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Substituted thienyl stibines and bismuthines: syntheses, structures and cytotoxicity

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New stibine and bismuthine substituted thienyl ring compounds, i.e. tris(3-methyl-2-thienyl)stibine (1), tris(3-methyl-2-thienyl)bismuthine (2), tris(3-thienyl)stibine (3), tris(3-thienyl)bismuthine (4) and tris(5-chloro-2-thienyl)stibine (5), have been synthesized and characterized by IR, mass, ^{1}H, ^{13}C, COSY, and HETCOR NMR spectroscopy. The metal centres in all compounds are pyramidal, and molecules in the stibine compound (1) and bismuthine compound (2) associate via Sb···S or Bi···S interactions to form supramolecular chains.

The cytotoxicity of compounds 1 and 5 was determined. For compound 5, 85% of carcinogenic cell growth inhibition (U, K and H) was observed. Compound 1 shows a significant selectivity (>80%) for carcinogenic cell growth (K and U) inhibition. Both the compounds are highly toxic for the growth of normal lymphocytes with ∼95% lethality. Compound 1 is approximately 20 times more toxic than 5 against *Artemia salina*.

KEYWORDS: stibine; bismuthine; substituted thienyl; crystal structure; cytotoxicity

INTRODUCTION

Tertiary stibines R_3Sb or bismuthines R_3Bi (R = alkyl or aryl) are very well known, but there exist only a few reports on tertiary stibines or bismuthines where antimony is directly attached to an aromatic heterocycle.[1–6] Studies on organometallic compounds containing thienyl or substituted thienyl, furyl or *N*-methylpyrrolyl with silicon, germanium, tin or mercury, and even with lighter pnictogens (phosphorus, arsenic), are reported in literature.[7–11]

Recently, we reported some new stibines and bismuthines containing C-attached 2-thienyl, 2-furyl and 2-(*N*-methylpyrrolyl) groups.[12,13] X-ray structures of tris(2-thienyl)stibine and tris(2-furyl)bismuthine have also been reported.[10,11] The ligation properties of these types of stibine have also been reported previously with palladium and silver.[4,12]

Apart from the above, there are very few reports available on the biological activity of organostibine(III) compounds, though a number of reports exist on the biological activities of organoantimony compounds where the pnictogen element is in oxidation state V.[14] In view of our interest in structural aspects of organoantimony and organobismuth compounds and the scant reports in the literature on stibines or bismuthines[15,16] containing C-heterocyclic thiophene and very few reports on the biological activities of stibines, we undertook this work.

RESULTS AND DISCUSSION

The new stibines and bismuthines (**1**–**5**) were synthesized by the reaction of MCl_3 (M = Sb or Bi) with suitable organolithium or organomagnesium precursors. The extraction and slow concentration from $CHCl_3$ solution permits the isolation of crystals. The structures were determined by spectroscopy, elemental analyses and X-ray diffraction. These new tertiary stibines and bismuthines containing a substituted thienyl ring remain unaffected by water; thus, the Sb–C and Bi–C bonds in these compounds are not hydrolysed by water alone. These substituted thienyl antimony(III) or bismuth(III) derivatives behave like other triaryl-stibines or -bismuthines and are thermally stable and melt without decomposition. These

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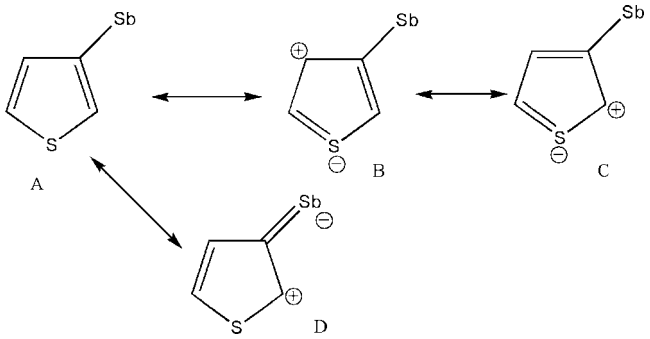
compounds show a very slow degree of decomposition at room temperature in air. The decomposition products could not be identified because of their insolubility in common organic solvents.

Electron impact (EI) mass spectral analyses of these stibines and bismuthines show some common fragmentation patterns. The fragmentation peaks observed for the thienyl part are not of much importance and are according to those reported in the literature. In the EI mass spectra of the tris(3-thienyl)bismuthine(III) molecular ion peak could not be observed; however, a molecular ion peak was observed in the FAB^+ spectra, but the peak percentage was very low.

The proton NMR spectra of all these stibines and bismuthines show characteristic chemical shift patterns of 2,3-disubstituted, 3-substituted and 2,5-disubstituted thiophene in the aromatic region. In all cases, assignment of individual proton signals was based on J_{HH} coupling constant values and was confirmed by COSY. For thiophene substituted at the third position by antimony or bismuth, it was observed that H_2 and H_4 are more deshielded compared with parent the unsubstituted heterocycle, which may be due to $p\pi-d\pi$ bonding and can be explained by the contribution of canonical forms B and C respectively in Scheme 1.

At ambient temperature, four ^{13}C NMR signals were observed for these compounds in the aromatic region. In bismuthine, most of the protons are deshielded in comparison with stibines; similar observations were also reported earlier.[13]



Scheme 1.

The crystal and molecular structures of each of **1**–**5** have been determined, and the results are given in Tables 1 and 2 and in Figures 1–5. As expected, all molecules exhibit pyramidal geometries. The molecules in each of **1, 2** and **4** (two independent but similar molecules) are located on a crystallographic threefold axis, whereas molecule **5** has mirror symmetry. The isomorphous stibine **1** and bismuthine **2** structures show supramolecular Sb···S and Bi···S interactions that are less than the sum of the respective van der Waals radii, as detailed in Table 3. Thus, the coordination geometry for the antimony and bismuth centres in **1** and **2** may be described as $3+3$ with the supramolecular association leading to chains aligned along the crystallographic *c*-axis. The average Sb–C bond distance in **3** is similar to the

Table 1. Crystallographic data for compounds **1**–**5**

	1	**2**	**3**	**4**	**5**
Empirical formula	$C_{15}H_{15}S_3Sb$	$C_{15}H_{15}BiS_3$	$C_{12}H_9S_3Sb$	$C_{12}H_9BiS_3$	$C_{12}H_6Cl_3S_3Sb$
Formula weight	413.20	500.43	371.12	458.35	474.44
Crystal system	Rhombohedral	Rhombohedral	Monoclinic	Rhombohedral	Monoclinic
Space group	*R*3	*R*3	$P2_1/n$	*R*3	$P2_1/m$
a (Å)	16.162(1)	16.426(1)	8.749(1)	9.5199(4)	6.8851(5)
b (Å)	16.162(1)	16.426(1)	16.923(1)	9.5199(4)	13.900(1)
c (Å)	5.4889(4)	5.332(1)	9.723(1)	26.129(3)	8.4535(6)
β (°)	90	90	110.267(1)	90	97.224(2)
V, (Å^3)	1241.7(1)	1245.9(3)	1350.5(2)	2050.8(3)	802.6(1)
Z	3	3	4	6	2
D_c (Mg cm^{-3})	1.658	2.001	1.825	2.227	1.963
μ(mm^{-1})	2.029	10.975	2.476	13.324	2.590
F(000)	612	708	720	1272	456
θ range (°)	2.5 to 32.5	2.5 to 32.6	2.4 to 32.6	2.4 to 28.0	2.4 to 33.2
Reflections collected	5741	5768	18 457	7142	11 413
Independent reflections	2003 ($R_{int} = 0.037$)	2003 ($R_{int} = 0.047$)	4877 ($R_{int} = 0.054$)	2210 ($R_{int} = 0.145$)	3119 ($R_{int} = 0.045$)
R indices (all data)	$R = 0.036$, $wR = 0.058$	$R = 0.042$, $wR = 0.050$	$R = 0.124$, $wR = 0.122$	$R = 0.059$, $wR = 0.092$	$R = 0.068$, $wR = 0.057$
Min./max. residual electron density (e$^-$Å^{-3})	1.44/−0.30	1.20/−1.07	0.94/0.46	2.45/−0.68	1.26/−0.41
CCDC deposition number	264 845	264 846	264 847	264 848	264 849

Table 2. Selected bond lengths (Å) and bond angles (°) for compounds **1**–**5**[a]

1	Sb1–C2	2.133(3)	C2–Sb1–C2A	94.17(11)
2	Bi1–C2	2.241(5)	C2–Bi1–C2A	92.47(16)
3	Sb1–C3	2.125(5)	Sb1–C8	2.134(5)
	Sb1–C13	2.135(4)	C3–Sb–C8	95.85(16)
	C3–Sb–C13	96.85(16)	C8–Sb–C13	95.86(16)
4	Bi1–C3	2.26(2)	C3–Bi1–C3A	90.4(8)
	Bi2–C8	2.250(18)	C8–Bi2–C8B	91.8(6)
5	Sb1–C5	2.122(3)	Sb1–C9	2.119(3)
	C5–Sb1–C9	99.24(9)	C5–Sb1–C5A	95.60(13)

[a] Symmetry operations. **1**: (A) $1-y, x-y, z$; **2**: (A) $y-x, 1-x, z$; **4**: (A) $1-y, x-y+1$; (B) $y-x, 1-x, z$; **5**: (A) $x, 1/2-y, z$.

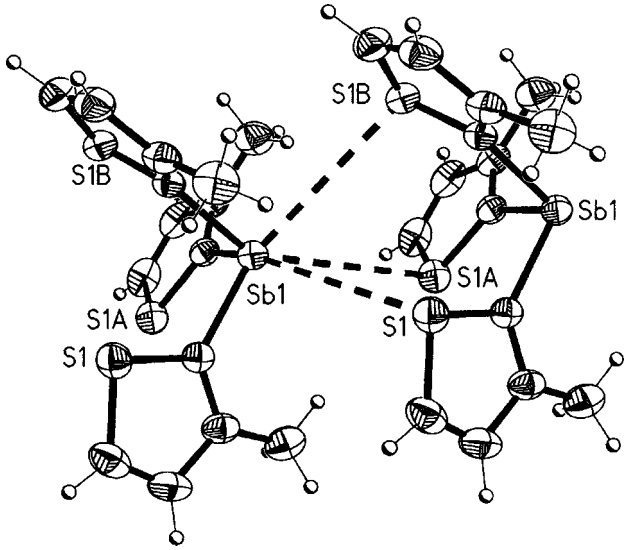


Figure 1. Supramolecular association in the structure of compound **1**. Right-hand molecule was generated by $1-x+y$, $1-x$, $1+z$ symmetry operations; atoms with suffixes A and B are generated by symmetry operation $1-y$, $x-y$, z and $y-x+1$, $1-x$, z respectively.

Sb–C bond length found in tris(2-thienyl)stibine (2.129(7) Å), but shorter than other tertiary stibines.[17–21] This may be due to the pπ–dπ bonding as suggested earlier in other reports based on the ^{1}H and ^{13}C NMR spectroscopy of similar compounds, i.e. 2-thienyl-stibine and -bismuthine.[12,13] In stibine **5**, the average Sb–C bond distance is 2.121(3) Å; to the best of our knowledge, this is the shortest Sb–C distance reported so far for compounds of this type. This may be due to the electronegativity of chlorine atoms present in the ring and pπ–dπ bonding between antimony and the carbon atom of the ring.

Both the stibines **1** and **5** show cytotoxicity against different cancer cell line cultivates. Compound **1** shows a significant selectivity (>80%) for carcinogenic cell leukaemia K562 on growth inhibition and shows less inhibition for colon HCT15 (<35%). Compound **5** inhibits growth of all three

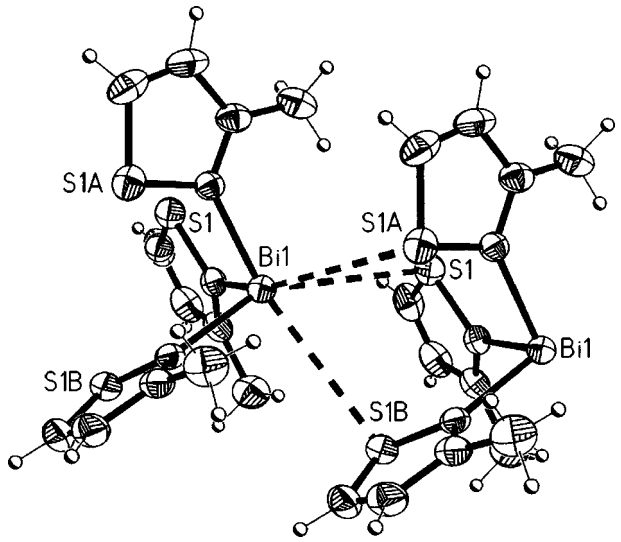


Figure 2. Supramolecular association in the structure of compound **2**. Right-hand molecule was generated by x, y, $1+z$ symmetry operations; atoms with suffixes A and B are generated by symmetry operation $x-y$, $1-x$, z and $1-y$, $x-y+1$, z respectively.

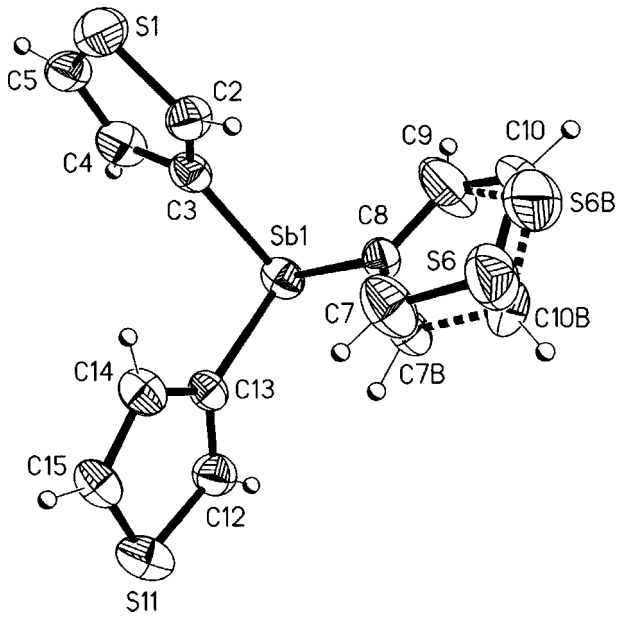


Figure 3. Molecular structure of compound **3**.

of the cell lines (leukaemia K562, colon HCT562 and SNC U251) studied in this work. Both compounds are highly toxic for the growth of normal lymphocytes with ~95% lethality.

The toxicity of tris(3-methyl-2-thienyl)stibine (**1**) and tris(5-chloro-2-thienyl)stibine (**5**) on larvae of *Artemia salina* was evaluated and LC_{50} value was determined. The LC_{50} value for compound **1** is 29.52 μM (with the concentration range

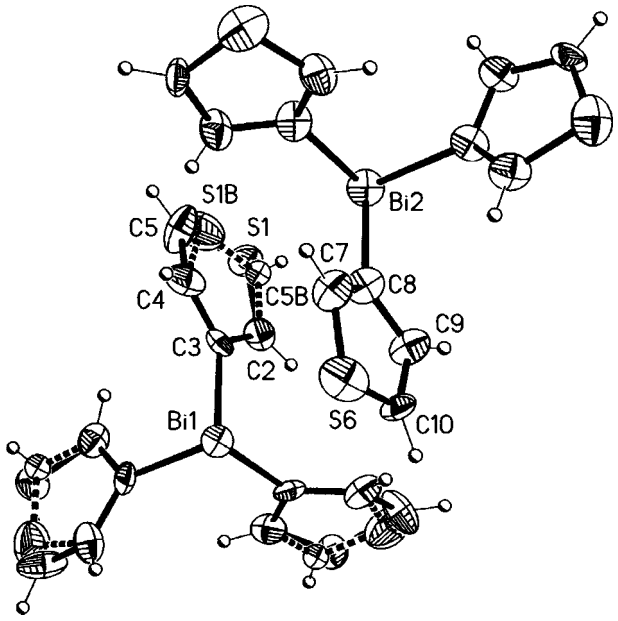


Figure 4. Molecular structure of compound **4**.

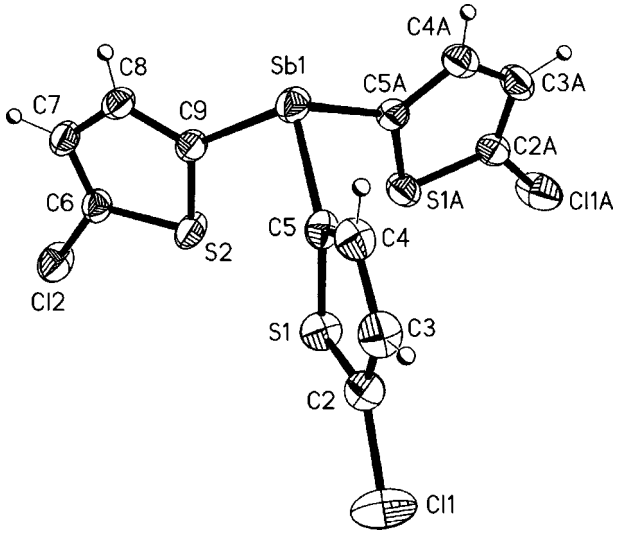


Figure 5. Molecular structure of compound **5**. Atoms with suffix A are generated by symmetry operation $x, 1/2 - y, z$.

Table 3. Secondary interactions in compounds **1, 2** and **4**

Compound	Atoms	Interatomic distance (Å)	Symmetry transformation
1	Sb1···S1A	3.8974(8)	$1-y, x-y, z$
2	Bi1···S1A	3.769(8)	$y-x, 1-x, z$
4	Bi2···S1B	3.98(4)	$y-x, 1-x, z$

being 23–38 μM). The LC_{50} value for compound **5** is 391.29 μM (with the concentration being 274–556 μM).

EXPERIMENTAL

All the solvents were distilled immediately prior to use. All the reactions were performed under an atmosphere of oxygen-free dry nitrogen. Melting points were obtained on a MEL-TEMP II Fisher and are uncorrected. The purity of the compounds was checked by thin-layer chromatography. Far-IR spectra were recorded in polyethylene on a Nicolet-Magna 750 spectrometer. EI and FAB^+ mass spectra were recorded on a JEOL SX102 double-focusing mass spectrometer with reverse geometry using a 6 kV xenon beam (10 am); nitrobenzyl alcohol was used as the matrix for recording the mass spectra. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ or CD_3OD using tetramethylsilane as an internal standard, on a JEOL ECLIPSE 300 spectrometer (^1H: 300.5311 MHz; ^{13}C: 75.5757).

X-ray structure determination

The X-ray intensity data were measured at 293 K on a Bruker SMART APEX CCD using monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) and SMART software.[22] An analytical face-indexed absorption correction was applied in each case. Structures were refined by full-matrix least squares on F^2 with SHELXTL.[23] In the crystals of compounds **3** and **4**, one of the independent thienyl rings is disordered. The disorder is twofold around the Sb–C and Bi–C bonds in each case, and superimposes the β and β' sulfur- and carbon-atom sites. The populations of sulfur and carbon scattering factors were refined for each of these sites, with the usual constraints—that the total population of each site be 1.0, and that each thienyl ring has the correct overall stoichiometry, i.e. C_4H_3S. Each site was refined with its own set of anisotropic displacement parameters (except for the carbon atom C5B in compound **4**) in order that the observed scattering density be modelled as accurately as possible. In compound **3**, S(6), C(7) and C(10) were refined to a site populations of 0.661(9), and their disordered congeners S(6B), C(7B) and C(10B) are complementary. For compound **4**, the refined site populations converged to 0.620(18) and 0.380(18) for S(1) and C(5) respectively, as well as for S(1B) and C(5B).

Toxicological studies on larvae of *A. salina*

A. salina larvae were obtained in 500 ml of seawater-type solution (prepared with Instant Ocean Aquatic Systems) with a concentration of 37.5 g l^{-1}. The eggs of *A. salina* were incubated at 25 °C for 48 h. A stock solution of 20 mM of compounds **1** and **5** in dimethylsulfoxide was diluted to 2 mM and 1 mM in sea-type water.

100 μl of the larvae solution was placed in a microplate NUNC with 96 wells to obtain a distribution of 10 larvae/well and 100 μl of stock solution. The latter gave total concentrations of 1 mM and 0.5 mM. The cultures were incubated for 24 h in order to determine the compounds' toxicity. The LC_{50} values were determined according to the Reed-Muench (Colegate) method and probit analysis

programme.[24] LC_{50} is the lethal concentration with 50% mortality.

Colon cancer (HCT-15), leukaemia (K-562 CML), and central nervous system (U-251 Glio) cell lines were supplied by the National Cancer Institute (USA). The cytotoxicity of the test compounds on tumour cells was determined using the protein-binding dye sulforhodamine B in micro-culture assay to measure cell viability and cell growth, as described in Ref. 25.

From the cell cultures of different tumour cell lines, i.e. central nervous system (U251), leukaemia (K562), colon (HCT-15) and normal lymphocytes, a suspension containing 5000 cells or 7500 cells in 100 µl were embedded in the microtitre plates and in another test compound. Both of these were incubated at 37 °C. After 24 h of incubation, 100 ml of each test compound was added with a concentration of 50 µM, and to test plate zero 100 µl of medium was added. These microplates were further incubated for 48 h and after the usual workup used for this test.[26] The results are obtained by IG (%) = 100 − (treatment/proteins content) × 100 (where IG is inhibition growth).

Syntheses

*Tris(3-methyl-2-thienyl)stibine (**1**)*

A solution of antimony trichloride (14.1 mmol) in diethyl ether (10 ml) was added dropwise and under a nitrogen atmosphere to 3-methyl-2-thienylmagnesium bromide (42.3 mmol; Aldrich, 1 M in tetrahydrofuran (THF)) at −20 °C with continuous stirring. The mixture was stirred for a further 3 h at room temperature (r.t.) and then the reaction was quenched with ice. After extraction with dichloromethane (3 × 10 ml) and drying over sodium sulfate, the solvent was removed under vacuum. Slow concentration from chloroform solution afforded single crystals suitable for X-ray analysis. Yield: 3.86 g (66%); m.p. = 56–58 °C. Anal. Found: C, 43.04; H, 3.31; S, 23.30. Calc. for $C_{15}H_{15}S_3Sb$: C, 43.68; H, 3.64; S, 24.17%. IR (cm^{-1}): 471 (Sb···C), 3064 (C–H aromatic), 727 (C–$S_{thiophene}$). ^1H NMR ($CDCl_3$, δ ppm): 7.5 (d, 1H J_{45} = 4.90, H_5), 7.0 (d, 1H, H_4), 2.39(s, 3H, $-CH_3$). ^{13}C NMR ($CDCl_3$, δ ppm): 17.47 (–Methyl), 126.46 (C_3), 145.77 (C_2), 132.32 (C_5), and 130.55 (C_4). MS (EI) *m/z* (%): 412 (14) [M^+], 314 (10) [M − (2-$C_4H_2SMe)^+$], 218 (100) [M − (2-$C_4H_2SMe)^+$], 193 (38) [(2-$C_4H_2SMe)_2$].

*Tris(3-methyl-2-thienyl)bismuthine (**2**)*

The compound was synthesized by a similar procedure to **1**. $BiCl_3$ (14.1 mmol) in THF (15 ml) was added in place of $SbCl_3$. Yield: 4.01 g (57%); m.p. = 147–148 °C. Anal.: Found: C, 36.09; H, 3.05; S, 19.53. Calc. for $C_{15}H_{15}BiS_3$: C, 36.0; H, 3.0; S, 19.2%. IR (cm^{-1}): 468.8 (Bi–C), 3093.9 (C–H aromatic), 718.3 (C–$S_{thiophene}$). ^1H NMR ($CDCl_3$, δ ppm): 7.6 (d, 1H J_{45} = 4.86, H_5), 6.93 (d, 1H, H_4), 2.37(s, 3H, $-CH_3$). ^{13}C NMR ($CDCl_3$, δ ppm): 18.55 (–Methyl), 126.73 (C_3), 145.29 (C_2), 133.87 (C_5), and 130.39 (C_4). MS (EI) *m/z* (%): 500 (0.7) [M^+], 403 (7.5) [M − (2-$C_4H_2SMe)^+$], 306 (100) [M − (2-$C_4H_2SMe)^+$], 209 (47) [M − (3-$C_4H_2SMe)^+$], 193 (17) [(2-$C_4H_2SMe)_2$].

*Tris(3-thienyl)stibine (**3**)*

A solution of antimony trichloride (12.13 mmol) in diethyl ether (10 ml) was added dropwise and under a nitrogen atmosphere to (3-thienyl)lithium, which was synthesized *in situ* according to the reported method[27] at −20 °C with continuous stirring. The mixture was stirred for a further 5 h at r.t. and then the reaction was quenched with ice. After extraction with dichloromethane (3 × 10 ml) and drying over sodium sulfate, the solvent was removed under vacuum. Slow concentration from chloroform solution afforded single crystals suitable for X-ray analysis. Yield: 2.15 g (48%); m.p. = 60 °C. Anal. Found: C, 38.70; H, 2.48; S, 24.94. Calc. for $C_{12}H_9S_3Sb$: C, 38.91; H, 2.43; S, 25.94%. IR (cm^{-1}): 480.1 (Sb–C), 3087.5 (C–H aromatic), 773.5 (C–$S_{thiophene}$). ^1H NMR ($CDCl_3$, δ ppm): 7.10 (d, 1H J_{45} = 4.94, H_5), 7.41 (d, 1H, H_4), 7.33 (s, 1H, H_2). ^{13}C NMR ($CDCl_3$, δ ppm): 133.22 (C_3), 133.0 (C_2), 132.66 (C_4), and 126.42 (C_5). MS (EI) *m/z* (%): 370 (11) [M^+], 287 (7) [M − (3-$C_4H_3S)^+$], 204 (100) [M − (3-$C_4H_3S)_2^+$], 166 (55) [(3-$C_4H_3S)_2$].

*Tris(3-thienyl)bismuthine (**4**)*

The compound was synthesized by a similar procedure to **3**. $BiCl_3$ (14.1 mmol) in THF (15 ml) was added in place of $SbCl_3$. Yield: 2.57 g (40%); m.p. = 74–75 °C; Anal. Found: C, 30.88; H, 2.01; S, 21.32. Calc. for $C_{15}H_{15}S_3Sb$: C, 31.44; H, 1.96; S, 20.96%. IR (cm^{-1}): 581.3 (Bi–C), 3077.6 (C–H aromatic), 767.10 (C–$S_{thiophene}$). ^1H NMR ($CDCl_3$, δ ppm): 7.19 (d, 1H J_{45} = 4.89, H_5), 7.42 (d, 1H, H_4), 7.21 (s, 1H, H_2). ^{13}C NMR ($CDCl_3$, δ ppm): 135.88 (C_3), 136.21 (C_2), 135.03 (C_4), and 127.88 (C_5). MS (EI) *m/z* (%): 458 (0.7) [M^+], 375 (4) [M − (3-$C_4H_3S)^+$], 292 (100) [M − (3- $C_4H_3S)_2^+$], 166 (55) [(3-$C_4H_3S)_2$].

*Tris(5-chloro-2-thienyl)stibine (**5**)*

A solution of antimony trichloride (14.1 mmol) in ether (10 ml) was added dropwise and under a nitrogen atmosphere to 5-chloro-2-thienylmagnesium bromide (42.3 mmol) (Aldrich, 1 M in THF) at −20 °C with continuous stirring. Yield: 3.05 g (46%); m.p. = 31–33 °C. Anal. Found: C, 29.87; H, 1.31; S, 20.90. Calc. for $C_{15}H_{15}S_3Sb$: C, 30.44; H, 1.26; S, 20.29%. IR (cm^{-1}): 474.1 (Sb–C), 3086 (C–H aromatic), 792.9 (C–$S_{thiophene}$). ^1H NMR ($CDCl_3$, δ ppm): 6.96 (d, 1H, J_{34} = 3.63, H_3), 7.08 (d, 1H, H_4). ^{13}C NMR ($CDCl_3$, δ ppm): 127.96 (C_3), 131.21 (C_2), 137.19 (C_4), and 137.36 (C_5). MS (EI) *m/z* (%): 473 (3) [M^+], 357 (6) [*M* − (5-Cl-2-$C_4H_2S)^+$], 240 (100) [M − (5-Cl-2-$C_4H_3S)_2^+$], 166 (55) [(5-Cl-2-$C_4H_3S)_2$].

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