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Structural study of di- and triorganotin(IV) dicarboxylates containing one double bond

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ABSTRACT

Tri- and diorganotin(IV) dicarboxylates derived from *trans*-glutaconic acid and acetone 1,3-dicarboxylic acid were prepared. Their structure was studied using NMR, IR, and MS data. All of these compounds (except for compound **2a**) are polymeric in the solid state and depolymerise upon dissolving in deuteriochloroform to give monomeric particles with four-coordinated central tin atoms. X-ray crystallography was used to characterize (*E*)-bis(tributylstannyl) pent-2-enedioate (**1a**). This compound crystallizes in a monoclinic space group system. The supramolecular organization of **1a** can be described as layered polymeric sheets constructed of forty-membered rings that are interconnected on four different sites to the third dimension. Each layer assembled of the forty-membered rings, is made up of six triorganotin fragments and six *trans*-glutaconic acids, where four of them are incorporated in the core of the ring and other two are bidentate bridging and participating in the ring system by three atoms of CO_2 group only.

1. Introduction

Organotin(IV) carboxylates have been studied very frequently up to now because of their well known catalytic and medical activity [1,2]. The structural motifs of these compounds are well established and studied by X-ray diffraction [3], Moessbauer and CP MAS NMR techniques in the solid state and, mainly, multinuclear NMR techniques in solution [3,4]. The tin atom in these compounds can be four-coordinated or five-coordinated (with major occurrence in the solid state). In the second case, the tin atom is surrounded by three carbon atoms originated from organic groups and two oxygen atoms from one asymmetrically bidentate carboxylate (intramoleculary chelated or two different carboxylate groups (intermolecularly bridging)).

Such compounds that are polymeric in the solid state usually depolymerise to give oligomeric or even monomeric structural units in solutions of various solvents [4].

Only relatively little is known about structure of bis(organotin (IV)) dicarboxylates (Refs. [5–7] and references therein).

In this contribution, we would like to present our results concerning the structure of organotin(IV) derivatives of acetone 1,3-dicarboxylic acid and *trans*-glutaconic acid. Acetone 1,3-dicarboxylic acid (3-oxopentanedioic acid, $HOOCCH_2C(=O)CH_2COOH$) is a "shorter" analogue of 4-ketopimelic acid [6,7] studied recently. In contrast to 4-ketopimelic acid, acetone 1,3-dicarboxylic acid exists partially in its enol form – $HOOCCH{=}C(-OH)CH_2COOH$. *Trans*-glutaconic acid ((*E*)-pent-2-enedioic acid, $HOOCCH{=}CHCH_2COOH$) is a suitable model compound for the enol form of acetone 1,3-dicarboxylic acid, having also two different carboxylic groups, one double bond and hydrogen instead of hydroxy group.

2. Results and discussion

2.1. Synthesis and NMR spectra

Bis(triorganostannyl) *trans*-glutaconates (**1a**,**b**) were prepared by the reaction of bis(tributyltin(IV)) oxide with *trans*-glutaconic acid in refluxing toluene and, analogously, **1b** by the reaction of *trans*-glutaconic acid with triphenyltin(IV) hydroxide. Both reactions gave good yields of products the purity of which was checked using ^{1}H and ^{119}Sn NMR spectra.

We observed $^{3}J(^{1}H, ^{1}H)$ coupling constant in the ^{1}H NMR spectra belonging to protons on the double bond being 15.6 Hz for **1a** and 15.7 Hz for **lb**, respectively. Their values mean that *trans* arrangement of double bond protons from starting acid was retained in both compounds. In line with the structure, two different ^{119}Sn

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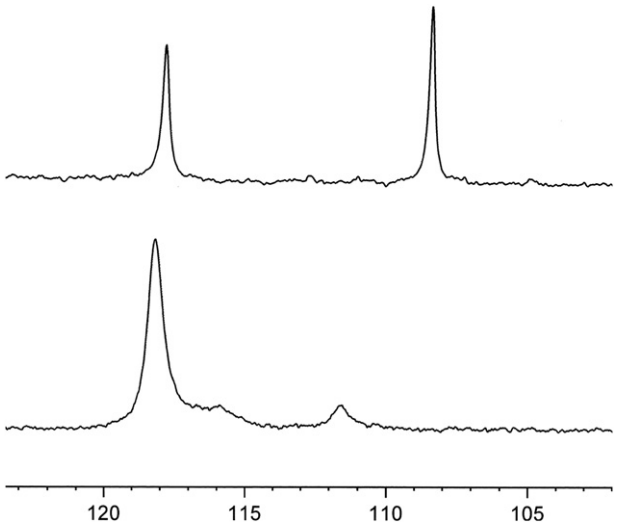


Fig. 1. ^{119}Sn NMR spectra of compounds **1a** (upper trace) and **3a** (bottom trace).

chemical shifts were detected in the ^{119}Sn NMR spectra of compounds **1a** (Fig. 1) and **1b**.

We tried to assign them experimentally using two-dimensional ^{1}H – ^{119}Sn HMQC spectra [8] based on $^{n}J(^{119}\mathrm{Sn}, ^{1}\mathrm{H})$ coupling constants of tin atoms with protons of glutaconic acid. No tin satellites were observable in the standard ^{1}H NMR spectra for protons of glutaconic acid, contrary to those in R_3Sn. Two-dimensional ^{1}H–^{119}Sn HMQC experiments were thus optimized for $^{n}J(^{119}\mathrm{Sn}, ^{1}\mathrm{H})$ coupling constants being very small (from 3 to 15 Hz). Unfortunately, only correlations of tin resonances with tributyl and triphenyl moieties were observable. We can conclude that $^{n}J(^{119}\mathrm{Sn}, ^{1}\mathrm{H})$ coupling constants of tin atoms with protons of glutaconic acid must be (if any) very close to zero.

The ^{13}C resonances of COO groups are well separated and were differentiated using proton-coupled ^{13}C NMR spectra: the signal with less complicated multiplet was assigned to =CHCOO ($\delta = 171.2$, the coupling with *one* proton via $^{2}J(^{13}\mathrm{C}, ^{1}\mathrm{H})$) while the more complicated one to CH_2COO carbon ($\delta = 175.3$, the coupling with *two* protons via $^{2}J(^{13}\mathrm{C}, ^{1}\mathrm{H})$). On the contrary, the ^{13}C resonances of butyl and phenyl groups in $COOSnR_3$ fragments in compounds **1a**,**b** were only slightly broadened and, except for *ipso* carbons of phenyl groups, were not resolved. 2D ^{1}H–^{13}C HMQC experiments were used for the assignment of proton resonances in butyl and phenyl groups since the unambiguous assignment of the ^{13}C resonances was straightforward using $^{n}J(^{119}\mathrm{Sn}, ^{13}\mathrm{C})$ coupling constants.

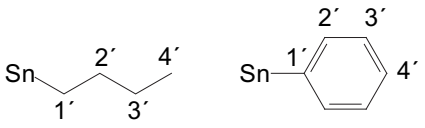
We performed the reaction of *trans*-glutaconic acid with dibutyltin oxide and with diphenyldichlorodistannane and obtained compounds **2a** and **2b**, respectively. The ^{119}Sn, ^{13}C and ^{1}H chemical shifts were determined for compound **2a** (Table 1) (compound **2b** is insoluble both in deuteriochloroform and hexadeuteriodimethyl sulfoxide). We obtained one set of sharp and resolved signals in ^{13}C and ^{1}H NMR spectra and only one signal in ^{119}Sn, NMR spectrum.

The problem in application of acetone 1,3-dicarboxylic acid consists in its rather low thermal stability. We performed the reaction of bis(tributyltin(IV)) oxide with acetone 1,3-dicarboxylic acid in refluxing benzene or toluene, however, under these experimental conditions 1,3-dicarboxylic acid undergoes decarboxylation to give CH_3COCH_2COOH first and, finally, acetone which is removed from the reaction mixture leaving, after removal of benzene or toluene, only traces of compounds having appropriate protons and carbons belonging to acetone 1,3-dicarboxylic acid. It was thus necessary to perform the reaction at 300 K and to use

Table 1
^{119}Sn, ^{13}C and ^{1}H chemical shifts and $^{n}J(^{119}\mathrm{Sn}, ^{13}\mathrm{C})$ and $^{3}J(^{1}\mathrm{HC{=}C^{1}H})$ coupling constants (Hz, ±0.3 Hz) in compounds **1a**,**b** and **2a** measured in deuteriochlorofom.

	1a	**1b**	**2a**
$\delta(^{119}\mathrm{Sn})$			
CH_2COOSn	117.3	−100.5	−139.1
=CHCOOSn	107.8	−111.8	−139.1
$\delta(^{13}\mathrm{C})$			
=CHCOO	171.2	172.2	175.2
=CHCOO	125.2	124.2	123.7
CH=CH–CH_2	140.5	141.9	142.4
CH_2COO	38.2	37.5	37.6
CH_2COO	175.3	176.1	179.2
1′	16.4 (358.8[a])	138.3 (635.7[a])	
137.8 (632.3[a])	25.3 (574.8[a])		
2′	27.6 (20.2[a])	136.8 (48.2[a])	26.5 (35.4[a])
3′	26.9 (66.1[a])	128.9 (63.3[a])	26.3 (99.1[a])
4′	13.6	130.1	13.5
$\delta(^{1}\mathrm{H})$			
=CHCOO	5.86 (15.6[b])	5.99 (15.7[b])	5.93 (15.7[b])
=CH-	6.90 (15.6[b])	7.12 (15.7[b])	7.16 (15.7[b])
CH_2COO	3.14[c]	3.30	3.29[c]
1′	1.20[c]	–[c]	1.62[c]
2′	1.55[c]	7.71[c]	1.62[c]
3′	1.28[c]	7.42[c]	1.34[c]
4′	0.86[c]	7.42[c]	0.87[c]

[a] $^{n}J(^{119}\mathrm{Sn}, ^{13}\mathrm{C})$.
[b] $^{3}J(^{1}\mathrm{H–C{=}C–^{1}H})$.
[c] The numbering of the butyl or phenyl atoms is indicated as 1′- 4″in the following scheme:



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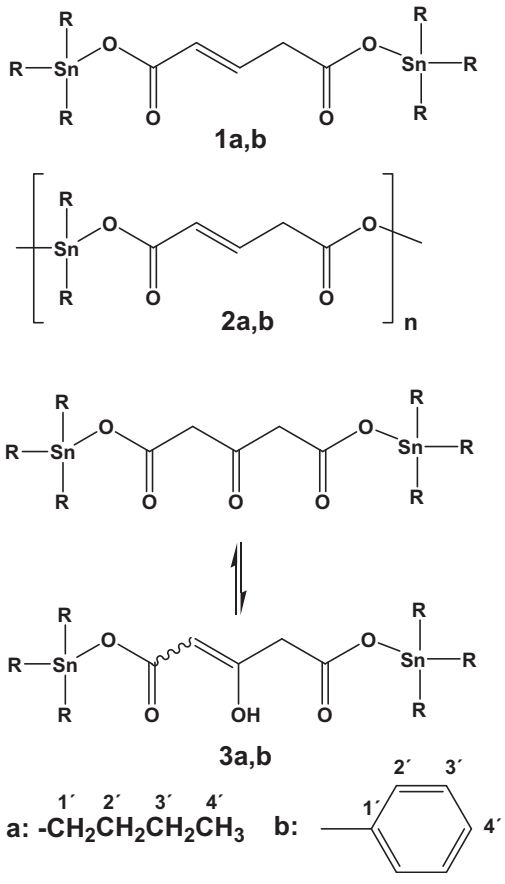
a reactive agent. An attempt to react acetone 1,3-dicarboxylic acid with Bu_3SnOCH_3 in a NMR tube afforded successfully compound **3a**. This compound is stable in the solution, however, it decomposes during separation. The compound **3b** was prepared using sodium methylate in methanol and Ph_3SnCl. The ^{119}Sn, ^{13}C and ^{1}H NMR data are given in Table 2. There were two sets of NMR signals in the NMR spectra of compounds **3a**,**b** (Scheme 1) corresponding to a mixture of keto and enol forms (keto to enol ratio being ca 8:1 for **3a** and ca 15:1 for **3b**). The keto forms are more abundant and symmetric and, thus, the assignment of all NMR resonances was straightforward. Two tin resonances were detected in enol forms in **3a** (Fig. 1) and **3b**, similarly to compounds **1a**,**b**. A comparison of ^{119}Sn chemical shifts allowed a tentative assignment of ^{119}Sn resonances in enol forms and compounds **1a**,**b**. Signals being closer to the ^{119}Sn chemical shift in keto form in compound **3a**,**b** were assigned to CH_2COOSn. The ^{119}Sn resonances in **3a** (Fig. 1) and **3b** were slightly more broadened than those in compounds **1a** (Fig. 1) and **1b**. This is very likely due to the existence of the dynamic keto–enol equilibrium involving an enol proton transfer in between the enol and keto tautomers of the organotin dicarboxylate compounds **3a**,**b**.

In the ^{13}C NMR spectra of the keto forms of compounds **3a**,**b**, two resonances are observed in relative intensity ratio 1:2 belonging to C=O and two equivalent COO while there are three resonances corresponding to two different COO groups and =C(OH)– in enol form of compounds **3a**,**b**. Proton-coupled spectrum was used for their assignment where a broadened signal was assigned to =CHCOO, quartet-like signal due to the interaction of carbon with CH_2 and OH protons to =C(OH)– and triplet due to the interaction of carbon with CH_2 protons to $C(OH)CH_2COO$.

Table 2
^{119}Sn, ^{13}C and ^{1}H chemical shifts and $^{n}J(^{119}Sn, ^{13}C)$ coupling constants (Hz, ±0.3 Hz) in compounds **3a**,**b** measured in deuteriochlorofom.

	3a (Keto)	**3a** (Enol)	**3b** (Keto)	**3b** (Enol)
$\delta(^{119}Sn)$				
CH_2COOSn	118.2	115.9	−82.3	−84.0
=CHCOOSn	–	111.5	–	−99.2
$\delta(^{13}C)$				
CH_2COO	171.8	–	173.2	–
CH_2COO	49.6	–	50.2	–
CO	198.2	–	201.4	–
=CHCOO	–	176.4	–	177.0
=CHCOO	–	92.5	–	89.8
=C(OH)-	–	170.3	–	172.2
$C(OH)CH_2COO$	–	41.6	–	50.2
$C(OH)CH_2COO$	–	173.4	–	173.2
1	16.5 (358.4[a])	[b]	138.3 (639.7[a])	[b]
2	27.6 (20.6[a])	[b]	136.2 (43.7[a])	[b]
3	26.8 (66.0[a])	[b]	128.3 (58.2[a])	[b]
4	13.4	[b]	129.3	[b]
$\delta(^{1}H)$				
CH_2COO	2.28	–	2.23	–
=CHCOO	–	5.03	–	5.12
=C(OH)COO	–	12.67	–	12.36
$C(OH)CH_2COO$	–	3.14	–	3.47
1	1.20	[b]	–	–
2	1.54	[b]	7.56	[b]
3	1.27	[b]	7.38	[b]
4	0.84	[b]	7.38	[b]

[a] $^{n}J(^{119}Sn, ^{13}C)$.
[b] Not resolved from signals of the prevailing keto form.



Scheme 1.

Table 3
Selected parameters of IR spectra for compounds **1**–**3** [cm^{-1}].

	Medium	ν(C=O)	$\nu_{as}(CO_2)$	$\nu_{s}(CO_2)$
1a	CH_2Cl_2	–	1651, 1617	1336
	KBr	–	1587, 1551	1378
	ATR[a]	–	1584, 1549	1377
1b	CH_2Cl_2	–	1652, 1620	1335
	KBr	–	1574, 1547	1350
	ATR[a]	–	1574, 1545	1347
2a	CH_2Cl_2	–	1606, 1583	1370
	KBr	–	1602, 1572	1378
	ATR[a]	–	1600, 1565	1378
2b	KBr	–	1560[b]	1389
	ATR[a]	–	1557[b]	1390
3a	$CDCl_3$	1724	1652	1340
3b	KBr	1722	1579	1380
	ATR[a]	1722	1579	1381

[a] Attenuated total reflection IR.
[b] Broad signal.

The reactions of acetone 1,3-dicarboxylic acid with dibutyldichlorodistannane and with diphenyldichlorodistannane gave white solid material completely insoluble both in deuteriochloroform and hexadeuteriodimethyl sulfoxide having high melting points. The reason might be that oxygen from enol form of acetone 1,3-dicarboxylic acid can participate as tridentate ligand and form a complicated structure of these insoluble materials.

2.2. Mass spectra

The results of electrospray ionization (ESI) mass spectrometry measurements in positive-ion mode are summarized in the Experimental Section. The typical feature of ESI mass spectra of organotin carboxylates is the cleavage of the most labile bond Sn–O in the molecules yielding two complementary ions where the cationic part of the molecule is measured in the positive-ion mode. The cationic part $[SnR_3]^+$ and subsequent fragment ions $[HSnR_2]^+$ and $[H_2SnR]^+$ are observed in the first-order positive ESI mass spectra.

2.3. Infrared spectra

The significant tool for evaluation of organotin carboxylate structures is IR spectroscopy, especially the values of ν_{as} and ν_S for carbonyl vibration in the CO_2 group [2].

These values and ν(C=O) for **1a**,**b**–**3a**,**b** in methylenedichloride solution (**3a** in deuteriochloroform), KBr pellets and using ATR (Attenuated Total Reflection) spectra, respectively, are collected in Table 3. The $\nu_{as}(CO_2)$ (1540–1590 cm^{-1}) and $\nu_s(CO_2)$ (1330–1390 cm^{-1}) values found for all compounds in solid state spectra except for **2a**, are in agreement with those reported earlier for a polymeric structure with bridging bidentate carboxylic groups. The increase of $\nu_{as}(CO_2)$ values in methylenedichloride (in deuteriochroform for **3a**) solution compared to the same parameter in KBr pellets and ATR corresponds to breaking up solid state polymeric structure into the monomers upon dissolving of these compounds. Only one absorption was obtained for the "symmetric" keto forms of compounds **3a**,**b** while in other compounds two absorptions were detected in line with the existence of two different –C(=O)OSn moieties. In other cases (Table 3), there are always two C=O frequencies, which are different in CH_2Cl_2 solution and the solid state IR while there are two C=O frequencies in **2a** which are the same in solution and the solid state IR. Two C=O frequencies mean two different structural motifs [6].

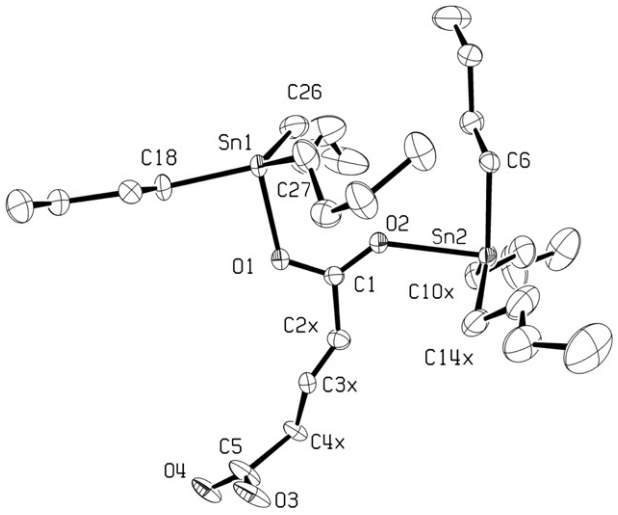


Fig. 2. Molecular structure of **1a**, ORTEP diagram, 30% probability level, hydrogen atoms as well as disordered groups are omitted for clarity. Selected interatomic distances and angles [Å, °]: Sn1C22 2.130(8), Sn1C18 2.137(6), Sn1C26 2.143(8), Sn1 O1 2.170(4), Sn1 O4 2.462(4), Sn2C6 2.122(6), Sn2 C10X 2.133(7), Sn2 C14X 2.138(9), Sn2 O3 2.177(4), Sn2 O2 2.434(4), O1C1 1.270(7), O2C1 1.248(6), O3C5 1.262(8), O4C5 1.243 (8), C1 C2X 1.489(15), C2X C3X 1.20(2), C3X C4X 1.569(19), C4X C5 1.586(14), C22 Sn1C18 119.9(3), C22 Sn1C26 120.8(3), C18 Sn1C26 116.0(3), C22 Sn1 O1 100.2(3), C18 Sn1 O1 90.0(2), C26 Sn1 O1 97.6(2), C22 Sn1 O4 82.9(3), C18 Sn1 O4 82.4(2), C26 Sn1 O4 86.7(2), O1 Sn1 O4 172.34(14), C6 Sn2 C10X 116.7(3), C6 Sn2 C14X 118.2(3), C10X Sn2 C14X 123.3(3), C6 Sn2 O3 90.0(2), C10X Sn2 O3 96.6(2), C14X Sn2 O3 96.5(3), C6 Sn2 O2 83.69(18), C10X Sn2 O2 86.8(2), C14X Sn2 O2 85.9(2), O3 Sn2 O2 173.68(15), O2 C1 O1 122.9(5), O4C5 O3 123.8(6).

The values of ν(C=O) in carbonyl group in compounds **3a**,**b** are very similar (1722–4 cm^{-1}). Though ν(C=O) of the CO_2 groups in the minor enol forms in **3a**,**b** are very likely overlapped by stronger absorptions of the keto forms, the sharp signal of the enolic OH was detected at 3631 cm^{-1} (chloroform), 3616 cm^{-1} (KBr) and 3617 cm^{-1}(ATR).

2.4. X-ray crystallography

The solid state structure of **1a** was determined by diffraction techniques. Compound **1a** crystallizes in a monoclinic space group system. The supramolecular organization of **1a** can be described as layered polymeric sheets (Fig. 2) constructed of forty-membered rings which are interconnected on four different sites to the third dimension. Each layer assembled of the forty-membered rings, is made up of six triorganotin fragments and six *trans*-glutaconic acids (Fig. 3), where four of them are incorporated in the core of the ring and two other are bidentate bridging and participating in the ring system by three atoms of CO_2 group only. Each ring is composed of (–Sn–A–Sn–A–Sn–B–Sn–A–Sn–A–Sn–B–) sequence; where A is the core acid, B is the bridging one and Sn is $SnBu_3$ moiety. This is in strong contrast with the supramolecular arrangement of triorganotin(IV) carboxylates with a longer chain-ketopimelic acid [6,7] where only twenty eight-, twenty-membered rings or monomeric structures were found. The ring sequence consisted of four alternating terminal and bridging acids between four organotin moieties for the unit with the largest ring. This is probably caused by the non-symmetric structure of *trans*-glutaconic acid and the restricted rotation around the double bond. The *n*-butyl chains are located within the cavities (17.8 × 17.8 × 10.5 Å) determined by the rings in the crystal lattice.

The *trans*-glutaconic acid is interconnecting two geometrically different tin atoms as a bridge in a non-symmetrical bidentate bridging mode (Fig. 2). The mutual separations of C and O atoms within each carboxylic group differ by 0.02 Å. The shorter distance C–O is associated with the closer contact to the tin atom (C1, O1, Sn1 and C5, O3, Sn2) and the parallel orientation of the contact to the carboxylic acid chain. The second type of Sn–O bond, for example Sn2–O2, which is oriented almost perpendicularly to the acid chain, is significantly elongated (difference about 0.3 Å, Fig. 3). Both types of the tin atom have almost perfect trigonal bipyramidal geometry with oxygen atoms in axial positions and O1–Sn1–O4, and O3–Sn2–O2 angles approaching the ideal value (172.34(14) and 173.68(15)°). The equatorial girdles have also nearly perfect planar fashion with the values of sums of interatomic angles being around 357°. The significant differences between the C–C distances in the *trans*-glutaconic acid chain determine the C=C double bond position.

3. Experimental part

The syntheses were performed without protection from air. *Trans*-glutaconic acid ((*E*)-pent-2-enedioic acid), di- and tri-organotin chlorides, oxides or methoxide, methanol, toluene and deuteriochloform were obtained from Sigma-Aldrich and acetone 1,3-dicarboxylic acid (3-oxopentanedioic acid) from the Research Institute for Organic Syntheses, Pardubice.

3.1. NMR spectroscopy

The solution state ^{1}H (500.13 MHz), ^{119}Sn (186.50 MHz) and ^{13}C NMR (125.76 MHz) spectra of the studied compounds were measured on a Bruker Avance 500 spectrometer equipped with 5 mm tuneable probe with *z*-gradient at laboratory temperature. The samples were dissolved in deuteriochloroform. The ^{1}H NMR spectra were obtained using standard procedure; proton-decoupled and proton-coupled ^{13}C NMR as well as two-dimensional $^{1}H–^{13}C$ HMQC and $^{1}H–^{13}C$ HMBC spectra were measured. The ^{1}H and ^{13}C chemical shifts were referred to the signal of internal tetramethylsilane ($\delta = 0.0$). One-dimensional ^{119}Sn NMR spectra were measured using the inverse gated-decoupling mode. Two-dimensional $^{1}H–^{119}Sn$ HMQC experiments were optimized for ^{n}J (^{119}Sn, ^{1}H) coupling constants from 3 to 15 Hz. The ^{119}Sn chemical shifts are referred to external neat tetramethylstannane ($\delta = 0.0$). The numbering system for the NMR spectral data is shown in Scheme 1.

3.2. Mass spectrometry

Positive-ion electrospray ionization (ESI) mass spectra (MS) were measured on the LCQ ion trap analyser (Thermo Fisher Scientific, Waltham, MA, USA) in the range *m*/*z* 100–2000. The samples were dissolved in methanol and analysed by direct infusion at the flow rate 3 μl/min. The ESI ion source spray voltage was set to 3.5 kV, capillary temperature was 250 °C, capillary voltage 27 V and tube lens offset −5 V.

3.3. IR spectroscopy

IR spectra were recorded on a Thermo Scientific Nicolet 6700 FT-IR spectrometer in dichloromethane solution (in deuteriochloroform for **3a**), in KBr pellet or by ATR (Attenuated Total Reflection) equipment (Diamond/ZnSe, range 4000–640 cm^{-1}) at laboratory conditions.

3.4. X-ray crystallography

The X-ray data for colorless crystals of **1a** were obtained at 150 K using Oxford Cryostream low-temperature device on a Nonius

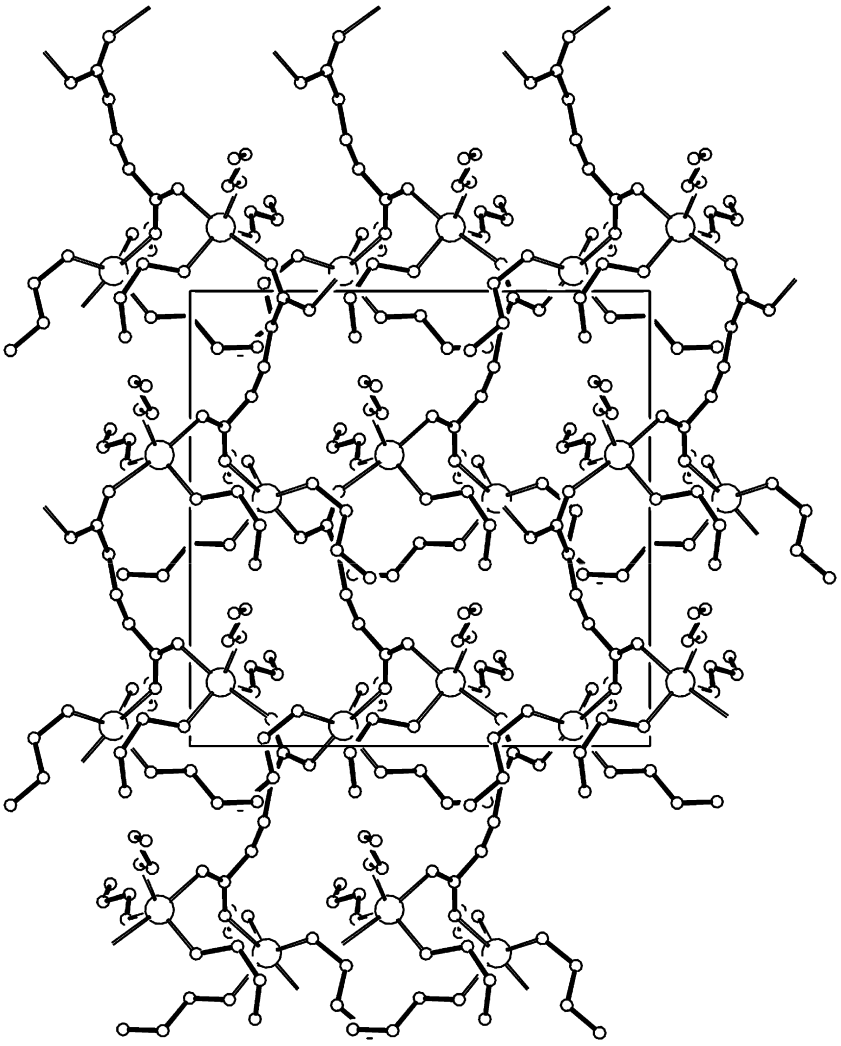


Fig. 3. Supramolecular architecture of **1a**, PLUTON view, hydrogen atoms as well as disordered groups are omitted for clarity.

KappaCCD diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å), a graphite monochromator, and the ϕ and χ scan mode. Data reductions were performed with DENZO-SMN [9]. The absorption was corrected by integration methods.[10] Structures were solved by direct methods (Sir92) [11] and refined by full matrix least-square based on F^2 (SHELXL97) [12]. Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of treatment of crystal, all hydrogen were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2\ U_{eq}$(pivot atom) or of $1.5\ U_{eq}$ for the methyl moiety with C–H = 0.96 Å, 0.97, and 0.93 Å for methyl, methylene and the vinyl hydrogen atoms, respectively.

Crystallographic data for **1a**: $C_{29}H_{58}O_4Sn_2$, $M = 708.13$, monoclinic, *Cc*, $a = 13.8651(10)$, $b = 15.8783(9)$, $c = 16.4918(6)$Å, $\beta = 107.56(8)^\circ$, $Z = 4$, $V = 3461.4(2)$ Å^3, $D_c = 1.359$ g cm^{-3}, $\mu = 1.470$ mm^{-1}, $T_{min} = 0.621$, $T_{max} = 0.827$; 14,942 reflections measured ($\theta_{max} = 27.5^\circ$), 7056 independent ($R_{int} = 0.0467$), 6213 with $I > 2\sigma(I)$, 356 parameters, $S = 1.116$, $R1$(obs. data) = 0.0378, $wR2$(*all data*) = 0.0788; max, min residual electron density = 0.764, −0.524 eÅ^{-3}.

$R_{int} = \Sigma|F_o^2 - F_{o,mean}^2|/\Sigma F_o^2$, $GOF = [\Sigma(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{1/2}$ for all data, $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for observed data, $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{1/2}$ for all data.

In the crystal of **1a** there are a couple of disordered atoms mainly in *n*-butyl moieties; the dicarboxylic acid chain reveals a positional disorder maybe due to the low mechanical stability of crystals when removed from mother liqueur. When the disordered atoms are split into two positions, these disorders have no influence to the quality of the data and molecular nor supramolecular structure of **1a**. These disorders were treated by different methods while the best result has been obtained by using SADI and EADP instructions in SHELXL software package and data refinements.

3.5. Synthesis

3.5.1. (*E*)-Bis(tributylstannyl) pent-2-enedioate (***1a***)

The mixture of (*E*)-pent-2-enedioic acid (130 mg; 1 mmol) and $(Bu_3Sn)_2O$ (598 mg; 1 mmol) was refluxed in toluene (25 ml) and water was removed azeotropically. The residual toluene was evaporated to give **1a** as white crystalline product (646 mg; 91%), mp: 88–91 °C. The ^{119}Sn, ^{13}C and ^{1}H, NMR data are given in Table 1. Molecular weight = 708.15. MS: *m*/*z* 1443, $[2M + Na]^+$, 38%; *m*/*z* 1001, $[M + SnBu_3]^+$, 100%; *m*/*z* 733, $[M + Na]^+$, 25%; *m*/*z* 711, $[M + H]^+$, 4%; *m*/*z* 653, $[M + H\text{-butane}]^+$, 6%; *m*/*z* 609, $[M + H - butane - CO_2]^+$, 5%. IR analysis ($\nu_{max}$, cm^{-1}): CH_2Cl_2 solution: 2959, 2925, 2872, 2855, 1651, 1617, 1465, 1336, 1076, KBr pellet: 2957, 2923, 2871, 2856, 1657, 1587, 1551, 1464, 1378, 1078, 976, 742, 673.

ATR: 2956, 2922, 2871, 2855, 1657, 1584, 1549, 1463, 1377, 1077, 976, 742, 670. Elemental analysis found: C, 49.5%; H, 8.1%. Calculated: C, 49.19%; H, 8.26%.

3.5.2. (E)-Bis(triphenylstannyl) pent-2-enedioate (**1b**)

The mixture of (*E*)-pent-2-enedioic acid (130 mg; 1 mmol) and Ph_3SnOH (736 mg; 2 mmol) was refluxed in toluene (25 ml) and water was removed azeotropically. The residual toluene was evaporated to give **1b** as a white crystalline product (714 mg; 86%), mp: 156–9 °C. The ^{119}Sn, ^{13}C and ^{1}H, NMR data are given in Table 1. Molecular weight = 828.09. MS: *m/z* 1683, $[2M + Na]^+$, 11%; *m/z* 1181, $[M + SnPh_3]^+$, 12%; *m/z* 853, $[M + Na]^+$, 16%; m/z 831, $[M + H]^+$, 4%; *m/z* 747, $[SnPh_3OCHO + SnPh_3]^+$, 50%; *m/z* 383, $[SnPh_3OCH_3 + H]^+$, 100% *m/z* 351, $[SnPh_3]^+$, 43%. IR analysis (ν_{max}, cm^{-1}): CH_2Cl_2 solution: 1652, 1482, 1335, 1077, 1023, 997, 985, 449, KBr pellet: 3066, 3047, 1658, 1574, 1547, 1481, 1430, 1350, 1076, 1023, 997, 984, 729, 697, 452, ATR: 3066, 3047, 1660, 1574, 1545, 1481, 1429, 1347, 1076, 1023, 997, 983, 729, 696. Elemental analysis found: C, 59.2%; H, 4.4%. Calculated: C, 59.47%; H, 4.14%.

3.5.3. Reaction of dibutyltin oxide with (E)-pent-2-enedioic acid (**2a**)

The mixture of (*E*)-pent-2-enedioic acid (260 mg; 2 mmol) and dibutyltin oxide (500 mg; 2 mmol) was refluxed in toluene (25 ml) and water was removed azeotropically. The residual toluene was evaporated to give **2a** as white solid product (650 mg; 90%), mp: 216–9 °C. The ^{119}Sn, ^{13}C and ^{1}H, NMR data are given in Table 1. IR analysis (ν_{max}, cm^{-1}): CH_2Cl_2 solution: 2961, 2929, 2873, 2860, 1660, 1606, 1583, 1465, 1370, KBr pellet: 2958, 2927, 2872, 2858, 1657, 1602, 1572, 1464, 1378, 1287, 1211, 1083, 779, 687, 613, ATR: 2955, 2923, 2871, 2858, 1657, 1600, 1565, 1462, 1378, 1286, 1209, 1089, 780, 688. Elemental analysis found: C, 45.1%; H, 6.7%. Calculated: C, 44.84%; H, 6.45%.

3.5.4. Reaction of diphenyldichlorostannane with (E)-pent-2-enedioic acid) (**2b**)

To the mixture of (*E*)-pent-2-enedioic acid (260 mg; 2 mmol), 1 M sodium methylate (2 mmol), methanol (15 ml), Ph_2SnCl_2 (688 mg; 2 mmol) was added and heated for 20 min. The solvent was evaporated and sodium chloride was extracted twice with water to give **2b** as white solid (641 mg; 81%), mp: >300 °C. IR analysis (ν_{max}, cm^{-1}): KBr pellet: 3050, 1654, 1560, 1481, 1431, 1389, 1076, 1023, 998, 985, 730, 695, 449, ATR: 3049, 1653, 1557, 1481, 1431, 1390, 1076, 1023, 998, 984, 730, 695. Elemental analysis found: C, 50.7%; H, 3.3%. Calculated: C, 50.92%; H, 3.52%.

3.5.5. Bis(tributylstannyl) 3-oxopentanedioate (**3a**)

Bu_3SnOCH_3 (321 mg; 1 mmol) was added to a suspension of 3-oxopentanedioic acid (74 mg; 0.5 mmol) in 1 ml of deuteriochloroform in a NMR tube. After a short time the solid dissolved and compound **3a** (as a mixture of keto and enol forms) is formed. The ^{119}Sn, ^{13}C and ^{1}H, NMR data are given in Table 2. IR analysis (ν_{max}, cm^{-1}): $CDCl_3$ solution: 3631, 2960, 2925, 2873, 2855, 1724, 1652, 1465, 1340, 1292, 1076, 1017, 606, 524.

3.5.6. Bis(triphenyltin) 3-oxopentanedioate (**3b**)

The mixture of 3-oxopentanedioic acid (146 mg; 1 mmol) 1 M sodium methylate (2 mmol) and methanol (20 ml), Ph_3SnCl (722 mg; 2 mmol) was added and the mixture was stirred at laboratory temperature for 1 h. Methanol was removed by evaporation *in vacuo* at laboratory temperature and sodium chloride was extracted twice with water to give **3b** as yellowish solid (660 mg; 78%), mp: >300 °C. The ^{119}Sn, ^{13}C and ^{1}H, NMR data are given in Table 1. Molecular weight = 844.09. MS: *m/z* 747, $[SnPh_3OCHO + SnPh_3]^+$, 47%; *m/z* 383, $[SnPh_3OCH_3 + H]^+$, 100%; *m/z* 351, $[SnPh_3]^+$, 49%. IR analysis (ν_{max}, cm^{-1}): KBr pellet: 3616, 3064, 3045, 1722, 1636, 1579, 1480, 1428, 1380, 1078, 1022, 997, 896, 775, 723, 694, 447, ATR: 3617, 3064, 3045, 1722, 1579, 1480, 1428, 1381, 1078, 1022, 997, 895, 774, 723, 694. Elemental analysis found: C, 57.9%; H, 3.7%. Calculated: C, 58.34%; H, 4.06%.

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Appendix A. Supplementary material

CCDC 765425 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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