APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 12, 13–23 (1998)

Triphenyltin(IV) Compounds with Biologically Active Anionic Groups: Crystal and Molecular Structures of the *p*-Ethoxybenzoic Acid, Acetylsalicylic Acid, Phthalic Acid and Salicylaldehyde Derivatives

Bruce D. James,[1]* Loretta M. Kivlighon,[1] Brian W. Skelton[2] and Allan H. White[2]
[1] School of Chemistry, La Trobe University, Bundoora, Victoria 3083, Australia
[2] Department of Chemistry, University of Western Australia, Nedlands, WA 6907, Australia

Triphenyltin(IV) compounds of *p*-ethoxybenzoic acid and acetylsalicylic acid contain molecular units with Sn–O bonds and distorted tetrahedral tin centers. The phthalic acid derivative contains two four-coordinate tin atoms between which the phthalic acid unit effectively forms a bridge. The salicylaldehydato compound is polymeric with trigonal bipyramidal tin centers in which the phenyl groups take equatorial positions. The polymerization occurs via the aldehyde oxygen atom bonding to a neighboring tin atom.

Appl. Organometal. Chem. **12**, 13–23, (1998)

Keywords: X ray structure; triphenyltin; *p*-ethoxybenzoic acid; acetylsalicylic acid; phthalic acid; salicylaldehydato; polymer

Received 16 January 1997; accepted 24 April 1997

INTRODUCTION

The determination of structures of organotin(IV) compounds is a field of continuing interest as it is a means of gaining insight into their biocidal activity. Despite the richness of the spectroscopic data yielded by various tin isotopes,[1] it has proved difficult to assign unambiguous structures on this basis alone; hence the increasing reliance placed on the crystallographic endeavours, of which numerous examples have been presented in this journal.[2]

In exploring the expectation that the incorporation of biologically active entities into a triorganotin system would lead to the formation of potent biocides,[3,4] a range of triphenyltin(IV) compounds with simple, biologically active anionic groups were synthesized and initially investigated spectroscopically.[4] Ambiguous spectroscopic data led to further crystallographic investigations on two of the tin–sulfur-bonded compounds; such materials have been shown to be especially active against *Ceratocystis ulmi*.[6]

We have now turned our attention to some of the other triphenyltin(IV) compounds in our original list[4] where we felt that the spectrosopic data warranted either confirmation or clarification. Four compounds were studied: triphenyltin(IV) derivatives of *p*-ethoxybenzoic acid (PEB) (**I**) acetylsalicylic acid (ASA); (**II**), phthalic acid (PTA) (**III**) and salicyaldehyde (SAL) (**IV**). Two of these (**III** and **IV**) have already been shown to have significant activity towards a range of fungi (*Agaricus bisporus, Verticillium fungicola, Colletotrichum gloeosporiodes, Alternaria brassicae, Fusarium culmorum, Sclerotinia fructicola, Rhizoctonia solani* and *Trichoderma viride*).[7] The structures of compounds **I–IV** are presented here.

EXPERIMENTAL

Syntheses

These followed the methods from triphenyltin hydroxide outlined previously,[4] except for the

* Correspondence to: Bruce D. James, School of Chemistry, La Trobe University, Bundoora, Victoria 3083, Australia.
Contract grant sponsor: Australian Research Council

 CCC 0268–2605/98/010013–11$17.50

aspirinate **II** (which appears to be particularly moisture-sensitive), for which it was found to be beneficial to include anhydrous magnesium sulfate desiccant in the synthetic mixture and then to induce crystallization of the concentrated solution by prolonged refrigeration in the presence of hexane.

Structure determinations

Unique room-temperature diffractometer data sets ($2\theta/\theta$) scan mode; monochromatic Mo Kα radiation, $\lambda = 0.7107_3$ Å; $T \sim 295$ K) were measured yielding N independent reflections, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the full matrix least-squares refinement after gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Conventional R, R_w on $|F|$ are quoted at convergence [statistical weights, derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$]. Neutral-atom complex scattering factors were used; for computation the XTAL program system was used,[8] as implemented by Hall. Individual variations in procedure are noted in the footnote to Table 1, which details crystal and refinement parameters.

In the figures, 20% thermal ellipsoids are shown for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å.

Fractional atomic coordinates for compounds **I–IV** are given in Tables 2–5 respectively and the bond lengths and angles pertinent to the geometry about the tin atoms are summarized in Table 6. Tables of structure factors, hydrogen-atom positional and isotropic thermal parameters and non-hydrogen atom anisotropic thermal parameters are deposited with the Editor.

RESULTS AND DISCUSSION

Syntheses and chemical characterizations are recorded as mentioned above for a number of compounds (**I–IV**) of the triphenyltin(IV) moiety with anionic oxygen donor ligands, the stoichiometry $(Ph_3Sn)_nL$ (n = formal charge on the

Table 1. Crystallographic data[a]

	I	II	III	IV
Molecular formula	$C_{27}H_{24}O_3Sn$	$C_{27}H_{22}O_4Sn$	$C_{44}H_{34}O_4Sn_2$	$[C_{25}H_{20}O_2Sn]_{\infty\|\infty}$
Molecular weight	515.18	529.16	864.14	471.13
F_{000}	520	1064	1720	944
a (Å)	15.050(7)	13.794(8)	25.413(9)	16.98(1)
b (Å)	9.540(4)	9.801(3)	15.907(3)	14.823(6)
c (Å)	9.043(4)	18.02(1)	9.136(5)	17.33(1)
α (°)	71.15(3)			
β (°)	76.13(3)	100.30(5)		105.70(6)
γ (°)	89.59(2)			
V (Å^3)	1189	2397	3693	4197
Space group	$P\bar{1}$	$P2_1/n$	$P2_12_12_1$	$P2_1/c$
Z	2	4	4	4
$2\theta_{max}$ (°)	50	50	55	50
ρ (g cm^{-3})	1.43_8	1.46_6	1.55_4	1.49_1
μ(MoK$_\alpha$) (cm^{-1})	11.0	11.0	13.9	12.3
Crystal dimensions (mm)	$0.40 \times 0.18 \times 0.40$	$0.51 \times 0.75 \times 0.38$	$0.08 \times 0.21 \times 0.65$	$0.40 \times 0.44 \times 0.10$
A* (min, max)	1.20, 1.43	1.40, 2.06	1.12, 1.31	1.16, 144
N	3104	4218	4720	7363
N_0	2796	3657	3409	5481
R	0.036	0.028	0.034	0.051
R_w	0.045	0.034	0.032	0.057

[a] Variata: **I, II, IV**: Additional hemispheres of data were measured to $2\theta_{max}$ 40°, R_{int} 0.038, 0.019, 0.075.
III: For the opposite chirality, R, R_w were 0.037, 0.036.

Table 2. Non-hydrogen positional and isotropic displacement parameters for **I**

Atom	*x*	*y*	z	*U* (eq) (Å^2)
Sn	0.82743(2)	0.64872(4)	0.91425(4)	0.0531(2)
C(11)	0.8344(4)	0.7189(6)	1.1098(7)	0.059(2)
C(12)	0.9192(4)	0.7696(6)	1.1160(7)	0.072(3)
C(13)	0.9274(6)	0.8042(7)	1.252(1)	0.088(4)
C(14)	0.8529(7)	0.7876(8)	1.3780(9)	0.093(4)
C(15)	0.7691(6)	0.7413(8)	1.3731(7)	0.088(3)
C(16)	0.7599(5)	0.7049(7)	1.2386(8)	0.078(3)
C(21)	0.9579(3)	0.6884(6)	0.7437(6)	0.053(2)
C(22)	1.0033(5)	0.8275(6)	0.6756(9)	0.074(3)
C(23)	1.0851(5)	0.8530(7)	0.559(1)	0.090(4)
C(24)	1.1228(4)	0.7379(9)	0.5110(8)	0.084(3)
C(25)	1.0785(5)	0.5997(8)	0.580(1)	0.087(4)
C(26)	0.9964(4)	0.5748(6)	0.6938(8)	0.070(3)
C(31)	0.7787(3)	0.4269(6)	0.9612(6)	0.056(2)
C(32)	0.7236(4)	0.3934(7)	0.8731(8)	0.083(3)
C(33)	0.7006(5)	0.2466(9)	0.892(1)	0.098(4)
C(34)	0.7339(5)	0.1343(7)	0.995(1)	0.096(4)
C(35)	0.7880(5)	0.1668(7)	1.081(1)	0.102(4)
C(36)	0.8113(4)	0.3133(7)	1.0632(7)	0.077(3)
C(1)	0.6292(4)	0.9257(6)	0.7420(7)	0.054(2)
C(101)	0.6783(4)	0.8087(6)	0.8373(8)	0.058(3)
O(101)	0.7621(3)	0.7951(4)	0.7618(4)	0.066(2)
O(102)	0.6447(3)	0.7331(5)	0.9775(5)	0.078(2)
C(2)	0.6702(4)	1.0093(7)	0.5844(8)	0.067(3)
C(3)	0.6272(4)	1.1226(7)	0.4959(7)	0.074(3)
C(4)	0.5418(4)	1.1537(6)	0.5677(8)	0.067(3)
O(4)	0.4947(3)	1.2651(5)	0.4902(5)	0.087(2)
C(41)	0.5393(5)	1.3607(8)	0.330(1)	0.102(4)
C(42)	0.4764(6)	1.474(1)	0.274(1)	0.146(5)
C(5)	0.4988(4)	1.0692(8)	0.7239(9)	0.085(3)
C(6)	0.5424(4)	0.9567(7)	0.8110(7)	0.069(3)

anionic ligand) being confirmed by the results of the single crystal X-ray structure determinations.

Two of the compounds, **I** and **II**, are of a mononuclear (Ph_3Sn)L form wherein the functionality of the anionic entity is the carboxylate group of a substituted benzoate ligand. As is frequently the case, the carboxylate is unsymmetrically bidentate, the long Sn···C(*n*O2) contacts comprising significant perturbations on a basically four-coordinate array about the tin[9] (Fig. 1). The geometries are closely similar to each other and to those of the two independent components of **III**, where the bifunctional dicarboxylate array bridges a pair of Ph_3Sn moieties (Fig. 2). In **I** and **II**, the coordinated carboxylate planes are quasi-parallel to the parent phenyl-ring planes, although deviations of the tin atoms are non-trivial; in **III** the carboxylate planes are not coplanar with the parent-ring plane, and different patterns of phenyl-ring dispositions are observed, both presumably contingent upon interference of the coordinated components disposed at *ortho* sites of the phenyl ring. For similar steric reasons, presumably, the acetyl plane is quasi-normal [interplanar dihedral angle 86.8(1)°] to the parent-phenyl plane in **II**. In **I**, the C(3)–C(4)–O(4)–C(41) torsion angle is −5(1)°, with the C(4)–O(4)–C(41)–C(42) angle −178.4(7)°, i.e. as usual the alkoxy substituent is closely coplanar with the ring, and as usual O(4)–C(4)–C(3,5) are unsymmetrical [123.0(5), 116.9(5)°]. In each of the three compounds one discrete $(Ph_3SN)_nL$ unit makes up the asymmetric unit of the structure. The infrared modes ν(C═O) for the three compounds are consistent with those observed for other triphenyltin benzoates,[10] being 1630, 1640 and 1650 cm^{-1} respectively. Previous spectroscopic studies[4] of **III** had suggested a polymeric array, consistent

Table 3. Non-hydrogen positional and isotropic displacement parameters for **II**

Atom	*x*	*y*	*z*	*U*(eq) (Å^2)
Sn	0.42584(1)	0.08090(2)	0.11888(1)	0.04215(8)
C(11)	0.3097(2)	0.1379(3)	0.0309(1)	0.0456(9)
C(12)	0.2786(2)	0.0446(3)	−0.0263(2)	0.054(1)
C(13)	0.2056(3)	0.08(304)	−0.0870(2)	0.068(1)
C(14)	0.1636(3)	0.2063(5)	−0.0895(2)	0.077(2)
C(15)	0.1935(3)	0.2998(4)	−0.0336(2)	0.084(2)
C(16)	0.2664(3)	0.2654(4)	0.0265(2)	0.066(1)
C(21)	0.4494(2)	−0.1327(3)	0.1253(1)	0.0446(9)
C(22)	0.3716(2)	−0.2230(3)	0.1257(2)	0.054(1)
C(23)	0.3871(3)	−0.3603(4)	0.1366(2)	0.065(1)
C(24)	0.4814(3)	−0.4121(3)	0.1442(2)	0.070(1)
C(25)	0.5592(3)	−0.3251(4)	0.1427(2)	0.070(1)
C(26)	0.5434(2)	−0.1868(3)	0.1337(2)	0.054(1)
C(31)	0.5592(2)	0.1913(3)	0.1279(1)	0.047(1)
C(32)	0.6300(3)	0.1821(5)	0.1924(2)	0.083(2)
C(33)	0.7164(3)	0.2537(6)	0.1988(3)	0.112(2)
C(34)	0.7335(3)	0.3368(5)	0.1420(3)	0.098(2)
C(35)	0.6647(3)	0.3485(4)	0.0778(2)	0.080(2)
C(36)	0.5781(2)	0.2762(3)	0.0708(2)	0.059(1)
C(1)	0.3850(2)	0.2510(3)	0.3258(1)	0.0451(9)
C(101)	0.3809(2)	0.2220(3)	0.2440(2)	0.048(1)
O(101)	0.3917(2)	0.0958(2)	0.2254(1)	0.0547(7)
O(102)	0.3706(2)	0.3125(2)	0.1972(1)	0.0712(9)
C(2)	0.3860(2)	0.1535(3)	0.3816(2)	0.049(1)
O(201)	0.3704(2)	0.0167(2)	0.3643(1)	0.0564(8)
C(201)	0.4495(3)	−0.0602(3)	0.3558(2)	0.059(1)
O(202)	0.5309(2)	−0.0166(3)	0.3668(1)	0.087(1)
C(202)	0.4191(3)	−0.2004(4)	0.3314(2)	0.084(2)
C(3)	0.3947(2)	0.1898(4)	0.4569(2)	0.062(1)
C(4)	0.4015(3)	0.3248(4)	0.4766(2)	0.071(1)
C(5)	0.3991(3)	0.4249(3)	0.4224(2)	0.066(1)
C(6)	0.3910(2)	0.3883(3)	0.3481(2)	0.056(1)

with its insolubility in $CDCl_3$; NMR data were recorded in coordinating dimethyl sulfoxide (DMSO), perhaps contributing to the ambiguous conclusion regarding its complexity.

In contrast to **I**–**III**, the salicylaldehyde derivative, **IV** of stoichiometry $(Ph_3Sn)L$, has two such formula units in the asymmetric unit of the structure, comprising the independent asymmetric/repeat units of two independent strands of a polymeric structure (Fig. 3). The strands lie parallel to *b* and to each other in space group $P2_1/c$, the generator of each being a crystallographic 2_1 screw axis. The phenoxide and aldehyde functionalities of the symmetry-related anions of the same type coordinate different, symmetry-related tin atoms of the same type within a given polymer strand, the array being head-to-tail and the overall structure

–Sn(1)–HL(1)T–Sn(1′)–HL(1′)T–

parallel to

–Sn(2)–HL(2)T–Sn(2′)–HL(2′)T–

The tin atoms are both five-coordinate and similar in the dispositions of ligand components about each. Sn–O(phenoxide) [2.108(4), 2.087(5) Å] are appreciably shorter than the Sn–O(aldehyde) [2.427(4), 2.459(5) Å], not surprisingly so, since it is the phenoxide oxygen which is formally charged; more surprisingly, in the quasi-trigonal-bipyramidal tin environments in which, as in triphenyltin formate,[12] the phenyl groups are equatorial, O(*n*2)–Sn–C(*nm*1) [range: 89.6(2)–99.6(2)°] are uniformly greater than O(*n*101)–Sn(*n*)–C(*nm*1) [range: 83.3(2)–88.3(2)°], contrary to intuitive electron-pair repulsion arguments. Angles Sn–O(phenoxide)–

Table 4. Non-hydrogen positional and isotropic displacement parameters for **III**

Atom	*x*	*y*	*z*	*U* (eq) ($Å^2$)
Sn(1)	0.34489(2)	0.62409(3)	0.80137(5)	0.0456(1)
C(111)	0.3214(2)	0.5021(4)	0.8759(7)	0.055(2)
C(112)	0.2825(3)	0.4592(5)	0.800(1)	0.085(3)
C(113)	0.2672(3)	0.3804(5)	0.840(1)	0.099(4)
C(114)	0.2889(3)	0.3433(4)	0.960(1)	0.087(4)
C(115)	0.3269(3)	0.3828(5)	1.032(1)	0.094(4)
C(116)	0.3435(3)	0.4632(4)	0.9916(8)	0.069(3)
C(121)	0.3790(2)	0.6079(4)	0.5912(7)	0.046(2)
C(122)	0.3538(3)	0.5578(5)	0.4906(9)	0.081(3)
C(123)	0.3740(4)	0.5424(6)	0.3566(9)	0.107(4)
C(124)	0.4215(3)	0.5761(5)	0.3165(9)	0.084(3)
C(125)	0.4476(3)	0.6245(5)	0.4134(8)	0.072(3)
C(126)	0.4270(3)	0.6407(4)	0.5485(7)	0.060(3)
C(131)	0.2805(2)	0.7062(4)	0.8480(7)	0.050(2)
C(132)	0.2375(3)	0.6721(5)	0.917(1)	0.079(3)
C(133)	0.1947(3)	0.7204(5)	0.956(1)	0.104(4)
C(134)	0.1959(3)	0.8045(6)	0.933(1)	0.090(4)
C(135)	0.2383(3)	0.8408(5)	0.867(1)	0.084(3)
C(136)	0.2809(3)	0.7917(4)	0.8255(9)	0.065(3)
C(1)	0.4639(2)	0.7573(4)	1.0138(7)	0.047(2)
C(101)	0.4219(2)	0.7218(4)	0.9202(7)	0.047(2)
O(101)	0.4038(2)	0.6476(2)	0.9532(5)	0.051(2)
O(102)	0.4019(2)	0.7626(3)	0.8185(5)	0.057(2)
C(2)	0.5097(2)	0.7144(4)	1.0477(7)	0.046(2)
C(201)	0.5242(2)	0.6335(4)	0.9732(7)	0.052(2)
O(201)	0.5558(2)	0.5836(3)	1.0421(5)	0.060(2)
O(202)	0.5088(2)	0.6179(3)	0.8491(5)	0.056(2)
C(3)	0.5460(3)	0.7503(4)	1.1438(7)	0.058(3)
C(4)	0.5379(3)	0.8294(5)	1.203(1)	0.075(3)
C(5)	0.4930(3)	0.8725(5)	1.1644(9)	0.080(3)
C(6)	0.4562(3)	0.8376(4)	1.0713(9)	0.066(3)
Sn(2)	0.57219(2)	0.48434(3)	0.90061(5)	0.0511(1)
C(211)	0.6208(2)	0.4210(4)	1.0555(7)	0.048(2)
C(212)	0.6334(3)	0.3367(4)	1.0347(8)	0.062(3)
C(213)	0.6617(3)	0.2924(4)	1.1352(9)	0.073(3)
C(214)	0.6787(3)	0.3298(5)	1.2627(9)	0.066(3)
C(215)	0.6672(3)	0.4131(5)	1.2842(8)	0.067(3)
C(216)	0.6379(3)	0.4571(4)	1.1827(8)	0.062(3)
C(221)	0.5041(2)	0.4130(4)	0.8478(7)	0.054(2)
C(222)	0.4702(3)	0.4342(5)	0.7401(8)	0.069(3)
C(223)	0.4292(3)	0.3825(5)	0.7009(9)	0.074(3)
C(224)	0.4220(3)	0.3088(4)	0.7734(9)	0.070(3)
C(225)	0.4548(3)	0.2869(4)	0.883(1)	0.076(3)
C(226)	0.4964(3)	0.3378(4)	0.9206(8)	0.061(3)
C(231)	0.6158(3)	0.5350(4)	0.7234(8)	0.055(2)
C(232)	0.5917(3)	0.5646(5)	0.5993(9)	0.081(3)
C(233)	0.6200(4)	0.6001(5)	0.488(1)	0.097(4)
C(234)	0.6722(4)	0.6076(5)	0.494(1)	0.110(4)
C(235)	0.6974(3)	0.5807(6)	0.615(1)	0.116(4)
C(236)	0.6702(3)	0.5425(5)	0.731(1)	0.090(4)

Table 5. Non-hydrogen positional and isotropic displacement parameters for **IV**

Atom	*x*	*y*	*z*	*U* (eq) ($Å^2$)
Sn(1)	0.48117(3)	0.50722(3)	0.26161(3)	0.0528(2)
C(111)	0.5959(4)	0.4414(4)	0.2914(4)	0.054(3)
C(112)	0.6579(5)	0.4566(5)	0.3618(4)	0.071(3)
C(113)	0.7323(5)	0.4123(6)	0.3750(5)	0.082(4)
C(114)	0.7486(5)	0.3554(6)	0.3210(5)	0.082(4)
C(115)	0.6885(5)	0.3383(5)	0.2510(5)	0.073(4)
C(116)	0.6138(4)	0.3809(5)	0.2365(4)	0.063(3)
C(121)	0.3995(4)	0.5185(4)	0.3317(4)	0.056(3)
C(122)	0.3565(5)	0.4470(6)	0.3499(5)	0.084(4)
C(123)	0.2948(6)	0.4536(6)	0.3882(6)	0.095(4)
C(124)	0.2730(6)	0.5359(7)	0.4091(5)	0.094(4)
C(125)	0.3127(5)	0.6095(6)	0.3934(5)	0.087(4)
C(126)	0.3735(5)	0.6032(5)	0.3553(5)	0.073(3)
C(131)	0.4643(4)	0.5924(4)	0.1604(4)	0.051(3)
C(132)	0.4075(5)	0.6622(5)	0.1446(5)	0.072(3)
C(133)	0.3996(6)	0.7174(6)	0.0793(5)	0.092(4)
C(134)	0.4458(6)	0.7046(6)	0.0279(6)	0.101(5)
C(135)	0.4996(5)	0.6347(7)	0.0401(6)	0.099(5)
C(136)	0.5097(5)	0.5797(5)	0.1077(5)	0.071(3)
C(11)	0.3883(4)	0.2718(4)	0.1125(4)	0.044(2)
C(1101)	0.4378(4)	0.2097(4)	0.1704(4)	0.050(3)
O(1101)	0.4457(3)	0.1297(3)	0.1567(3)	0.065(2)
C(12)	0.3847(4)	0.3631(4)	0.1328(4)	0.045(2)
O(12)	0.4226(3)	0.3899(3)	0.2052(3)	0.064(2)
C(13)	0.3363(4)	0.4201(4)	0.0749(4)	0.056(3)
C(14)	0.2942(5)	0.3879(5)	0.0021(4)	0.072(3)
C(15)	0.2980(5)	0.2971(5)	−0.0175(4)	0.080(3)
C(16)	0.3452(5)	0.2408(4)	0.0356(4)	0.070(3)
Sn(2)	0.99089(3)	0.31932(3)	0.74426(3)	0.0466(2)
C(211)	0.9135(4)	0.2491(4)	0.6448(4)	0.047(2)
C(212)	0.9202(5)	0.2631(5)	0.5677(4)	0.069(3)
C(213)	0.8707(6)	0.2127(6)	0.5039(5)	0.088(4)
C(214)	0.8171(5)	0.1518(6)	0.5175(5)	0.091(4)
C(215)	0.8114(5)	0.1375(5)	0.5926(6)	0.089(4)
C(216)	0.8607(4)	0.1854(5)	0.6573(5)	0.069(3)
C(221)	1.1174(4)	0.3262(5)	0.7560(4)	0.060(3)
C(222)	1.1597(5)	0.2485(5)	0.7431(5)	0.071(3)
C(223)	1.2410(5)	0.2528(6)	0.7463(5)	0.087(4)
C(224)	1.2841(5)	0.3314(7)	0.7664(5)	0.091(4)
C(225)	1.2445(5)	0.4079(6)	0.7775(5)	0.079(4)
C(226)	1.1630(4)	0.4052(5)	0.7718(4)	0.061(3)
C(231)	0.9390(4)	0.4127(4)	0.8081(4)	0.049(3)
C(232)	0.9845(5)	0.4751(5)	0.8625(4)	0.062(3)
C(233)	0.9471(5)	0.5367(5)	0.8998(5)	0.077(4)
C(234)	0.8652(5)	0.5385(5)	0.8850(5)	0.079(4)
C(235)	0.8180(5)	0.4797(6)	0.8310(5)	0.085(4)
C(236)	0.8551(5)	0.4166(5)	0.7943(4)	0.069(3)
C(21)	1.0488(4)	0.0898(4)	0.9056(4)	0.046(2)
C(2101)	1.0180(4)	0.0242(4)	0.8432(4)	0.056(3)

Table 5. Continued.

O(2101)	1.0231(3)	−0.0573(3)	0.8534(3)	0.065(2)
C(22)	1.0381(4)	0.1818(4)	0.8866(4)	0.052(3)
O(22)	0.9924(3)	0.2059(3)	0.8159(3)	0.068(2)
C(23)	1.0758(5)	0.2434(5)	0.9466(4)	0.073(3)
C(24)	1.1198(5)	0.2141(5)	1.0203(5)	0.082(4)
C(25)	1.1277(5)	0.1225(5)	1.0402(4)	0.070(3)
C(26)	1.0919(4)	0.0620(4)	0.9829(4)	0.059(3)

C [138.0(4), 133.2(4)°] are comparable with Sn–O(aldehyde)–C [132.7(4), 130.3(4)°]; the *'trans'* O–C–C–C torsion angles of the aldehyde group [−178.3(7), −179.1(7)°] and associated Sn′–O–C–C [−178.1(5), −162.4(5)°] are indicative of a substantial coplanarity throughout the string. The parent C_6-ring planes lie quasi-parallel to the polymer axis *b* and thus to successive members of each polymer strand (at 11.4 and 1.6° respectively to the axis), presenting an orientation appropriate for possible conjugation within each strand. This provides a possible basis for the rationalization of the bright green–yellow colour of the complex which is

Table 6. Tin environments in compounds **I–IV**

	I	**II**	**III/1**	**111/2[a]**	**IV/1**	**IV/2[a]**
Distances (Å)						
Sn–C(11)	2.107(7)	2.118(3)	2.142(7)	2.132(6)	2.113(7)	2.134(6)
Sn–C(21)	2.135(5)	2.119(3)	2.122(7)	2.125(6)	2.082(8)	2.105(7)
Sn–C(31)	2.119(6)	2.115(3)	2.136(6)	2.120(7)	2.116(7)	2.108(7)
Sn–O(101)	2.050(4)	2.061(2)	2.075(4)	2.082(5)	2.108(4)[b]	2.087(5)
Sn–O(102)	2.837(4)	2.848(2)	2.642(4)	2.708(4)	2.427(4)[b]	2.459(5)
Angle (deg.)						
C(11)–Sn–C(21)	110.6(2)	112.9(1)	107.0(2)	111.7(2)	127.6(3)	119.4(3)
C(11)–Sn–C(31)	119.0(2)	117.0(1)	106.1(2)	112.6(2)	112.8(3)	119.4(2)
C(11)–Sn–O(101)	111.2(2)	114.2(1)	98.7(2)	93.6(2)	91.1(2)	89.6(2)
C(11)–Sn–O(102)	83.5(2)	85.83(9)	152.9(2)	146.2(2)	84.9(2)	83.3(2)
C(21)–Sn–C(31)	107.4(2)	112.2(1)	124.5(2)	117.1(3)	118.2(3)	118.5(3)
C(21)–Sn–O(101)	95.3(2)	94.44(9)	109.4(2)	112.5(2)	91.8(2)	97.7(2)
C(21)–Sn–O(102)	145.9(2)	144.34(9)	86.0(2)	84.0(2)	85.2(2)	86.3(2)
C(31)–Sn–O(101)	110.7(2)	103.4(1)	108.0(2)	106.9(2)	99.6(2)	99.0(2)
C(31)–Sn–O(102)	90.7(2)	82.0(1)	84.2(2)	83.1(2)	88.3(2)	84.1(2)
O(101)–Sn–O(102)	50.7(1)	49.92(7)	54.2(1)	52.7(2)	172.1(2)	172.9(2)
Sn–O(101)–C(101)	111.3(3)	111.3(2)	105.3(4)	106.7(4)	138.0(4)	133.2(4)
Sn–O(102)–C(101)	76.1(3)	75.7(2)	80.3(3)	78.9(4)	132.7(4)	130.3(4)
Torsion angle (deg.)						
O(101)–Sn–C(11)–C(12)	−109.6(4)	−124.3(2)	−177.8(6)	163.6(5)	−145.1(6), 28.1(6)	−145.4(6), 35.2(5)
O(101)–Sn–C(21)–C(22)	59.5(6)	69.1(2)	151.7(5)	84.3(6)	23.9(6), −148.7(6)	49.7(6), −124.4(6)
O(101)–Sn–C(31)–C(32)	11.0(5)	39.0(3)	−103.6(6)	−90.7(6)	105.2(6), −75.8(6)	99.1(6), −87.4(6)
C_2O_2/C_6 plane parameters: dihedral angle, θ (deg.) and deviation (δÅ) of Sn from C_2O_2, C_6 planes						
θ	3.5(2)	9.8(1)	50.3(2)	29.2(2)	—	—
$\delta(C_2O_2)$	0.210(8)	0.548(4)	0.010(9)	0.122(9)	0.61(1), −0.04(2)	0.52(1), 0.92(2)
$\delta(C_6[1])$	0.19(1)	0.084(5)	0.04(1)	0.13(1)	0.08(1)	0.07(1)
$\delta(C_6[2])$	0.10(1)	0.153(5)	0.08(1)	0.17(1)	0.25(1)	0.05(1)
$\delta(C_6[3])$	0.24(1)	0.021(5)	0.12(1)	0.08(1)	0.03(1)	0.09(1)

[a] Read 2 as the first digit of the ligand atom number, as appropriate.
[b] For O(101, 2) read O(12), O(1101′); similarly for part 2. The two entries in the torsion angles pertain to phenoxide and aldehyde functionalities respectively and in the δ values for δSn from the associated C_6 plane.

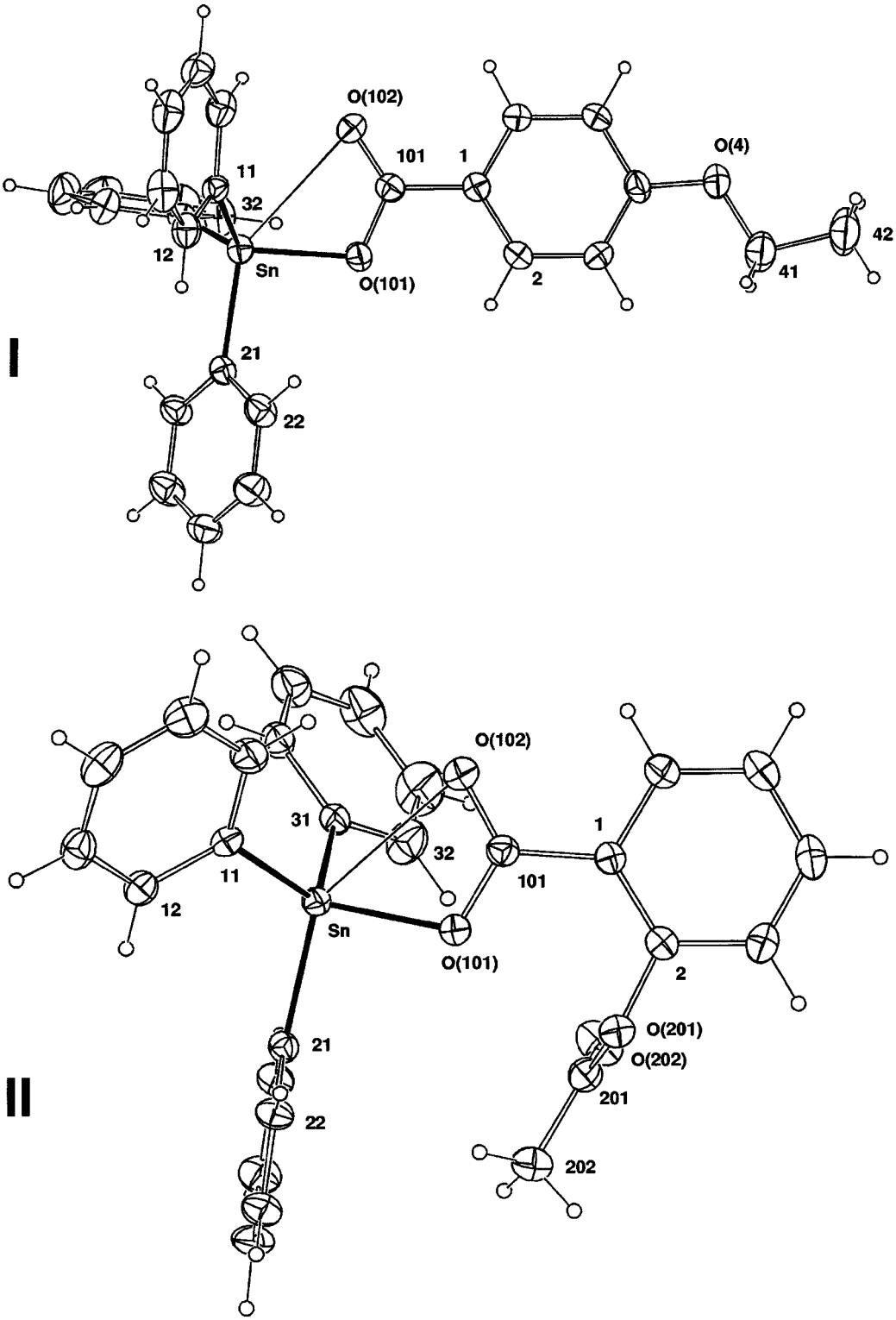

Figure 1 Projections of individual molecules of **I** and **II**.

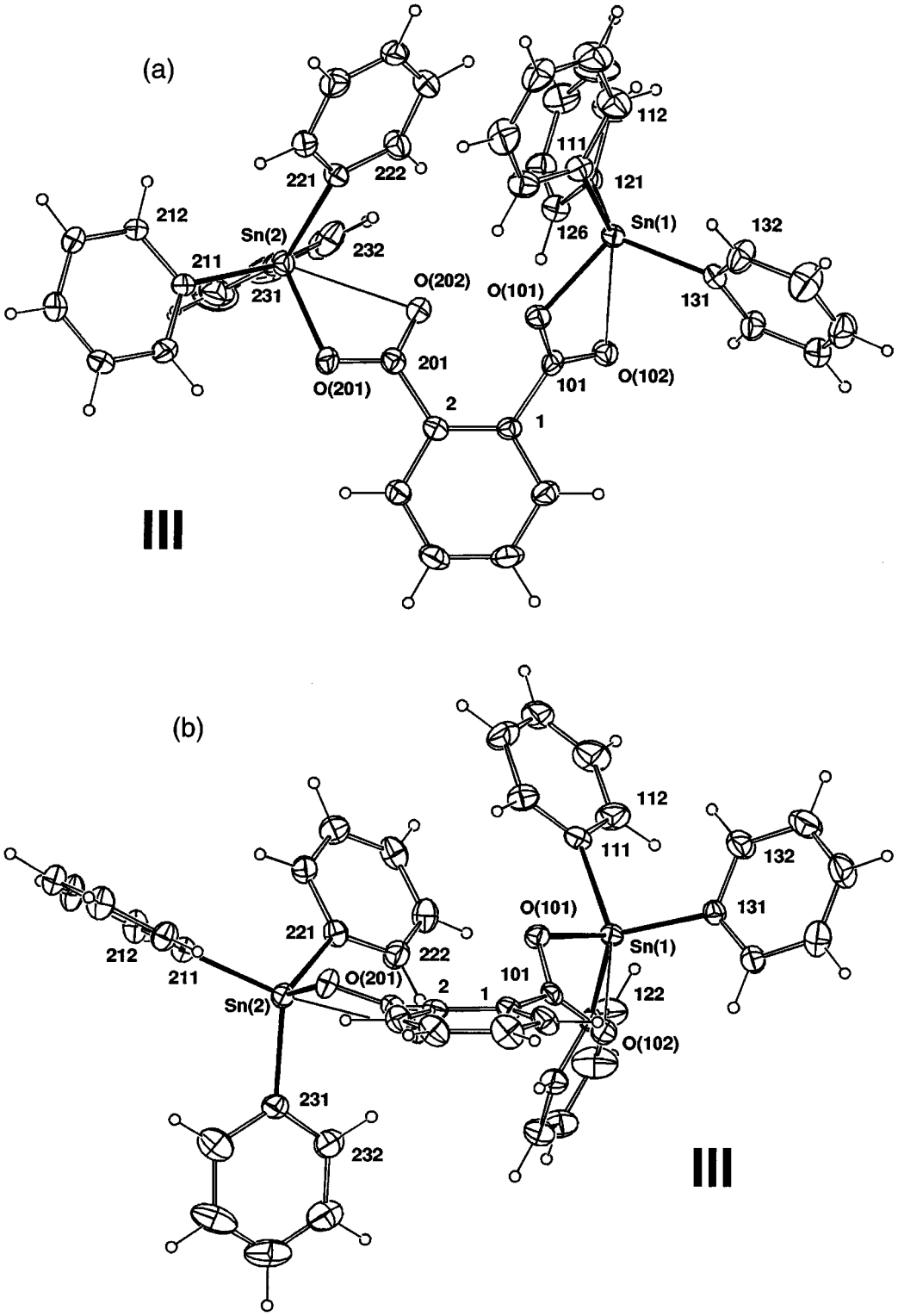

Figure 2 Projections of **III** (a) normal to and (b) (approximately) through the central C_6 plane.

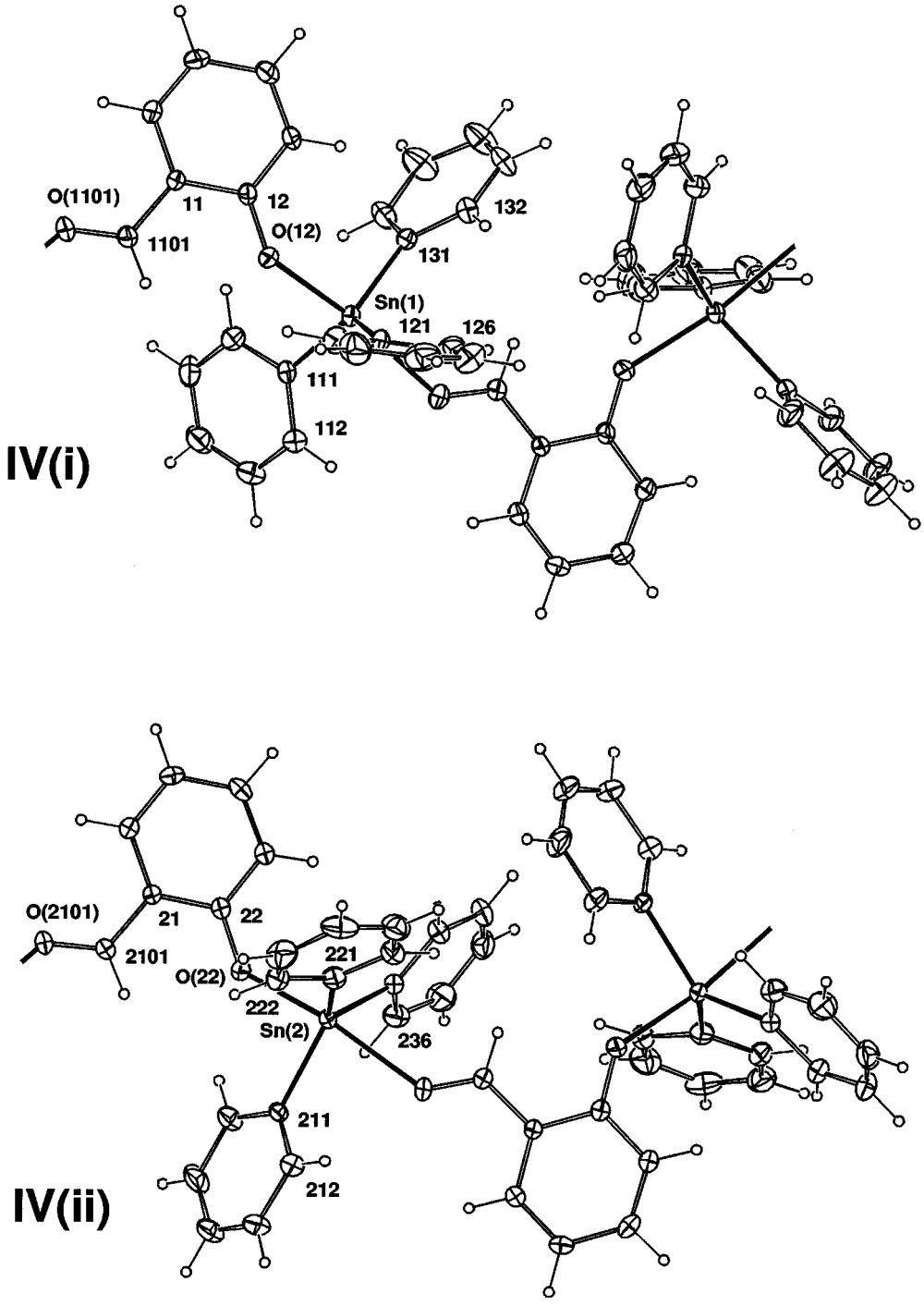

Figure 3 The two independent strands of the polymer of **IV**, projected normal to the central salicylate C_6 plane.

completely discharged in solution (ethanol or chloroform), the NMR data being consistent with a four-coordinate structure,[4] and the fungicidal activity possibly related to the ability of the complex to dissociate in this manner, an effect previously noted for triphenyltin benzoates.[10] The ν(C═O) is shifted from 1661 cm^{-1} in the parent ligand to 1622 cm^{-1} in the present complex.

It is interesting to note that in studies of fungitoxicity[7] the phthalic acid derivative was somewhat less active than that of salicylaldehyde. This may reflect the different molecular sizes involved in the mechanism,[12] although the role of hydrolysis (or aquation) in the test matrix is rather unclear.

Acknowledgements We thank the Australian Research Council for support of this work (BDJ, AHW).

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