Synthesis, characterisation and crystal structures of asymmetric (*Z*)-1-[2-(triphenylstannyl)vinyl]-1-indanol and its diphenylbromostannyl derivative

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Asymmetric (*Z*)-1-[2-(triphenylstannyl)vinyl]-1-indanol **1** and (*Z*)-1-[2-(bromo- diphenylstannyl)vinyl]-1-indanol **2** were synthesised and characterised by elemental analysis, ^{1}H NMR, FT–IR spectroscopy and X-ray diffraction analysis.

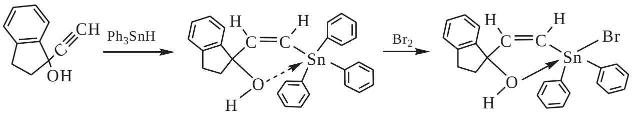
Keywords: organotin compounds, phenyltin compounds, FT–IR spectroscopy, ^{1}H NMR spectroscopy, X-ray crystal structure

Recently, the synthesis and antitumour activity of organotin compounds of the type $(Z)\text{-}\overline{CH_2(CH_2)_nC}(OH)CH{=}CHSnAr_3$ (Ar = phenyl and *p*-tolyl; *n* = 3, 4 and 5), with intramolecular O→Sn coordination have been actively studied. In particular, the effects of the symmetric 1-vinyl-1-hydroxy $[\overline{CH_2(CH_2)_n(HO)C}CH{=}CH\text{-}]$ alkyl groups on both the structure and the antitumour activity of this type of compound have been extensively reported.[1–4] To the best of our knowledge, asymmetric (at C-1) 1-vinyl-1-hydroxy alkyl group-substituted organotin compounds have not yet been reported. We report here the synthesis and structure of asymmetric (*Z*)-1-[2-(triphenylstannyl)vinyl]-1-indanol **1** and (*Z*)-1-[2-(bromodiphenylstannyl)vinyl]-1-indanol **2**. Their structural features, particularly the HO→Sn coordination interaction, are discussed. These compounds are likely to serve as new models for further investigations of structure–antitumour activity relationships.

The compounds **1** and **2** were synthesised according to Scheme 1. The indanol **1** was prepared by the addition of triphenyltin hydride to the triple bond of 1-ethynylindanol and the reaction of **1** with bromine in a 1:1 molar ratio yielded **2**.

The molecular structures of **1** and **2** are given in Figs 1 and 2 and selected distances and bond angles are listed in Table 1. The Sn atom in **1**, bonded to three phenyl groups and the C(19) atom of the vinyl residue, adopts a distorted tetrahedral geometry, with C–Sn(1)–C angles ranging from 101.9(3) to 117.5(3)°. The C(7)–Sn(1)–C(19) angle [117.5(3)°] is significantly larger than the other C–Sn(1)–C angles due to weak coordination of the O(1) atom of the indanol hydroxyl group. The distance between the O(1) and the Sn(1) atoms is 2.778(8) Å, which is significantly less than the sum of their van der Waals radii [3.70 Å].[5] The weak coordination of the O(1) atom also influences the strength of the Sn(1)–C(phenyl) bond and as a result[6], the Sn(1)–C(1) is longer by 0.02 Å than the other two Sn–C(phenyl) bonds. The fact that the *Z* isomer rather than the *E* isomer was obtained from this type of reaction may be attributed to the weak intramolecular O→Sn coordination.[2,4]

The Sn atom in **2** is five coordinate and the molecule has a distorted trigonal bipyramidal geometry with the trigonal plane defined by the C(1), C(11) and C(21) atoms and the axial positions occupied by the Br(1) and O(1) atoms. This is similar to the reported analogue (*Z*)-1-[2-(chlorodi-*p*-tolylstannyl)vinyl]-1-cycloheptanol.[2] The Sn(1)···O(1) distance of 2.375(6) Å is in the range of a normal Sn–O coordination bond length,[2,3,4] indicating that the Sn atom in **2** is formally coordinated by the O(1) atom of the hydroxyl group and that the Lewis acidity of the Sn atom in the $(phenyl)_2SnBr$ moiety is greater than that in the $(phenyl)_3Sn$ moiety. On the other hand, the O(1)–C(31) bond (1.456(10) Å) in **2** is weaker than the corresponding bond (1.435(8) Å) in **1** due to the strong coordination interaction between the O(1)



1 **2**

Scheme 1

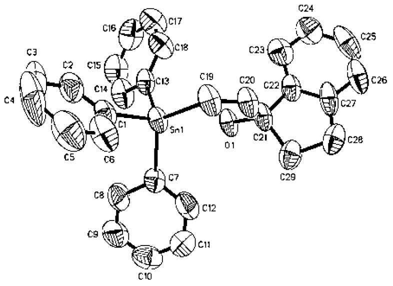


Fig. 1 The molecular structure and crystallographic numbering scheme for **1**.

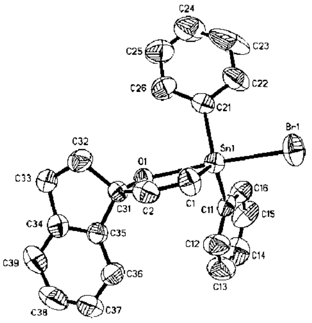


Fig. 2 The molecular structure and crystallographic numbering scheme for **2**.

Table 1 Selected bond distances (/Å) and angles (°) in 1 and 2

Parameter	1	Parameter	2
Sn(1)–C(7)	2.116(8)	Sn(1)–C(1)	2.112(9)
Sn(1)–C(19)	2.139(7)	Sn(1)–C(21)	2.145(9)
Sn(1)–C(13)	2.140(8)	Sn(1)–C(11)	2.156(8)
Sn(1)–C(1)	2.161(7)	Sn(1)–Br(1)	2.6204(15)
Sn(1)–O(1)	2.778(8)	Sn(1)–O(1)	2.375(6)
O(1)–C(21)	1.435(8)	O(1)–C(31)	1.456(10)
C(19)–C(20)	1.303(11)	C(1)–C(2)	1.345(12)
C(20)–C(21)	1.514(10)	C(2)–C(31)	1.503(12)
C(7)–Sn(1)–C(19)	117.5(3)	C(1)–Sn(1)–C(21)	120.9(4)
C(7)–Sn(1)–C(13)	113.6(3)	C(1)–Sn(1)–C(11)	121.3(4)
C(19)–Sn(1)–C(13)	113.1(3)	C(21)–Sn(1)–C(11)	113.0(3)
C(7)–Sn(1)–C(1)	102.8(3)	C(1)–Sn(1)–Br(1)	96.1(2)
C(19)–Sn(1)–C(1)	101.9(3)	C(11)–Sn(1)–Br(1)	98.4(2)
C(13)–Sn(1)–C(1)	105.8(3)	C(21)–Sn(1)–Br(1)	97.5(2)
Sn(1)–C(19)–C(20)	127.8(6)	Br(1)–Sn(1)–O(1)	169.12(15)
O(1)–C(21)–C(20)	105.7(6)	Sn(1)–C(1)–C(3)	120.9(7)
		O(1)–C(31)–C(2)	107.8(7)

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and the Sn(1) atoms. The Sn(1)–C(1)–C(2) angle (120.9(7)°) in **2** is considerably smaller than the equivalent angle (127.8(6)°) in **1** and the C(1)–C(2) bond (1.345(12) Å) in **2** is longer than the corresponding bond (1.303(11) Å) in **1**, which apparently results from the strain of the five-membered ring.

The solution ^{1}H NMR spectra of **1** and **2** are consistent with their structures. All spectra show characteristic ethylenic proton signals of doublet of doublets with $^3J_{(HC=CH)}$ = 12.0–13.6 Hz in the regions of 6.41–6.42 and 6.95–6.96 ppm. The $^3J_{(HC=CH)}$ coupling constant of 13.6 Hz observed for **1** is quite large, since the *cis* coupling constants in similar compounds with a five-membered ring substituent are usually 8 Hz or less.[7] With regard to the stannyl group, the $^3J_{(HC=CH)}$ coupling constant decreases in the order Sn(phenyl)$_3$ > Sn(phenyl)$_2$Br. The chemical shift of the OH proton shifts to high field in the same order, which indicates that the strength of the HO→Sn interaction increases with the decrease in the steric hindrance of the stannyl group.

Experimental

Melting points were determined on a Yanaco melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded in CDCl$_3$ on a Varian Mercury 300 MHz spectrometer. Infrared spectra (KBr pellets) were recorded on an Alpha Centauri FI/IR spectrometer (400–4000cm^{-1} range). Elemental analyses were carried out on a Perkin-Elmer PE 2400 CHN instrument and gravimetric analysis was used for Sn.

CAUTION: Triphenyltin hydride, dibenzoyl peroxide and benzene should be handled with appropriate precautions.

Preparation of (Z)-1-[2-(triphenylstannyl)vinyl]-1-indanol **1**: 1-Ethynylindanol and triphenyltin hydride were prepared according to the literature methods.[8,9]

A mixture of 1-ethynylindanol (15.82 g, 100 mmol) and triphenyltin hydride (35.10 g, 100 mmol) was placed in a 3-necked flask (250 ml) equipped with a condenser carrying a CaCl$_2$ tube and benzene (100ml) and dibenzoyl peroxide (200mg) were then added to this mixture under nitrogen. After magnetic stirring for 35 h at room temperature, the benzene was evaporated and the residue was crystallised from ethanol. Product **1** was obtained in 57% yield (35.24 g), m.p. 134.3–135.1 °C. Elemental analysis: Found (Calcd) $C_{29}H_{26}OSn$: C, 68.25 (68.40); H, 5.21 (5.15); Sn, 23.17 (23.31)%. IR (KBr pellets): ν_{CO}: 1072 cm^{-1}, ν_{OH}: 3555 cm^{-1}. ^{1}H NMR (CDCl$_3$, ppm): δ: 1.58 (s, OH); 6.41 (d, J_{HH}= 13.6 Hz, =CH-Sn); 6.95 (d, J_{HH} = 13.6 Hz, CH=); 7.02–7.75 (m, Ph); 2.11–2.34, 2.85–3.14 (m, CH$_2$-CH$_2$).

Preparation of (Z)-1-[2-(bromodiphenylstannyl)vinyl]-1-indanol **2**: A solution of bromine (0.48 g, 3.0 mmol) in 20 ml of chloroform was added dropwise with magnetic stirring to a solution of **1** (1.52 g, 3.0 mmol) in 20 ml of the same solvent at room temperature. The colour disappeared immediately. After having added the last drop of bromine yielding a persistent colour, the reaction mixture was stirred for 2 h and the solvent was then evaporated. The residue was recrystallised from cyclohexane. Product **2** was obtained in 87% yield (1.34 g). m.p. 159–160 °C. Elemental analysis: Found (Calcd) $C_{23}H_{21}BrOSn$: C, 53.81 (53.95); H, 4.24 (4.13); Sn, 23.28 (23.18)%. IR (KBr pellets): ν_{CO}: 1075 cm^{-1}, ν_{OH}: 3410 cm^{-1}. ^{1}H NMR (CDCl$_3$, ppm): δ: 2.64 (s, OH); 6.42 (d, J_{HH}= 12.0 Hz, =CH-Sn); 6.96 (d, J_{HH} = 12.0 Hz, CH=); 7.06–7.72 (m, Ph); 2.08–2.96, 2.85–3.16 (m, CH$_2$-CH$_2$).

Crystal data **1**: $C_{29}H_{26}OSn$, *Mr* = 509.19, triclinic, $P\bar{1}$, *a* = 9.152(4) Å, *b* = 11.461(2) Å, *c* = 12.454(5) Å, α = 76.39(3)°, β = 77.17(3)°, γ = 76.07(2)°, *V* = 1213.2(7) Å^3, *Z* = 2, D_x = 1.394 gcm^{-3}, *F*(000) = 516, μ = 1.070 cm^{-1}, *T* = 298 K. Diffraction data for **1** were collected on a Siemens P4 diffractometer with graphite monochromatised Mo K$_\alpha$ (λ = 0.71073 Å) at ambient temperature. The structures were solved by the direct methods (SHELXS 97),[10] and were refined by full-matrix least squares techniques (SHELXL 97).[11] Non-hydrogen atoms were refined anisotropically. The hydrogen atoms were generated geometrically. A total of 4665 reflections were collected. The final cycle of full-matrix least-squares refinement was based on 3445 observed reflections (I>2α(I)) and 280 variable parameters and converged with R_1 = 0.0735 and wR_2 = 0.1958.

Crystal data **2**: $C_{23}H_{21}BrOSn$, *Mr* = 512.00, monoclinic, *P*2(1)/n, *a* = 11.891(2) Å, *b* = 13.586(3) Å, *c* = 16.403(3) Å, β = 104.20(3)°, *V* = 2568.9(9) Å^3, *Z* = 4, D_x = 1.321 g cm^{-3}, *F*(000) = 1004.0, μ = 2.557 cm^{-1}, *T* = 298 K. The colourless block crystals for X-ray determination were obtained by evaporating an ethanol solution slowly at room temperature over one week. The data were collected at room temperature using a Rigaku R-AXISRAPID diffractometer with graphite monochromatised Mo–K$_\alpha$ radiation (λ = 0.7107 Å) by the ω scan mode. Empirical absorption corrections were applied in each case. The data were collected in the ω scan mode and were corrected for Lorentz and polarisation effects. The structures were solved by the heavy-atom method (SHELXS 97),[9] and were refined by full-matrix least squares techniques (SHELXL 97).[10] Non-hydrogen atoms were refined anisotropically. The hydrogen atoms were generated geometrically. A total of 5801 reflections were collected. The final cycle of full-matrix least-squares refinement was based on 3783 observed reflections (I>2α(I)) and 235 variable parameters and converged with R_1 = 0.0839 and wR_2 = 0.2778.

The hydroxyl hydrogen on O atom was not located in the refinement for molecules **1** and **2**.

Full crystallographic details have been deposited at the Cambridge Crystallographic Data Centre, CCDC No. 210845 for **1**, CCDC No. 210846 for **2**.

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