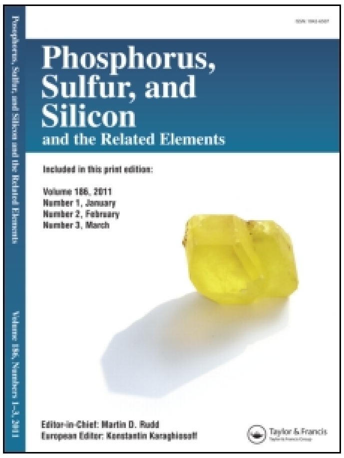

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Sharma, Pankaj K. , Rai, A. K. and Singh, Yashpal(2006) 'Triphenylantimony(v) Derivatives of 2,2-Disubstituted Benzothiazoline Ligands: Synthetic and Spectroscopic Studies', Phosphorus, Sulfur, and Silicon and the Related Elements, 181: 9, 2147 — 2154

To link to this Article: DOI: 10.1080/10426500600614477

URL: http://dx.doi.org/10.1080/10426500600614477

Phosphorus, Sulfur, and Silicon, 181:2147–2154, 2006
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500600614477

Triphenylantimony(v) Derivatives of 2,2-Disubstituted Benzothiazoline Ligands: Synthetic and Spectroscopic Studies

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*The reactions of triphenylantimony(v) isopropoxide with 2,2-disubstituted benzothiazolines in a 1:2 molar ratio in refluxing benzene solution yielded the corresponding triphenylantimony(v) derivatives (**1–5**) of the type $Ph_3Sb[SC_6H_4N{:}C(R)CH_2C(O)R']_2$, [Where, $R{=}CH_3$, $R'{=}CH_3$(**1**); $R{=}CH_3$, $R'{=}C_6H_5$(**2**); $R{=}CH_3$, $R'{=}4\text{-}CH_3C_6H_4$(**3**); $R{=}CH_3$, $R'{=}4\text{-}ClC_6H_4$(**4**); and $R{=}CF_3$, $R'{=}C_6H_5$(**5**)]. All of these newly synthesized derivatives have been characterized by elemental analyses and molecular weight measurements as well as IR and NMR [^1H and ^{13}C] spectral studies. On the basis of spectral data, seven-coordination around central antimony atom has been assigned to these derivatives.*

Keywords Triphenylantimony(v) derivatives; benzothiazoline; bidentate ligands; seven coordinated antimony(v) atom

INTRODUCTION

Compounds of organoantimony are well known for their applications in chemotherapy, as these compounds exhibit significant antimicrobial,[1] antiparasitic,[2] and antitumor[3–5] activities, which are associated with cytostatic activity.[4] The biological toxicity of these derivatives is much less than those of Pt and Pd anticancer substances.[4,6] A large number of antimony compounds have also been tested as bactericides,[7] fungicides,[8] and antifertility agents.[9,10]

Although an array of structural types for organoantimony complexes has been established ranging from monomeric[11,12] and dimeric[13,14] complexes to structures with infinite polymeric chains,[5,15] an interest in the

Received October 1, 2005; accepted December 30, 2005.

The award of a senior research fellowship to Pankaj K. Sharma by the University Grants Commission, New Delhi, is gratefully acknowledged.

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chemistry of organoantimony derivatives with a higher-coordinated antimony atom has increased during the last two decades, with special interest in their molecular structure, as antimony may attain a coordination number of 5, 6, and even 7 in some special cases.[16–21] A number of trialkyl- or triaryl-antimony(v) derivatives of multidentate ligands with seven-coordinated antimony have been synthesized and characterized.[16,17,22,23]

Benzothiazolines constitute an important class of bidentate as well as multidentate ligands.[24–26] The use of these Lewis-base functionalized ligands can be effective in increasing the coordination number of the central metal atom at the expense of the benzothiazoline ring to the corresponding Schiff base derivatives, leading to greater stability of the resulting compounds. In view of the previously discussed and in continuation of our analogous studies on organoantimony(v) derivatives,[27] we report herein the synthesis and characterization of triphenylantimony(v) derivatives of these ligands.

RESULTS AND DISCUSSION

Triphenylantimony(v) derivatives **1–5** (numbered according to the scheme given in Table I) of the benzothiazoline ligands have been prepared by the reactions of triphenylantimony(v) isopropoxide with the corresponding 2,2-disubstituted benzothiazoline ligands in a 1:2 molar ratio in refluxing benzene solution for ~6 h.

$$\mathrm{Ph_3Sb(OPr^i)_2 + 2\,H\overline{NC_6H_4S}C(R)CH_2C(O)R'} \xrightarrow[\text{Reflux}]{\mathrm{C_6H_6}}$$

$$\mathrm{Ph_3Sb[SC_6H_4N{:}C(R)CH_2C(O)R']_2 + 2Pr^iOH} \qquad (1)$$

All these reactions are quantitative and quite facile. The progress as well as the completion of reactions have been checked by estimating the isopropanol liberated during the course of reactions and fractionated as azeotrope with benzene. All these newly synthesized derivatives are hygroscopic, light-to-dark brown colored, viscous compounds, and soluble

TABLE I Numbering Scheme of the Derivatives (1–5)

Compound	Ligand	R	R′
1	L^1H	CH_3	CH_3
2	L^2H	CH_3	C_6H_5
3	L^3H	CH_3	$4\text{-}CH_3C_6H_4$
4	L^4H	CH_3	$4\text{-}ClC_6H_4$
5	L^5H	CF_3	C_6H_5

in common organic solvents. Ebullioscopic molecular weight measurements reveal their monomeric nature in benzene solution.

Infra-Red Spectra

A comparison of the IR spectra of the derivatives **1–5** with those of the corresponding free ligands reveals the following features: a disappearance of the broad stretching vibration (observed at 3225–3335 cm^{-1} due to the >NH group in the spectra of free ligands), which suggests the deprotonation of this group and rearrangement of the benzothiazoline ring during the formation of organoantimony(v) derivatives. This rearrangement of the benzothiazoline ring is also supported by the appearance of three new bands at 1622–1630 cm^{-1}, 422–430 cm^{-1}, and 365–383 cm^{-1} due to ν >C=N, νSb←N[28], and νSb—S[29] vibrations, respectively. No shift has been observed in the position of the >C=O absorption band (1720–1730 cm^{-1}) in the spectra of metal derivatives as compared to its position in the ligand's spectra; this indicates that this group does not participate in bonding, i.e., the ligand behaves as a bidentate ligand only. The Sb—Ph vibrations (Y-mode) have been observed in the range 448–470 cm^{-1}.[30]

^{1}H NMR Spectra

The characteristic signals in ^{1}H NMR spectra of these derivatives are summarized in Table II. The broad signal observed at δ 4.53–6.46 ppm, due to the >NH group resonance in the spectra of free benzothiazolines, is found to be absent in the spectra of corresponding triphenylantimony(v) derivatives, indicating the deprotonation of the >NH proton and the rearrangement of the benzothiazoline ring during complex formation. A sharp singlet observed in the region of δ 2.87–3.62 ppm has been assigned to —CH_2—protons. The absence of =CH as well as —C—OH

TABLE II ^{1}H NMR Data (δ ppm) of Triphenylantimony(v) Derivatives (1–5)

Complex	R	R′	—CH_2—	—NC_6H_4S—	Sb—Ph
1	2.42 (s)	1.71 (s)	2.92 (s)	7.29–7.54 (m)	7.73–7.96 (m)
2	2.87 (s)	7.30–7.70 (m)	2.87 (s)	7.30–7.70 (m)	7.77–7.98 (m)
*3	2.78 (s)	7.31–7.68 (m)	2.88 (s)	7.31–7.68 (m)	7.76–7.98 (m)
4	2.73 (s)	7.36–7.72 (m)	3.53 (s)	7.36–7.72 (m)	7.79–8.05 (m)
5	—	7.39–7.80 (m)	3.62 (s)	7.39–7.80 (m)	7.89–8.12 (m)

(s) = Singlet; (m) = Multiplet.

*A singlet for CH_3 protons has been observed at δ2.13 ppm.

signals and the presence of a —CH_2—signal in the spectra of both ligands and their corresponding triphenylantimony(v) derivatives indicate the absence of enolization of the >C=O group in these ligands, i.e., these ligands do not behave as bifunctional moieties in these derivatives. Different R and R′ group protons have been observed at their expected positions with small downfield shifts as compared to their positions in corresponding free ligands. Sb—Ph protons appear as a complex pattern in the region δ 7.73–8.12 ppm.

^{13}C NMR Spectra

Some useful information about the complexation behavior of benzothiazolines with the central Sb atom and the geometry of these derivatives have been obtained from ^{13}C NMR spectral data, summarized in Table III. The signal for the >C=N carbon has been observed in the range of 165.81–169.27 ppm. This signal was observed in the range 161.39–165.74 ppm (observed as C—N) in the spectra of free benzothiazolines. This small downfield shift (~5–7 ppm) in its position suggests the participation of this group in bonding with the rearrangement of the benzothiazoline ring on complexation followed by the formation of Sb←N and Sb—S bonds. The formation of the Sb—S bond is also supported by the shift of ~5–8 ppm in the position of the carbon signal attached to sulphur. The signals for various R, R′, and —CH_2— carbons show a small downfield shift in comparison to their position in free ligands.

Enolization of the ligands has been ruled out due to the absence of a =CH signal and appearance of a >C=O signal in the ^{13}C NMR spectra of ligands as well as complexes. The signal for a >C=O carbon does not show any shift in its position when compared with its position in the ^{13}C NMR spectra of free ligands. This may be due to the fact that the oxygen of this group is not coordinated to the central metal atom. Thus these ligands behave as monofunctional bidentate moieties

TABLE III ^{13}C NMR Data (δ ppm) of Triphenylantimony(v) Derivatives (1–5)

Complex	R	R′	—CH_2—	>C=O	>C=N	—NC_6H_4S—	Sb—Ph
1	28.74	19.05	63.06	193.47	165.93	120.34–128.83	130.25–152.93
2	28.82	120.29–124.81	62.45	194.09	165.81	126.60–131.98	134.18–152.26
*3	28.98	123.76–128.74	63.69	193.86	167.34	126.72–132.07	133.16–152.27
4	28.95	124.02–130.45	63.88	194.27	169.27	125.28–131.68	133.07–153.09
5	111.84	120.59–125.28	65.62	194.45	168.03	126.53–129.94	134.26–153.17

*^{13}C signal for the CH_3 group has been observed at δ25.67 ppm.

in these derivatives. The Sb—Ph carbons appear in the region 130.25–153.27 ppm.

Structural Elucidation

Although it is quite difficult to comment on the molecular structure of these derivatives in a solid state without actual X-ray crystal structure analysis of at least one of the products, on the basis of the previous IR and NMR (^{1}H and ^{13}C) spectral data (which indicate the monofunctional bidentate nature of these ligands) and in view of the presence of three phenyl groups and two monofunctional bidentate ligands, a structure with seven-coordinated antimony may be tentatively proposed for these triphenylantimony(v) derivatives.

EXPERIMENTAL

Moisture was carefully excluded throughout the whole experiment. All chemicals used were of reagent grade. Solvents (E. Merck) were carefully dried by standard methods before use. The benzothiazoline ligands[24–26] were prepared by equimolar condensation reactions of 2-aminothiophenol with corresponding β-diketones in refluxing benzene solution and were purified by distillation under vacuum before use. Triphenylantimony(v) isopropoxide was prepared by the reaction of Ph_3SbBr_2 with sodium isopropoxide in a 1:2 molar ratio.[31] Ph_3SbBr_2 was prepared by the literature method.[32] Antimony was estimated iodometrically.[33] Nitrogen and sulphur were estimated by Kjeldahl's and Messenger's methods, respectively.[33] Liberated isopropanol was estimated by the dichromate oxidimetric method.[34]

Molecular weight measurements were carried out by the ebullioscopic method in benzene solution using a Beckmann's thermometer. The IR spectra were recorded on a Nicolet DX FT IR spectrophotometer in the range 4000–200 cm^{-1} on a CsI cell. ^{1}H and ^{13}C NMR spectra were recorded in DMSO-d_6 solution on JEOL-FX-90Q MHz NMR spectrometer, using TMS as an internal and external reference, respectively.

The Synthesis of (1)

A benzene solution of the ligand $H\overline{NC_6H_4S}C(CH_3)CH_2C(O)CH_3$ (1.71 g, 8.25 mM) was added to a benzene solution of the $Ph_3Sb(OPr^i)_2$ (1.94 g, 4.12 mM), and the mixture was refluxed for ~6 h under a fractionating column. The progress as well as completion of the reaction was checked by estimating the liberated isopropanol in the azeotrope. After the completion of the reaction, excess solvent was distilled off and

TABLE IV Synthetic and Analytical Data of Triphenylantimony(v) Derivatives 1–5

	Reactants g (mM)		Molecular formula color physical state and % yeild	PriOH (g) found (Calc.)	Elemental analysis (%) found (Calc.)			Molecular weight found (Calc.)
Complex	$Ph^3Sb(OPr^i)_2$	Ligand			Sb	N	S	
1	1.94 (4.12)	1.71 (8.25)	$C_{40}H_{39}N_2O_2S_2Sb$ Dark brown Viscous 89	0.47 (0.50)	15.82 (15.90)	3.62 (3.66)	8.30 (8.38)	756 (765.64)
2	1.46 (3.10)	1.67 (6.20)	$C_{50}H_{43}N_2O_2S_2Sb$ Light brown Viscous 91	0.32 (0.37)	13.59 (13.68)	3.08 (3.15)	7.11 (7.21)	878 (889.78)
3	1.58 (3.33)	1.90 (6.70)	$C_{50}H_{47}N_2O_2S_2Sb$ Light brown Viscous 87	0.34 (0.40)	13.21 (13.27)	2.96 (3.05)	6.85 (6.99)	903 (917.83)
4	1.21 (2.57)	1.56 (5.13)	$C_{50}H_{41}Cl_2N_2O_2S_2Sb$ Light brown Viscous 86	0.27 (0.31)	12.59 (12.70)	2.83 (2.92)	6.59 (6.69)	949 (958.67)
5	1.03 (2.19)	1.42 (4.39)	$C_{50}H_{37}F_6N_2O_2S_2Sb$ Gray Viscous 83	0.24 (0.23)	12.13 (12.20)	2.74 (2.81)	6.29 (6.43)	985 (997.72)

traces of solvent were removed under reduced pressure to give a viscous product. This product was purified by dissolving it in a small amount of anhydrous benzene and then adding well-dried petroleum benzene (40–60°) until the compound began to separate. This solution was kept overnight at -10°C. After decanting off the solvent, the compound was dried under vacuum [Yield 89% (2.81 g)].

All the other derivatives were prepared by adopting a similar method. The synthetic and analytical data of these derivatives have been summarized in Table IV.

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