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Structure of azo dye organotin(IV) compounds containing a C,N-chelating ligand, part II,† and their *in vitro* antifungal activity‡

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Eight complexes of azo dyes used in routine industrial processes and the [(2-dimethylaminomethyl) phenyl](R_2)tin(IV) moiety (R = Ph or *n*-Bu) have been prepared, their NMR, electrospray ionization mass spectrometry, IR and UV–VIS spectra measured, and the X-ray structure of {[2-(*N*,*N*-dimethylaminomethyl)phenyl](diphenyl)}tin(IV)-2-{[*N*′-(2-oxo-1-phenylcarbamoylpropyliden)hydrazo]}benzoate (3a), determined. The compounds reveal similar structures in chloroform solution (NMR) and in the solid state (X-ray, IR). Four compounds exist in the hydrazone tautomeric form. The central tin atoms in all compounds exist in slightly distorted *trans*-trigonal bipyramidal geometry with the 'negative' atoms (nitrogen, oxygen) in axial and the carbon atoms in equatorial positions; no intramolecular attacks from the dyes' cores were observed. The *in vitro* antifungal activity of the compounds studied was comparable to similar organotin(IV) compounds and antifungal drugs in clinical use. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: organotin(IV) compounds; azo dyes; C,N-chelating ligand; NMR; X-ray diffraction; electrospray ionization mass spectrometry; azo-hydrazone tautomerism

INTRODUCTION

Organotin(IV) compounds with the possibility of hypercoordination have been investigated for the last three decades,[1,2] but results on the field of additional ligand exchange reactions (halogens are commonly used as additional ligands) are rather scarce.[3,4] The substances of our interest represent new types of compound containing a bulky substituent instead of the halogen atom typically used in previous studies. The strength of the intramolecular Sn–N interaction in these types of compound is taken as the most important parameter for prediction of some properties, and can be evaluated in the solid state and in solution by various parameters and experimental techniques.[5,6] We reported previously[7] that organotin derivatives of the simple azo dyes methyl orange (**1a**) and *para*-methyl red (**2a**)) (also used as acid–base indicators) when containing the C,N-chelating ligand (2-(*N*,*N*-dimethylaminomethyl)phenyl-) are different in physico-chemical properties[7] from the free azo dyes and some organotin complexes of azo dyes without an intramolecular Sn–N bond. The products of reactions of triorganotin

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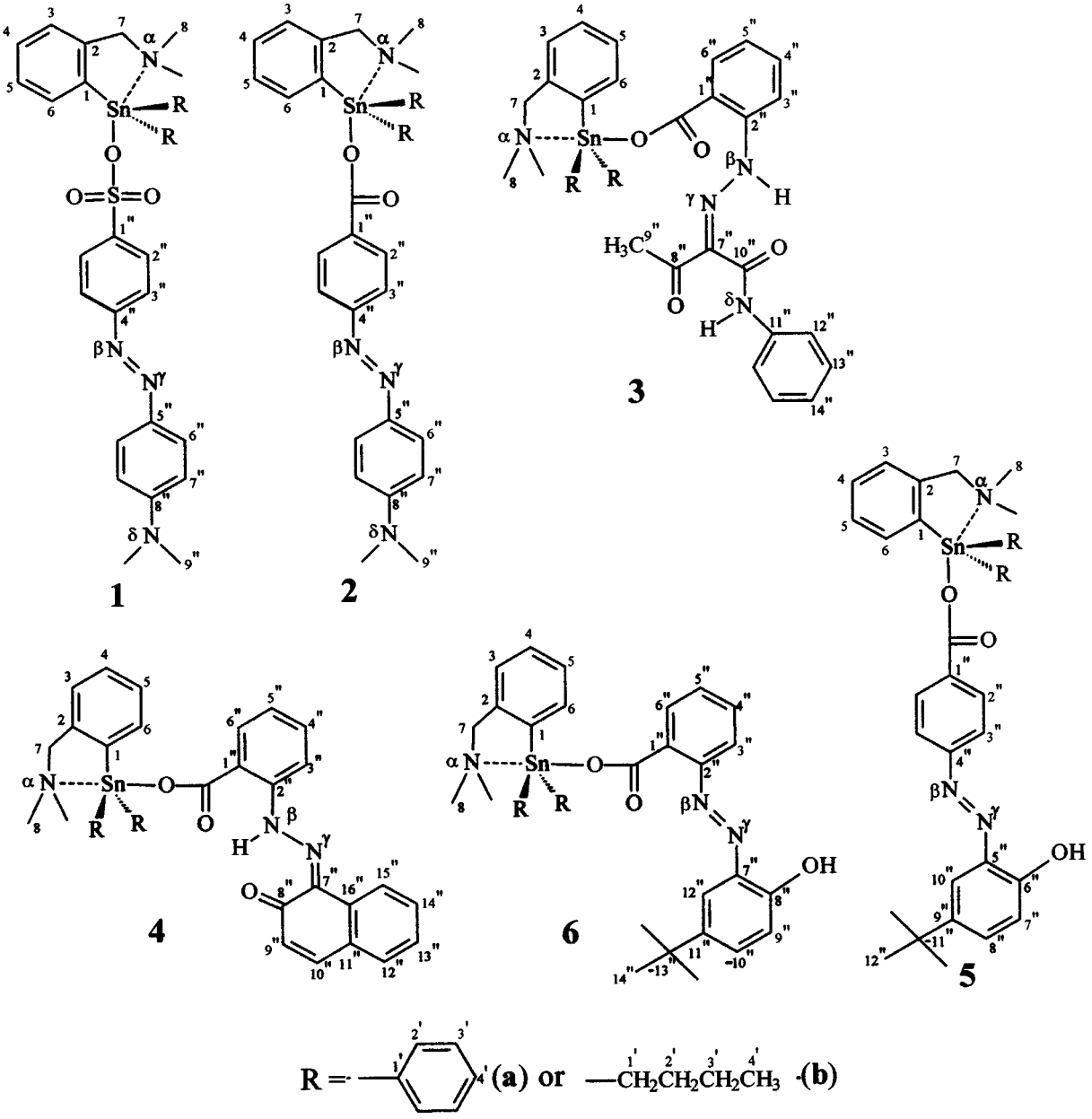

Figure 1. Numbering of the compounds studied.

halides with azo dye silver salts are intensively colored and represent a special sort of metallacomplex dye stuff that is extensively studied for its special (mainly optical) properties.[8–11]

Organotin(IV) compounds have also been studied extensively and screened for *in vitro* and *in vivo* for antitumor activity.[12,13] Recently, considerable attention has been paid to triorganotin(IV) derivatives because of their high *in vitro* antifungal activities against some medically important fungi.[4,14]

Now we would like to pay more attention to the organotin complexes in which the same chelating ligand is present, but with different, and more complicated, azo dyes (Fig. 1), which are also involved in many industrial applications.[8–11] Some of the compounds can occur in two tautomeric forms (**3**–**6**), and there is also the theoretical possibility of increasing the tin coordination number via the coordination of the dye intrinsic donor atoms.

We report here on the structural investigation of the various compounds studied using different solid-state and solution techniques with the aim of characterizing the coordination sphere of the tin(IV) atom, and compare the main characteristics of the compounds prepared with their precursors and/or similar organotin(IV) compounds. Another topic was to explore the biological activity of these compounds against potentially pathogenic fungi.

EXPERIMENTAL

General comments

The starting chemicals and all solvents were obtained from commercial sources (Acros and Sigma-Aldrich). Some dyes used as ligands were prepared and characterized using NMR spectra as described in Ref. 15. Other dyes were prepared and analyzed analogously. All reactions described were carried out in air and in commercially available solvents, without any drying or further purification; only methanol was dried, by distillation from sodium methoxide. An aluminum foil was used for reaction-flask light protection in the cases of reactions where the silver(I) compounds were employed. The syntheses of the starting organotin chlorides and compounds **1a** and **2a** have been reported previously.[5–7]

Synthesis

{[2-(N,N-dimethylaminomethyl)phenyl](diphenyl)} tin(IV)-2- {[N′-(2-oxo-1-phenylcarbamoylpropyliden) hydrazo]}benzoate (3a) (a typical procedure)

2-{[*N*′-(2-oxo-1-phenylcarbamoylpropyliden)hydrazo]} benzoic acid (0.25 g, 0.77 mmol) was dissolved in warm ethanol and in a solution of sodium salt (titration with NaOH, $c = 0.1736$ mol dm^{-3}). To this solution (80 °C) was added an equimolar amount of $AgNO_3$, the mixture was stirred at the elevated temperature for 2 h, then cooled to 10 °C and filtered. The crude product was washed twice with a small amount of cold water and twice with dried methanol. The precipitate was dried overnight *in vacuo* at room temperature. The resulting silver(I) complex (0.3 g, 0.671 mmol; yield 96%) was suspended in toluene (200 ml) and added to solution of 0.34 g (0.671 mmol) {[2-(dimethylaminomethyl)phenyl](diphenyl)}tin chloride in toluene (100 ml). The mixture was refluxed for 3 h and then filtered. The filtrate was concentrated *in vacuo* to 15 ml and cooled to −40 °C. The crystals that appeared after several days were recrystallized from a chloroform–hexane mixture (1 : 5) to give **3a** as a pure bright yellow solid. Yield: 0.43 g (87.7%); m.p. 110–114 °C. ^{1}H NMR: 8.26 (d, 1H, Ph–C(6)H, $^3J(^{119}Sn, ^1H) = 69.7$ Hz), 8.06 (d, 4H, Ph–C(2′)H, $^3J(^{119}Sn, ^1H) = 62.3$ Hz), 3.70 (s, 2H, NC(7)H_2), 1.85 (s, 6H, NC(8)H_3), 2.56 (s, 3H, COC(9″)H_3), 15.56 (s, 1H, N(β)–H), 11.25 (s, 1H, Ph–N(δ)H), 8.01 (d, 1H, Ph–C(6″)H), 7.92 (dd, 2H, Ph–C(4 and 5)H), 7.80 (d, 1H, Ph–C(3)H), 7.36 (m, 6H, Ph–C (3′, 4′, 3″, 12″ and 13″)H), 7.19 (dd, 2H Ph–C(14″)H). ^{13}C NMR: 138.1 (C(1)), $^1J(^{119}Sn, ^{13}C) = 752.9$ Hz, 142.8 (C(2), $^2J(^{119}Sn, ^{13}C) = 38.4$ Hz), 128.5 (C(4)), 126.7 (C(3), $^4J(^{119}Sn, ^{13}C) = 55.9$ Hz), 64.8 (C(7), $^3J(^{119}Sn, ^{13}C) = 27.9$ Hz), 45.7 (C(8)), 140.9 (C(1′), $^1J(^{119}Sn, ^{13}C) = 784.8$ Hz), 136.6 (C(2′), $^2J(^{119}Sn, ^{13}C) = 45.4$ Hz), 136.5 (C(3′), $^3J(^{119}Sn, ^{13}C) = 45.3$ Hz), 128.5 (C(4′)), 170.5 (COO), 199.9 (C(8″)), 26.3 (C(9″)), 161.1 (C(10″)), 116.2 (C(1″)), 144.5 (C(2″)), 116.5 (C(3″)), 133.6 (C(4″)), 123.6 (C(5″)), 131.9 (C(6″)), 130.5 (C(7″)), 120.7 (C(12″)), 137.6 (C(11″)), 129.5 (C(13″)), 124.5 (C(14″)). ESI-MS, positive-ion mode: $[M + H]^+$, m/z 733, 10%; $[Cat]^+$, m/z 408, 100%; negative-ion mode: $[An]^-$, m/z 268, 100%; m/z 280, $[An - CO_2]^-$, 15%. Mol. wt 698.40. Analysis: found (calc.): C, 62.3 (62.23); H, 5.3 (5.22); N, 7.7 (7.64). λ_{max} (nm)/ε_{max}(m^2 mol^{-1}): 377/2710. ν_{as}(C═O) (cm^{-1})/ν_s(C═O) (cm^{-1}): 1636/1345.

{[2-(N,N-dimethylaminomethyl)phenyl](diphenyl)} tin(IV)-2-{[N′-(2-oxo-2H-naphthalen-1-yliden) hydrazo]}benzoate (4a)

The compound was prepared from appropriate silver complex (0.255 g, 0.638 mmol) and {[2-(dimethylaminomethyl) phenyl](di(*n*-butyl))}tin chloride (0.282 g, 0.638 mmol). Yield: 0.365 g (82%); m.p. 201–204 °C. ^{1}H NMR: 7.45 (dd, 1H, Ph–C(5)H), 8.26 (d, 1H, Ph–C(6)H, $^3J(^{119}Sn, ^1H) = 70.0$ Hz), 8.07 (d, 4H, Ph–C(2′)H, $^3J(^{119}Sn, ^1H) = 66.2$ Hz), 3.55 (s, 2H, NC(7)H_2), 1.87 (s, 6H, NC(8)H_3), 7.29 (dd, 4H, Ph–C(3′)H), 7.34 (dd, 2H, Ph–C(4′)H), 16.48 (s, 1H, N(β)–H), 8.00 (d, 1H, Ph–C(12″)H)), 8.17 (d, 1H, Ph–C(3″)H)), 8.05 (d, 1H, Ph–C(6″)H)), 7.48 (d, 1H, Ph–C(15″)H)), 6.63 (d, 1H, Ph–C(9″)H)), 7.10 (d, 1H, Ph–C(10″)H)), 7.39 (m, 6H, Ph–C(3, 4, 4″, 5″, 13″ and 14″)H). ^{13}C NMR: 138.3 (C(1), $^1J(^{119}Sn, ^{13}C) = 652.9$ Hz), 142.8 (C(2), $^2J(^{119}Sn, ^{13}C) = 36.4$ Hz), 128.5 (C(4)), 126.7 (C(3), $^4J(^{119}Sn, ^{13}C) = 55.9$ Hz), 64.8 (C(7), $^3J(^{119}Sn, ^{13}C) = 28.9$ Hz), 45.6 (C(8)), 140.7 (C(1′), $^1J(^{119}Sn, ^{13}C) = 804.8$ Hz), 136.6 (C(2′), $^2J(^{119}Sn, ^{13}C) = 45.4$ Hz), 136.5 (C(3′), $^3J(^{119}Sn, ^{13}C) = 45.3$ Hz), 128.5 (C(4′)), 170.7 (COO, $^nJ(^{119}Sn, ^{13}C) = 10.6$ Hz), 179.5 (C(8″)), 133.2 (C(1″)), 144.5 (C(2″)), 116.5 (C(3″)), 132.5 (C(4″)), 124.4 (C(5″)), 131.9 (C(6″)), 130.5 (C(7″)), 128.2 (C(9″)), 141.2 (C(10″)), 128.7 (C(12″)), 128.6 (C(11″)), 127.5 (C(13″)), 128.5 (C(14″)), 122.3 (C(15″)), 134.6 (C(16″)). ESI-MS, positive-ion mode: m/z 700, $[M + H]^+$, 2%; $[Cat]^+$, m/z 408, 100%; m/z 722, $[M + Na]^+$, 6%; negative-ion mode, $[An]^-$, m/z 291, 100%; m/z 247, $[An - CO_2]^-$, 81%. Mol. wt 697.66. Analysis: found (calc.): C, 65.4 (65.35); H, 4.8 (4.76); N, 6.1 (6.02). λ_{max} (nm)/ε_{max}(m^2 mol^{-1}): 496/2670. ν_{as}(C═O) (cm^{-1})/ν_s(C═O) (cm^{-1}): 1625/1344.

{[2-(N,N-dimethylaminomethyl)phenyl](diphenyl)} tin(IV)-2-{[2′-(hydroxy)-4′-(2″, 2″-dimethylethyl) phenyl]azo}benzoate (5a)

The compound was prepared from the appropriate silver complex (0.240 g, 0.6 mmol) and {[2-(dimethylaminomethyl) phenyl](diphenyl)}tin chloride (0.256 g, 0.6 mmol) Yield: 0.266 g (63%); m.p. 113–115 °C of orange crystals. ^{1}H NMR: 7.45 (dd, 1H, Ph–C(5)H), 8.29 (d, 1H, Ph–C(6)H, $^3J(^{119}Sn, ^1H) = 70.0$ Hz), 7.86 (d, 4H, Ph–C(2′)H, $^3J(^{119}Sn, ^1H) = 67.2$ Hz), 3.56 (s, 2H, NC(7)H_2), 1.74 (s, 6H, NC(8)H_3), 7.43 (dd, 4H, Ph–C(3′)H), 7.40 (dd, 2H, Ph–C(4′)H), 1.37 (s, 9H, Ph–C(12″)H)), 7.81 (d, 2H, Ph–C(3″)H)), 12.76 (s, 1H, OH)), 7.38 (s, 1H, Ph–C(10″)H)), 7.20 (d, 1H, Ph–C(3)H), 7.41 (dd, 1H, Ph–C(4)H), 8.17 (d, 2H, Ph–C(2″)H), 6.97 (d, 1H, Ph–C(7″)H), 7.96 (d, 1H, Ph–C(8″)H). ^{13}C NMR: 138.0 (C(1), $^1J(^{119}Sn, ^{13}C) = 808.2$ Hz), 143.4 (C(2), $^2J(^{119}Sn, ^{13}C) = 41.2$ Hz), 129.3 (C(4), $^4J(^{119}Sn, ^{13}C) = 14.2$ Hz), 127.3 (C(3), $^3J(^{119}Sn, ^{13}C) = 63.2$ Hz), 64.8 (C(7), $^3J(^{119}Sn, ^{13}C) = 29.0$ Hz), 45.7 (C(8)), 140.7 (C(1′), $^1J(^{119}Sn, ^{13}C) = 805.7$ Hz), 136.1 (C(2′), $^2J(^{119}Sn, ^{13}C) = 46.1$ Hz), 128.6 (C(3′), $^3J(^{119}Sn, ^{13}C) = 70.4$ Hz),

129.3 (C(4′)), 169.8 (COO, $^{n}J(^{119}Sn, ^{13}C) = 10.9$ Hz), 129.8 (C(8″)), 136.6 (C(1″)), 131.1 (C(2″)), 121.5 (C(3″)), 152.2 (C(4″)), 137.0 (C(5″)), 150.5 (C(6″)), 117.7 (C(7″)), 142.9 (C(9″)), 129.9 (C(10″)), 31.3 (C(12″)), 34.1 (C(11″)), 128.6 (C(5), $^{3}J(^{119}Sn, ^{13}C) = 70.4$ Hz), 138.2 (C(6), $^{2}J(^{119}Sn, ^{13}C) = 31.5$ Hz). ESI-MS, positive-ion mode: m/z 408, $[Cat]^+$ 100%; negative-ion mode: $[An]^-$, m/z 297, 100%; m/z 253, $[An - CO_2]^-$, 35%. Mol. wt 703.66. Analysis: found (calc.): C, 64.9 (64.79); H, 5.6 (5.58); N, 6.0 (5.97). λ_{max} (nm)/ε_{max}(m^2 mol^{-1}): 333/1953 and 408/789. ν_{as}(C═O) (cm^{-1})/ν_s(C═O) (cm^{-1}): 1632/1333.

{[2-(N,N-dimethylaminomethyl)phenyl]di(n-butyl)tin(IV)-4-{[4′-(dimethylamino)phenyl]azo} benzenesulfonate (1b)

The compound **1b** was obtained from the reaction of methyl orange silver(I) complex (0.192 g, 0.46 mmol) and 0.187 g (0.46 mmol) {[2-(dimethylaminomethyl)phenyl](di(*n*-butyl))}tin chloride in toluene. The resulting red crystals were crystallized from chloroform–hexane mixture (1 : 5) to give **1b** as a pure red solid. Yield: 0.166 g (53%); m.p. 128–132 °C. ^{1}H NMR: 7.31 (m, 2H, Ph–C(3)H), 7.13 (t, 1H, Ph–C(4)H), 7.31 (m, 2H, Ph–C(5)H), 8.07 (d, 1H, Ph–C(6)H, $^{3}J(^{119}Sn, ^{1}H) = 58.6$ Hz), 3.65 (s, 2H, NC(7)H_2), 2.40 (s, 6H, NC(8)H_3), 1.65 (t, 4H, C(1′)H), 1.41 (m, 4H, C(2′)H_2), 1.32 (m, 4H, C(3′)H), 0.83 (t, 6H, C(4′)H), 8.00 (d, 1H, Ph–C(2″)H), 7.85 (m, 1H, Ph–C(3″)H), 7.85 (m, 2H, Ph–C(6″)H), 6.74 (d, 2H, Ph–C(7″)H), 3.08 (s, 6H, NC(9″)H_3). ^{13}C NMR: 139.8 (C(1)), 141.7 (C(2), $^{2}J(^{119}Sn, ^{13}C) = 38.5$ Hz), 126,5 (C(3), $^{3}J(^{119}Sn, ^{13}C) = 26.6$ Hz), 129.6 (C(4), $^{4}J(^{119}Sn, ^{13}C) = 12.8$ Hz), 128.5 (C(5), $^{3}J(^{119}Sn, ^{13}C) = 64.2$ Hz), 138.2 (C(6), $^{2}J(^{119}Sn, ^{13}C) = 38.8$ Hz), 65.9 (C(7), $^{3}J(^{119}Sn, ^{13}C) = 25.8$ Hz), 45.9 (C(8), $^{5}J(^{119}Sn, ^{13}C) = 5.9$ Hz), 15.9 (C(1′), $^{1}J(^{119}Sn, ^{13}C) = 484.8$ Hz), 27.0 (C(2′), $^{2}J(^{119}Sn, ^{13}C) = 92.6$ Hz), 27.8 (C(3′), $^{3}J(^{119}Sn, ^{13}C) = 31.2$ Hz), 13.5 (C(4′)), 143.6 (C(1″)), 127.1 (C(2″)), 122.0 (C(3″)), 152.7 (C(4″)), 144.1 (C(5″)), 125.3 (C(6″)), 111.5 (C(7″)), 154.3 (C(8″)), 40.3 (C(9″)). ESI-MS, positive-ion mode: $[Cat]^+$, m/z 368, 100%; negative-ion mode: $[An]^-$, m/z 304, 100%. Mol. wt 671.48. Analysis: found (calc.); C, 55.5 (55.45); H, 6.6 (6.65); N, 8.4 (8.34); S, 4.8 (4.78). λ_{max} (nm)/ε_{max}(m^2 mol^{-1}): 421/2990. ν_{as}(S═O) (cm^{-1})/ν_s(S═O) (cm^{-1}): 1274/1108.

{[2-(N,N-dimethylaminomethyl)phenyl]di(n-butyl)tin(IV)-4-{[4′-(dimethylamino)phenyl]azo} benzoate (2b)

The analogous reactions as for **1b** provided **2b** as bright orange crystals. Yield: 0.21 g (59%); m.p. 131–133 °C. ^{1}H NMR: 7.12 (d, 1H, Ph–C(3)H), 7.32 (t, 1H, Ph–C(4)H), 7.33 (t, 1H, Ph–C(5)H), 8.02 (d, 1H, Ph–C(6)H, $^{3}J(^{119}Sn, ^{1}H) = 51.9$ Hz), 3.60 (s, 2H, NC(7)H_2), 2.34 (s, 6H, NC(8)H_3), 1.66 (t, 4H, C(1′)H), 1.50 (m, 4H, C(2′)H), 1.36 (m, 4H, C(3′)H), 0.85 (t, 6H, C(4′)H), 7.89 (d, 1H, Ph–C(2″)H), 7.85 (d, 1H, Ph–C(3″)H), 8.23 (d, 1H, Ph–C(6″)H), 6.75 (d, 1H, Ph–C(7″)H), 3.10 (s, 6H, NC(9″)H_3). ^{13}C NMR: 141.8 (C(1), 142.7 (C(2), $^{2}J(^{119}Sn, ^{13}C) = 38.5$ Hz), 126.8 (C(3), $^{3}J(^{119}Sn, ^{13}C) = 55.9$ Hz), 128.9 (C(4), $^{4}J(^{119}Sn, ^{13}C) = 13.4$ Hz), 127.8 (C(5), $^{3}J(^{119}Sn, ^{13}C) = 56.6$ Hz), 137.7 (C(6), $^{2}J(^{119}Sn, ^{13}C) = 28.4$ Hz), 65.7 (C(7), $^{3}J(^{119}Sn, ^{13}C) = 22.9$ Hz), 45.7 (C(8)), 16.5 (C(1′), $^{1}J(^{119}Sn, ^{13}C) = 515.0$ Hz), 27.0 (C(2′), $^{2}J(^{119}Sn, ^{13}C) = 86.1$ Hz), 28.1 (C(3′), $^{3}J(^{119}Sn, ^{13}C) = 31.2$ Hz), 13.7 (C(4′)), 170.7 (COO), 135.5 (C(1″)), 130.7 (C(2″)), 121.6 (C(3″)), 152.6 (C(4″)), 143.8 (C(5″)), 125.2 (C(6″)), 111.5 (C(7″)), 154.9 (C(8″)), 40.2 (C(9″)). ESI-MS, positive-ion mode MS: m/z 637, $[M + H]^+$, 4%; $[Cat]^+$, m/z 368, 100%; negative-ion mode MS: $[An]^-$, m/z 268, 100%. Mol. wt 635.42. Analysis: found (calc.): C, 60.5 (60.49); H, 7.0 (6.98); N, 8.9 (8.82). λ_{max} (nm)/ε_{max}(m^2 mol^{-1}): 422/3660. ν_{as}(C═O) (cm^{-1})/ν_s(C═O) (cm^{-1}): 1636/1329.

{[2-(N,N-dimethylaminomethyl)phenyl]di(n-butyl)}tin(IV)-2-{[N′-(2-oxo-1-phenylcarbamoyl-propyliden)hydrazo]benzoate (3b)

The compound **3b** was prepared analogously to **3a**. From the appropriate silver complex (0.105 g, 0.244 mmol) and {[2-(dimethylaminomethyl)phenyl](di(*n*-butyl))}tin chloride (0.098 g, 0.244 mmol) was obtained 0.124 g (74%; m.p. 153–156 °C) of bright yellow crystals. ^{1}H NMR: 7.07 (d, 1H, Ph–C(3)H), 7.47 (dd, 1H, Ph–C(4)H), 7.93 (d, 1H, Ph–C(6)H, $^{3}J(^{119}Sn, ^{1}H = 55.9$ Hz)), 3.56 (s, 2H, NC(7)H_2), 2.32 (s, 6H, NC(8)H_3), 1.65 (t, 4H, C(1′)H), 1.52 (m, 4H, C(2′)H), 1.35 (t, 4H, C(3′)H), 0.81 (t, 2H, C(4′)H), 2.58 (s, 3H, COC(9″)H_3), 8.18 (d, 2H, Ph–C(12″)H), 15.67 (s, 1H, N(β)–H), 11.25 (s, 1H, Ph–N(δ)H), 8.01 (d, 1H, Ph–C(6″)H), 7.72 (d, 1H, Ph–C(3)H), 7.06 (m, 3H, Ph–C(4, 5 and 13″)H), 7.19 (dd, 2H Ph–C(14″)H). ^{13}C NMR: 137.9 (C(1), $^{1}J(^{119}Sn, ^{13}C) = 652.9$ Hz), 142.6 (C(2), $^{2}J(^{119}Sn, ^{13}C) = 39.4$ Hz), 128.2 (C(4)), 125.9 (C(3), $^{4}J(^{119}Sn, ^{13}C) = 57.8$ Hz), 65.7 (C(7), $^{3}J(^{119}Sn, ^{13}C) = 28.9$ Hz), 45.7 (C(8)), 16.8 (C(1′), $^{1}J(^{119}Sn, ^{13}C) = 510.5$ Hz), 28.2 (C(2′), $^{2}J(^{119}Sn, ^{13}C) = 90.73$ Hz), 27.0 (C(3′), $^{3}J(^{119}Sn, ^{13}C) = 30.2$ Hz), 13.7 (C(4′), 170.5 (COO), 200.2 (C(8″)), 26.4 (C(9″)), 161.1 (C(10″)), 116.2 (C(1″)), 144.5 (C(2″)), 116.5 (C(3″)), 133.6 (C(4″)), 123.6 (C(5″)), 131.9 (C(6″)), 130.5 (C(7″)), 120.7 (C(12″)), 137.6 (C(11″)), 129.5 (C(13″)), 124.5 (C(14″)), 128.8 (C(5), $^{3}J(^{119}Sn, ^{13}C) = 59.0$ Hz), 138.2 (C(6), $^{2}J(^{119}Sn, ^{13}C) = 32.9$ Hz). ESI-MS, positive-ion mode: $[M + H]^+$, m/z 693, 17%; $[Cat]^+$, m/z 368, 100%; negative-ion mode: $[An]^-$, m/z 324, 100%; m/z 280, $[An - CO_2]^-$, 13%. Mol. wt 693.46. Analysis: found (calc.): C, 58.8 (58.84); H, 6.7 (6.69); N, 8.1 (8.08). λ_{max} (nm)/ε_{max}(m^2 mol^{-1}): 377/3100. ν_{as}(C═O) (cm^{-1})/ν_s(C═O) (cm^{-1}): 1631/1347.

{[2-(N,N-dimethylaminomethyl)phenyl](di(n-butyl))}tin(IV)-2-{[N′-(2-oxo-2H-naphthalen-1-yliden)hydrazo]}benzoate (4b)

The compound was prepared from the appropriate silver complex (0.105 g, 0.550 mmol) and {[2-(dimethylaminomethyl)phenyl](di(*n*-butyl))}tin chloride (0.222 g, 0.550 mmol). Yield: 0.279 g (77%; m.p. 61–62 °C) of bright orange crystals. ^{1}H NMR: 7.27 (dd, 1H, Ph–C(5)H), 8.00 (d, 1H, Ph–C(6)H, $^{3}J(^{119}Sn, ^{1}H) = 66.0$ Hz), 1.71 (m, 4H, C(2′)H), 3.61 (s, 2H, NC(7)H_2), 2.36 (s, 6H, NC(8)H_3), 1.36 (m, 4H, C(3′)H), 0.83 (t, 6H, C(4′)H), 16.48 (s, 1H, N(β)–H), 7.45 (d, 1H, Ph–C(12″)H)), 8.29 (d, 1H, Ph–C(3″)H)), 8.20 (d, 1H, Ph–C(6″)H)), 8.48 (d, 1H, Ph–C(15″)H)), 7.55

(d, 1H, Ph–C(10″)H)), 6.66 (d, 1H, Ph–C(9″)H)), 7.25 (d, 1H, Ph–C(3)H)), 7.12 (dd, 1H, Ph–C(4)H)), 1.45 + 1.57 anisochronous protons (m, 4H, C(1′)H)), 7.55 (dd, 1H, Ph–C(4″)H)), 7.20 (dd, 1H, Ph–C(5″)H)), 7.32 (dd, 1H, Ph–C(13″)H)), 7.48 (dd, 1H, Ph–C(14″)H)). ^{13}C NMR: 141.8 (C(1), $^{1}J(^{119}Sn, ^{13}C) = 646.6$ Hz), 142.6 (C(2), $^{2}J(^{119}Sn, ^{13}C) = 36.8$ Hz), 128.8 (C(4)), 126.7 (C(3), $^{4}J(^{119}Sn, ^{13}C) = 55.3$ Hz), 65.7 (C(7), $^{3}J(^{119}Sn, ^{13}C) = 23.7$ Hz), 45.7 (C(8), 16.8 (C(1′), $^{1}J(^{119}Sn, ^{13}C) = 513.4$ Hz), 28.2 (C(2′), $^{2}J(^{119}Sn, ^{13}C) = 30.4$ Hz), 26.9 (C(3′), $^{3}J(^{119}Sn, ^{13}C) = 88.3$ Hz), 13.5 (C(4′)), 170.6 (COO, $^{n}J(^{119}Sn, ^{13}C) = 10.6$ Hz), 179.1 (C(8″)), 134.6 (C(1″)), 144.2 (C(2″)), 116.1 (C(3″)), 132.1 (C(4″)), 124.0 (C(5″)), 132.0 (C(6″)), 130.6 (C(7″)), 126.0 (C(9″)), 141.1 (C(10″)), 128.8 (C(12″)), 128.7 (C(11″)), 127.7 (C(13″)), 128.6 (C(14″)), 122.2 (C(15″)), 134.6 (C(16″)), 127.8 (C(5), $^{3}J(^{119}Sn, ^{13}C) = 58.0$ Hz), 137.8 (C(6), $^{2}J(^{119}Sn, ^{13}C) = 30.8$ Hz). ESI-MS, positive-ion mode: m/z 368, 100%; negative-ion mode: $[An]^-$, m/z 291, 100%; m/z 247, $[An - CO_2]^-$, 61%. Mol. wt 658.41. Analysis: found (calc.): C, 62.1 (62.02); H, 6.3 (6.28); N, 6.4 (6.38). λ_{max} (nm)/ε_{max}(m^2 mol^{-1}); 496/1339. ν_{as}(C═O) (cm^{-1})/ν_s(C═O) (cm^{-1}): 1629/1340.

{[2-(N,N-dimethylaminomethyl)phenyl](di(n-butyl))}tin(IV)-4-{[2′-(hydroxy)-4′-(2″,2″-dimethylethyl)phenyl]azo}benzoate (6b)

The compound was prepared from the appropriate silver complex (0.120 g, 0.296 mmol) and {[2-(dimethylaminomethyl)phenyl](di(*n*-butyl))}tin chloride (0.222 g, 0.055 mmol). Yield: 0.160 g (81%) of deep-red oil. ^{1}H NMR: 7.19 (dd, 1H, Ph–C(5)H), 7.95 (d, 1H, Ph–C(6)H, $^{3}J(^{119}Sn, ^{1}H) = 66.0$ Hz), 1.71 (m, 4H, C(2′)H), 3.58 (s, 2H, NC(7)H_2), 2.33 (s, 6H, NC(8)H_3), 1.33 (m, 4H, C(3′)H), 0.83 (t, 6H, C(4′)H), 7.97 (d, 1H, Ph–C(12″)H)), 7.87 (d, 1H, Ph–C(3″)H)), 12.78 (s, 1H, OH)), 7.36 (d, 1H, Ph–C(10″)H)), 7.09 (d, 1H, Ph–C(3)H), 7.24 (dd, 1H, Ph–C(4)H), 7.54 (dd, 1H, Ph–C(4″)H), 7.49 (dd, 1H, Ph–C(5″)H), 7.87 (d, 1H, Ph–C(6″)H), 6.93 (d, 1H, Ph–C(9″)H), 1.37 (s, 9H, Ph–C(14″)H), 1.45 + 1.57 anisochronous protons (m, 4H, C(1′)H)). ^{13}C NMR: 141.5 (C(1), $^{1}J(^{119}Sn, ^{13}C) = 647.0$ Hz), 142.6 (C(2), $^{2}J(^{119}Sn, ^{13}C) = 36.7$ Hz), 128.7 (C(4), $^{4}J(^{119}Sn, ^{13}C) = 12.6$ Hz), 126.7 (C(3), $^{3}J(^{119}Sn, ^{13}C) = 55.4$ Hz), 65.6 (C(7), $^{3}J(^{119}Sn, ^{13}C) = 23.6$ Hz), 45.6 (C(8)), 16.7 (C(1′), $^{1}J(^{119}Sn, ^{13}C) = 512.9$ Hz), 28.1 (C(2′), $^{2}J(^{119}Sn, ^{13}C = 30.3$ Hz)), 26.9 (C(3′), $^{3}J(^{119}Sn, ^{13}C) = 90.8$ Hz), 13.5 (C(4′)), 171.1 (COO, $^{n}J(^{119}Sn, ^{13}C) = 9.6$ Hz), 150.5 (C(8″)), 133.5 (C(1″)), 149.2 (C(2″)), 115.5 (C(3″)), 130.7 (C(4″)), 130.0 (C(5″)), 131.1 (C(6″)), 137.7 (C(7″)), 118.1 (C(9″)), 130.4 (C(10″)), 129.6 (C(12″)), 141.9 (C(11″)), 127.6 (C(5), $^{3}J(^{119}Sn, ^{13}C) = 56.9$ Hz), 137.8 (C(6), $^{2}J(^{119}Sn, ^{13}C) = 31.5$ Hz), 33.9 (C(13″)), 31.3 (C(14″)). ESI-MS, positive-ion mode: m/z 368, 100%; negative-ion mode: $[An]^-$, m/z 297, 100%; m/z 253, $[An - CO_2]^-$, 44%. Mol. wt 664.46. Analysis: found (calc.): C, 61.5 (61.46); H, 7.2 (7.13); N, 6.4 (6.32). λ_{max} (nm)/ε_{max}(m^2 mol^{-1}): 343/1672 and 765/2670. ν_{as}(C═O) (cm^{-1})/ν_s(C═O) (cm^{-1}): 1624/1347.

NMR measurements

The ^{1}H (500.13 MHz), ^{13}C (125.76 MHz), ^{119}Sn (186.50 MHz) and ^{15}N (50.65 MHz) NMR spectra of all compounds in deuteriochloroform (30–50 mg in 0.6 ml) were recorded at ambient temperature on a Bruker Avance 500 spectrometer equipped with a 5 mm broadband probe with *z*-gradient and an SGI O2 computer. The ^{13}C and ^{1}H chemical shifts were referenced to the signals of $CDCl_3$ and residual $CHCl_3$ respectively ($\delta(^{13}C) = 77.0$, $\delta(^{1}H) = 7.25$), the ^{119}Sn chemical shifts were referenced to external neat tetramethylstannane ($\delta(^{119}Sn) = 0.0$), and the ^{15}N chemical shifts referenced to external neat nitromethane ($\delta(^{15}N) = 0.0$). Two-dimensional gradient-selected (gs)-H,H-COSY, gs-^{1}H–^{13}C—HSQC, gs-^{1}H–^{13}C—HMBC and gs-^{1}H–^{15}N-HMBC[16,17] spectra were recorded using standard microprograms provided by Bruker. ^{119}Sn NMR spectra were measured using the inverse gated-decoupling mode. The ^{1}H and ^{13}C chemical shifts were assigned from gs-H,H-COSY, gs-^{1}H–^{13}C and gs-^{1}H–^{13}C-HMBC[16,17] spectra (latter-two optimized for $^{1}J(^{13}C, ^{1}H) \approx 150$ Hz and $^{3}J(^{13}C, ^{1}H)$ 8 Hz respectively). The ^{15}N chemical shifts were assigned using gs-^{1}H–^{15}N-HMBC spectra optimized for $^{n}J(^{15}N, ^{1}H) = 4–5$ Hz. The assignment of ^{15}N chemical shifts of –N═N–moiety is in line with data published for ^{15}N selectively mono-enriched azobenzenes.[18]

Mass spectrometry (MS)

Electrospray ionization (ESI) mass spectra were measured on an Esquire 3000 (Bruker Daltonics, Bremen, Germany) ion trap mass analyzer within the mass range m/z 50–800. The mass spectrometer was tuned to give an optimum response for m/z 300 or 400. The samples were dissolved in acetonitrile and analyzed by direct infusion at a flow rate of 2–5 µl min^{-1} in both the positive-ion and negative-ion modes. The ion source temperature was 300 °C, and the flow rate and the pressure of nitrogen were 4 l min^{-1} and 10 psi respectively. For all MS/MS measurements, the isolation width was $m/z = 8$, and the collision amplitude was 0.7–1.0 V. Mass spectra were averaged over 10 scans. The ions with relative abundances lower than 2% are neglected. 'Cat' means cationic part and 'An' means anionic part of the molecule (see discussion below for the explanation).

Crystallography

Single crystals were obtained by vapor diffusion of hexane into an approximately 3% dichloromethane solution of **3a**. The X-ray data were collected on a Nonius KappaCCD diffractometer fitted with Mo Kα radiation ($\lambda = 0.71073$ Å) at 150(2) K. The absorption correction was performed using a multi-scan procedure (SORTAV[19]), the structure was solved by direct methods (SIR92[20]), and full-matrix least-squares refinements on F^2 were carried out using the program SHELXL97.[21]

With the exception of the *ipso*-carbon atoms, the three tin-bound phenyl moieties exhibit large positional disorder, resulting in large displacement parameters; hence, there was a necessity to restrict the phenyl-group geometry during

refinement. Despite this, the coordination sphere of tin and parameters defining the azo dye moiety could be clearly established. All non-hydrogen atoms were refined anisotropically, all hydrogen atoms on carbon were calculated into idealized positions (riding model) and assigned displacement factors $U_{iso}(H) = 1.2U_{eq}$ (pivot atom) or of $1.5U_{eq}$ for the methyl group. The positions of the remaining hydrogen along were found using a difference Fourier map and refined as riding on nitrogen with isotropic displacement factors.

Crystallographic data for $C_{38}H_{36}N_4O_4Sn{\cdot}CH_2Cl_2$, $M = 816.32$, triclinic, $P\bar{1}$, $a = 9.6660(3)$, $b = 12.5050(3)$, $c = 16.8890(3)$ Å, $\alpha = 87.197(2)$, $\beta = 74.709(2)$, $\gamma = 73.083(2)^\circ$, $Z = 2$, $V = 1883.09(9)$ Å^3, $D_c = 1.440$ g cm^{-3}, $\mu = 0.865$ mm^{-1}, 36 351 reflections measured ($\theta_{max} = 27.2^\circ$), 8300 independent, 7413 with $I > 2\sigma(I)$, 400 parameters, $S = 1.18$, $R(F) = 0.065$ (obs. data), $wR(F^2) = 0.154$, $\Delta\rho_{max} = 1.28$ e$^-$ Å^{-3} (between atoms N11 and C18). CCDC deposition number: 248304.

IR and UV–VIS spectroscopies

IR spectra were recorded on a Perkin–Elmer 684 spectrophotometer in Nujol mulls under laboratory conditions.

Electronic absorption spectra were recorded on a V-550 JASCO spectrophotometer in quartz cuvettes (optical length 1 cm) in the UV and VIS region (10 000–35 000 cm^{-1}) in CH_3OH.

In vitro antifungal screening

The *in vitro* testing was carried out by the modified microdilution broth method according to the M27-A guideline.[22] Quality-control strains (*Candida albicans* ATCC 90028, *Candida parapsilosis* ATCC 22019, *Candida krusei* ATCC 6258) and amphotericin B (Sigma), fluconazole (Pfizer), ketoconazole (Janssen-Cilag, Beerse) were involved as reference drugs. All fungal strains were passaged on Sabouraud dextrose agar at 35 °C prior to being tested.

The minimum inhibitory concentration (MIC) and the minimum fungicidal concentration (MFC) were determined by the following method.[22] Dimethyl sulfoxide (DMSO) served as a diluent for all compounds tested. DMSO did not exceed a final concentration of 2%. RPMI 1640 medium (Sevapharma, Prague) supplemented with L-glutamine and buffered with 0.165 M morpholinepropanesulfonic acid (Serva) to pH 7.0 by using 10 M NaOH was used as a test medium. Each well of the microdilution tray was filled with 200 µl of the RPMI 1640 medium with a diluted compound tested and then inoculated with 10 µl of suspension of a given fungal strain in sterile water. Fungal inoculum was prepared to give a final size of $(5 \pm 0.2) \times 10^3$ CFU ml^{-1}. The trays were incubated at 35 °C and the MICs read after 24 and 48 h. Owing to slow growth, *Trichophyton mentagrophytes* strain was read at 72 and 120 h. The MICs were determined visually and defined as 80% inhibition of the growth of control.

RESULTS AND DISCUSSION

The compounds studied were prepared by the reaction of azo dye–silver(I) complex and either [(2-dimethylaminomethyl) phenyl](diphenyl)tin(IV) or [(2-dimethylaminomethyl)phenyl](*n*-butyl)tin(IV) chloride in 1 : 1 ratio in warm toluene suspension. All compounds reveal satisfactory elemental analyses and the ^{1}H NMR spectra are in good conformity with the proposed compositions. The ESI-MS spectra can also be taken as indirect proof for the compounds' identities. Attempts to prepare the analogous compounds **5b** and **6a** were also made, but we were not able to purify them via crystallization.

ESI-MS

The typical feature of the ESI mass spectra of the compounds studied is the cleavage of the Sn–O bond as the most labile one in both molecules. This cleavage primarily yields two complementary ions, which we call the cationic ('Cat') and anionic ('An') parts of the molecule (see observed ions in the Experimental section). The cationic part is identical for compounds **3a, 4a** and **5a** (m/z 408) and for compounds **1b, 2b, 3b, 4b** and **6b** (m/z 368). The anionic parts differ by masses.

Positive-ion ESI mass spectra

The first-stage mass spectrum of compounds **1b, 2b, 3b, 4b** and **6b** exhibits only the ion m/z 368 and in the case of compounds **3a, 4a** and **5a** only the ion m/z 408. In addition to these ions, the spectra also show the ion $[M + H]^+$ (**2b, 3a, 3b**) or $[M + Na]^+$ (**3b**). Owing to the characteristic isotopic distribution of the tin element, the presence or absence of the tin atom in individual fragment ions can easily be recognised.[4] The structures of the observed ions are easily proposed by correlation with the known structures of the cationic parts.

Negative-ion ESI mass spectra

The negative-ion ESI mass spectrum of compound **1b** shows only the anionic part of the molecule (m/z 304). In the case of compounds **2b, 3a, 3b, 4a, 4b, 5a** and **6b** the fragment ion $[An - CO_2]^-$ is also present in the first-stage mass spectrum (see Experimental section).

ESI-MS in positive-ion and negative-ion modes gives complementary information for the structure confirmation of organotin complexes with a labile bond, where the cationic part of the molecule can be measured in the positive-ion mode and the anionic part in the negative-ion mode.

Solid-state study: crystallography

The ORTEP drawing with the numbering scheme of compound **3a** is depicted in Fig. 2; selected parameters of the crystal structure of this compound are presented in the Fig. 2 caption. In the structure, the tin atom exists in slightly distorted *trans*-trigonal bipyramidal geometry defined by three *ipso*-carbon atoms of the phenyl groups in equatorial positions, with the intramolecularly bound

nitrogen atom for the $CH_2N(CH_3)_2$ group and the oxygen atom of the carboxylate group in apical positions (Sn1–O11 2.121(3) Å for **3a**, 2.1400(16) Å for **2a**, 2.073(2) Å for triphenyltin benzoate[7,23]). The remaining oxygen atom (Sn1–O12 3.126(4) Å, and 2.997(2) Å for **2a**) is not involved in the first coordination sphere of the tin atom. The monodentate mode of coordination of the carboxylate is reflected in the disparate C41–O11 and C41–O12 bond distances (see Fig. 2 caption), the longer separation between carbon and oxygen being associated with the stronger Sn–O interaction. The Sn–N1 distance of 2.541(5) Å (for comparison, 2.5392(19) Å for **2a**) is in the range of relatively strong intramolecular contacts. This compares with the Sn–N distances found in the Cambridge Structural Database[24] (the shortest distance for tin and nitrogen in the aminomethylphenyl moiety is 2.355(2) Å), as well as in the [(2-dimethylaminomethyl)phenyl](diphenyl)tin(IV) bromide (2.511(12) Å),[25] chloride (2.519(2) Å),[26] $[Ph_2P(S)S]^-$ (2.548(3) Å),[26] $[Ph_2P(S)O]^-$ (2.481(2) Å),[26] $[Ph_2P(O)CH_2COO]^-$ (2.488(2) Å) and $[Ph_2P(S)CH_2COO]^-$ (2.534(2) Å).[27] A further comparison can be made with the same molecules for the N–Sn–O and N–Sn–X angles (X = Br, Cl, S and O): 163.8(2)° for **3a**, 163.5° for **1a**, 168.56(6)° for **2a**, 171.0(1)° for the bromide, 170.49(6)° for the chloride, 169.06(8)° for $[Ph_2P(S)S]^-$, 168.58(8)° for $[Ph_2P(S)O]^-$, 165.16(7)° for $[Ph_2P(O)CH_2COO]^-$ and 172.22(5)° for $[Ph_2P(S)CH_2COO]^-$. The remaining donor groups of **3a** do not ligate the tin center. The geometry of the azo dye is in agreement with the ketohydrazone form, similar to the closely related pigments. Important bond lengths in this respect are the N41–N42 1.315(7) Å, N42–C48 1.297(9) Å and the ketone C51–O42 1.229(8) Å and C49–O41 1.233(10) Å. The system of three intramolecular hydrogen bonds ensures the planarity of the whole ketohydrazone group. Other distances and angles are in agreement with previously published studies.[28]

Solution-state study

The ^1H, ^{13}C, ^{119}Sn and ^{15}N chemical shifts and $^nJ(^{119}Sn, ^{13}C)$ coupling constants for all compounds were measured in $CDCl_3$ at 300 K; the ^{119}Sn and ^{15}N parameters are collected in Table 1, and the rest are given in the Experimental section.

The solution structures of the triorganotin(IV) compounds studied can be described on the basis of several NMR spectra parameters. The most important parameters for the direct evaluation of the structure arise from nuclei involved directly in the coordination polyhedra of the central tin atom.[5,6] On the basis of this approach, we can consider all structures as *trans*-trigonal bipyramids with the more electronegative nitrogen and oxygen atoms in axial and carbon atoms in equatorial planes, with relatively strong intramolecular donor–acceptor Sn–N interaction. The values of $\delta(^{119}Sn)$ (Table 1) are in the

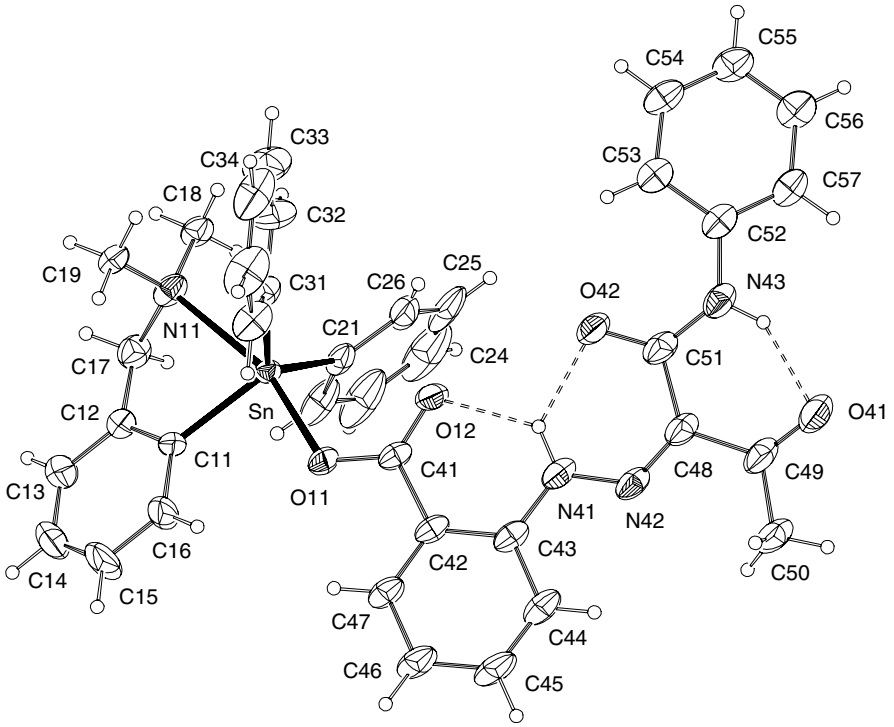

Figure 2. Molecular structure of compound **3a** with atom numbering scheme. (ORTEP 30% probability level); the solvent is omitted for clarity. Selected interatomic distances (Å) and angles (°): Sn–O(11) 2.121(3), Sn–C(11) 2.142(2), Sn–C(21) 2.147(2), Sn–C(31) 2.137(2), Sn–N(11) 2.541(5), O(11)–Sn–C(11) 89.5(1), O(11)–Sn–C(21) 100.8(1), O(11)–Sn–C(31) 97.3(1), O(11)–Sn–N(11) 163.8(2), C(11)–Sn–C(21) 113.8(1), C(11)–Sn–C(31) 119.5(1), C(21)–Sn–C(31) 123.4(1), N(11)–Sn–C(11) 74.4(1), N(11)–Sn–C(21) 88.1(1), N(11)–Sn–C(31) 88.9(1), C(41)–O(11) 1.289(7), C(41)–O(12) 1.230(7).

Table 1. Selected NMR parameters

Compound	$\delta(^{119}Sn)$ (ppm)	$\delta(^{15}N)$ (ppm)			
		N(α)	N(β)	N(γ)	N(δ)
3a	−214.6	—[a]	−205.2	−5.1	−250.2
4a	−212.6	—[a]	−195.7	−21.4	—
5a	−217.2	−347.4	65.6	127.6	—
1b	−83.7	—[a]	90.9	123.6	−328.7
2b	−83.6	−345.7	93.8	122.5	−324.0
3b	−77.3	−346.2	−203.5	−2.9	−247.8
4b	−78.5	−347.1	−194.3	−20.3	—
6b	−80.0	−348.1	74.6	124.1	—

[a] Not detected

Table 2. Results of antifungal screening of **1**–**6**

Strain (code)[a]		MIC/MFC (μmol l^{-1})							
		1a	**2a**	**3a**	**5a**	**1b**	**2b**	**4b**	**6b**
MIC									
CA	24 h	7.81	15.63	15.63	3.91	0.977	1.91	1.91	1.91
	48 h	15.63	15.63	62.5	7.81	7.81	7.81	15.63	3.91
CT	24 h	15.63	7.81	>125	15.63	1.95	0.488	3.91	7.81
	48 h	15.63	15.63	>125	62.5	15.63	7.81	7.81	15.63
CK	24 h	3.91	3.91	3.91	1.95	0.977	3.91	3.91	1.91
	48 h	3.91	7.81	3.91	3.91	1.95	3.91	7.81	1.91
CG	24 h	31.25	>62.5	>125	15.63	15.63	>125	62.5	7.81
	48 h	62.5	>62.5	>125	62.5	15.63	>125	125	15.63
TB	24 h	7.81	31.25	15.63	15.63	0.977	1.95	3.91	7.81
	48 h	15.63	>62.5	62.5	62.5	7.81	>125	15.63	15.63
AF	24 h	15.63	15.63	7.81	7.81	3.91	3.91	7.81	3.91
	48 h	15.63	31.25	7.81	15.63	7.81	>125	15.63	7.81
AC	24 h	1.95	7.81	3.91	3.91	0.488	0.122	0.977	1.91
	48 h	3.91	7.81	3.91	3.91	0.488	0.977	0.977	3.91
TM	72 h	3.91	7.81	3.91	3.91	0.977	1.91	3.91	1.91
	120 h	7.81	15.63	15.63	7.81	1.91	3.91	7.81	3.91
MFC									
CA	48 h	31.25	>62.5	>125	15.63	7.81	15.63	125	7.81
CT	48 h	15.63	15.63	>125	>125	31.25	15.63	>125	31.25
CK	48 h	31.25	31.25	62.5	7.81	31.25	>125	>125	7.81
CG	48 h	>250	>62.5	>125	>125	62.5	>125	>125	15.63
TB	48 h	>250	>62.5	>125	>125	>500	>125	>125	>125
AF	48 h	>250	>62.5	>125	>125	>500	>125	>125	>125
AC	48 h	3.91	7.81	7.81	31.25	15.63	3.91	7.81	31.25
TM	120 h	31.25	15.63	>125	>125	62.5	31.25	125	31.25

[a] CA: *Candida albicans* ATCC 44859; TB: *Trichosporon beigelii* 1188; CT: *Candida tropicalis* 156; TM: *Trichophyton mentagrophytes* 445; CK: *Candida krusei* E28; AF: *Aspergillus fumigatus* 231; CG: *Candida glabrata* 20I; AC: *Absidia corymbifera* 272.

range from −217.2 to −212.6 ppm for the **a** series (Ph) and from −83.7 to −78.5 ppm for the **b** series (Bu) and are exactly in the range[29] for five-coordinated triorganotin sulfonates and carboxylates respectively, which is in line with the proposed structure. These values are also comparable with $\delta(^{119}Sn)$ for the starting chlorides (−177.1 and −51.7 ppm) and analogous bromides (−180.8 and −44.9 ppm).[5,6] All ^{119}Sn chemical shifts for **1**–**6** are shifted significantly downfield in comparison with

analogous compounds having distorted tetrahedral geometry (e.g. triphenyltin benzoate, −111.7 ppm[23]).

The C–Sn–C angle of the two phenyl or butyl *ipso*-carbon atoms is 122–125° for all compounds, as calculated according to the procedure reported in Refs 30 and 31 from $^{1}J(^{119}Sn, ^{13}C)$ coupling-constant values. These angles compare with those calculated for the starting chlorides (average 123.0° and 124° respectively), and those obtained from X-ray solid-state study (125.7(2)° for **1a**, 122.38(9)° for **2a**, and 123.4(1)° for **3a**). On the other hand, triphenyltin benzoate has a lower value for this coupling constant (650 Hz), which is typical for triphenyltin compounds with distorted tetrahedral geometry. The are two additional types of the coupling constants, which can be used for intramolecular interaction Sn–N strength evaluation ($^{n}J(^{119}Sn, ^{13}C(7))$[5] and $^{3}J(^{119}Sn, ^{1}H(6 \text{ or } 2'))$[32]). The magnitudes of these coupling constants are in line with those previously published for organotin(IV) compounds bearing the TBP structure. We arrive at the same conclusion on the basis of $\delta(^{15}N(\alpha))$ values[5] (Table 1) with respect to the chemical shift value of free amine (−353.0 ppm[6]). The $\delta(^{13}C(COO))$ values (~170 ppm) are comparable to values for four-coordinated triorganotin benzoates[33] and can be taken as additional information about the tin–carboxylate monodentate bond fashion. Four of the compounds studied (**3a, 3b, 4a** and **4b**) occur in the hydrazone tautomeric form (based mainly on $\delta(^{15}N(\beta))$ values).[15,18]

Electronic and vibrational spectra

The electronic spectra were recorded in order to make a comparison of spectral parameters for **1–6** and their precursors (free acids and monosodium salts). All carboxylate and sulfonate sodium salts have similar electronic spectra with one maximum (except **5a** and **6b**, which have two maxima) in the visible region 330–450 nm. When the sodium ion is replaced by a [2-$(C_6H_4)CH_2N(CH_3)_2$(Ph or Bu)$_2$Sn] ligand, the energy and extinction coefficient of this band is only minimally changed. This fact suggests that there is no interaction between tin and the rest of the dye fragment.

The complexes prepared were investigated by IR spectroscopy in $CHCl_3$ solution. Bands characteristic for functional groups (carboxyl, sulfonyl, azo group and benzene ring) were found in all spectra measured. The difference between the asymmetric ν_a(C=O) and symmetric ν_s(C=O) band frequencies is characteristic for monodentate-bonded carboxylic groups.

In vitro antifungal activity

The results of *in vitro* antifungal testing of the compounds **1–6** (compounds **4a** and **3b** were not soluble in the media used) are summarized in the Table 2. The *in vitro* antifungal effect of the compounds with alkyl substituents (series **b**) was found to be slightly higher than for the aryl-substituted compounds. The values for **1b–6b** were comparable with those for the antimycotic drugs (ketoconazole, fluconazole, amphotericin B)[4] used for the treatment of systemic mycoses, but **1b–6b** were less active than the previously published tributyltin(IV) compounds with a four-coordinated tin atom.[34] The MFC values suggest that all the compounds studied are fungistatic rather than fungicidal (Table 2).

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REFERENCES

1. Jastrzebski JTBH, van Koten G. *Adv. Organometal. Chem.* 1993; **35**: 241.
2. Smith PJ (ed.). *Chemistry of Tin*. Blackie Academic & Professional: Glasgow, 1998.
3. Jurkschat K, Pieper N, Seemeyer S, Schürmann M, Biesemans M, Verbruggen I, Willem R. *Organometallics* 2001; **20**: 686.
4. Růžička A, Dostál L, Jambor R, Brus J, Císařová I, Holčapek M, Holeček J. *Appl. Organometal. Chem.* 2002; **16**: 315.
5. Růžička A, Pejchal V, Holeček J, Lyčka A, Jacob K. *Collect. Czech. Chem. Commun.* 1998; **63**: 997.
6. Růžička A, Jambor R, Brus J, Císařová I, Holeček J. *Inorg. Chim. Acta* 2001; **323**: 163.
7. Růžička A, Lyčka A, Jambor R, Novák P, Císařová I, Holčapek M, Erben M, Holeček J. *Appl. Organometal. Chem.* 2003; **17**: 168.
8. Price R. In *The Chemistry of Synthetic Dyes*, Vol. III, Venkataraman K (ed.). Academic Press: New York, 1997; chapter VII.
9. Baumann H. In *Ullmanns Encyclopaedie der Technischen Chemie*, Vol. 16. VCH: Weinheim, 1978.
10. Beffa F, Back G. *Rev. Prog. Color Relat. Top.* 1984; **14**: 33.
11. Zollinger H. In *Color Chemistry. Syntheses, Properties and Application of Organic Dyes and Pigments*. VCH: Weinheim, 1987.
12. Crowe AJ. In *Metal Complexes in Cancer Chemotherapy*, Keppler BK (ed.). VCH: Weinheim, 1993; 369–379 and references cited therein.
13. Gielen M. *Appl. Organometal. Chem.* 2002; **16**: 481 and references cited therein.
14. Nath M, Yadav R, Eng G, Musingarimi P. *Appl. Organometal. Chem.* 1999; **13**: 29 and references cited therein.
15. Lyčka A, Luštinec D, Holeček J, Nádvorník M, Holčapek M. *Dyes Pigments* 2001; **50**: 203.
16. Hull W. In *Two-Dimensional NMR Spectroscopy. Application for Chemists and Biochemists*, second edition, Croasmun WR, Carlson RMK (eds). VCH: New York, 1994.
17. Braun S, Kalinowski H-O, Berger S. *150 and More Basic NMR Experiments*, second edition. Wiley VCH: Weinheim, 1998.
18. Lyčka A. *Collect. Czech. Chem. Commun.* 1982; **47**: 1112.
19. Blessing RH. *J. Appl. Crystallogr.* 1997; **30**: 421.
20. Altomare A, Cascarone G, Giacovazzo C, Guagliardi A, Burla MC, Polidori G, Camalli M. *J. Appl. Crystallogr.* 1994; **27**: 435.
21. Sheldrick GM. *SHELXL-97, a program for crystal structure refinement*. University of Göttingen, Germany, 1997.
22. National Committee for Clinical Laboratory Standards. Reference method for broth dilution antifungal susceptibility testing of yeasts. Approved standard. Document M27-A, National Committee for Clinical Laboratory Standards, Wayne, PA, 1997.
23. Willem R, Bouhdid A, Mahieu B, Ghys L, Biesemans M, Tiekink ERT, de Vos D, Gielen M. *J. Organometal. Chem.* 1997; **531**: 151.

24. Allen FH, Kennard O. *Chem. Des. Automat. News* 1993; **8**: 1, 31–37.
25. Van Koten G, Noltes JG, Spek AL. *J. Organometal. Chem.* 1976; **118**: 183.
26. Varga RA, Schuerman M, Silvestru C. *J. Organometal. Chem.* 2001; **623**: 161.
27. Zoufalá P, Císařová I, Růžička A, Štěpnička P. *Appl. Organometal. Chem.* **18**: in press.
28. Tiekink ERT. *Appl. Organometal. Chem.* 1991; **5**: 1.
29. Holeček J, Nádvorník M, Handlíř K, Lyčka A. *J. Organometal. Chem.* 1983; **241**: 177.
30. Holeček J, Handlíř K, Nádvorník M, Lyčka A. *Z. Chem.* 1990; **30**: 265.
31. Holeček J, Lyčka A. *Inorg. Chim. Acta* 1986; **118**: 115.
32. Biesemans M, Martins J, Willem R, Lyčka A, Růžička A, Holeček J. *Magn. Reson. Chem.* 2002; **40**: 65.
33. Lyčka A, Nádvorník M, Handlíř K, Holeček J. *Collect. Czech. Chem. Commun.* 1984; **49**: 2903.
34. Smička A, Buchta V, Handlíř K. *Metal Based Drugs* 2001; **8**: 165.

