta$=3), **3** ($\Delta\delta$=56.4) and **4** ($\Delta\delta$=6.6). All those changes are indicative in the compounds **1** and **2** of the presence of tin fragment; meanwhile the biggest changes for compounds **3** and **4** are indicative of

the high coordination number in the tin atom.

Table 1. Chemical shits of ^{119}Sn and ^{13}C, in $CDCl_3$, in brackets are coupling constants $^{n}J(^{13}C\text{-}^{117/119}Sn)$

Comp.	**I**[a]	**1**[a]	**2**[a]	**3**[b]	**4**[b]
^{119}Sn	--	-112.0	110.9	-260.2	-20.0
C1	134.1	135.0	137.2	135.5	135.7
C2	128.4	129.9	128	129.9	128.1
C3	129.0	128.4	128.8	128.2	129.3
C4	130.7	128.8	129.8	128.2	129.7
C5	129.0	128.4	128.8	128.2	129.3
C6	128.4	129.9	128.0	129.9	128.1
C7	147.1	144.7	143.7	141.6	141.1
C8	117.4	119.7	120.4	123.8	124.0
C9	172.8	173.4	172.2	170.4	170.5
C10	--	138.9 (NO)	16.9 (~351.9)	144.0 (829)	19.2 (475,454)
C11	--	136.9 (NO)	28.16 (19.8)	136.9 (453)	28.3 (26.9)
C12	--	128.9 (63.3)	27.0 (67.2)	128.8 (69.2)	27.0 (73.8)
C13	--	130.1	13.99	129.3	14.2
C14	--	128.9	--	128.8	--
C15	--	136.9	--	136.9	--

[a] $CDCl_3$ [b] DMSO-d_6, NO not observed

The coupling constants $^{n}J(^{13}C\text{-}^{117/119}Sn)$ that are in brackets in Table 1 correspond to assigned atom and all of them are indicative of the tin geometry, according to the literature.[13]

The ^{1}H NMR for compounds **1-4** are summarized in Table 2, the H7 signals for different compounds are shifted to lower frequency than the starting material **I**, while H8 almost does not have changes. The rest of the protons have not important changes. The *trans*- coupling constant $^{3}J(^{1}H7\text{-}^{1}H8)$ was confirmed in all compounds around 16 Hz for phenyltin- derivatives and 15 Hz for butyltin- derivatives, all of them are close to starting material **I**.

Table 2. Chemical shifts (δ, ppm) of ^{1}H for compounds **1**-**4**, The coupling constant $^{3}J(^{1}H\text{-}^{1}H)_{trans}$ is showing between parenthesis (Hz)

Comp.	**I**[a]	**1**[a]	**2**[a]	**3**[b]	**4**[b]
H2	7.56	7.92	7.43	7.31	7.55
H3	7.40	7.55	7.27	7.56	7.33
H4	7.42	7.54	7.27	7.56	7.33
H5	7.40	7.55	7.27	7.56	7.33
H6	7.56	7.92	7.43	7.31	7.55
H7	7.81(16.1)	7.81(15.6)	7.55(16.0)	7.37(16.1)	7.37(15.1)
H8	6.46(16.1)	6.65(15.6)	6.44(16.0)	6.46(16.1)	6.42 (15.1)
H10	--	--	1.25	--	1.12
H11	--	7.44	1.57	7.88	1.59
H12	--	7.41	1.25	7.45	1.30
H13	--	7.40	0.84	7.43	0.85
H14	--	7.41	--	7.45	--
H15	--	7.44	--	7.88	--

[a] $CDCl_3$ [b] DMSO-d_6

X-Ray analyses

Compound **1** crystallizes in the monoclinic space group $P2_1/n$ from chloroform, the crystal data, selected bonds and angles are given in Tables 3, 4. Figure 1 shows the ORTEP diagram, three phenyl groups in a equatorial position and *trans*-cinnamic acid is occupying axial position, in the opposite site, from this, an empty space shows coordination to the tin atom by other electron donor group.

In the lattice, (Figure 2) two triphenyltin groups are bridged by carboxylic group of *trans*-cinnamic acid, with two different distances d(O1-Sn1) = 2.275(2) Å and d(O2-Sn1) = 2.230(2) Å with the angle (O1-Sn1-O2) = 172.30(7)°, making a polymeric rearrangement where tin atom is in trigonal bipyramidal (BPT) geometry.

The net shows, Figures 2 and 3, that crystal packing is structured by non-classical hydrogen bonds (C-H···A) related to (C-H···π) interactions as soft acid and soft base[14a]. In Table 5 are listed the hydrogen contacts geometries. In the Figure 2, C17-H17 is acting as a bifurcate donor because it is interacting with O1*, as a true hydrogen bond[14b], and C9*, against C27-H17 is acting as a normal donor group to C15* and C15*-H15* is a normal donor of C17.[14c,d] The individual interactions are not important; but they are essential to the supramolecular structure, so they manage the growing of the crystal packing, Figure 4.

Table 3. The crystal data of compound **1**

Formula	C27 H22 O2 Sn1
Formula Weight	497.16
Crystal System	Monoclinic
Space group	P21/n, (No. 14)
Å [Å]	12.8222(2)
b [Å]	11.4892(2)
c [Å]	16.0870(3)
α [°]	90,
β [°]	102.3586(7),
γ [°]	90
V [Å^3]	2314.97(7)
Z	4
D(calc) [g/cm**3]	1.426
Mu(MoKa) [/mm]	1.123
F(000)	1000
Crystal Size [mm]	0.08 x 0.14 x 0.20
Data Collection	
Temperature (K)	293
Radiation [Angstrom]	MoKa, 0.71070
Theta Min-Max [Deg]	3.7, 27.5
Dataset	-15: 15; -12: 14; -20: 20
Tot., Uniq. Data, R(int)	9337, 5170, 0.021
Observed data [I > 3.0 sigma(I)]	3457
Refinement	
Nref, Npar	3457, 338
R, wR2, S	0.0257, 0.1719, 1.10
w = 0.276 0.696E-01 0.466E-01 -0.871E-02	
Max. and Av. Shift/Error	0.00, 0.00
Min. and Max. Resd. Dens. [e/Ang^3]	-0.35, 0.62

Table 4. Selected bond distances and angles of compound **1**

Atoms	Distance (Å)	Atoms	Angle (°)	Atoms	Angle (°)
C1 C2	1.396(6)	C2 C1 C6	117.9(4)	C10 Sn1 C16	119.88(12)
C1 C6	1.379(6)	C2 C1 C7	118.7(4)	O1 Sn1 C22	92.23(10)
C1 C7	1.466(5)	C6 C1 C7	123.4(4)	O2 Sn1 C22	92.03(10)
C2 C3	1.382(8)	C1 C2 C3	120.5(6)	C10 Sn1 C22	117.67(12)
C3 C4	1.360(10)	C2 C3 C4	120.7(6)	C16 Sn1 C22	122.45(11)
C4 C5	1.365(10)	C3 C4 C5	119.5(5)	C24 C25 C26	119.8(4)
C5 C6	1.383(7)	C4 C5 C6	120.8(7)	C25 C26 C27	120.5(4)
C7 C8	1.306(5)	C5 C6 C1	120.7(6)	C22 C27 C26	120.8(4)
C8 C9	1.476(4)	C1 C7 C8	128.4(4)	C9 O1 Sn1	138.00(18)
C9 O1	1.257(3)	C7 C8 C9	123.3(3)	Sn1 O2 C9	140.1(2)
C9 O2	1.263(3)	C8 C9 O1	119.9(3)	O1 Sn1 O2	172.30(7)
C10 C11	1.364(6)	C8 C9 O2	117.0(3)	O1 Sn1 C10	86.79(10)
C10 C15	1.386(5)	O1 C9 O2	123.0(3)	O2 Sn1 C10	85.55(10)
C10 Sn1	2.127(3)	C11 C10 C15	118.2(4)	O1 Sn1 C16	90.82(10)
C11 C12	1.402(7)	C11 C10 Sn1	120.4(3)	O2 Sn1 C16	92.31(11)
C12 C13	1.380(11)	C15 C10 Sn1	121.4(3)		
C13 C14	1.335(11)	C10 C11 C12	120.8(6)		
C14 C15	1.388(6)	C11 C12 C13	119.2(6)		
C16 C17	1.374(5)	C12 C13 C14	120.8(5)		
C16 C21	1.380(5)	C13 C14 C15	120.0(6)		
C16 Sn1	2.124(3)	C14 C15 C10	121.1(5)		
C17 C18	1.386(6)	C17 C16 C21	117.9(3)		
C18 C19	1.353(7)	C17 C16 Sn1	120.1(2)		
C19 C20	1.354(7)	C21 C16 Sn1	122.0(2)		
C20 C21	1.397(6)	C16 C17 C18	120.9(4)		
C22 C23	1.376(5)	C17 C18 C19	120.6(4)		
C22 C27	1.387(5)	C18 C19 C20	119.6(4)		
C22 Sn1	2.121(3)	C19 C20 C21	120.5(4)		
C23 C24	1.387(6)	C20 C21 C16	120.3(4)		
C24 C25	1.361(8)	C23 C22 C27	117.8(3)		
C25 C26	1.356(8)	C23 C22 Sn1	121.2(3)		
C26 C27	1.383(6)	C27 C22 Sn1	121.0(2)		
O1 Sn1	2.275(2)	C22 C23 C24	120.8(4)		
O2 Sn1	2.230(2)	C23 C24 C25	120.3(5)		

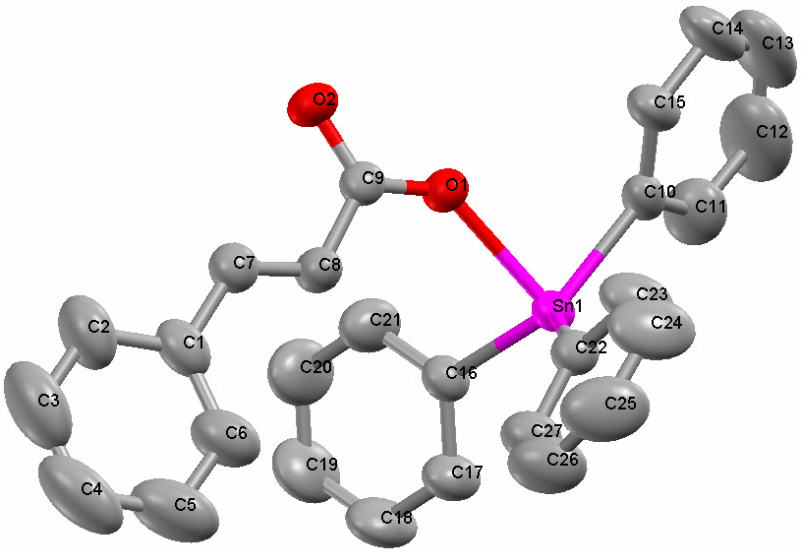


Figure 1. ORTEP diagram of compound **1**, showing the atom-numbering scheme and displacements ellipsoids at the 50 % probability, hydrogen atoms are omitted for clarity.

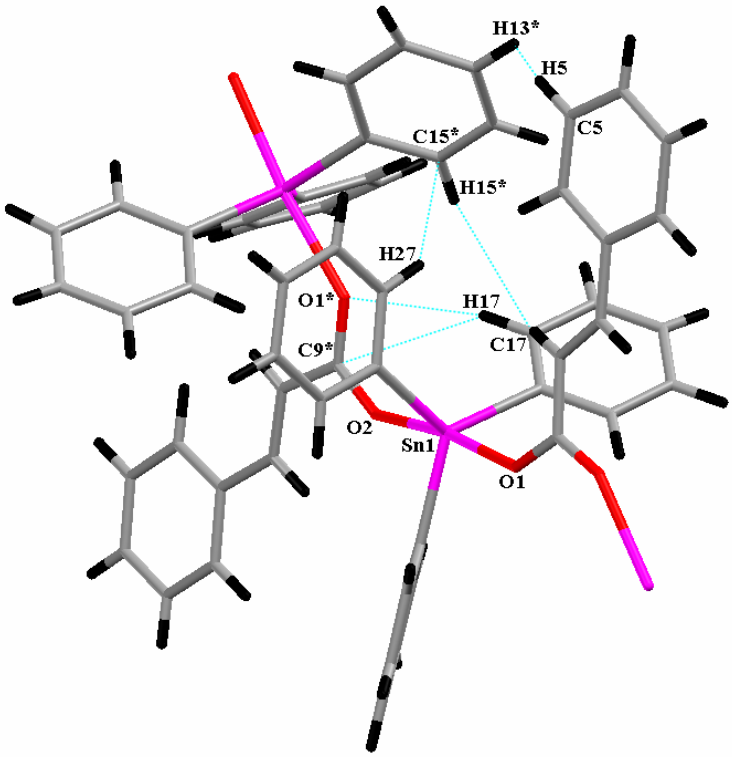


Figure 2. Non-classical intramolecular interactions. The marked atoms are at the symmetry positions: * 1.5-x,1/2+y,1/2-z.

Figure 3 shows two C-H···π intermolecular interactions, that connect two different polymer lines, those interactions are considered as strong hydrogen bonds[15], because the short distances and angles (C26-H26···C17) = 146.17 and (C26-H26···C17) = 162.49; in both cases C-H···π acts as a C-H(guest)/π(host) interaction[16]. All such interactions are important because they contribute that the molecule **1** stays in a supramolecular polymeric structure.

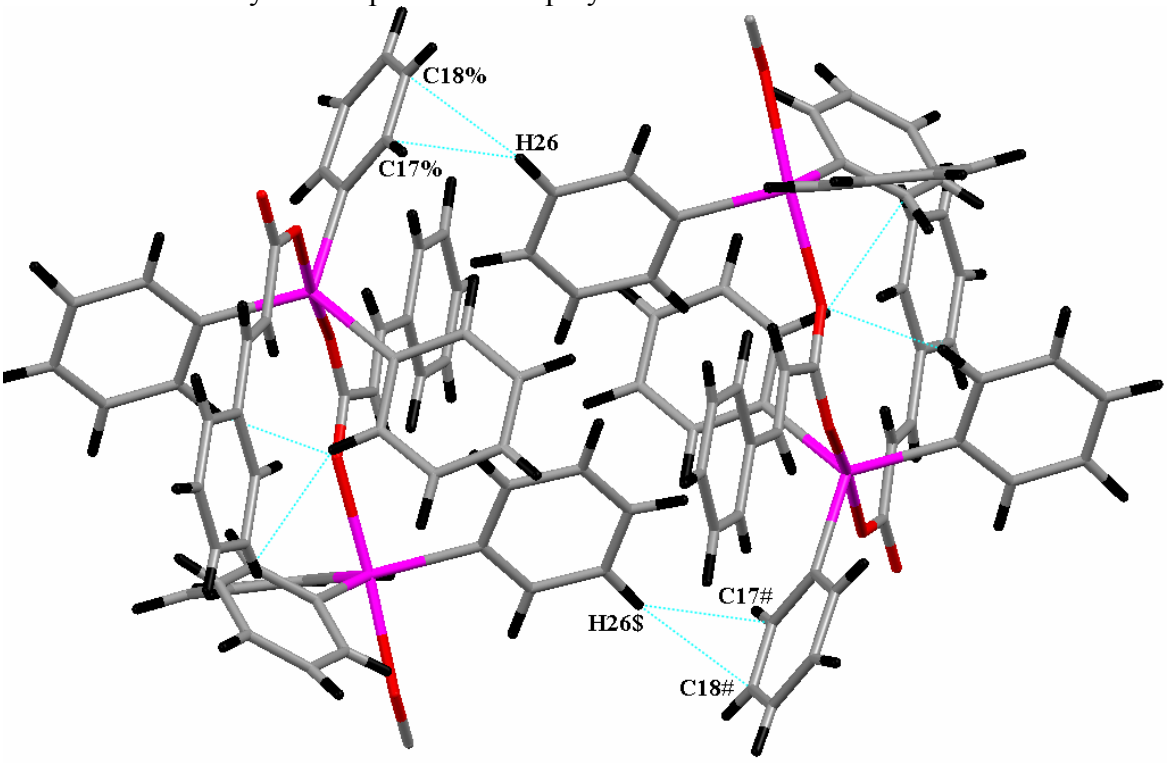


Figure 3. Non-classical intermolecular interactions. The marked atoms are at the symmetry positions: (%) 1/2 + x, 1/2 - y, 1/2 + z; ($) 2 - x, -y, 1 – z; (#) 1.5-x, - ½ + y, ½ - z.

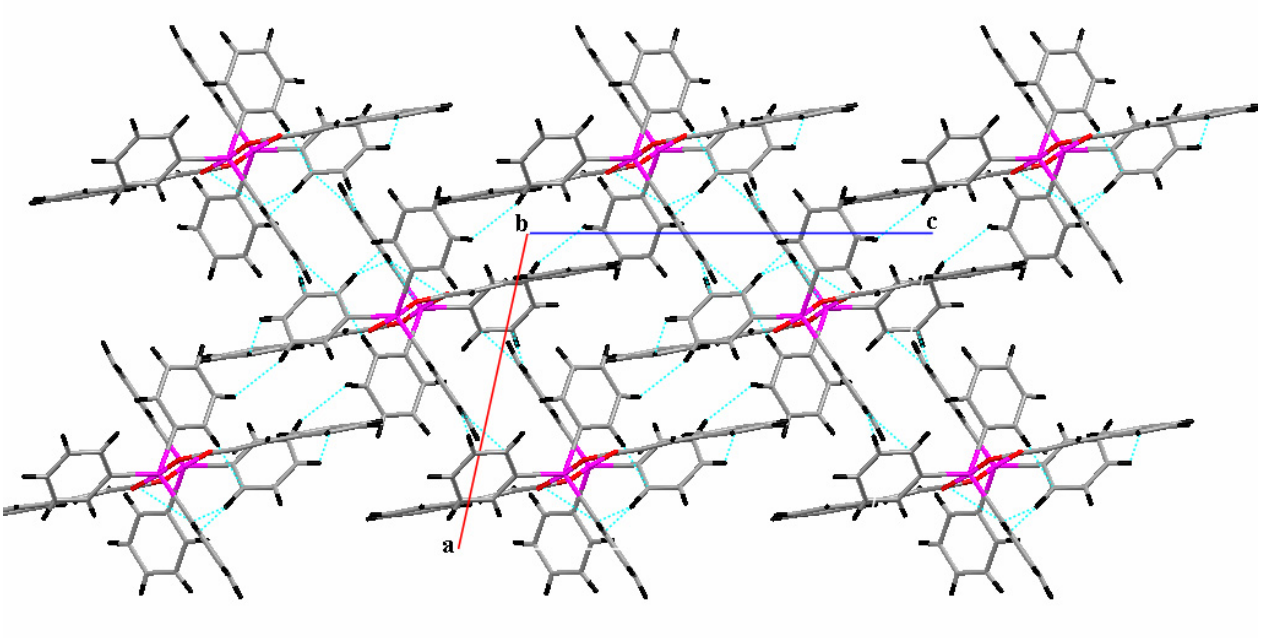


Figure 4. Supramolecular structure of compound **1**, packing is controlled by non-classical interactions, view along b exe.

Table 5. Hydrogen contacts geometry (Å) for **1**

#	Atom 1	Atom 2	Symm. op. 1	Symm. op. 2	Length	Length-VdW
1	C17	H15*	x,y,z	1.5-x,1/2+y,1/2-z	2.819	-0.081
2	H5	H13*	x,y,z	1.5-x,1/2+y,1/2-z	2.389	-0.011
3	H17	C9*	x,y,z	1.5-x,1/2+y,1/2-z	2.812	-0.088
4	H17	O1*	x,y,z	1.5-x,1/2+y,1/2-z	2.557	-0.163
5	H27	C15*	x,y,z	1.5-x,1/2+y,1/2-z	2.896	-0.004
6	H26	C17%	x,y,z	1/2+x,1/2-y,-1/2+z	2.789	-0.111
7	H26	C18%	x,y,z	1/2+x,1/2-y,-1/2+z	2.694	-0.206
8	C17#	H26$	1.5-x,-1/2+y,1/2-z	2-x,-y,1-z	2.789	-0.111
9	C18#	H26$	1.5-x,-1/2+y,1/2-z	2-x,-y,1-z	2.694	-0.206

Conclusions

From spectroscopy data we found different tin compounds: for **1** (penta-coordinated, ^{119}Sn = -112.0), for **2** (tetra-coordinated, ^{119}Sn = + 109.9), for **3** (hexa-coordinated, ^{119}Sn = - 260.2) and for **4** (penta-coordinated^{119}Sn = - 20.0). The structure of **1** was corroborated by X-ray diffraction, we found a polymeric triphenyltin-*trans*-cinnamete structure, because the acidity of tin center, causes that the carboxylic group in the *trans*-cinnamic acid acts as a bridge between two tin

groups, the lattice are govern by non classical intra- and inter-molecular interactions (D-H···π). Compound **3** and **4** were obtained dissolving **1** and **2** in DMSO-d_6, the chemical shift of ^{119}Sn shows signals at lower frequency than the starting materials, showing the acidity of the tin center.

Acknowledgements

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Supplementary Information

X-ray Crystallography data (excluding structure factors) for compound **1** have been deposited with the Cambridge Crystallographic Data Center: CCDC 651003. Complete copies may be obtained free of charge on application to the Director: Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, United Kingdom. For further information on submission to the CCDC consult their web site at www.ccdc.cam.ac.uk.

Experimental Section

General Procedures. *trans*-Cinnamic acid, triphenyltin chloride, tributhyltin chloride, triethylamine, benzene and DMSO-d_6 were commercially available. The compounds **1** and **2** were performed using a Schlenk technique, with fresh distilled solvents and were stored at room temperature. Melting points were getting from Melt-Temp from capillaries, and are uncorrected. IR spectrum was recorded on an FT-IR 1600 Perkin Elmer spectrophotometer using solid compounds KBr pellets in the 4000-400 cm^{-1} range. Mass spectra in the FAB+ technique was performed in a Jeol MStation 700 spectrometer of high resolution in the range of 1 to 5000 m/z. The elemental analyzes were performed in a Thermofinniga, Flash 112 under standard conditions. The NMR spectrums were obtained in $CDCl_3$ and DMSO-d_6 in the Bruker 300 MHz and Jeol Eclipse 400 MHz spectrometers. For ^{1}H (300.13185 MHz or 399.78219 MHz), for ^{13}C (75.47564 MHz or 100.52530 MHz) using TMS as internal reference; and Me_4Sn for ^{119}Sn (111.92607 MHz or 149.08124), respectively.[17] Chemical Shifts (δ) are reported in ppm, the coupling constants $^nJ(^{13}C\text{-}^{119/117}Sn)$ were got from the satellite signal in the ^{13}C spectrum, the values are reported in Hertz (Hz). X-ray diffraction for compound **1** was performed with Enraf Nonius FR590 Kappa CCD ($\lambda_{MoK\alpha}$ = 0.71073 Å) the crystals were mounted in a fiver glass. Relevant crystallographic data are summarized in table 3, structure solution and refinement were

performed in *Crystals*[18] program. Graphics were performed in ORTEP[19] and Mercury[20] programs.

Triphenyltin-*trans*-cinnamate 1 [$(C_9H_7O_2)Sn(C_6H_5)_3$]. A solution of 0.5 g (3.3 mmol) of **I** and 0.4702 ml (0.3414 gr, 3.374 mmol) of triethylamine in 20 ml of benzene was prepared under continue stirring. A separated solution was prepared by addition of 1.2515 gr (3.3 mmol) triphenyltin chloride and 0.4702 ml (0.3414 gr, 3.374 mmol) of triethylamine in 20 ml of benzene. Then the solutions were mixed under strong and continue stirring, the reaction mixture was refluxed by 3 h after that the solution was stirred by 3 h at room temperature. The mixture of reaction was filtered off and the solvent was removed at low pressure, the white solid was washed two times with benzene and was crystallized with chloroform. The white solid, 1.58 g (94 %), pf = 133-135 C, **IR** (solid): 1385.3 (C=O sym), 1499.9(C=O asym), 1499 (-C=C-), 1636 (-C=N-), (-C-Sn-), (-C-S-), (-S=C-). **NMR** ($CDCl_3$): **^{119}Sn**: - 112.0. **^{1}H**: H2(7.92), H3(7.55), H4(7.54), H5(7.55), H6(7.92), H7(6.65), H8(7.81), H11(7.44), H12(7.41), H13(7.40), H14(7.41), H15(7.44). **^{13}C**: C1(135.0), C2(129.9), C3(128.4), C4(128.8), C5(128.4), C6(129.9), C7(119.7), C8(144.7), C9(173.4), C10(138.9,[48.1]), C11(136.9), C12(128.9,[63.3]), C13(130.1), C14(128.9), C15(136.9). **e/m** (FAB+): 267 ($C_9H_7O_2Sn$, 10%), 351 ($C_{18}H_{15}Sn$, 100%), 421 ($C_{21}H_{17}O_2Sn$, 93 %), 497 ($C_{27}H_2O_2Sn$, 5 %). **Anal. Calc.** for $C_{27}H_{22}O_2Sn$: C, 65.23; H, 4.46. Found: C, 64.88; H, 4.51.

Tributyltin-*trans*-cinnamate 2 [$(C_9H_7O_2)Sn(C_4H_9)_3$]. Using the same procedure described for compound **1**, a solution of 0.5 g (3.3 mmol) of **I** and 0.4702 ml (0.3414 gr, 3.3 mmol) of triethylamine in 20 ml was mixed with a separated solution of 0.9151ml (1.0982 gr, 3.3 mmol) tributhyltin chloride and 0.4702 ml (0.3414 gr, 3.374 mmol) of triethylamine in 20 ml of benzene to produced a white solid 1.37 g (93 %), pf = 65-69 C. **IR** (solid): 1386 (C=O sym), 1542.5 (C=O asym), 1542 (-C=C-), 1640 (-C=N-), (-C-Sn-), (-C-S-), (-S=C-). **NMR** ($CDCl_3$): **^{119}Sn NMR**: + 110.9. **^{1}H NMR**: H2(7.43), H3(7.27), H4(7.27), H5(7.27), H6(7.43), H7(6.44), H8(7.55), H10(1.25), H11(1.57), H12(1.25), H13(0.84). **^{13}C NMR**: C1(137.2), C2(128), C3(128.8), C4(129.8), C5(128.8), C6(128.0), C7(120.4), C8(143.7), C9(172.2), C10(16.9,[~351.9]), C11(28.16,[19.8]), C12(27.0,[67.2]), C13(13.99). **e/m** (FAB+): 291 ($C_{12}H_9Sn$, 30%), 381 ($C_{17}H_{25}O_2Sn$, 100%), 439 ($C_{21}H_{34}O_2Sn$, 5%), 727 ($C_{33}H_{25}O_2Sn_2$, 28%), 817 ($C_{42}H_{32}O_4Sn_2$,15%). **Anal. Calc.** for $C_{21}H_{34}O_2Sn$: C, 57.69; H, 7.84. Found: C, 57.88; H, 8.59.

Compounds **3 [$(C_9H_7O_2)(DMSO\text{-}d_6)\cdot Sn(C_6H_5)_3$]** and **4 [$(C_9H_7O_2)(DMSO\text{-}d_6)\cdot Sn(C_4H_9)_3$]** were analyzed dissolving them in DMSO-d_6.

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