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# Triphenyltin derivatives of isothiazol-3(2*H*)-one 1,1-dioxides. Synthesis, Mössbauer spectra, some fungitoxicity data, and crystal structure of triphenylstannyl 1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide · *N,N*-dimethylformamide

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## Abstract

The syntheses and tin-119m Mössbauer spectroscopic data are reported for two series of stannylimides, 2-triphenylstannyl 1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide·L (L = *O*-donor ligand) and 2-triphenylstannyl 4,5-substituted isothiazol-3(2*H*)-one 1,1-dioxides, and for the stannylester, triphenyltin 1,2-benzisothiazol-3(2*H*)-onyl-2-acetate 1,1-dioxide. The observed quadrupole splitting (QS) values (3.12–3.25 mm s<sup>-1</sup>) are interpreted in terms of *trans*-C<sub>3</sub>SnNO trigonal bipyramidal structures for the (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnNC(O)C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>·L [L = (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>C<sub>2</sub>CO, (CH<sub>3</sub>)<sub>2</sub>NCHO, C<sub>6</sub>H<sub>7</sub>NO, (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)<sub>2</sub>SO, (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PO, (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>AsO] adducts. A crystal structure determination of the *N,N*-dimethylformamide adduct confirms the Mössbauer assignment. The *ipso*-carbons [Sn–C 2.120(4), 2.120(5), 2.122(5) Å] comprise the equatorial girdle of the trigonal bipyramid, the apical positions being occupied by the imido nitrogen [Sn–N 2.242(5) Å] and amido oxygen [Sn–O 2.402(5) Å] atoms. A similar five-coordinate structure is assigned to (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnNC(O)C(R')C(R'')SO<sub>2</sub> [QS 2.95–3.32 mm s<sup>-1</sup>; R' = R'' = CH<sub>3</sub>; R' = H, R'' = C<sub>6</sub>H<sub>5</sub>; R'R'' = -(CH<sub>2</sub>)<sub>4</sub>-; R'R'' = -(CH<sub>2</sub>)<sub>5</sub>-], but for the R' = CH<sub>3</sub>, R'' = C<sub>6</sub>H<sub>5</sub> derivative, the lower QS value (2.54 mm s<sup>-1</sup>) is more consistent with a four-coordinate tetrahedral structure. A *trans*-C<sub>3</sub>SnO<sub>2</sub> trigonal bipyramidal structure for the (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnO<sub>2</sub>CCH<sub>2</sub>NC(O)C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub> stannylester is indicated by its large QS (3.53 mm s<sup>-1</sup>). Results on fungitoxicity tests on some of the triphenyltin compounds are presented.

## Introduction

There are a number of examples of triorganotin derivatives of inorganic acids in which the inorganic anion engages the tin atom in intermolecular coordination. The intermolecular linkages can be broken by hard *O*-donor ligands to give rise to five-coordinate structures [1], and an illustrative example is provided by triphenyltin nitrate, which forms crystalline adducts with  $N \rightarrow O$  [2,3],  $P \rightarrow O$  [4–6] and  $As \rightarrow O$  [5,7] ligands. In contrast, the triorganotin derivatives of organic acids such as imides, carboxylic acids or mercaptans rarely yield isolable adducts, except for some *O*-donor adducts of triphenyltin trifluoroacetate [8], trichloroacetate [9] and ethylxanthate [10], and a methanol-coordinated triorganotin carboxylate [11] that has been structurally verified. Recently, we reported the ability of the 2-triphenylstannyl derivative of saccharin [1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide], an imido acid, to form five-coordinate adducts with ethanol [12] and glycolic acid [13]. The ability of the feebly-basic hydroxylic group in both these compounds to coordinate to tin suggests that triphenyltin saccharin must be strongly Lewis acidic. With other triorganotin saccharins, however, the nature of the organic groups appears to influence the acceptor ability since the trimethyltin [14] but not the tributyltin [15] analogue forms an adduct with water. We assumed that the ligand in the triphenyltin saccharin · ethanol adduct could be replaced by somewhat stronger Lewis bases, and this has been indeed realized in the present study, which involved the preparation of several 1/1 triphenyltin saccharin adducts as well as that of the triphenylstannyl derivatives of the 'aliphatic' saccharin [isothiazol-3(2*H*)-one 1,1-dioxide] analogues [16]. The assignments of the structures of the triphenylstannyl compounds were based on their tin-119m Mössbauer quadrupole splitting values, and for the *N,N*-dimethylformamide (DMF) adduct the structure was confirmed in an X-ray diffraction study. Preliminary fungitoxic data on selected compounds are also presented.

## Experimental

### Synthesis

An aqueous solution of commercially-available hydrated sodium saccharin\* when neutralized with dilute hydrochloric acid gave a white precipitate; the solid upon recrystallization from ethanol was found to be anhydrous saccharin. Anal. Found: C, 45.90; H, 2.68; N, 7.62.  $C_7H_5NO_3S$  calcd.: C, 45.89; H, 2.75; N, 7.64%. Tributyltin saccharin was prepared by heating bis(tributyltin) oxide and saccharin in a 1/2 molar ratio in the absence of solvent; the melt was cooled and recrystallized from hexane to give a white solid, m.p. 93–95 °C (Lit. 91 °C [15]). Except for diphenylcyclopropenone [17] which was prepared by a published procedure, the other *O*-donor ligands used in this study were obtained from commercial sources. Triphenyl saccharin · ethanol was prepared by heating equimolar amounts of triphenyltin hydroxide and saccharin in ethanol, as described previously [12]. The triphenyltin saccharin · *N,N*-dimethylformamide adduct was obtained as large clear

\* Listed as sodium saccharin · *x* water in chemical catalogs; the actual value of *x* is 2/3: G. Jovanovski and B. Kamenar, *Cryst. Struct. Commun.*, 11 (1982) 247.

Table 1

Analytical data for 2-triphenylstannyl benzisothiazol-3(2*H*)-one 1,1-dioxide adducts and 4,5-substituted 2-triphenylstannyl isothiazol-3(2*H*)-one 1,1-dioxides

| Compound                                | m.p.<br>(°C) | Anal. (Found (calc.) (%)) |             |             |
|-----------------------------------------|--------------|---------------------------|-------------|-------------|
|                                         |              | C                         | H           | N           |
| $(C_6H_5)_3SnNC(O)C_6H_4SO_2 \cdot L$   |              |                           |             |             |
| L = ethanol                             | 243–244      | 56.20 (56.08)             | 3.56 (4.35) | 2.69 (2.42) |
| diphenylcyclopropanone                  | 188–190      | 65.00 (65.06)             | 3.88 (3.95) | 1.88 (1.89) |
| <i>N,N</i> -dimethylformamide           | 243–244      | 55.30 (55.56)             | 4.28 (4.32) | 4.59 (4.62) |
| quinoline <i>N</i> -oxide               | 204–205      | 60.30 (60.29)             | 3.81 (3.86) | 4.09 (4.13) |
| dibenzylsulfoxide                       | 146–148      | 61.70 (61.43)             | 4.28 (4.36) | 1.71 (1.83) |
| triphenylphosphine oxide                | 193–194      | 64.00 (63.72)             | 4.20 (4.22) | 1.76 (1.72) |
| triphenylarsine oxide                   | 205–207      | 60.60 (60.44)             | 3.92 (4.01) | 1.63 (1.63) |
| $(C_6H_5)_3SnNC(O)C(CH_3)C(CH_3)SO_2$   | 174–176      | 54.50 (54.14)             | 4.15 (4.14) | 2.64 (2.74) |
| $(C_6H_5)_3SnNC(O)C(H)C(C_6H_5)SO_2$    | 180–181      | 58.60 (58.09)             | 4.00 (3.79) | 2.42 (2.50) |
| $(C_6H_5)_3SnNC(O)C(CH_3)C(C_6H_5)SO_2$ | 191–192      | 58.20 (58.76)             | 3.81 (4.05) | 2.55 (2.44) |
| $(C_6H_5)_3SnNC(O)C(CH_2)_4CSO_2$       | 206–208      | 56.10 (55.99)             | 4.24 (4.32) | 2.55 (2.61) |
| $(C_6H_5)_3SnNC(O)C(CH_2)_5CSO_2$       | 212–213      | 56.60 (56.75)             | 4.54 (4.57) | 2.52 (2.54) |

crystals upon recrystallization of the ethanol adduct from DMF. Other adducts were prepared by heating together equimolar amounts of triphenyltin hydroxide, saccharin, and the appropriate Lewis base in ethanol. The 4- and/or 5-substituted isothiazol-3(2*H*)-one 1,1-dioxides [16] were converted into the triphenylstannyl derivatives by mixing ethanolic solutions containing equimolar amounts of the corresponding imido acid and triphenyltin hydroxide, and then evaporating the solution to a small volume. The products were recrystallized from ethanol to give slightly tan-colored powders, except for the dimethyl derivative, which was a crystalline solid that became flaky when exposed to air. Analytical data are listed in Table 1. Tin-119m Mössbauer isomer shifts (IS), quadrupole splittings (QS) and linewidths ( $\Gamma_1$ ,  $\Gamma_2$ ) at 78 K (Table 2) were obtained on a Cryophysics constant-acceleration spectrometer operating in the sawtooth wave mode. The velocity

Table 2

Mössbauer data <sup>a</sup> for 2-triphenylstannyl benzisothiazol-3(2*H*)-one 1,1-dioxide adducts and 4,5-substituted 2-triphenylstannyl isothiazol-3(2*H*)-one 1,1-dioxides

| Compound                                | IS   | QS   | $\Gamma_1$ , $\Gamma_2$ |
|-----------------------------------------|------|------|-------------------------|
| $(C_6H_5)_3SnNC(O)C_6H_4SO_2 \cdot L$   |      |      |                         |
| L = ethanol                             | 1.23 | 3.13 | 1.05, 1.03              |
| diphenylcyclopropanone                  | 1.27 | 3.14 | 0.89, 0.87              |
| <i>N,N</i> -dimethylformamide           | 1.23 | 3.13 | 1.02, 0.99              |
| quinoline <i>N</i> -oxide               | 1.22 | 3.16 | 0.91, 0.97              |
| dibenzylsulfoxide                       | 1.24 | 3.19 | 0.94, 0.97              |
| triphenylphosphine oxide                | 1.23 | 3.25 | 0.90, 0.96              |
| triphenylarsine oxide                   | 1.19 | 3.12 | 0.93, 0.88              |
| $(C_6H_5)_3SnNC(O)C(CH_3)C(CH_3)SO_2$   | 1.31 | 3.25 | 1.13, 1.12              |
| $(C_6H_5)_3SnNC(O)C(H)C(C_6H_5)SO_2$    | 1.35 | 3.09 | 0.90, 0.91              |
| $(C_6H_5)_3SnNC(O)C(CH_3)C(C_6H_5)SO_2$ | 1.30 | 2.54 | 0.86, 0.86              |
| $(C_6H_5)_3SnNC(O)C(CH_2)_4CSO_2$       | 1.31 | 2.96 | 0.99, 0.98              |
| $(C_6H_5)_3SnNC(O)C(CH_2)_5CSO_2$       | 1.31 | 2.95 | 0.92, 0.92              |

<sup>a</sup> In mm s<sup>-1</sup>.

calibration was based on the room temperature spectrum of natural iron, with calcium stannate set to be the zero-velocity reference.

1,2-Benzisothiazol-3(2*H*)-onyl-2-acetic acid (saccharinacetic acid),  $\overline{\text{C}}(\text{O})\text{C}_6\text{H}_4\text{-SO}_2\text{NCH}_2\text{CO}_2\text{H}$ , was obtained by acid hydrolysis of the product arising from the reaction of sodium saccharin and chloroacetonitrile [18]. Triphenyltin saccharinate, m.p. 176–177°C, prepared by mixing hot alcoholic solutions containing equimolar amounts of triphenyltin hydroxide and the acid, was obtained as an analytically pure compound upon cooling the solution. Anal. Found: C, 54.80; H, 3.53; N, 2.34.  $\text{C}_{27}\text{H}_{21}\text{NO}_5\text{SSn}$  calcd.: C, 54.94; H, 3.58; n, 2.37%. Mössbauer IS 1.26, QS 3.53,  $I_1$  0.99,  $I_2$  1.01 mm s<sup>-1</sup>.

### *X-ray structural analysis*

Cell parameters were determined from 25 Mo- $K_\alpha$  reflections of a  $0.20 \times 0.36 \times 0.42$  mm triphenyltin saccharin·DMF adduct crystal mounted on an  $R3m/V$  diffractometer, and 5045 independent ( $h, k, \pm l$ ) reflections were then collected at 294 K up to  $2\theta_{\text{max}}$  65°. The intensity data were corrected for Lorentz and polarization effects and for absorption ( $\mu_{\text{Mo}}$  10.52 cm<sup>-1</sup>; max/min 0.801/0.659). The Patterson method yielded the position of the heavy atom, and the non-H atoms were then derived from successive difference-Fourier syntheses. The non-H atoms were subjected to anisotropic refinement but the H-atoms were placed in calculated positions (C–H bonds fixed at 0.96 Å) and allowed to ride on their respective parent C-atoms; they were assigned an isotropic  $U$  temperature factor of 0.10 Å<sup>2</sup>. The model was refined by a full-matrix least-squares routine, converging to a final  $R_F$  index of 0.035 ( $R_w$  0.038;  $w = [\sigma^2 |F_o| + 0.00025 |F_o|^2]^{-1}$ ) for 3959 observed reflections obeying the  $|F_o| > 6\sigma |F_o|$  criterion. Calculations were performed by using the SHELXTL-PLUS program package [19] on a DEC MicroVAX-II computer.

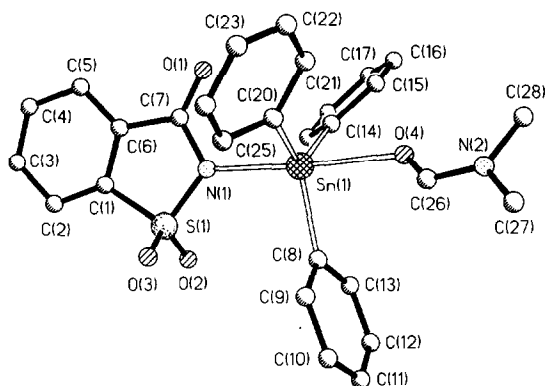


Table 3

Atomic coordinates ( $\times 10^5$  for Sn;  $\times 10^4$  for other atoms) and equivalent isotropic temperature factors <sup>a</sup> ( $\text{\AA}^2 \times 10^4$  for Sn and S;  $\times 10^3$  for other atoms) for triphenyltin saccarin·DMF

| Atom  | x        | y        | z        | $U_{\text{eq}}$ |
|-------|----------|----------|----------|-----------------|
| Sn(1) | 24217(3) | 0        | 9566(3)  | 363(1)          |
| S(1)  | 1890(1)  | 604(1)   | 4234(1)  | 417(4)          |
| O(1)  | 1159(5)  | 1860(2)  | 824(4)   | 55(2)           |
| O(2)  | 820(4)   | -15(4)   | 4218(4)  | 63(1)           |
| O(3)  | 3468(5)  | 470(3)   | 5258(5)  | 66(2)           |
| N(1)  | 1778(5)  | 798(2)   | 2515(4)  | 40(1)           |
| C(1)  | 1255(5)  | 1581(3)  | 4537(6)  | 42(2)           |
| C(2)  | 1070(7)  | 1869(4)  | 5785(7)  | 59(2)           |
| C(3)  | 590(8)   | 2694(4)  | 5714(9)  | 72(3)           |
| C(4)  | 335(8)   | 3164(4)  | 4466(9)  | 68(3)           |
| C(5)  | 535(7)   | 2862(3)  | 3202(8)  | 57(2)           |
| C(6)  | 1011(5)  | 2052(3)  | 3254(6)  | 40(2)           |
| C(7)  | 1308(6)  | 1586(3)  | 2051(6)  | 40(2)           |
| C(8)  | 2975(6)  | -1097(3) | 2256(6)  | 44(2)           |
| C(9)  | 4488(7)  | -1248(4) | 3323(6)  | 57(2)           |
| C(10) | 4899(9)  | -2022(4) | 3968(7)  | 72(3)           |
| C(11) | 3823(10) | -2644(4) | 3570(8)  | 74(3)           |
| C(12) | 2347(9)  | -2513(4) | 2523(8)  | 70(3)           |
| C(13) | 1914(8)  | -1744(3) | 1866(8)  | 58(3)           |
| C(14) | 205(5)   | 71(4)    | -856(5)  | 40(1)           |
| C(15) | 13(5)    | 70(5)    | -2370(5) | 46(2)           |
| C(16) | -1447(6) | 110(5)   | -3546(6) | 60(2)           |
| C(17) | -2728(6) | 146(4)   | -3220(7) | 58(2)           |
| C(18) | -2566(6) | 140(4)   | -1739(8) | 61(2)           |
| C(19) | -1114(5) | 104(5)   | -535(6)  | 55(2)           |
| C(20) | 4308(5)  | 759(3)   | 1118(6)  | 43(2)           |
| C(21) | 4470(10) | 1040(6)  | -174(9)  | 63(3)           |
| C(22) | 5721(10) | 1528(5)  | -38(12)  | 88(5)           |
| C(23) | 6790(9)  | 1734(5)  | 1292(13) | 90(4)           |
| C(24) | 6678(8)  | 1459(5)  | 2570(11) | 97(4)           |
| C(25) | 5421(7)  | 998(4)   | 2518(7)  | 66(2)           |
| O(4)  | 3115(5)  | -771(3)  | -810(4)  | 54(1)           |
| C(26) | 4361(10) | -1121(5) | -453(9)  | 61(3)           |
| N(2)  | 4918(7)  | -1416(3) | -1365(7) | 63(2)           |
| C(27) | 6355(9)  | -1854(5) | -859(13) | 106(5)          |
| C(28) | 4013(11) | -1341(5) | -2995(9) | 93(4)           |

<sup>a</sup>  $U_{\text{eq}}$  defined as one third of the trace of the orthogonalized  $U$  tensor.

The atomic coordinates for the adduct are listed in Table 3 and the structure is depicted in Fig. 1. The absolute structure was not determined (cf. ref. 12).

Crystal data:  $\text{C}_{25}\text{H}_{19}\text{NO}_3\text{SSn} \cdot \text{C}_3\text{H}_7\text{NO}$ , MW 605.31, monoclinic, space group  $P2_1$  (No. 4),  $a$  9.462(1),  $b$  16.317(3),  $c$  9.581(2) Å,  $\beta$  113.76(1)°,  $V$  1353.8(4) Å<sup>3</sup>,  $D_c$  1.48 g cm<sup>-3</sup> for  $Z = 2$ .

## Results and discussion

$(\text{C}_6\text{H}_5)_3\text{Sn}\overline{\text{NC}(\text{O})\text{C}_6\text{H}_4\text{SO}_2} \cdot \text{L}$  ( $\text{L} = \text{O-donor}$ ),  $(\text{C}_6\text{H}_5)_3\text{Sn}\overline{\text{NC}(\text{O})\text{C}(\text{R}')\text{C}(\text{R}'')\text{SO}_2}$  and  $(\text{C}_6\text{H}_5)_3\text{SnO}_2\text{CCH}_2\overline{\text{NC}(\text{O})\text{C}_6\text{H}_4\text{SO}_2}$

2-Triphenylstannyl 1,2-benzisothiazol-3(2H)-one 1,1-dioxide (triphenyltin, sac-

charin) forms 1/1 adducts with several *O*-donor ligands (Table 1). The C=O (diphenylcyclopropenone, *N,N*-dimethylformamide), N→O (quinoline *N*-oxide), S=O (dibenzylsulfoxide), P→O (triphenylphosphine oxide) and A→O (triphenylarsine oxide) ligands, being 'pointed' [20] Lewis bases, would coordinate through their oxygen ends, as has been established, for example, for the diphenylcyclopropenone [20], quinoline *N*-oxide [21] and dibenzylsulfoxide [22] complexes of organotin halides. The Mössbauer QS values (Table 2) for the adducts fall within a narrow range (3.12–3.25 mm s<sup>-1</sup>), and are indicative of a five-coordinate, *trans*-trigonal bipyramidal structure. Since this geometry is known to give rise to QS values of 3.00–4.00 mm s<sup>-1</sup> for triorganotin compounds [1], the observed QS values, being near the lower limit, can be interpreted in terms of a distorted *trans*-C<sub>3</sub>SnNO trigonal bipyramidal structure. Although there is overwhelming evidence in the coordination chemistry of organotin compounds for oxygen coordination to tin for these ligands, spectroscopic evidence for this feature could not be obtained by means of infrared spectroscopy, since the bands of the saccharin fragment overlap with the ligand bands.

The QS values of the triphenyltin derivatives of the 'aliphatic' saccharins also fall in a narrow range (2.95 to 3.25 mm s<sup>-1</sup>) for which the *trans*-C<sub>3</sub>SnNO trigonal bipyramidal geometry is also envisaged. The exception to this is provided by (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnNC(O)C(CH<sub>3</sub>)C(C<sub>6</sub>H<sub>5</sub>)SO<sub>2</sub>, whose lower QS value of 2.54 mm s<sup>-1</sup> together with a QS/IS ratio [23] of less than 2.1 implies a tetrahedral structure. There is no obvious explanation for this result, since all five compounds have similar steric constraints around the carbonyl oxygen, and the QS/IS ratios clearly attest to higher-than-four coordination about tin for the other four compounds. Since none of the compounds contain coordinated ethanol, although this was used as solvent in their syntheses, the five-coordinate status of tin in the four compounds must arise from intermolecular coordination by either the sulfonyl or the carbonyl oxygen. Coordination through the sulfonyl oxygen is unlikely since the sulfonyl group is a weaker Lewis base than the carbonyl group [12]. Coordination by the carbonyl oxygen is expected to be weak, however, as can be seen from the long intermolecular Sn–O bonds in trimethylstannyl succinimide (QS 3.14 [24], 3.35 mm s<sup>-1</sup> [25]), triethylstannyl succinimide [26] (3.44 mm s<sup>-1</sup> [25]) and trimethylstannyl phthalimide [27] (3.22 mm s<sup>-1</sup> [25]). In the infrared spectra of the five triphenyltin 'aliphatic' saccharins, the shifts of the carbonyl bands to smaller wavenumbers relative to the parent imido acids are small; for example the band in (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnNC(O)C(H)C(C<sub>6</sub>H<sub>5</sub>)SO<sub>2</sub> is shifted by only 33, and that in (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnNC(O)C(CH<sub>3</sub>)C(C<sub>6</sub>H<sub>5</sub>)SO<sub>2</sub> by 27 cm<sup>-1</sup> only.

Triphenyltin saccharinacetate, having a –CH<sub>2</sub>CO<sub>2</sub>– linkage between the triphenyltin and saccharin halves, is assigned a *trans*-C<sub>3</sub>SnO<sub>2</sub> trigonal bipyramidal structure, one that is common for triphenyltin esters of alkanolic acids which adopt distorted helical conformations [28]. However, the ester may possibly exist as a cyclic hexamer, [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnO<sub>2</sub>CCH<sub>2</sub>NC(O)C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>]<sub>6</sub>, rather than as a distorted helical polymer, since its atomic composition is similar to that of triphenyltin phthaloylglycinate (Mössbauer QS 3.86 mm s<sup>-1</sup>) which has a CO group in place of the SO<sub>2</sub> group; in the crystal structure of the latter, six molecules are bridged to form a cyclic hexamer [29].

Thermogravimetric analyses were performed on tributyltin saccharin and the adducts of triphenyltin saccharin with ethanol, glycolic acid, and DMF. The

thermogram of tributyltin saccharin shows a one-stage decomposition pattern consistent with the sublimation of the compound, and the thermograms of the adducts show initial losses of the coordinated ligands.

*Crystal structure of  $(C_6H_5)_3Sn\overline{NC(O)C_6H_4SO_2} \cdot O=CHN(CH_3)_2$*

The DMF adduct of triphenyltin saccharin, depicted in Fig. 1, is isomorphous with the ethanol [12] and glycolic acid [13] adducts, the three compounds crystallizing with matching unit-cell dimensions and atomic coordinates. Isomorphism in organotin compounds has been previously documented only for the triphenyltin esters of acetic [30] and chloroacetic [31] acids.

The crystal structure of the DMF adduct confirms the *trans*- $C_3SnNO$  trigonal bipyramidal assignment made on the basis of the Mössbauer QS value. The Sn–N bond (2.242(5) Å) in the DMF adduct is of the same length as those in the ethanol (2.240(7) Å [12]) and glycolic acid (2.242(8) Å [13]) adducts. Although the Lewis basicity of DMF is greater than that of alcohols, the Sn–O bond (2.402(5) Å) in the DMF adduct is not shorter than those (2.394(8), 2.409(7) Å) found in the ethanol and glycolic acid adducts; in fact, there are no significant structural differences in the triphenyltin saccharin molecule among the three adducts. This suggests that packing forces dominate in their crystal structures.

The DMF ligand in the adduct is planar, but the C–N bond length of 1.28(1) Å is significantly shorter than the reported average value (1.325(9) Å) for the C–N bond [32]. In the DMF adduct, the angle at oxygen (123.5(4)°) is also typical of  $sp^2$ -hybridized angles found in the carbonyl-donor complexes of organotin halides [33], and the C–O bond of 1.23(1) Å in the adduct agrees well with values found in the DMF adducts of methyltin [34] and dimethyltin [35] halides. The tin–oxygen bond is as long as that (2.399(4) Å) found in the triphenyltin chloride adduct with the carbonyl-donor caprolactam [36].

Table 4

ED<sub>50</sub> values <sup>a</sup> for four triphenyltin compounds containing the isothiazol-3(2*H*)-one 1,1-dioxide unit against fungi <sup>b</sup>

| Fungus                                                | Triphenyltin<br>saccharin·<br>ethanol | Triphenyltin<br>saccharin·<br>glycolic acid | 2-Triphenyl-<br>stannyl<br>thiazolone<br>1,1-dioxide | Triphenyltin<br>saccharin-<br>acetate |
|-------------------------------------------------------|---------------------------------------|---------------------------------------------|------------------------------------------------------|---------------------------------------|
| <i>Alternaria padwickii</i>                           | 1.54                                  | 1.31                                        | 1.70                                                 | 1.49                                  |
| <i>Botryodiplodia theobromae</i> (isolate 122)        | 1.67                                  | 2.27                                        | 1.78                                                 | 1.41                                  |
| <i>Colletotrichum gloeosporoides</i><br>(isolate 282) | 2.01                                  | 1.66                                        | 2.36                                                 | 2.47                                  |
| <i>Colletotrichum musae</i>                           | 0.75                                  | 0.77                                        | 0.91                                                 | 0.78                                  |
| <i>Colletotrichum musae</i> (isolate 246)             | 0.34                                  | 0.77                                        | 0.54                                                 | 0.77                                  |
| <i>Colletotrichum musae</i> (isolate 273)             | 0.75                                  | 0.89                                        | 0.72                                                 | 0.68                                  |
| <i>Ganoderma boninense</i>                            | 0.72                                  | 1.38                                        | 1.72                                                 | 1.93                                  |
| <i>Pestalotiopsis guepini</i>                         | 9.42                                  | 1.90                                        | 1.68                                                 | 3.04                                  |
| <i>Phytophthora palmivora</i> (isolate 56)            | 1.42                                  | 1.45                                        | 1.47                                                 | 1.41                                  |
| <i>Phytophthora palmivora</i> (isolate 139)           | 2.27                                  | 1.47                                        | 3.70                                                 | 3.84                                  |
| <i>Pyricularia oryzae</i>                             | 0.71                                  | 0.57                                        | 0.13                                                 | 0.45                                  |

<sup>a</sup> In ppm. <sup>b</sup> Using the radial-growth method on malt extract agar at 27 ± 2°C (Ref. 37).

### Fungitoxicity tests

The radial-growth method was used to evaluate the toxicity of triphenyltin saccharin · ethanol, triphenyltin saccharin · glycolic acid, 2-triphenylstannyl dimethylisothiazol-3(2*H*)-one 1,1-dioxide and triphenyltin saccharinacetate towards several plant-pathogenic fungi, and the ED<sub>50</sub> values are listed in Table 4. The compounds have ED<sub>50</sub> values that compare favorably in most cases with those of two commercial fungicides, triphenyltin hydroxide and triphenyltin acetate [37], and their spectrum of activity is in the main as that of these fungicides. Only *Pestalotiopsis guepini* reveals a differential activity among the four compounds, with the ethanol adduct being the least active.

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