

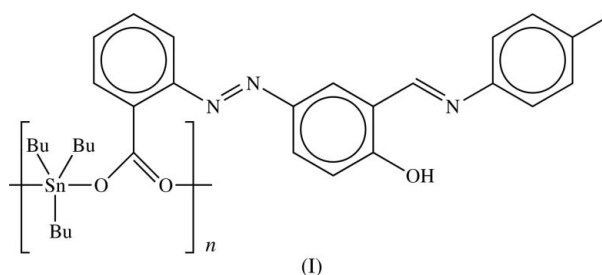
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Key indicators

Single-crystal X-ray study
 $T = 160$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
Disorder in main residue
 R factor = 0.037
 wR factor = 0.088
Data-to-parameter ratio = 17.7For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.**catena-Poly[[tri-*n*-butyltin(IV)]- μ -2-{(E)-4-hydroxy-3-[(E)-4-methylphenyliminomethyl]phenyldiazenyl]-benzoato- $\kappa^2\text{O}:\text{O}'$]**The title compound, $[\text{Sn}(\text{C}_4\text{H}_9)_3(\text{C}_{21}\text{H}_{16}\text{N}_3\text{O}_3)]_n$, is a one-dimensional polymer in which the two carboxylate O atoms of a single benzoate ligand bridge adjacent SnBu_3 groups. The Sn atom has a slightly distorted *trans*- Bu_3SnO_2 trigonal-bipyramidal coordination geometry.

Comment

The title compound, (I), was prepared during an ongoing study of the coordination chemistry of organotin carboxylates of polyaromatic compounds containing an azo and a Schiff base linkage (Basu Baul *et al.*, 2004; Basu Baul, Singh, Holčapek, Jirásko, Linden *et al.*, 2005; Basu Baul, Singh, Holčapek, Jirásko, Rivarola & Linden, 2005; Basu Baul, Singh, Lyčka *et al.*, 2005; Butcher *et al.*, 2005). These compounds, particularly the tri-*n*-butyltin(IV) complexes, have been demonstrated to possess significant biological activity towards *Aedes aegypti* and *Anopheles stephensi* mosquito larvae (Basu Baul *et al.*, 2004; Basu Baul, Singh, Holčapek, Jirásko, Linden *et al.*, 2005) and sea urchin (*Paracentrotus lividus* and *Sphaerechinus granularis*) early development stages (Basu Baul, Rynjah *et al.*, 2005). Critical to the rationalization of the mode of action of organotin carboxylates is an understanding of their molecular structure and, as a consequence, the crystal structures of many members of this class of compound have been studied. It was in this context that the title compound, (I), was investigated.The solid-state structure of complex (I) is a one-dimensional polymer. The asymmetric unit of the crystal structure contains just one of the principal chemical units (Fig. 1). The two carboxylate O atoms of a single benzoate ligand bridge adjacent SnBu_3 groups (Bu = *n*-butyl) and the pattern then repeats to give a continuous single-stranded polymeric structure, as illustrated in Fig. 2. The primary coordination sphere of the Sn atom has a slightly distorted *trans*- Bu_3SnO_2 trigonal bipyramidal geometry (Table 1) with equatorial *n*-butyl groups and carboxylate O atoms occupying axial positions, one being from each of two symmetry-related benzoate ligands. The carboxylate C—O bond lengths are not equiva-

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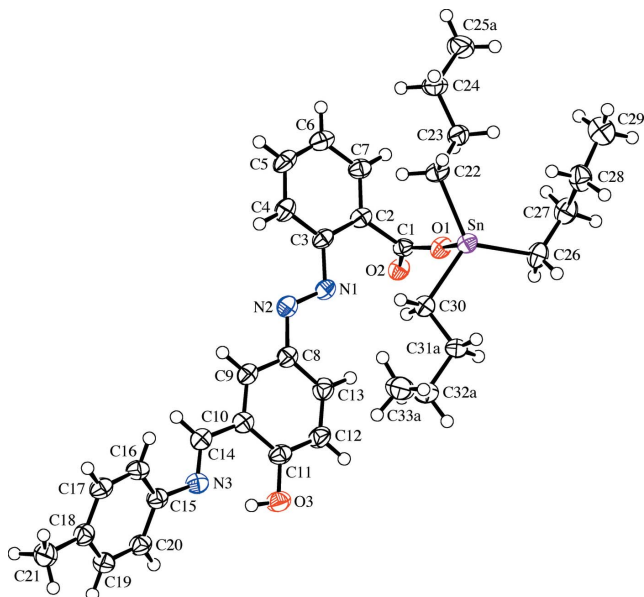


Figure 1
View of the asymmetric unit of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. Only one conformation of the disordered *n*-butyl groups is shown.

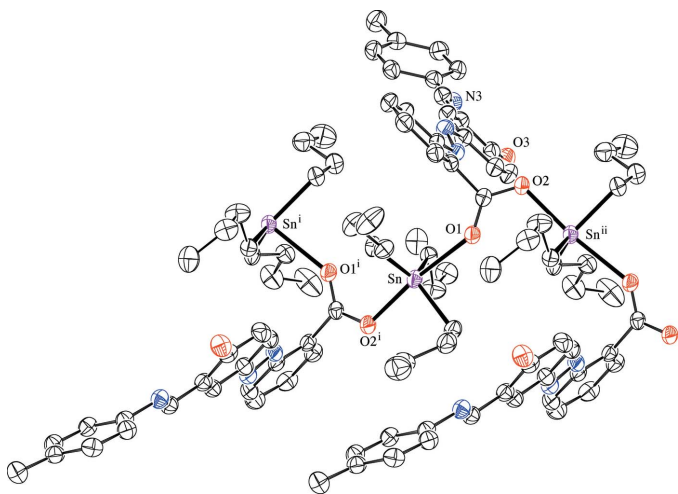


Figure 2
A three-unit segment of the polymeric chain in (I). Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. [Symmetry codes: (i) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$.]

lent, which shows some distinction between the carbonyl and carboxylic acid O atoms. Correspondingly, the Sn—O bond lengths involving these O atoms are also not equivalent, with the Sn—O bond to the carbonyl O atom being the longer, as would be expected on electronic grounds. The carboxylate O atom involved in the longer of the axial Sn—O bonds also has a weak interaction with the next Sn atom in the chain, with an Sn···O distance of 3.1371 (18) Å, thus generating six-coordination in the extended coordination sphere of the Sn atom. Although this distance is well inside the sum of the van der Waals radii of the Sn and O atoms (*ca* 3.6 Å), the trigonal-bipyramidal geometry of the primary coordination sphere is distorted minimally as a result of this contact. The phenolic

hydroxy group in each ligand forms an intraligand hydrogen bond with the adjacent imine N atom (Table 2). The terminal methyl group in one of the *n*-butyl ligands and the terminal propyl segment of another *n*-butyl ligand are disordered over two conformations. Such disorder is common for complexes involving the Bu₃Sn core.

Complex (I) has a 4-methylphenyl group in the benzoate ligand and is isomorphous and isostructural with the 4-chlorophenyl analogue (Basu Baul *et al.*, 2004). The structure of (I) corresponds with the type II polymeric motif described by Willem *et al.* (1998) for similar R₃SnO₂CR' compounds and observed in the crystal structures of the 4-chlorophenyl and 4-methoxyphenyl analogues of (I) (Basu Baul *et al.*, 2004; Basu Baul, Singh, Holčapek, Jirásko, Linden *et al.*, 2005), and in the tri-*n*-butyltin(IV) complexes with the 2-[(*E*)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]benzoate and 2-hydroxyphenylmethylimino- β -alaninate ligands (Basu Baul *et al.*, 2004, 2006). In (I), the repeat Sn···Sn distance is 5.2583 (3) Å, which agrees well with the mean repeat distance found in other type II carboxylate-bridged triorganotin species of 5.19±0.21 Å (Ng *et al.*, 1988) and shows again that the repeat distance is independent of the nature of the tin-bound substituents and carboxylate residues. As in the earlier reports (Willem *et al.*, 1998; Basu Baul *et al.*, 2004, 2006), the polymeric chain in the structure of (I) propagates in a 2₁ screw fashion coincident with a crystallographic 2₁ screw axis.

Experimental

The preparation and spectroscopic data of the title compound have been described by Basu Baul *et al.* (2004). Red prismatic crystals were obtained from the slow evaporation of a solution of (I) in hexane-dichloromethane (m.p. 362–364 K).

Crystal data

[Sn(C₄H₉)₃(C₂₁H₁₆N₃O₃)]
M_r = 648.32
 Monoclinic, P2₁/n
a = 14.1439 (2) Å
b = 9.9908 (2) Å
c = 23.2964 (4) Å
 β = 105.1374 (9)°
V = 3177.76 (10) Å³
Z = 4

D_x = 1.355 Mg m⁻³
 Mo K α radiation
 Cell parameters from 66752 reflections
 θ = 2.0–27.5°
 μ = 0.84 mm⁻¹
T = 160 (1) K
 Prism, red
 0.32 × 0.17 × 0.10 mm

Data collection

Nonius KappaCCD area-detector diffractometer
 φ and ω scans with κ offsets
 Absorption correction: multi-scan (Blessing, 1995)
T_{min} = 0.752, *T_{max}* = 0.929
 66753 measured reflections

7243 independent reflections
 5802 reflections with *I* > 2 σ (*I*)
R_{int} = 0.075
 θ_{max} = 27.4°
h = -18 → 18
k = -12 → 12
l = -30 → 30

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.037
wR (*F*²) = 0.088
S = 1.06
 7241 reflections
 409 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0358P)^2 + 3.0855P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.002$
 $\Delta\rho_{max} = 1.16 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{min} = -0.62 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Sn—C30	2.135 (3)	Sn—O1 ⁱ	3.1371 (18)
Sn—C26	2.148 (3)	O1—C1	1.244 (3)
Sn—C22	2.149 (3)	O2—C1	1.277 (3)
Sn—O2 ⁱ	2.2087 (18)	N1—N2	1.264 (3)
Sn—O1	2.4560 (18)	N3—C14	1.282 (4)
C30—Sn—C26	115.99 (11)	C22—Sn—O2 ⁱ	96.22 (9)
C30—Sn—C22	122.01 (11)	C30—Sn—O1	86.40 (9)
C26—Sn—C22	121.00 (11)	C26—Sn—O1	84.17 (9)
C30—Sn—O2 ⁱ	93.88 (9)	C22—Sn—O1	89.32 (9)
C26—Sn—O2 ⁱ	89.67 (9)		

Symmetry code: (i) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$.**Table 2**

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O3—H3...N3	0.87 (4)	1.79 (4)	2.591 (3)	152 (3)

The terminal methyl group in one of the butyl ligands and the terminal propyl segment of another butyl ligand are disordered over two conformations each. Two sets of overlapping positions were defined for the disordered atoms and the refinement of constrained site occupation factors yielded values of 0.52 (5) and 0.707 (12), respectively, for the major conformations of the disordered groups. Similarity restraints were applied to the chemically equivalent bond lengths and angles involving disordered C atoms, while neighbouring disordered atoms were restrained to have similar atomic displacement parameters. The hydroxy H atom was located in a difference Fourier map and its position was refined freely along with an isotropic displacement parameter. The methyl H atoms were constrained to an ideal geometry with C—H = 0.98 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$, but were allowed to rotate freely about the C—C bonds. All remaining H atoms were placed in geometrically idealized positions (C—H = 0.95–0.99 Å) and constrained to ride on their parent atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Two low-angle reflections were omitted from the final cycles of refinement because their observed intensities were much lower than the calculated values as a result of being partially

obscured by the beam stop. The highest residual electron-density peak is located 1.43 Å from C3 and 1.47 Å from N1, thus forming a triangle leaning towards the Sn atom.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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