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Synthesis, Structure, and Fungicidal Activity of Triorganotin (4*H*-1,2,4-triazol-4-yl)benzoates

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ABSTRACT: *A series of triorganotin (4H-1,2,4-triazol-4-yl)benzoates have been synthesized by the reaction of 4-(4H-1,2,4-triazol-4-yl)benzoic acid and 3-(4H-1,2,4-triazol-4-yl)benzoic acid with* $(R_3Sn)_2O$ *(R = Et, n-Bu and Ph) or* R'_3SnOH *(R′ = p-tolyl and cyclohexyl). The molecular structure of tri(p-tolyl)tin 3-(4H-1,2,4-triazol-4-yl)benzoate determined by X-ray crystallography displays that the tin atom adopts a five-coordinate distorted trigonal bipyramidal geometry with the carboxyl oxygen atom and the nitrogen atom on 1-position of triazole ring occupying the apical position. Moreover, this complex forms a polymeric chain by the intermolecular Sn–N interactions. All these complexes show good antifungal activities in vitro against Alternaria solani, Cercospora arachidicola, Gibberella zeae, Physalospora piricola, and Botrytis cinerea.* © 2010 Wiley Periodicals, Inc. Heteroatom Chem 20:411–417, 2009; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20566

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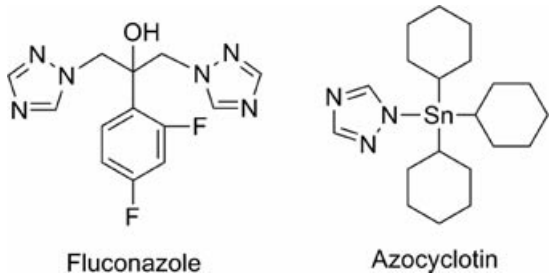
INTRODUCTION

Organotin compounds have been used widely in industry and agriculture owing to their significant biological activities, in spite of their toxicity and environmental effects partially limiting their applications. Among these organotin derivatives, organotin carboxylates have attracted extensive attention because of their versatile structures [1,2] as well as significant biological activities [3–5], especially anticancer activity [6]. In recent years, more and more investigations have focused on the synthesis of organotin carboxylates of functionalized carboxylic acids with additional O, S, or N donor groups [7–13]. Owing to the presence of additional coordinating atoms, these organotin carboxylates show considerable structural diversity. It is known that triazole and its derivatives possess versatile biological activities, such as antimicrobial and antifungal activities. Many triazole derivatives, for example, fluconazole and propiconazole, have been commercially available antifungal agents. Some organotin derivatives with triazole, such as azocyclotin (Scheme 1), have also been used as agrochemicals. Recently, we are interested in the synthesis and bioactivity of organotin carboxylates with additional sulfur or nitrogen donor groups, which exhibit considerable structural diversity and good antifungal activity [14–16]. Taking into consideration of the important biological activity of triazole derivatives as well as the versatile coordinating ability of triazole [17], as an extension of our investigations on biologically active organotin



SCHEME 1 Chemical structures of fluconazole and azocyclotin.

complexes, we herein report the synthesis and the fungicidal activity in vitro of organotin (4*H*-1,2,4-triazol-4-yl)benzoates.

EXPERIMENTAL

IR spectroscopic data were obtained from a Nicolet 380 spectrometer as KBr disks. Multinuclear NMR spectra were recorded on a Bruker 400 spectrometer, and the chemical shifts were reported in ppm with respect to reference standards (internal $SiMe_4$ for ^1H NMR and ^{13}C NMR spectra, external $SnMe_4$ for ^{119}Sn NMR). Elemental analyses were carried out on an Elementar Vairo EL analyzer. Melting points were measured with an X-4 digital micro melting-point apparatus and were uncorrected. 4-(4*H*-1,2,4-Triazol-4-yl)benzoic acid (**1**) and *N*,*N*-dimethylformamide azine dihydrochloride were prepared by the published methods [18]. Organotin oxide and organotin hydroxide are commercially available and are used as received without further purification.

*Synthesis of 3-(4H-1,2,4-triazol-4-yl)benzoic Acid (**2**)*

The mixture of *N*,*N*-dimethylformamide azine dihydrochloride (10 g, 46.65 mmol) and 3-aminobenzoic acid (6.40 g, 46.65 mmol) in benzene (125 mL) was stirred and was heated at reflux for 7 h to yield a pale yellow solid. After cooling to room temperature, the solid was filtered and washed with EtOH (20 mL) and ether (40 mL) to give compound **2** (8.45 g, 96%); mp 292–294°C. ^1H NMR (DMSO-d_6, ppm): 7.68–7.72, 7.97–7.80, 8.19 (m, m, s, 1H, 2H, 1H, C_6H_4), 8.85 (s, br, 1H, O*H*), 9.24 (s, 2H, protons of triazole). ^{13}C NMR (DMSO-d_6, ppm): 121.7, 125.6, 128.7, 130.4, 132.6, 134.2 (C_6H_4), 141.4 (carbons of triazole), 166.3 (*C*OO). IR (cm^{-1}): ν (OH), 3421 (br); ν (C=O), 1701.

*Synthesis of Triethyltin 4-(4H-1,2,4-triazol-4-yl) benzoate (**3**)*

The mixture of **1** (0.38 g, 2 mmol) and $(Et_3Sn)_2O$ (0.43 g, 1 mmol) in anhydrous benzene (40 mL) was stirred and was heated at reflux for 12 h. After cooling to room temperature, the white solid was filtered and was washed with *n*-hexane (10 mL) to give compound **3**. Yield: 0.51 g (65%); mp 257–258°C. ^1H NMR (DMSO-d_6, ppm): 1.10–1.28 (m, 15H, C_2H_5), 7.75 (d, J = 8.0 Hz, 2H, C_6H_4), 8.03 (d, J = 8.0 Hz, 2H, C_6H_4), 9.19 (s, 2H, protons of triazole). ^{13}C NMR (DMSO-d_6, ppm): 10.1 [^2J (^{13}C-$^{119/117}Sn$) = 33 Hz], 10.4 [^1J (^{13}C-$^{119/117}Sn$) = 497/475 Hz] (ethyl carbons), 120.5, 130.8, 134.4, 135.8 (C_6H_4), 141.2 (carbons of triazole), 168.4 (*C*OO). ^{119}Sn NMR (DMSO-d_6, ppm): −25.9. IR (cm^{-1}): ν_{as} (COO), 1621; ν_s (COO), 1356; $\Delta\nu$, 265. Anal. Calcd for $C_{15}H_{21}N_3O_2Sn$: C, 45.72; H, 5.37; N, 10.66. Found: C, 45.92; H, 5.36; N, 10.59.

*Synthesis of Tri(n-butyl)tin 4-(4H-1,2,4-triazol-4-yl)benzoate (**4**)*

This compound was obtained similarly using $[(n\text{-}C_4H_9)_3Sn]_2O$ instead of $(Et_3Sn)_2O$ as described above for **3**. After completion of the reaction, the solvent was removed in vacuo, and the crude product was recrystallized from benzene to afford white solids of **4**. Yield: 84%; mp 193–195°C. ^1H NMR ($CDCl_3$, ppm): 0.93 (t, J = 7.0 Hz, 9H, CH_3), 1.36–1.46, 1.60–1.77 (m, m, 12H, 6H, $CH_2CH_2CH_2$), 7.48 (d, J = 7.8 Hz, 2H, C_6H_4), 8.24 (d, J = 7.8 Hz, 2H, C_6H_4), 8.58 (s, 2H, protons of triazole). ^{13}C NMR ($CDCl_3$, ppm): 13.7, 16.9 [^1J (^{13}C-$^{119/117}Sn$) = 365/349 Hz], 27.0 [^3J (^{13}C-$^{119/117}Sn$) = 65 Hz], 27.8 [^2J (^{13}C-$^{119/117}Sn$) = 21 Hz] (butyl carbons), 121.3, 132.3, 133.3, 136.3 (C_6H_4), 141.1 (carbons of triazole), 169.7 (*C*OO). ^{119}Sn NMR ($CDCl_3$, ppm): 111.2. IR (cm^{-1}): ν_{as} (COO), 1632; ν_s (COO), 1355; $\Delta\nu$, 277. Anal. Calcd for $C_{21}H_{33}N_3O_2Sn$: C, 52.74; H, 6.96; N, 8.79. Found: C, 52.57; H, 7.03; N, 8.79.

*Synthesis of Triphenyltin 4-(4H-1,2,4-triazol-4-yl)benzoate (**5**)*

This compound was obtained similarly using $(Ph_3Sn)_2O$ instead of $(Et_3Sn)_2O$ as described above for **3**. Yield: 92%; mp 244–246°C. ^1H NMR (DMSO-d_6, ppm): 7.41–7.48, 7.88–7.90 (m, m, 9H, 6H, C_6H_5), 7.74 (d, J = 8.4 Hz, 2H, C_6H_4), 7.99 (d, J = 8.4 Hz, 2H, C_6H_4), 9.18 (s, 2H, protons of triazole). ^{13}C NMR (DMSO-d_6, ppm): 120.5, 128.3 [^3J (^{13}C-$^{119/117}Sn$) = 69 Hz], 128.9, 130.9, 133.9, 136.0, 136.2 [^2J (^{13}C-$^{119/117}Sn$) = 46 Hz], 141.2 (C_6H_5 and C_6H_4), 143.0 (carbons of triazole), 168.0 (*C*OO).

^{119}Sn NMR (DMSO-d_6, ppm): −262.9. IR (cm^{-1}): ν_{as} (COO), 1629; ν_s (COO), 1336; $\Delta\nu$, 293. Anal. Calcd for $C_{27}H_{21}N_3O_2Sn$: C, 60.26; H, 3.93; N, 7.81. Found: C, 60.25; H, 4.00; N, 7.79.

*Synthesis of Tri(p-tolyl)tin 4-(4H-1,2,4-triazol-4-yl)benzoate (**6**)*

This compound was obtained similarly using (p-$CH_3C_6H_4)_3SnOH$ instead of $(Et_3Sn)_2O$ as described above for **3**, but in a 1:1 molar ratio. Yield: 42%; mp 272–274°C. ^{1}H NMR (DMSO-d_6, ppm): 2.32 (s, 9H, CH_3), 7.26 (d, J = 7.6 Hz, 6H, SnC_6H_4), 7.67–7.83 (m, 8H, SnC_6H_4 and C_6H_4), 7.95 (d, J = 7.8 Hz, 2H, C_6H_4), 9.17 (s, 2H, protons of triazole).^{13}C NMR (DMSO-d_6, ppm): 21.0 (*C*H$_3$), 120.5, 128.9 [^3J (^{13}C-$^{119/117}$Sn) = 72 Hz], 130.8, 134.0, 135.9, 136.1 [^2J (^{13}C-$^{119/117}$Sn) = 47 Hz], 138.1, 139.4 (C_6H_5 and C_6H_4), 141.2 (carbons of triazole), 167.7 (*C*OO). ^{119}Sn NMR (DMSO-d_6, ppm): −251.2. IR (cm^{-1}): ν_{as} (COO), 1632; ν_s (COO), 1345; $\Delta\nu$, 287. Anal. Calcd for $C_{30}H_{27}N_3O_2Sn$: C, 62.10; H, 4.69; N, 7.24. Found: C, 61.99; H, 4.67; N, 7.23.

*Synthesis of Tricyclohexyltin 4-(4H-1,2,4-triazol-4-yl)benzoate (**7**)*

This compound was obtained similarly using tricyclohexyltin hydroxide instead of $(Et_3Sn)_2O$ as described above for **3**, but in a 1:1 molar ratio. After completion of the reaction, the solvent was removed in vacuo, and the crude product was recrystallized from CH_2Cl_2/*n*-hexane to afford white solids of **7**. Yield: 66%; mp 205–206°C. ^{1}H NMR ($CDCl_3$, ppm): 1.33–1.39, 1.66–1.76, 1.98–2.03 (m, m, m, 9H, 15H, 9H, C_6H_{11}), 7.46 (d, J = 8.4 Hz, 2H, C_6H_4), 8.24 (d, J = 8.4 Hz, 2H, C_6H_4), 8.55 (s, 2H, protons of triazole).^{13}C NMR ($CDCl_3$, ppm): 26.8, 28.9 [^3J (^{13}C-$^{119/117}$Sn) = 64 Hz], 31.1 [^2J (^{13}C-$^{119/117}$Sn) = 15 Hz], 34.1 [^1J (^{13}C-$^{119/117}$Sn) = 334/321 Hz] (C_6H_{11}), 121.3, 132.3, 133.1, 136.3 (C_6H_4), 141.1 (carbons of triazole), 169.5 (*C*OO). ^{119}Sn NMR ($CDCl_3$, ppm): 25.6. IR (cm^{-1}): ν_{as} (COO), 1626; ν_s (COO), 1353; $\Delta\nu$, 273. Anal. Calcd for $C_{27}H_{39}N_3O_2Sn$: C, 58.29; H, 7.07; N, 7.55. Found: C, 58.35; H, 7.15; N, 7.51.

*Synthesis of Triethyltin 3-(4H-1,2,4-triazol-4-yl) benzoate (**8**)*

The mixture of **2** (0.38 g, 2 mmol) and $(Et_3Sn)_2O$ (0.43 g, 1 mmol) in anhydrous benzene (40 mL) was stirred and was heated at reflux for 12 h. After cooling to room temperature, the solvent was removed in vacuo, and the crude product was recrystallized from benzene/*n*-hexane to afford white solids of **8**. Yield: 0.61 g (77%); mp 178–179 °C. ^{1}H NMR ($CDCl_3$, ppm): 1.35–1.45 (m, 15H, C_2H_5), 7.61–7.63, 8.17, 8.23 (m, s, d, J = 7.2 Hz, 2H, 1H, 1H, C_6H_4), 8.63 (s, 2H, protons of triazole). ^{13}C NMR ($CDCl_3$, ppm): 9.4 [^1J (^{13}C-$^{119/117}$Sn) = 424/405 Hz], 10.1 [^2J (^{13}C-$^{119/117}$Sn) = 30 Hz] (ethyl carbons), 123.4, 124.7, 130.1, 130.7, 133.2, 136.4 (C_6H_4), 141.3 (carbons of triazole), 169.3 (*C*OO). ^{119}Sn NMR ($CDCl_3$, ppm): 54. IR (cm^{-1}): ν_{as} (COO), 1628; ν_s (COO), 1342; $\Delta\nu$, 286. Anal. Calcd for $C_{15}H_{21}N_3O_2Sn$: C, 45.72; H, 5.37; N, 10.66. Found: C, 45.92; H, 5.31; N, 10.64.

*Synthesis of Tri(n-butyl)tin 3-(4H-1,2,4-triazol-4-yl)benzoate (**9**)*

This compound was obtained similarly using [(n-$C_4H_9)_3Sn]_2O$ instead of $(Et_3Sn)_2O$ as described above for **8**. Yield: 89%; mp 109–110°C. ^{1}H NMR ($CDCl_3$, ppm): 0.93 (t, J = 7.3 Hz, 9H, CH_3), 1.37–1.45, 1.69–1.71 (m, m, 12H, 6H, CH_2CH_2CH_2), 7.58–7.65, 8.13, 8.19 (m, s, d, J = 7.3 Hz, 2H, 1H, 1H, C_6H_4), 8.59 (s, 2H, protons of triazole). ^{13}C NMR ($CDCl_3$, ppm): 13.6, 17.2 [^1J (^{13}C-$^{119/117}$Sn) = 383/367 Hz], 27.0 [^3J (^{13}C-$^{119/117}$Sn) = 67 Hz], 27.6 [^2J (^{13}C-$^{119/117}$Sn) = 22 Hz] (butyl carbons), 123.4, 124.9, 130.1, 130.5, 133.5, 135.7 (C_6H_4), 141.2 (carbons of triazole), 169.3 (*C*OO). ^{119}Sn NMR ($CDCl_3$, ppm): 90.1. IR (cm^{-1}): ν_{as} (COO), 1629; ν_s (COO), 1349; $\Delta\nu$, 280. Anal. Calcd for $C_{21}H_{33}N_3O_2Sn$: C, 52.74; H, 6.96; N, 8.79. Found: C, 52.54; H, 7.09; N, 8.72.

*Synthesis of Triphenyltin 3-(4H-1,2,4-triazol-4-yl)benzoate (**10**)*

This compound was obtained similarly using $(Ph_3Sn)_2O$ instead of $(Et_3Sn)_2O$ as described above for **8**. After cooling to room temperature, the white solid was filtered and washed with *n*-hexane (10 mL) to give compound **10**. Yield: 88%; mp 205–207°C. ^{1}H NMR ($CDCl_3$, ppm): 7.39–7.54, 7.77–7.92 (m, m, 9H, 6H, C_6H_5), 7.33, 8.04, 8.18 (s, s, d, J = 7.7 Hz, 2H, 1H, 1H, C_6H_4), 8.32 (s, 2H, protons of triazole). ^{13}C NMR ($CDCl_3$, ppm): 123.9, 125.5, 128.3, 129.1 [^3J (^{13}C-$^{119/117}$Sn) = 65 Hz], 130.3, 130.9, 133.6, 134.2, 136.9 [^2J (^{13}C-$^{119/117}$Sn) = 47 Hz], 138.5 (C_6H_5 and C_6H_4), 141.4 (carbons of triazole), 170.2 (*C*OO). ^{119}Sn NMR ($CDCl_3$, ppm): −126.8. IR (cm^{-1}): ν_{as} (COO), 1647; ν_s (COO), 1345; $\Delta\nu$, 302. Anal. Calcd for $C_{27}H_{21}N_3O_2Sn$: C, 60.26; H, 3.93; N, 7.81. Found: C, 60.21; H, 3.95; N, 7.66.

*Synthesis of Tri(p-tolyl)tin 3-(4H-1,2,4-triazol-4-yl)benzoate (**11**)*

This compound was obtained similarly using (p-$CH_3C_6H_4)_3SnOH$ instead of $(Et_3Sn)_2O$ as

described above for **8**, but in a 1:1 molar ratio. After cooling to room temperature, the white solid was filtered and washed with *n*-hexane (10 mL) to give compound **11**. Yield: 44%; mp 261–262°C. ^{1}H NMR (DMSO-d_6, ppm): 2.32 (s, 9H, CH_3), 7.24–7.28, 7.62–7.94 (m, m, 5H, 11H, SnC_6H_4 and C_6H_4), 9.15 (s, 2H, protons of triazole). ^{13}C NMR (DMSO-d_6, ppm): 21.0 (CH_3), 121.8, 125.4, 128.7, 128.9 [^3J (^{13}C-$^{119/117}$Sn) = 71 Hz], 130.2, 133.9, 134.1, 136.1 [^2J (^{13}C-$^{119/117}$Sn) = 48 Hz], 138.1, 139.4 (C_6H_5 and C_6H_4), 141.5 (carbons of triazole), 166.6 (*C*OO). ^{119}Sn NMR (DMSO-d_6, ppm): −251.3 ppm. IR (cm^{-1}): ν_{as} (COO), 1638; ν_s (COO), 1346; $\Delta\nu$, 292. Anal. Calcd for $C_{30}H_{27}N_3O_2Sn$: C, 62.10; H, 4.69; N, 7.24. Found: C, 61.95; H, 4.79; N, 7.24.

*Synthesis of Tricyclohexyltin 3-(4H-1,2,4-triazol-4-yl)benzoate (**12**)*

This compound was obtained similarly using tricyclohexyltin hydroxide instead of $(Et_3Sn)_2O$ as described above for **8**, but in a 1:1 molar ratio. After the solvent was removed in vacuo, the crude product was recrystallized from CH_2Cl_2/*n*-hexane to afford white solids of **12**. Yield: 68%; mp 118–120°C. ^{1}H NMR ($CDCl_3$, ppm): 1.33–1.39, 1.65–1.72, 1.93–2.03 (m, m, m, 9H, 15H, 9H, C_6H_{11}), 7.53–7.63, 8.09, 8.18 (m, s, d, J = 7.7 Hz, 2H, 1H, 1H, C_6H_4), 8.54 (s, 2H, protons of triazole).^{13}C NMR ($CDCl_3$, ppm): 26.8, 28.8 [^3J (^{13}C-$^{119/117}$Sn) = 64 Hz], 31.1 [^2J (^{13}C-$^{119/117}$Sn) = 15 Hz], 33.8 [^1J (^{13}C-$^{119/117}$Sn) = 312/303 Hz] (C_6H_{11}), 123.6, 125.1, 130.1, 130.6, 133.8, 135.0 (C_6H_4), 141.3 (carbons of triazole), 169.3 (*C*OO). ^{119}Sn NMR ($CDCl_3$, ppm): 29.3. IR (cm^{-1}): ν_{as} (COO), 1640; ν_s (COO), 1331; $\Delta\nu$, 309. Anal. Calcd for $C_{27}H_{39}N_3O_2Sn$: C, 58.29; H, 7.07; N, 7.55. Found: C, 58.45; H, 7.05; N, 7.59.

Crystal Structure Determination of **11**

Crystals of **11** suitable for X-ray analyses were obtained by slowly cooling the hot ethanol/*n*-hexane solution of **11**. Intensity data were collected on a Rigaku Saturn CCD detector using the ω/2θ scan technique, and a semiempirical absorption correction was applied. The structure was solved by direct methods and was refined by full-matrix least squares on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. A summary of the fundamental crystal data is listed in Table 1. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as CDCC No. 749359. These data can be obtained free of charge from the CCDC at: www.ccdc.cam.ac.uk/data request/cif.

TABLE 1 Crystallographic Data for Compound **11**

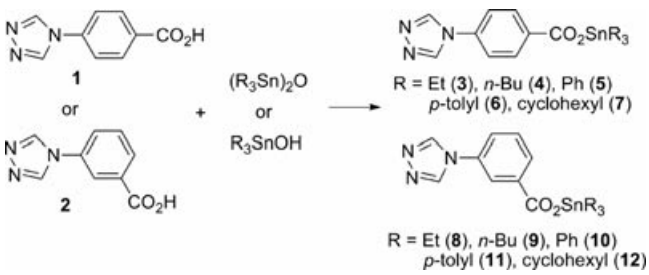
Formula	$C_{30}H_{27}N_3O_2Sn$
Formula weigh	580.24
Crystal size (mm)	0.20 × 0.18 × 0.12
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a (Å)	9.4679(19)
b (Å)	16.487(3)
c (Å)	17.475(4)
T (K)	113(2)
λ (Å)	0.71073
V (Å^3)	2727.7(9)
$D_{calc.}$ (g cm^{-3})	1.413
2θ Range (°)	3.40–50.02
Absorption coefficient (mm^{-1})	0.967
Z	4
F(000)	1176
Reflections collected	21511
Independent reflections (R_{int})	4818 (0.0290)
No. of observed reflections ($I > 2\sigma(I)$)	4738
No. of parameters	327
Residuals *R*, *R* w [$I > 2\sigma(I)$]	0.0176, 0.0452
Goodness-of-fit	1.106

RESULTS AND DISCUSSION

Synthesis and Characterization of Complexes

3-(4*H*-1,2,4-Triazol-4-yl)benzoic acid (**2**) was synthesized similarly using 3-aminobenzoic acid instead of 4-aminobenzoic acid as described in the preparation of 4-(4*H*-1,2,4-triazol-4-yl)benzoic acid (**1**) [18]. Upon treatment of these two acids with organotin oxide or organotin hydroxide in anhydrous benzene, a series of triorganotin (4*H*-1,2,4-triazol-4-yl)benzoates were obtained (Scheme 2), which have been characterized by IR and NMR (^{1}H, ^{13}C, and ^{119}Sn) spectra as well as elemental analyses.

IR Spectra. Compared to those of the free acids, the remarkable changes in the IR spectra of complexes **3–12** are the absence of the broad band ascribed to the COOH group as well as the lower carbonyl stretching frequencies, indicating the



SCHEME 2 Synthesis of triorganotin (4*H*-1,2,4-triazol-4-yl)benzoates.

deprotonation of the carboxylic acids and the carboxylate coordination [19]. The differences ($\Delta\nu$) between asymmetric and symmetric stretching vibrations of the carboxylate groups are observed in the region of 265–309 cm^{-1} in these complexes, larger than those detected in the corresponding sodium salts of acids **1** (217 cm^{-1}) and **2** (224 cm^{-1}), in which the asymmetric and symmetric stretching vibrations of the carboxylate groups appear at 1605 and 1388 cm^{-1} for **1**, and 1618 and 1394 cm^{-1} for **2**, respectively, implying the monodentate manner of the carboxylate groups in these complexes to the tin atom [20].

NMR Spectra. The NMR spectroscopic data also support the suggested structures. The ^1H NMR spectra display the expected integration values and peak multiplicities. The ^{13}C NMR spectra clearly show the carbonyl carbon resonances at 168.4–170.2 ppm, slightly downfield shift compared with those in free acids **1** and **2**. Holeček and coworkers have shown that the $^1J(^{13}C–^{119/117}Sn)$ coupling constants depend significantly on the coordination number of the tin atom in triorganotin complexes [21,22]. For example, the $^1J(^{13}C–^{119/117}Sn)$ coupling constants for four-coordinated tributyltin complexes in $CDCl_3$ solution exhibit the values of 326–390 Hz [22]. In the present work, the ^1J (^{13}C-$^{119/117}Sn$) coupling constants of tributyltin complexes **4** (365/349 Hz) and **9** (383/367 Hz) in $CDCl_3$ solution are in accordance with the values for four-coordinate tributyltin complexes. The estimated C–Sn–C angles (~111° in **4** and ~113° in **9**, respectively) calculated from their ^1J ($^{13}C–^{119}Sn$) coupling constants in solution [23] are also consistent with the tetrahedral tin atom. In addition, the ^{119}Sn NMR resonances of complexes in $CDCl_3$ solution also suggest the four-coordinated tetrahedral geometry of the tin atom. The ^{119}Sn NMR chemical shifts of tributyltin complexes **4** (111.2 ppm) and **9** (90.1 ppm) and triphenyltin complex **10** (−126.8 ppm) are compared to those values reported in the corresponding four-coordinated tributyltin (100–145 ppm) and triphenyltin (−83 to −122 ppm) carboxylates [2]. It is worthy of note that although these complexes possibly exhibit polymeric linkage structures in solid (one case shown in Fig. 1), these complexes should be monomeric four coordinated structures in noncoordinating solvent, based on the above results. The polymeric structures lost in solution possibly owing to the weak Sn ··· N interactions.

The Crystal Structure of Complex **11**

The molecular structure of **11** is presented in Fig. 1. 3-(4*H*-1,2,4-Triazol-4-yl)benzoate acts as a bridging bidentate ligand by the carboxylate oxygen atom and 1-position nitrogen atom of triazole, which results in the formation of a linkage coordination polymer through the intermolecular Sn–N interactions. The tin atom adopts a five-coordinate slightly distorted trigonal bipyramidal geometry. The electronegative nitrogen and oxygen atoms occupy the apical positions with an angle N1–Sn1–O1A of 175.74(6)°, and three *p*-tolyl groups lie in the equatorial plane. The Sn1–N1 distance is 2.4509(18) Å, slightly shorter than those in linkage polymeric triaryltin derivatives with nitrogen-functionalized carboxylate ligands, such as $[2\text{-}(4\text{-}PyCH_2S)]C_6H_4CO_2SnPh_3$ (2.524(2) Å) [15], but similar to those in organotin derivatives with triazole ligands, such as $CH_2Tz_2SnPh_2Br_2$ (2.454(7) Å, Tz: 1,2,4-triazol-1-yl) [24]. The nonbond Sn1 ··· O2A distance is 3.269(2) Å, markedly longer than the covalent Sn1–O1A bond distance (2.1518(15) Å), but still shorter than the sum of the van der Waal's radii for the Sn and O atoms of 3.57 Å [25], suggesting that some weak interactions possibly exist between these two atoms. The triazolyl plane and the phenyl plane formed by the C3–C8 atoms are noncoplanar, and the dihedral angle between them is 140.6°.

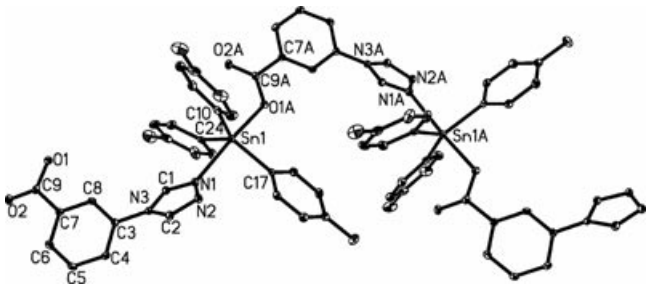


FIGURE 1 Polymeric chain structure of **11** with the thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Sn1–C10 2.130(2), Sn1–C17 2.131(2), Sn1–C24 2.126(2), Sn1–N1 2.4509(18), Sn1–O1A 2.1518(15), Sn1···O2A 3.269(2), C9–O1 1.295(3), C9–O2 1.221(3) Å; N1–Sn1–O1A 175.74(6), C10–Sn1–C17 121.05(9), C10–Sn1–C24 120.04(8), C17–Sn1–C24 117.95(9), C7–C9–O1 113.26(19), C7–C9–O2 121.0(2), O1–C9–O2 125.7(2), Sn1–O1A–C9A 122.46(13)°. Symmetric operations: A = $-x+1.5, -y, z+0.5$.

Fungicidal Activity

Preliminary in vitro tests for fungicidal activity of all compounds have been carried out by the fungi growth inhibition method [26]. The data are summarized in Table 2, which indicate that all compounds involving in complexes **3–12** as well as the free acids

TABLE 2 Antifungal Activity Data of the Free Acid Ligand and Complexes (Percent Inhibition)[a]

Compound	*Alternaria solani*	*Cercospora arachidicola*	*Gibberella zeae*	*Physalospora piricola*	*Botrytis cinerea*
1	22.2	26.1	32.1	50.0	95.0
2	27.8	30.4	32.1	54.8	95.0
3	100.0	78.3	100.0	100.0	100.0
4	100.0	91.3	100.0	98.8	100.0
5	83.3	82.6	71.7	94.1	95.0
6	66.7	56.5	60.4	95.2	100.0
7	66.7	82.6	77.4	78.6	95.0
8	100.0	69.6	100.0	100.0	100.0
9	100.0	69.6	100.0	100.0	100.0
10	83.3	82.8	71.7	73.8	85.0
11	72.2	78.3	60.4	78.6	95.0
12	66.7	82.6	67.9	96.4	100.0
Positive control[b]	88.9	91.3	94.3	100.0	100.0

[a]Concentration: 50 μg/mL of DMF.
[b]Positive control: propiconazole.

1 and **2** display high activities to *Botrytis cinere*. Compared with free acids **1** and **2**, their complexes **3–12** are more active for *Alternaria solani*, *Cercospora arachidicola*, *Gibberella zeae*, and *Physalospora piricola*, possibly due to the increased lipophilic nature, led by the complexation with organotin moiety, which strengthens the interactions of complexes with the cells [27]. Moreover, the inhibition percentage of triethyltin and tributyltin complexes in vitro for *Alternaria solani*, *Gibberella zeae,* and *Physalospora piricola* are approximate to 100%, respectively, and higher than the corresponding values of triaryl and tricyclohexyltin complexes, in accordance with high toxicity of trialkyltin derivatives [28]. It is worthy of note that the tributyltin derivative **4** of acid **1** is more active against *Cercospora arachidicola* than the corresponding derivative **9** of acid **2**. In addition, the derivatives **5** and **6** of acid **1** also show high activities against *Physalospora piricola* than the corresponding derivatives **10** and **11** of acid **2**. However, the activity of derivative **7** of acid **1** against *Physalospora piricola* is lower than that of derivative **12** of acid **2**. Even though no remarkable rules are found so far, the differences between para- and meta-substitution may inspire further investigations.

CONCLUSION

In conclusion, a series of triorganotin (4*H*-1,2,4-triazol-4-yl)benzoates have been successfully synthesized and characterized. The crystal structural analysis of one of them displays that a polymeric chain with intermolecular Sn–N interactions is formed in solid. All these complexes, especially triethyltin and tributyltin complexes, show good antifungal activities in vitro.

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