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Supramolecular organotin(IV) dithiocarboxylates as potential antimicrobial agents

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A series of tri-, chlorodi-, and diorganotin(IV) derivatives of 4-(2-methoxyphenyl)piperazine-1-carbodithioate (L) {R = *n*-C_4H_9 (**1**), C_6H_{11} (**2**), CH_3 (**3**) and C_6H_5 (**4**)}, (*n*-C_4H_9)$_2$SnClL (**5**) and R_2SnL_2 {R = *n*-C_4H_9 (**6**), C_2H_5 (**7**), CH_3 (**8**)} have been synthesized by refluxing organotin(IV) chlorides with the ligand-salt in the appropriate molar ratio. Elemental analysis, Raman, IR, multinuclear NMR (^{1}H, ^{13}C and ^{119}Sn), mass spectroscopic, and single-crystal X-ray crystallographic studies were undertaken to elucidate the structures of the new compounds both in solution and in the solid state. The X-ray diffraction work reveals supramolecular structures for **4** and **6**, with distorted trigonal-bipyramidal and distorted octahedral geometries around Sn, respectively. The ligand and several of the new compounds are good antimicrobial agents.

Keywords: Organotin(IV) dithiocarboxylate; Molecular spectroscopy; Single-crystal X-ray structures; Antifungal and antibacterial activity

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1. Introduction

Dithiocarboxylate salt and their complexes have industrial and biological applications [1–3], being used as pesticides, as an antidote for copper poisoning, i.e., Wilson's disease and have application in ameliorating nephrotoxicity associated with platinum-based chemotherapy [4–6]. Pyrrolidine dithiocarboxylate salts have been investigated for antitumor and antiviral activities [7]. Diethyldithiocarbamate salts have application in chronic alcoholism therapy [8] and treatment of HIV-patients [9]. Metal-based dithiocarboxylates, such as *ziram* (zinc-dimethyldithiocarboxylate) and *zineb* (zinc ethylene-1,2-bis-dithiocarboxylate), are marketed as fungicides for use on seed foliages, fruit and vegetable crops.

The importance of the Sn–S bond in biology has led to the study of organotin dithiocarboxylates [10], which also have fascinating structural motifs and biological

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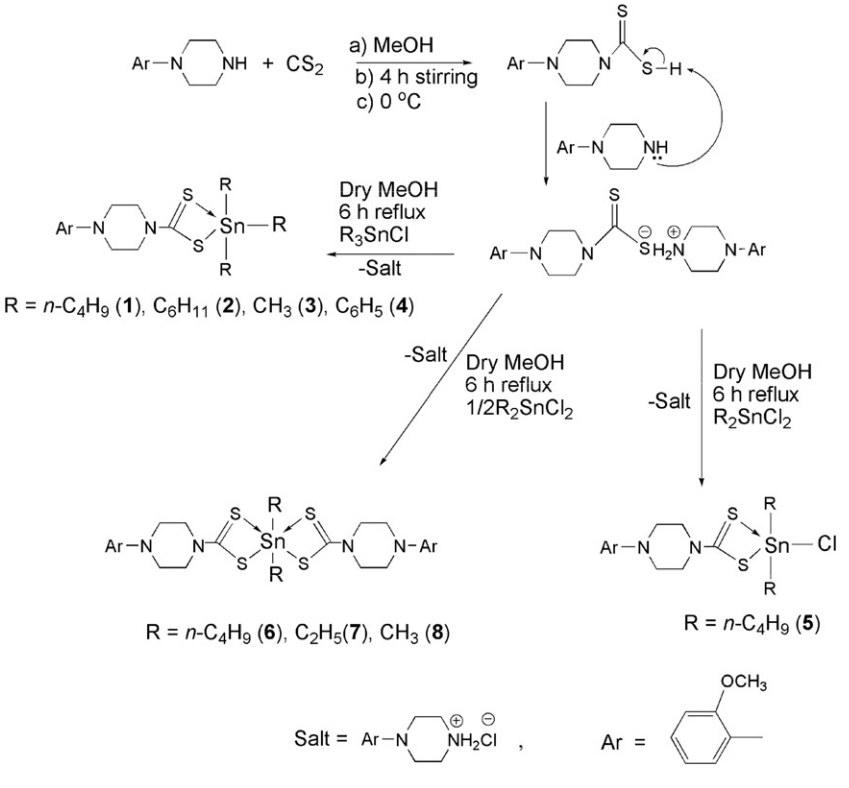
applications as fungicidal, bactericidal, insecticidal, and antitumor agents [11, 12]. Our group recently showed that these compounds exert anticancer action by arresting DNA replication through intercalation with DNA-bases [13]. In order to broaden the scope of these compounds, we synthesized Sn-based dithiocarboxylates of 4-(2-methoxyphenyl)-piperazine-1-carbodithioate and screen them for fungicidal and bactericidal activities (scheme 1).

2. Experimental

2.1. *Materials and methods*

Reagents, organotin(IV) chlorides and 4-benzylpiperidine were obtained from Aldrich and CS_2 was purchased from Riedal-de Haën; methanol was dried before use by the literature procedure [14]. Microanalyses were done using a Leco CHNS 932 apparatus. IR spectra ($\pm 1\,cm^{-1}$) were recorded as KBr pellets from 4000 to 400 cm^{-1} on a Bio-Rad Excaliber FT-IR, model FTS 300 MX spectrometer (USA). Raman spectra ($\pm 1\,cm^{-1}$) were measured with an InVia Renishaw spectrometer using both argon-ion (514.5 nm) and near-infrared diode (785 nm) lasers. The Renishaw WiRE 2.0 software was used for data acquisition and spectral manipulations. NMR spectra (DMSO-d_6) were obtained



Scheme 1. Synthesis of ligand and its organotin(IV) derivatives.

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on a Bruker AVANCE 300-MHz and Varian Mercury 300-MHz spectrometers (^{1}H and ^{13}C) using TMS as a reference and a Varian Unity 500-MHz instrument [^{119}Sn; $SnMe_4$ (ext) ref]. Electron impact (70 eV) mass spectra were recorded on a Kratos MS25RFA instrument.

The X-ray diffraction data were collected on a Bruker SMART APEX CCD diffractometer equipped with a 4K CCD detector. Data integration and global cell refinement were performed with SAINT. The program suite SAINTPLUS was used for space group determination (XPREP). The structure was solved by the Patterson method; extension of the model was accomplished by direct methods and applied to different structure factors using the program DIRDIF. All refinement calculations and graphics were performed with the program PLUTO and PLATON package. Hydrogen atoms were generated by geometrical considerations, constrained to idealized geometries, and allowed to ride on the carrier atoms with an isotropic displacement parameter related to the equivalent displacement parameter of their carrier, with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}$(methyl C). The methyl groups were refined as rigid groups and allowed to rotate freely. Assigned values of bond distances: secondary C–H_2 = 0.99 Å, methyl C–H_3 = 0.98 Å, and aromatic C–H = 0.95 Å.

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2.2. *Synthesis*

The synthesis of the ligand and the complexes are presented in this section together with Raman, IR and mass spectral data. The ^{1}H- and ^{13}C-NMR data for the ligand are also presented here. For the complexes, ^{1}H-NMR spectra are given in table 1, while the ^{13}C- and ^{119}Sn-NMR data are listed in table 2.

2.2.1a. 4-(2-Methoxyphenyl)piperazinium 4-(2-methoxyphenyl)piperazine-1-carbodithioate (L). Dropwise addition of CS_2 (in excess) in methanol (50 mL) to 4-(2-methoxyphenyl)piperazine (5.00 g, 26.04 mmol) in methanol (50 mL) was followed by stirring for 4 h at 273 K. The solvent was evaporated under reduced pressure giving a white product (scheme 1), which was washed with diethyl ether. (Yield: 5.10 g, 85%). m.p. 161–163°C. Anal. Calcd (Found, %), for $C_{23}H_{32}N_4O_2S_2$ (460.7): C, 59.97 (59.69); H, 7.00 (6.91); N, 12.16 (12.11); S, 13.92 (13.77). Raman (cm^{-1}): 569 ν(C–S), 1215 ν(C=S), 1466 ν(C–N). IR (cm^{-1}): 1020 ν(C–S), 1444 ν(C–N). ^{1}H-NMR (ppm): 3.63–3.60, 3.12–3.09 (m, $H_{2,2',2a,2'a}$, 8H), 4.64–4.63, 3.39–3.38 (m, $H_{3,3',3a,3'a}$, 8H), 3.90, 3.86 (s, OCH_3, 6H), 7.07–6.84 (m, Ar-H, 8H), 8.5 (s, NH_2, 2H). ^{13}C-NMR (ppm): 209.6 (C-1), 48.3, 44.7 (C-2, 2′, 2a, 2′a), 50.8, 50.7 (C-3, 3′, 3a, 3′a), 55.5, 55.4 (OCH_3), 140.6, 140.2 (C-4, 4a), 152.3, 152.1 (C-5, 5a), 111.4, 111.3 (C-6, 6a), 121.1, 121.0 (C-7, 7a), 123.8, 123.4 (C-8, 8a), 118.4, 118.3 (C-9, 9a). EI–MS, m/z (%): $[C_{11}H_{17}N_2O]^+$ 192 (100), $[C_9H_{12}NO]^+$ 150 (82.4), $[C_8H_9NO]^+$. 135 (26), $[C_7H_6NO]^+$ 120 (21), $[C_6H_4O]^+$ 92 (4.4), $[C_6H_4]^+$ 76 (75).

2.2.1b. General procedure for the synthesis of complexes. Triorganotin(IV) chloride (1 : 1) or diorganotin(IV) dichloride (1 : 1 and 2 : 1) in methanol (30 mL) was added dropwise to the ligand in methanol (50 mL) in the appropriate molar ratio and the mixture was refluxed for 6 h with constant stirring. The solvent was rotary evaporated and the product thus obtained was recrystallized from a chloroform–ethanol (4 : 1)

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Table 1. ^{1}H-NMR data[ab] of **1–8**.

^{1}H	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
2,2′	3.14–3.12 (m)	3.17–3.14 (m)	3.18–3.15 (m)	3.19–3.16 (m)	3.22–3.19 (m)	3.22–3.19 (m)	3.18–3.15 (m)	3.21–3.16 (m)
3,3′	4.36–4.32 (m)	4.42–4.39 (m)	4.3–4.28 (m)	4.33–4.30 (m)	4.20–4.17 (m)	4.20–4.17 (m)	4.33–4.30 (m)	4.17–4.14 (m)
Ar–H	7.01–6.84 (m)	7.08–6.89 (m)	7.09–6.90 (m)	7.12–6.91 (m)	7.12–6.89 (m)	7.12–6.87 (m)	7.09–6.90 (m)	7.12–6.89 (m)
OCH_3	3.85 (s)	3.90 (s)	3.90 (s)	3.91 (s)	3.91 (s)	3.91 (s)	3.91 (s)	3.74 (s)
α	1.67–1.19 (m)	2.05–1.28 (m)	1.58 (s), [81]	–	1.90–1.34 (m)	1.86–1.32 (m)	2.11 (q), (9)	1.19 (s), [98]
β	1.67–1.19 (m)	2.05–1.28 (m)	–	7.89–7.66 (m)	1.90–1.34 (m)	1.86–1.32 (m)	1.63 (t), (9)	–
γ	1.67–1.19 (m)	2.05–1.28 (m)	–	7.48–7.39 (m)	1.90–1.34 (m)	1.86–1.32 (m)	–	–
δ	0.94 (t), (6)	2.05–1.28 (m)	–	7.48–7.39 (m)	0.96 (t), (6)	0.96 (t), (6)	–	–

[a]Chemical shift (δ) in ppm. ^{2}J[^{119}Sn, ^{1}H], ^{3}J(^{1}H, ^{1}H) in Hz are listed in square brackets and parenthesis, respectively. Multiplicity is given as s = singlet, q = quartet, m = muliplet.
[b]Numbering in accordance with scheme 2.

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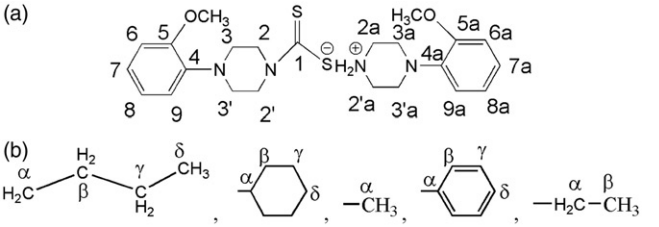
Table 2. ^{13}C and ^{119}Sn-NMR data[abc] of **1**–**8**.

^{13}C	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
1	190.6	198.8	199.3	196.1	196.9	197.4	200.4	196.2
2,2′	45.9	50.3	50.1	50.1	49.9	49.9	50.2	44.0
3,3′	51.2	52	51.3	52.6	51.9	51.9	51.3	48.2
Ar–C [c](4–9)	141.4, 152.5, 111.5, 121.2, 123.5, 118.6	140.2, 152.2, 111.3, 121.1, 123.7, 118.5	139.9, 152.2, 111.3, 121.1, 123.8, 118.5	139.9, 152.2, 111.3, 121, 1, 123.9, 118.6	139.5, 152.2, 111.4, 121.1, 124.3, 118.6	139.5, 152.2, 111.4, 121.1, 124.1, 118.6	140.0, 152.2, 111.3, 121.1, 123.8, 118.5	140.8, 152.6, 112.6, 121.5, 123.9, 118.8
OCH_3	55.6	55.5	55.5	55.5	55.5	55.5	55.5	56.0
α	17.7 [331.0, 315.0]	36.9 [340.0, 319.0]	15.5	142.3	26.5	26.5 [592.0, 572.0]	27.9 [621.0, 594.0]	12.1
β	28.1 [17.0]	32.1 [16.5]	–	136.8 [47.3, 45.0]	29.3	29.2	1.89 [49.5, 45.7]	–
γ	27.1 [63.0]	29.3 [67.5]	–	128.6 [61.5, 59.2]	27.9	27.1	–	–
δ	13.8	27.0 [7.5]	–	129.2 [12.8]	13.7	13.7	–	–
^{119}Sn	−13.4	−26.9	−167.0	−183.1	−193.2	−200.2	−186.4	−331.2

[a]Chemical shifts (δ) in ppm. $^{n}J[^{119,117}Sn, ^{13}C]$ in Hz are listed in square brackets.
[b]Number in accordance with scheme 2.
[c]Chemical shifts of carbons 4–9 of methoxyphenyl moiety.



Scheme 2. Numbering scheme for ligand (a) and organic moieties attached to Sn (b).

mixture (scheme 1). The numbering systems for the ligand and the organic groups attached to Sn are given in scheme 2.

2.2.2. Tributyltin(IV) 4-(2-methoxyphenyl)piperazine-1-carbodithioate (1). (Yield: 0.78 g, 75%) liquid. Anal. Calcd (Found), for $C_{24}H_{42}N_2OS_2Sn$ (557.4): C, 51.71 (51.61); H, 7.59 (7.56); N, 5.03 (5.09); S, 11.50 (11.41) %. Raman (cm^{-1}): 627 ν(C–S), 1157 ν(C=S), 1457 ν(C–N), 540 ν(Sn–C), 362 ν(Sn–S). IR (cm^{-1}): 977 ν(C–S), 1460 ν(C–N), 520 ν(Sn–C). EI-MS, *m/z* (%): $[C_{24}H_{42}N_2OS_2Sn]^+$ 558 (9), $[C_{20}H_{33}N_2OS_2Sn]^+$ 501 (32),$[C_{12}H_{15}N_2OS_2Sn]^+$ 387 (5), $[C_{13}H_{27}S_2Sn]^+$ 367 (5), $[C_9H_{18}S_2Sn]^+$ 310 (8), $[C_{12}H_{27}\ Sn]^+$ 291 (43), $[C_6H_{11}S_2Sn]^+$ 267 (100), $[C_8H_{18}Sn]^+$ 234 (35), $[C_4H_9Sn]^+$ 177 (100), $[Sn]^+$ 120 (58).

2.2.3. Tricyclohexyltin(IV) 4-(2-methoxyphenyl)piperazine-1-carbodithioate (2). (Yield: 0.82 g, 69%); m.p. 129–130°C. Anal. Calcd (Found, %), for $C_{30}H_{48}N_2OS_2Sn$ (635.6): C, 56.69 (56.55); H, 7.61 (7.65); N, 4.41 (4.54); S, 10.09 (9.86). Raman (cm^{-1}): 598 ν(C–S), 1163 ν(C=S), 1439 ν(C–N), 639 ν(Sn–C), 387 ν(Sn–S). IR (cm^{-1}): 990 ν(C–S), 1461 ν(C–N), 550 ν(Sn–C). EI-MS, *m/z* (%): $[C_{29}H_{45}N_2S_2Sn]^+$ 605 (5), $[C_{24}H_{37}N_2OS_2Sn]^+$ 533 (53), $[C_{17}H_{30}N_2S_2Sn]^+$ 446 (4), $[C_{12}H_{15}N_2OS_2Sn]^+$ 387 (14), $[C_{11}H_{19}N_2S_2Sn]^+$ 363 (68), $[C_9H_{15}NS_2Sn]^+$ 321 (100), $[C_{12}H_{22}Sn]^+$ 286 (4), $[C_6H_{11}Sn]^+$ 203 (87).

2.2.4. Trimethyltin(IV) 4-(2-methoxyphenyl)piperazine-1-carbodithioate (3). (Yield: 0.51 g, 63%); m.p. 123–126°C. Anal. Calcd (Found, %), for $C_{15}H_{24}N_2OS_2Sn$ (431.2): C, 41.78 (41.68); H, 5.61 (5.58); N, 6.50 (6.51); S, 14.87 (14.73). Raman (cm^{-1}): 554 ν(C–S), 1160 ν(C=S), 1433 ν(C–N), 514 ν(Sn–C), 386 ν(Sn–S). IR (cm^{-1}): 990 ν(C–S), 1463 ν(C–N), 507 ν(Sn–C). EI-MS, *m/z* (%): $[C_3H_6S_2Sn]^+$ 226 (2), $[C_3H_9Sn]^+$ 165 (25), $[C_2H_6Sn]^+$ 150 (100), $[C\ H_3Sn]^+$ 135 (40).

2.2.5. Triphenyltin(IV) 4-(2-methoxyphenyl)piperazine-1-carbodithioate (4). (Yield: 0.92 g, 80%); m.p. 156–158°C. Anal. Calcd (Found, %), for $C_{30}H_{30}N_2OS_2Sn$ (617.4): C, 58.36 (58.27); H, 4.90 (4.88); N, 4.54 (4.58); S, 10.39 (10.29). Raman (cm^{-1}): 617 ν(C–S), 1157 ν(C=S), 1480 ν(C–N), 267 ν(Sn–C), 390 ν(Sn–S). IR (cm^{-1}): 1007 ν(C–S), 1461 ν(C–N). EI MS, *m/z* (%): $[C_{24}H_{25}N_2OS_2Sn]^+$ 541 (9), $[C_{12}H_{15}N_2OS_2Sn]^+$ 387 (3), $[C_{18}H_{15}Sn]^+$ 351 (10), $[C_6H_5Sn]^+$ 197 (22).

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2.2.6. Chlorodibutyltin(IV) 4-(2-methoxyphenyl)piperazine-1-carbodithioate (5). (Yield: 0.81 g, 81%); m.p. 185–186°C. Anal. Calcd (Found, %), for $C_{20}H_{33}N_2OS_2SnCl$ (535.8): C, 44.83 (44.75); H, 6.21 (6.27); N, 5.23 (5.29); S, 11.97 (11.87). Raman (cm^{-1}): 626 ν(C–S), 1168 ν(C=S), 1457 ν(C–N), 513 ν(Sn–C), 361 ν(Sn–S), 259 ν(Sn–Cl). IR (cm^{-1}): 970 ν(C–S), 1470 ν(C–N), 509 ν(Sn–C). EI-MS, *m/z* (%): $[C_{20}H_{33}N_2OS_2Sn]^+$ 501 (4.5), $[C_{16}H_{24}N_2OS_2SnCl]^+$ 479 (10), $[C_{12}H_{15}N_2OS_2SnCl]^+$ 422 (10), $[C_{12}H_{15}N_2OS_2Sn]^+$ 387 (5), $[C_9H_{18}S_2SnCl]^+$ 345 (2), $[C_9H_{18}S_2Sn]^+$ 310 (2), $[C_8H_{18}SnCl]^+$ 269 (2), $[C_5H_9S_2Sn]^+$ 253 (8.6), $[C_4H_9SnCl]^+$ 212 (71), $[C_4H_9Sn]^+$ 177 (7), $[SnCl]^+$ 155 (53).

2.2.7. Dibutyltin(IV) bis[4-(2-methoxyphenyl)piperazine-1-carbodithioate] (6). (Yield: 0.59 g, 82%); m.p. 115–117°C. Anal. Calcd (Found, %), for $C_{32}H_{48}N_4O_2S_4Sn$ (767.7): C, 50.06 (49.77); H, 6.30 (6.29); N, 7.30 (7.32); S, 16.71 (16.59). Raman (cm^{-1}): 628 ν(C–S), 1153 ν(C=S), 1439 ν(C–N), 513 ν(Sn–C), 360 ν(Sn–S). IR (cm^{-1}): 980 ν(C–S), 1463 ν(C–N), 509 ν(Sn–C). EI-MS, *m/z* (%): $[C_{25}H_{41}N_4OS_4Sn]^+$ 661 (4), $[C_{17}H_{23}N_4OS_4Sn]^+$ 547 (3), $[C_{20}H_{33}N_2OS_2Sn]^+$ 501 (6), $[C_{12}H_{15}N_2OS_2Sn]^+$ 387 (4), $[C_4H_9Sn]^+$ 177 (12), $[Sn]^+$ 120 (20).

2.2.8. Diethyltin(IV) bis[4-(2-methoxyphenyl)piperazine-1-carbodithioate] (7). (Yield: 0.51 g, 76%); m.p. 185–186°C. Anal. Calcd (Found, %), for $C_{28}H_{40}N_4O_2S_4Sn$ (711.6): C, 47.26 (47.14); H, 5.67 (5.64); N, 7.87 (7.89); S, 18.02 (17.93). Raman (cm^{-1}): 624 ν(C–S), 1180 ν(C=S), 1457 ν(C–N), 486 ν(Sn–C), 385 ν(Sn–S). IR (cm^{-1}): 970 ν(C–S), 1461 ν(C–N), 509 ν(Sn–C). EI-MS, *m/z* (%): $[C_{26}H_{35}N_4O_2S_4Sn]^+$ 683 (0.7), $[C_{24}H_{30}N_4O_2S_4Sn]^+$ 654 (3), $[C_{16}H_{25}N_2OS_2Sn]^+$ 445 (10), $[C_{12}H_{15}N_2OS_2Sn]^+$ 387 (12), $[C_7H_{13}N_2S_2Sn]^+$ 309 (6), $[C_2H_5Sn]^+$ 149 (18).

2.2.9. Dimethyltin(IV) bis[4-(2-methoxyphenyl)piperazine-1-carbodithioate] (8). (Yield: 0.50 g, 79%); m.p. 191–194°C. Anal. Calcd (Found), for $C_{26}H_{36}N_4O_2S_4Sn$ (683.6): C, 45.68 (45.55); H, 5.31 (5.29); N, 8.20 (8.14); S, 18.76 (18.66). Raman (cm^{-1}): 626 ν(C–S), 1169 ν(C=S), 1458 ν(C–N), 512 ν(Sn–C), 361 ν(Sn–S). IR (cm^{-1}): 969 ν(C–S), 1463 ν(C–N), 514 ν(Sn–C). EI-MS, *m/z* (%): $[C_{24}H_{34}N_4O_2S_4Sn]^+$ 658 (100), $[C_{14}H_{21}N_2OS_2Sn]^+$ 417 (1), $[C_{13}H_{18}N_2OS_2Sn]^+$ 402 (2), $[C_3H_6S_2Sn]^+$ 226 (1), $[C_2H_3S_2Sn]^+$ 211 (4), $[S_2Sn]^+$ 184 (38), $[CS_2Sn]^+$ 196 (2), $[C_2H_6Sn]^+$ 150 (76), $[CH_3Sn]^+$ 135 (11), $[Sn]^+$ 120 (8).

3. Results and discussion

3.1. *Synthesis of ligand and 1–8*

Eight new organotin(IV) 4-(2-methoxyphenyl)piperazine-1-carbodithioates were prepared by reaction of L with the selected triorganotin(IV) chlorides and diorganotin(IV) dichlorides in the appropriate molar ratio in dry methanol (scheme 1). Compounds **1**–**8** are quite stable in moist-air and are also soluble in common organic solvents.

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3.2. *Raman and IR spectra*

In **1**–**8**, a new Raman peak (360–390 cm^{-1} region) due to Sn–S vibration indicates formation of the complexes. All spectra display a sharp Sn–C peak at 486–639 cm^{-1} except for the triphenyltin(IV) derivative, where a weak vibration at 267 cm^{-1} is due to Sn–C stretch. A ν(Sn–Cl) was observed only for the chlorodibutyltin(IV) derivative, indicating substitution of one chloride group from the diorganotin during the reaction.

For the organotin(IV) dithiocarboxylates, two main regions of the IR are of particular interest. First, 1450–1580 cm^{-1}, which is primarily associated with the "thioureide" band due to ν(N-CSS); second, the 940–1060 cm^{-1} region, which is associated with ν(C–S). The peak due to ν(N-CSS) was at ~1465 cm^{-1}, between the range reported for a C–N single bond (1250–1360 cm^{-1}) and a C=N double bond (1640–1690 cm^{-1}), and is an indication of partial double bond character in the C–N bond. From ligand to complexes, ν(N-CSS) shifts to higher energies, showing an increase of C–N double bond character [15]. For the chlorodibutyltin(IV) derivative, the ν(N-CSS) occurs at higher energy than for the dibutyltin(IV) complex owing to the electron-withdrawing chloride leading to a higher positive charge on nitrogen. The single band for C–S, in **1**–**8**, is in accord with bidentate 1,1-dithiolate to Sn [16].

3.3. *^{1}H, ^{13}C, and ^{119}Sn-NMR spectra*

^{1}H-NMR spectra were recorded for **1**–**8** in DMSO-d_6. The chemical shifts were identified from their relative intensities and multiplicity patterns. The total numbers of protons, calculated from the integration curves, are compatible with the proposed structures. The piperazine protons exhibit two triplets in the aliphatic region as demanded by the structure. The protons of phenyl resonate as a multiplet in the aromatic region, while the methoxy protons appear as a singlet at 3.85 ppm. The proton chemical shift assignments of the groups attached to Sn were a singlet at 1.19 ppm for **3** and **8** and a multiplet in the aliphatic region for **1**, **2**, **5**, and **6**. Ethyltin(IV) derivatives are a quartet and triplet as expected, while the aromatic protons of triphenyltin(IV) resonate as multiplets at 7.89–7.66 ppm. ^{2}J [^{119}Sn, ^{1}H] for **3** was 81 Hz, in the range normally expected for five-coordinate Sn and consistent with CSnC angle of 126.5°. The coupling constants, ^{2}J [^{119}Sn, ^{1}H], for the *n*-butyl-, cyclohexyl-, ethyl-, and triphenyltin(IV) derivatives could not be determined owing to the complex patterns. The geometry of the triphenyltin(IV) derivative was assessed from the difference in the chemical shift resonances of the *ortho* to *meta* and *para* protons (0.4 ppm), which matched well with anisobidentate bonding of 1,1-dithiolate moiety in solution [17].

The ^{13}C-NMR chemical shifts attributable to the organic groups attached to Sn were observed at positions comparable to those for similar compounds [18]. Moreover, the ^{13}C chemical shifts observed for the complexes were similar to that of the ligand except that the duplicate peak pattern disappeared and a small shift in the position of the CSS carbon was noted upon coordination. In the organotin compounds, the ^{1}J[^{119}Sn,^{13}C] coupling constant is a key parameter in assessing the coordination number of Sn. The coupling constants were 341 Hz for the tributyltin (**1**) and 331 Hz for the tricyclohexyltin (**2**), typical values for tetrahedral compounds [19] (table 3). A characteristic feature for triphenyltin derivatives is the observation of the ^{13}C chemical shift of the *ipso*-carbon at 142.3 ppm, which is attributed to a five-coordinate Sn [20].

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Table 3. (C–Sn–C) angles (°) based on NMR parameters of selected compounds.

Comp. No.	$^1J(^{119}Sn, ^{13}C)$ (Hz)	$^2J(^{119}Sn, ^1H)$ (Hz)	Angle (°)		Angle (°) from X-ray analysis
			^1J	^2J	
1	331	–	105.8	–	–
2	340	–	106.6	–	–
3	–	81	–	126.5	–
6	592	–	128.6	–	143.37(11)
7	621	–	131.2	–	–
8	–	98	–	144.9	–

The calculated ^1J [^{119}Sn, ^{13}C] coupling constant for **6** and **7** is 592 and 661 Hz, respectively, in accord with a five-coordinate Sn in these compounds.

The ^{119}Sn chemical shifts obtained for triorganotin(IV) complexes lie in the range expected for four- (**1** and **2**) and five-coordinate (**3** and **4**) Sn. The ^{119}Sn-NMR data for **5**, **6**, and **7** are in conformity with five-coordinate Sn. The −333.2 ppm value for **8** is compatible with octahedral geometry around Sn [21].

3.4. *Mass spectra*

The mass spectra for **1**–**8** showed rich ion distributions, but our interest lies in the Sn-containing ions. These ions were easily and quantitatively identified from the characteristic isotopic peak pattern for "Sn" and "SnCl" (only in case of chlorodibutyltin derivatives) [22]. Complexes **1**–**8** show no molecular ion (M^+), as is generally the case for main group organometallic compounds; however, the different fragments observed for these compounds are given in the Experimental section.

3.5. *X-ray structures*

3.5.1. Crystal structure of 4. The crystal data and selected interatomic parameters for **4** are shown in tables 4 and 5, respectively. The balls and sticks diagram, together with atomic numbering, is depicted in figure 1. The 1,1-dithiolate is coordinated asymmetrically to Sn, with a shorter Sn–S1 bond [2.4747(16) Å] and a longer Sn–S2 bond [3.0737(17) Å]. The difference between the two Sn–S bonds is 0.599 Å. The shorter bond length is close to the sum of the covalent radii of Sn and S (2.42 Å), and long Sn–S bond length is much shorter than the sum of the van der Waal's radii (4.0 Å) of the two atoms. The ligand is coordinated in an anisobidentate manner and chelated to Sn by two sulfurs, giving a trigonal-bipyramidal geometry around Sn. The geometry around Sn can also be characterized by the value of $\tau = (\beta - \alpha)/60$, where β and α are the consecutive largest of the basal angles around Sn. The calculated τ value for **4** is 0.59, indicating a highly distorted trigonal-bipyramidal geometry around Sn with C13 of a phenyl group and S2 of the ligand in axial positions, while C19A and C25A of the two phenyls and S1 of the ligand planar. The sum of the equatorial angles involving the two α-carbons of phenyl and S of 1 : 343.9° also shows marked deviation from the ideal

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Table 4. Crystal data and structure refinement parameters for **4** and **6**.

	4	**6**
Empirical formula	$C_{30}H_{30}N_2OS_2Sn$	$(C_{16}H_{24}N_2OS_2S)_2Sn$
Formula weight	617.42	767.73
Crystal system	Triclinic	Monoclinic
Space group	*P*-1, 2	*C*2/c, 15
Unit cell dimensions (Å, °)		
a	9.2973(8)	30.779(2)
b	11.9648(10)	7.0293(4)
c	13.5149(11)	22.3630(14)
α	88.9179(13)	–
β	77.7142(13)	133.0181(8)
γ	70.3200(13)	–
Volume (Å^3), *Z* (*Z*′)	1380.9(2), 2 (1)	3537.5(4), 4 (0.5)
Crystal size (mm^3)	$0.30 \times 0.27 \times 0.23$	$0.34 \times 0.21 \times 0.08$
Temperature (K)	100(1)	100(1)
Calculated density (cm^{-1})	11.02	9.93
Reflections collected	10,486	14,495
Independent reflections (all)	5292	4058
For $F_o \geq 4.0\sigma(F_o)$	4449	3426
$R(F) = \sum(\|\|F_o\| - \|F_c\|\|)/\sum\|F_o\|$	0.0604	0.0333
For $F_o > 4.0\sigma(F_o)$		
$wR(F^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$	0.1359	0.0805
Goodness-of-fit	1.047	1.197
θ range for data collection (°)	2.54–26.02	1.045
Data/restraints/parameters	5292/0/417	4058/0/197

Table 5. Selected bond lengths (Å) and angles (°) for **4.**

Sn–S1	2.4747(16)	Sn–S2	3.0737(17)
Sn–C13	2.164(9)	Sn–C19A	2.128(9)
Sn–C25A	2.316(8)	S1–C12	1.760(6)
S2–C12	1.693(6)		
S1–Sn–S2	63.84(5)	S1–Sn–C13	91.8(2)
S1–Sn–C19A	109.9(2)	S1–Sn–C25A	114.1(2)
S2–Sn–C13	155.6(2)	S2–Sn–C19A	85.4(3)
S2–Sn–C25A	79.51(19)	C13–Sn–C19A	103.4(4)
C13–Sn–C25A	113.8(4)	Sn–S1–C12	97.68(19)
Sn–S2–C12	79.3(2)	Sn–C13–C18A	114.5(6)
Sn–C19a–C20A	123.7(6)	Sn–C19a–C24A	116.0(7)
Sn–C25a–C26A	125.4(6)	Sn–C25a–C30A	114.6(5)

angle of 360°. C13 occupies one apical position of the trigonal-bipyramidal with S1–Sn–C13 angle being 91.8(2)°. As a result, 4-(2-methoxyphenyl)piperazine-1-carbodithioate is a chelating ligand with a small bite forming a four-membered ring and the S1–Sn–S2 angle is not 90°, but only 63.84(5)°. Therefore, S2 cannot occupy exactly the corresponding *trans* axial position to C13 and the C13–Sn–S2 angle is 155.6(2)° instead of 180°. The S–C bond lengths [S1–C12 = 1.760(6) Å and S2–C12 = 1.693(6) Å] also show the asymmetric nature of the dithiocarboxylate. Owing to the presence of intermolecular π–H and CH_3O–H interactions, a supramolecular structure results for **4** (figure 2).

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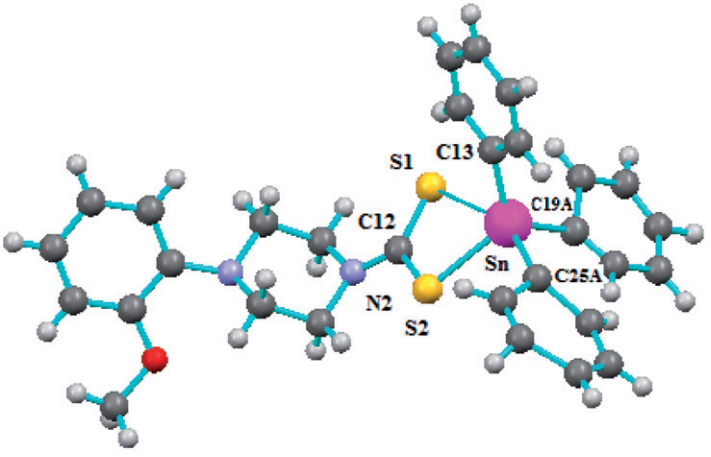

Figure 1. Balls and sticks drawing of **4** with atom numbering scheme.

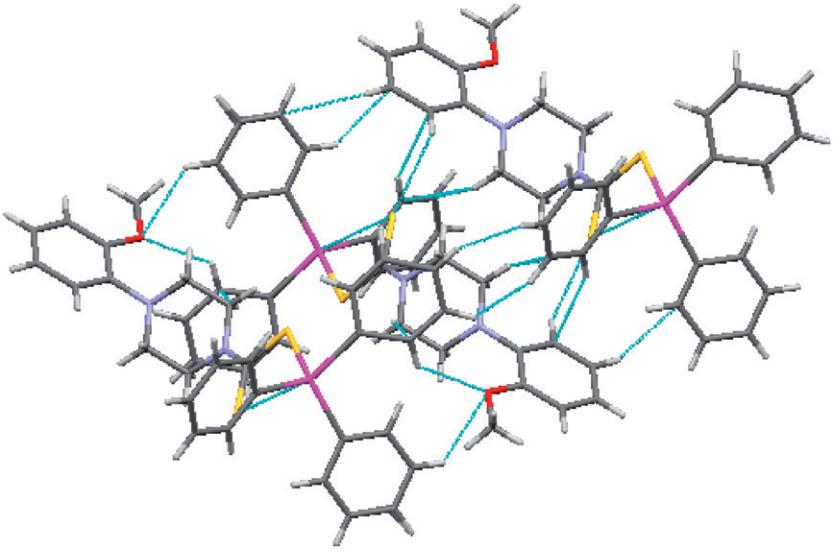

Figure 2. Supramolecular structure of **4** mediated by secondary π–H and CH_3O–H (2.587 Å) interactions.

3.5.2. X-ray structure of 6. Relevant bond lengths and angles are given in table 6, while table 4 lists the crystal data. A view of the molecule, including atom numbering scheme, is shown in figure 3. The two dithiocarboxylates are coordinated asymmetrically with short Sn–S2 [2.5364(9) Å] and Sn–S2_a [2.5364(9) Å] distances and longer Sn–S1 [2.9693(10) Å] and Sn–S1_a [2.9693(10) Å] distances. The longer Sn–S distances are significantly less than the sum of the van der Waal's radii (4.0 Å), and the coordination number of Sn is assigned as six. Further, the degree of asymmetry in the Sn–S bond distances is identical in the two dithiocarboxylates. The overall geometry at Sn is, however, highly distorted from *trans* octahedral with the C13–Sn–C13_a angle only 143.37(11)°, intermediate between *cis* and *trans*. The Sn and four sulfurs of the

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Table 6. Selected bond lengths (Å) and angles (°) for **6**.

Sn–S1	2.9693(10)	Sn–S2	2.5364(9)
Sn–C13	2.146(3)	Sn–S1_a	2.9693(10)
Sn–S2_a	2.5364(9)	Sn–C13_a	2.146(3)
S1–C12	1.703(2)	S2–C12	1.738(3)
S1–Sn–S2	64.95(2)	S1–Sn–C13	83.97(10)
S1–Sn–S1_a	148.37(2)	S1–Sn–S2_a	146.57(2)
S1–Sn–C13_a	86.21(10)	S2–Sn–C13	106.31(8)
S2–Sn–S1_a	146.57(2)	S2–Sn–S2_a	82.06(3)
S2–Sn–C13_a	101.15(10)	C13–Sn–S1_a	86.21(10)
C13–Sn–S2_a	101.15(9)	C13–Sn–C13_a	143.37(11)
S1_a–Sn–S2_a	64.95(2)	S1_a–Sn–C13_a	83.97(10)
S2_a–Sn–C13_a	106.31(8)	Sn–S1–C12	80.87(12)
Sn–S2–C12	94.29(9)		

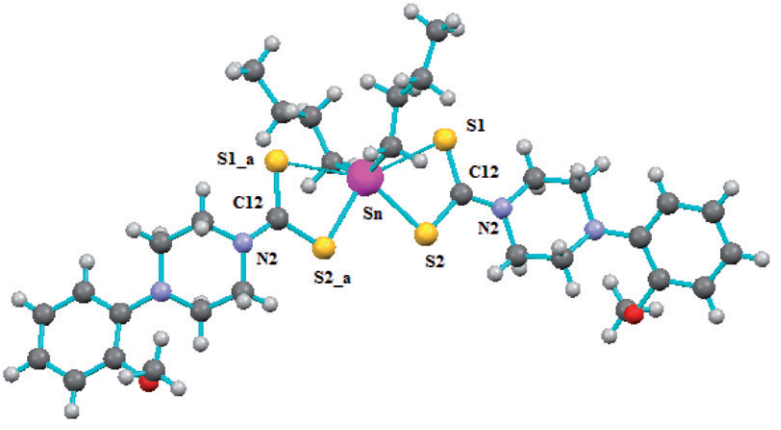

Figure 3. Balls and sticks drawing of **6** with atom numbering scheme.

ligands are nearly coplanar, but distorted from square-planar geometry, so that the *cis* S2–Sn–S2_a angle is only 82.06(3)° and the *cis* S1–Sn–S1_a angle is 148.37(2)°. In both anisobidentate ligands, each shorter Sn–S bond is associated with a longer C–S bond and *vice versa*, in accord with the bonding asymmetry of the ligands. The bond angles subtended at Sn by the methylene carbons and S2 and S2_a range from 106.31(8)° to 101.15(10)° demonstrating that the Sn–C bonds are bent toward the longer Sn–S bonds. This situation presumably arises because of repulsion between the bonding electron pairs around Sn. Thus, the coordination geometry about Sn in **6** is best described as distorted skew trapezoidal-bipyramidal. The geometry and bond lengths of the SnC_2S_4 core are comparable with those usually observed for related octahedral complexes [23]. The packing diagram (figure 4) shows that the supramolecular structure of **6** mediated by secondary π–H and CH_3O–H interactions.

3.6. *Biocidal activities*

The antibacterial and antifungal activities of **1**–**8**, together with those of **9** and **10** [chlorodiethyltin(IV) and chlorodimethyltin(IV) derivatives] of the ligand, were

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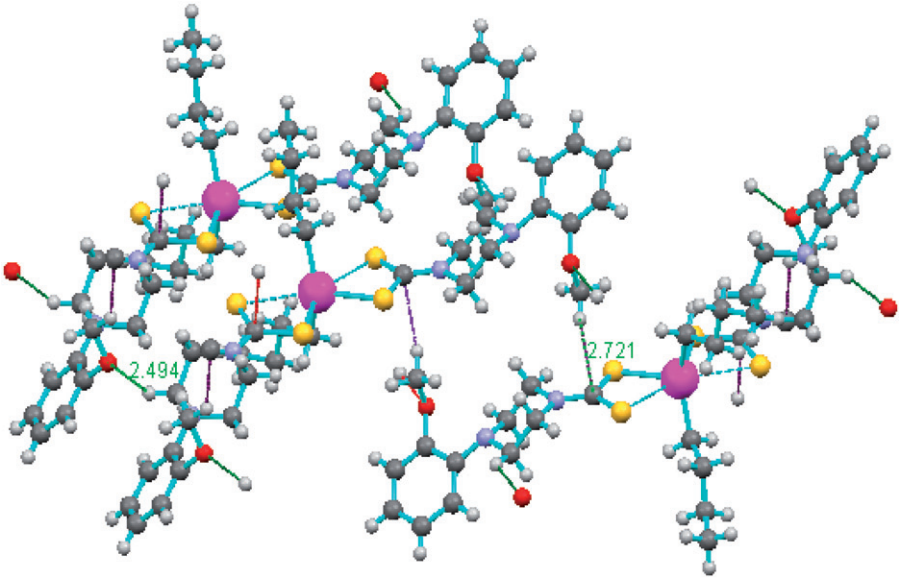

Figure 4. Supramolecular structure of **6** mediated by secondary π–H and CH_3O–H interactions.

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investigated. Spectroscopic data and the crystal structures for **9** and **10** have already been published by our group [24].

3.6.1. Antibacterial and antifungal activities. Compounds **1**–**10** were tested by the agar well diffusion method and the results are presented in table 7. The activity of these compounds against five different types of bacteria, *Escherichia coli*, *Salmonella typhi*, *Pseudomonas aeroginosa*, *Staphylococcus auerus*, and *Streptococcus*, were studied using *Streptomycin* as a reference drug. The antibacterial studies of the compounds showed better activity against the selected bacteria than did the ligand, but low activities when compared to the reference drug. Among the triorganotin(IV) derivatives, the bactericidal activities of **1** and **4** are fairly good; however, these two complexes demonstrated no activity against *S. aureus*. Complex **2** is the least active among the triorganotin(IV) complexes, while **3** was active against all the studied strains. In general, the chlorodibutyltin(IV) complex is more active than is its counterparts without a chloride substituent. The probable reason for this difference is the ease of hydrolysis of the former complexes [12].

The agar tube dilution protocol was employed to test the antifungal activities of the synthesized compounds against five different strains of fungi, *Aspergillus nigar*, *Aspergillus flavus*, *Helminthosporium solani*, *Alternia solani*, and *Fusarium* sp. The results are shown in table 8. The triorganotin(IV) derivatives are more active than are the chlorodi- and diorganotin(IV) complexes against the five strains. The activities of the triorganotin(IV) complexes are even more than for the standard drug and follow the trend: *n*-Bu_3SnL (**1**) > Me_3SnL (**3**) > Ph_3SnL (**4**) > $(C_6H_{11})_3SnL$ (**2**). The cytoplasmic membrane may be the possible target of action. This observation is further supported by high activities of the tributyltin(IV) derivatives, which alter the membrane fluidity

Table 7. Antibacterial activity data of ligand and its organotin(IV) derivatives.[ab]

Bacterium	Clinical implication	Zone of inhibition (mm)											
		L-salt	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	Ref. drug[b]
E. coli	Infection of wounds, urinary tractand dysentery	28	30	12	20	29	22	21	30	27	22	21	34
S. typhi	Typhoid fever, localized infection	14	30	22	24	28	28	22	31	31	24	20	31
P. aeruginosa	Infection of wounds, eyes, septicemia	0	8	0	20	6	10	14	22	20	16	18	24
S. aureus	Food poisoning, scaled skin syndrome, endrocarditis	0	0	0	20	0	23	23	28	23	24	16	38
Streptococcus	Strep throat	30	31	0	30	30	20	24	30	28	18	18	38

[a]*In vitro*, agar well diffusion method, conc. 1 mg mL^{-1} of DMSO.
[b]Reference drug, Streptomycin.

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[25] and the organism dies due to extensive K^+ leakage. In spite of the controversy around the toxicity of organotins toward higher species [26], it is possible that some of their complexes are not so hazardous. Therefore, **1**, **3**, and **4** represent a new class of drugs to be employed alone or in combination with others in current use, as new formulation for fungal diseases.

The mechanism of action of these compounds may be due to their ability to form secondary intermolecular interactions (as can be seen in crystal packing diagrams of **4** and **6**) with the cell constituents of the microorganisms, which in turn block the synthesis of protein by inhibiting the movement of ribosome along with RNA. This would inhibit synthesis of DNA in the cell nucleus [27]. The enhanced antimicrobial activity of the ligand on complexation with an organotin moiety may be due to chelation which reduces the polarity of the central Sn atom because of the partial sharing of its positive charge with donor groups and possible π-electron delocalization within the whole chelating ring. As a result, the lipophilic nature of the Sn increases, which favors the permeation of the complexes through the lipid layer of the cell membrane [28]. Our antimicrobial results supersede the findings of S. Jabbar *et al*. [29] for similar organotin(IV) dithiocarbamates. This fact may be attributed to the presence of methoxyphenyl substituent on piperazine ring, further enhancing the interaction of the complexes with microorganisms (see packing diagram).

4. Conclusions

Raman, IR and X-ray analyses of the new compounds illustrate that the mode of coordination of ligand, in all complexes, is bidentate in solid state. However, in solution, the coordination around Sn is decreased by one degree in **1**, **2**, and **6**, as validated by the multinuclear NMR spectroscopy. The *in vitro* antimicrobial assays of the complexes against selected bacterial and fungal strains have established their

Table 8. Antifungal activity[a] of ligand and its organotin(IV) derivatives.

	Tested fungi									
	A. nigar		*A. flavus*		*H. solani*		*A. solani*		*Fusarium* sp.	
Sample	Linear growth	% inhibition	Linear growth	% inhibition	Linear growth	% inhibition	Linear growth	% inhibition	Linear growth	% inhibition
Control	85	–	86	–	87	–	90	–	70	–
L	82.0	3.5	86	0.0	12	86.2	10	55.6	17	75.7
1	10.0	88.2	10	88.4	10	88.5	12	62.2	8	88.6
2	53.0	37.6	68	20.9	71	18.4	82	7.8	54	22.9
3	20.0	76.5	20	76.7	83	5.7	83	88.9	60	14.3
4	12.0	85.9	10	88.4	12	86.2	10	86.7	17	75.7
5	45.0	47.1	82	4.7	87	0.0	80	11.1	35	50.0
6	80.0	5.9	85	1.2	85	2.3	60	33.3	54	22.9
7	50	41.2	86	0.0	87	0.0	90	0.0	34	51.4
8	85	0.0	86	0.0	78	10.3	51	43.3	60	14.3
9	45.0	47.1	82	4.7	87	0.0	80	11.1	35	50.0
10	78.0	8.2	86	0.0	79	9.2	40	11.1	45	35.7
Clotrimazole	60	29.4	52	39.5	51	41.4	48	46.7	44	37.1

[a]Concentration: 200 μg mL^{-1} of DMSO.

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inhibitory effects. Moreover, the antifungal assays have confirmed that **1**, **3**, and **4** have the potency to be used fungicides.

Supplementary material

Crystallographic data for the structural analysis are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK on request quoting deposition numbers 718384 and 718385 for **4** and **6**, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CBZ, IEZ, UK (Fax: 44 1223336; E-mail: deposit@ccdc.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgments

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