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Triaryl Thioantimonites, $Sb(SAr)_3$. Chemical Reactions and Spectral Properties, Including ^{121}Sb Mössbauer Spectra

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$Sb(SC_6H_4X\text{-}p)_3$; X = H, Br, NH_2, NO_2, Me, Bu^t (I) were prepared by the metathetic reactions of $SbCl_3$ and p-XC_6H_4SH in the presence of a base. I, X = Me was shown to be thermally and photochemically stable but readily hydrolysed and oxidised [to $(SC_6H_4X\text{-}p)_2$ and Sb_2O_3]. Exchange of sulphide units occurred between I and $(ArS)_2$ on heating. Reactions of I, X = Me proceed readily with the electrophilic reagents, MeI, o-$NO_2C_6H_4SCl$ and SCl_2 to give $MeSC_6H_4Me$-p, o-$NO_2C_6H_4SSC_6H_4Me$-p and (p-$MeC_6H_4)_2S_3$ respectively.

The Sb–S frequencies occur in the ranges 340–380 cm^{-1} (stretch) and 240–290 cm^{-1} (bend). General fragmentation pathways in the mass spectra are successive loss of SC_6H_4X-p $\{\rightarrow [Sb(SC_6H_4X\text{-}p)_n]^+$, n = 1,2$\}$ (major) and loss of S $\{\rightarrow [SbS_{n-1}(C_6H_4X\text{-}p)_n]^+$, n = 2, 3$\}$. Also generally observed were $[SbSC_6H_3X\text{-}p]^+$, as reported previously for X = H.

The Mössbauer parameters (at 4 °K) for I were similar ($\delta = -12.5 \pm 0.3$ mm s^{-1} relative to $BaSnO_3$ and $e^2qQ = 13.6 \pm 0.3$ mm s^{-1}, X = Me, Bu^t, Br, NH_2) although the e^2qQ value for X = NO_2 was significantly different (= +11.8 mm s^{-1}).

Introduction

Triaryl thioantimonites, $Sb(SAr)_3$, have only received limited attention [1–5]. The most-frequently used method of preparation involves the metathetic reaction of $SbCl_3$ with a thiol or its sodium salt [1–4], while another reported preparation [5] used the free radical reaction of a thiol with $SbEt_3$. The susceptibility of $Sb(SC_6H_4X\text{-}p)_3$ (X = H and Me) [2] to hydrolysis in solution has also been pointed out, the isolated products being diaryl disulphides and antimony–oxygen compounds. The spectral properties (mass, infrared and n.q.r) of $Sb(SC_6H_5)_3$ were also given by Brill and Campbell [4].

In this paper we wish to report on some aspects of the stability of $Sb(SC_6H_4Me\text{-}p)_3$, its reactions with electrophilic reagents, and spectral properties (in particular, Mössbauer) of a series of $Sb(SC_6H_5X\text{-}p)_3$ compounds.

Experimental

The $Sb(SC_6H_4X\text{-}p)_3$ compounds were prepared under a nitrogen atmosphere by reactions of $SbCl_3$ and p-XC_6H_4SH in the presence of a base, either Et_3N (using CCl_4 as the solvent) or NaOEt (in EtOH). Analtyical data and m.p.'s. are given in Table I. The thiols, $SbCl_3$ and solvents were commercial samples of the highest available purity. The solvents were dried over calcium hydride and were distilled prior to use. Authentic diaryl disulphides used for purposes of comparison in this study were prepared as indicated [6] previously and had analyses, m.p.'s and physical properties in accord with the expected and published data. o-Nitrobenzenesulphenyl chloride was prepared as described by Zincke and Farr [7].

Stability of $Sb(SC_6H_4Me\text{-}p)_3$

(i) $Sb(SC_6H_4Me\text{-}p)_3$ (0.490 g, 1 mmol) was heated *in vacuo* (0.02 mm Hg) at 130 °C for 2 h. After cooling, the sample was shown by i.r., m.p., mixed m.p., and analysis to be unaltered.

(ii) $Sb(SC_6H_4Me\text{-}p)_3$ (0.490 g, 1 mmol) was heated at 130 °C in a stream of air for 2 h. From the cooled reaction residue, $(p\text{-}MeC_6H_4S)_2$ (0.270 g) was extracted by petroleum ether (60–80 °C); m.p. 41–42 °C (lit. [8] m.p. 46 °C). *Anal.* $C_{14}H_{14}S_2$ Calcd: C 68.3, H 5.7, S 26.0. Found: C 68.2. H 5.6, S 26.1%.

(iii) Oxygen was bubbled through a solution of $Sb(SC_6H_4Me\text{-}p)_3$ (0.490 g) in benzene for *ca.* 3 h. The solvent was removed and $(p\text{-}MeC_6H_4S)_2$ (0.168 g) in the residue was extracted with petroleum ether (60–80 °C); it was identical in all respects to an authentic sample.

(iv) A mixture of $Sb(SC_6H_4Me\text{-}p)_3$ (0.490 g) and $(p\text{-}MeC_6H_4S)_2$ (0.246 g) was heated *in vacuo* for 1½ h at 130 °C. The residue was a mixture of an oil and solid but totally solidified on cooling; petroleum

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TABLE I. Analytical Data.

Compound $Sb(SC_6H_4X\text{-}p)_3$ X	M.p. (°C) (lit. m.p.)		Analysis Found (Calc.)			
			C	H	S	N or Br
H	67–68	(67–68)[a]	48.8 (49.1)	3.3 (3.1)	21.1 (21.1)	
Me	100–101	(95 dec.)[a]	51.4 (51.3)	4.5 (4.3)	19.7 (19.6)	
Br	98–100		31.3 (31.5)	2.0 (1.8)	13.8 (14.0)	35.1 (34.9)
NO_2	178–180	(182–184)[b]	37.1 (37.0)	2.1 (2.1)	16.5 (16.5)	8.8 (8.5)
NH_2	175–177		43.7 (44.0)	3.7 (3.7)	19.0 (19.5)	8.8 (8.5)

[a] [2]. [b] [3].

ether (60–80 °C) extraction gave $(p\text{-}MeC_6H_4S)_2$ (0.305 g).

(v) A mixture of $Sb(SC_6H_4Me\text{-}p)_3$ (0.490 g) and $(p\text{-}ClC_6H_4S)_2$ (0.287 g) was heated *in vacuo* at 130 °C for 1 h. The cooled solid product was extracted with petroleum ether (60–80 °C). The extract was shown from mass spectra and t.l.c. to contain the three disulphides: $(p\text{-}ClC_6H_4S)_2$, $(p\text{-}MeC_6H_4S)_2$ and $p\text{-}ClC_6H_4SSC_6H_4Me\text{-}p$. The mass spectrum of the insoluble portion showed the parent ion clusters, all with the correct isotopic distributions, for $Sb(SC_6H_4Me\text{-}p)_3$, $Sb(SC_6H_4Me\text{-}p)_2(SC_6H_4Cl\text{-}p)$, $Sb(SC_6H_4Me\text{-}p)(SC_6H_4Cl\text{-}p)_2$ and $Sb(SC_6H_4Cl\text{-}p)_3$.

Other reactions of $Sb(SC_6H_4Me\text{-}p)_3$

Reaction of $Sb(SC_6H_4Me\text{-}p)_3$ and $o\text{-}NO_2C_6H_4SCl$

Solutions of $Sb(SC_6H_4Me\text{-}p)_3$ (0.68 g) and $o\text{-}NO_2C_6H_4SCl$ (0.79 g) in carbon tetrachloride were mixed and stirred for 2 h. After removing the solvent, the residue was chromatographed [silica column: benzene/petroleum ether (60–80 °C) eluent]. *p*-Tolyl *o*-nitrophenyl disulphide was collected and recrystallised from ethanol, m.p. 73 °C (lit. [9] m.p. 74°), 0.80 g, 70%. *Anal.* $C_{13}H_{11}NO_2S_2$ Calcd: C 56.3, H 4.0, S 23.2. Found: C 56.1, H 3.9, S 23.0%.

Reaction of $Sb(SC_6H_4Me\text{-}p)_3$ and SCl_2

To a solution of $Sb(SC_6H_4Me\text{-}p)_3$ (0.980 g, 2 mmol) in CCl_4 was added dropwise with vigorous stirring, a solution of SCl_2 (0.309 g, 3 mmol) in CCl_4. The resulting solution was stirred for 2 h at room temperature, the solvent removed and the residue chromatographed [preparative thin layer: alumina stationary phase with petroleum ether (60–80 °C) as eluent] to give $(p\text{-}MeC_6H_4)_2S_3$. 0.66 g, 80%, m.p. 80–81 °C (lit. [10] m.p. 82 °C). *Anal.* $C_{14}H_{14}S_3$ Calcd: C 60.4, H 5.0, S 34.6. Found: C 60.5 H 5.1, S 34.7%.

Reaction of $Sb(SC_6H_4Me\text{-}p)$ and MeI

A well-stoppered flask containing a solution of $Sb(SC_6H_4Me\text{-}p)_3$ (0.490 g, 1 mmol) in dry, oxygen-free and freshly-distilled MeI (50 ml) was kept in a N_2-filled desiccator for 13 days. After this time, the colour of the solution was yellow and a considerable amount of precipitate had formed. The solvent was removed to leave a residue, which was extracted with petroleum ether (60–80 °C). Methyl *p*-tolyl sulphide was shown to be present by chromatography, (t.l.c., g.l.c.) and by spectroscopy, (n.m.r. and mass).

Spectral Studies

^1H N.m.r. spectra were recorded on Varian HA 100D and Perkin-Elmer R12A instruments; g.l.c. were run on a Perkin-Elmer F11 instrument; mass spectra were determined using an AEI H30 instrument.

Mössbauer Spectra

The sample material was dispersed in pressed acrylic powder discs to give a concentration of natural Sb of about 25 mg/cm^2. The spectra were taken with both source (1 mci ^{129}Sb as $CaSnO_3$ – New England Nuclear Corporation) and absorber at liquid helium temperature, accumulating about 10^5 counts per channel. The constant acceleration spectrometer, based on an Intertechnique SA41 multi-channel analyser, has been described elsewhere [11]. In accord with the asymmetry of the spectra, they were fitted to an 8 line model, similar to that used by Ruby *et al.* [12] where the widths of the component lines were constrained to be equal. A typical spectrum and computer fit is shown in Figure 1. The asymmetry parameter (η) and the ratio of the quadrupole moments [13] of the excited and ground states of ^{129}Sb were taken as zero and 1.34, respectively.

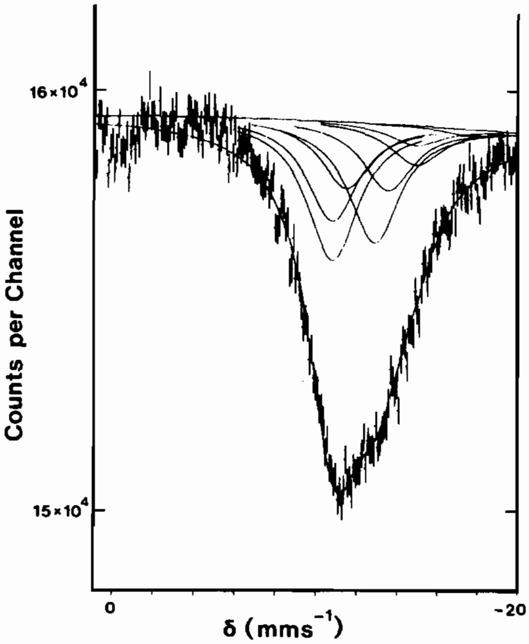


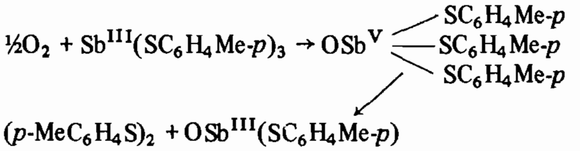
Figure 1. Mössbauer spectrum of $Sb(SC_6H_4Bu^t\text{-}p)_3$ at 4 °K.

Results and Discussion

All the triaryl thioantimonites were pale- to deep-yellow coloured crystalline solids. As mentioned by Klements [2] these compounds are prone to hydrolyses in solution. From the hydrolysis of $Sb(SC_6H_5)_3$ Klements isolated Sb_2O_3 and $(C_6H_5S)_2$, the latter assumed to be produced rapidly from the thiol on oxidation.

All our samples of $Sb(SC_6H_5)_3$, in contrast to all the other triaryl thioantimonites, had a faint thiol-like odour – very similar to that of benzenethiol but very much less intense. Our experiments on the stabilities of the triaryl thioantimonites were conducted with the odourless $Sb(SC_6H_4Me\text{-}p)_3$. The odour of $p\text{-}MeC_6H_4SH$ is sufficiently pronounced, in our experience, that only a very little of this compound need be present for its detection. In none of the reactions in which hydrolysis occurred was $p\text{-}MeC_6H_4SH$ detected. This included freshly hydrolysed solutions of $Sb(SC_6H_4Me\text{-}p)_3$ in aqueous ether through which nitrogen had been bubbled. We are forced to conclude that the concentration of *free* thiol produced in the solutions during hydrolysis is negligible and that the disulphide most probably forms directly on an antimony template.

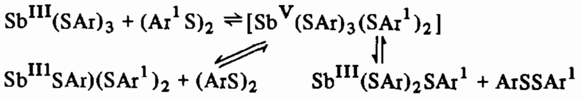
Triaryl thioantimonites are also directly oxidised by oxygen; this has been shown with the trialkyl analogues [14]. Passage of oxygen or air over molten $Sb(SC_6H_4Me\text{-}p)_3$ rapidly resulted in the formation of $(p\text{-}MeC_6H_4S)_2$ and Sb_2O_3. In the absence of air, $Sb(SC_6H_4Me\text{-}p)_3$ is thermally stable up to at least 130 °C. It is also photochemically stable at room temperature in benzene solution. The oxidation process with oxygen is envisaged to go through $OSb^V(SC_6H_4Me\text{-}p)_3$, formed *via* oxidative addition, and subsequent loss of the disulphide:



$$\tfrac{1}{2}O_2 + Sb^{III}(SC_6H_4Me\text{-}p)_3 \rightarrow OSb^V(SC_6H_4Me\text{-}p)_3 \rightarrow (p\text{-}MeC_6H_4S)_2 + OSb^{III}(SC_6H_4Me\text{-}p)$$

Further reactions of $OSb^{III}(SC_6H_4Me\text{-}p)$ to Sb_2O_3 and $(SC_6H_4Me\text{-}p)_2$ will occur in a similar manner. While $OSb(SR)_3$ compounds, unlike [2] $SSb(SC_6H_5)_3$, have not been isolated, Mehrotra [14] did assume their presence among the oxidation products from $Sb(SR)_3$ reactions (R = alkyl) from the elemental analysis data.

Exchange of sulphide groups occurred between triaryl thioantimonites and diaryl disulphides. Thus heating equimolar $Sb(SC_6H_4Me\text{-}p)$ and $(p\text{-}ClC_6H_4S)_2$ at 130 °C *in vacuo* led to a product mixture containing all three possible disulphides $p\text{-}XC_6H_4SSC_6H_4Y\text{-}p$ (X, Y = Cl, Me) and all four triaryl thioantimonites, $Sb(SC_6H_4Cl)_n(SC_6H_4Me\text{-}p)_{3-n}$ (n = 0, 1, 2, 3). The mechanism of the exchange process must involve thermally labile, penta-aryl thioantimonate species, formed by oxidative addition of the disulphides to the thioantimonites



$$Sb^{III}(SAr)_3 + (Ar^1S)_2 \rightleftharpoons [Sb^V(SAr)_3(SAr^1)_2] \rightleftharpoons Sb^{III}SAr)(SAr^1)_2 + (ArS)_2$$
$$[Sb^V(SAr)_3(SAr^1)_2] \rightleftharpoons Sb^{III}(SAr)_2SAr^1 + ArSSAr^1$$

etc.

Successive exchange reactions would lead to all products. Attempts to make $Sb^V(SR)_5$ (R = alkyl and aryl) have previously failed [2, 12], the sulphur-containing products from the reactions of Sb^VCl_5 and RSH always being of the types $Sb^{III}(SR)_3$ and R_2S_2. Other Sb^V thioesters have also limited thermal stability. Schmidbaur has reported [15, 16] that above room temperature Me_4SbSR (R = alkyl and phenyl) breaks down to Me_3Sb and MeSR, and $Me_3Sb(SR)_2$ to Me_3Sb and $(SR)_2$. We have found that $Ph_4SbSC_6H_4X\text{-}p$ (X = OMe, Br, Me, H) also have only limited thermal stability with decomposition occurring above 50 °C to give a number of products [17], including Ph_3Sb, $PhSC_6H_4X\text{-}p$ and $(SC_6H_4X\text{-}p)_2$ and also that $Ph_3Sb(SAr)_2$ does not survive even at –20 °C; an attempted preparation [18] involving Bu_3SnSAr and Ph_3SbCl_2 at that temperature led to the formation of Ph_3Sb and $(SAr)_2$ as well as of Bu_3SnCl. All this provides a reasonable basis for our exchange mechanism. Other combinations of $Sb(SAr)_3$ and disulphide behaved in the same basic manner.

As well as the exchange reactions, some decomposition of $Sb(SAr)_3$ also occurred during the

$Sb(SAr)_3/(ArS)_2$ reactions. As stated earlier, decomposition did not occur in the absence of the disulphide and thus the presence of the disulphide, or some material derived from the disulphide or even the labile intermediate $Sb^V(SAr)_5$ species, must be involved in this decomposition. This manifested itself in the production of more disulphide in the initial stages. Thus, heating equimolar $Sb(SC_6H_4Me\text{-}p)_3$ and $(SC_6H_4Me\text{-}p)_2$ (0.246 g) *in vacuo* for 1½ h led to a reaction mixture containing 0.30 g $(SC_6H_4Me\text{-}p)_2$. The subsequent decomposition products and final antimony products were not closely investigated. Only in one system – that containing $Sb(SC_6H_4Me\text{-}p)_3$ (0.490 g) and $(o\text{-}NO_2C_6H_4S)_2$ (0.308 g) – was the reaction time sufficiently long to assume complete reaction had occurred. However, by this time, a significant amount of charred material was present and the final antimony product or products (0.095 g) – pale yellow in colour, high melting (>350 °C), insoluble in organic solvents with broad i.r. bands at 1600, 1300, 1150, 960, 740, 620, 390 and 260 – might not be typical.

Reactions With Electrophilic Reagents

Reactions of $Sb(SC_6H_4Me\text{-}p)_3$ with weakly electrophilic reagents were investigated. The three reagents used – MeI, $o\text{-}NO_2C_6H_4SCl$ and SCl_2 – reacted under mild conditions to give the appropriate sulphur containing products (eqn. 1–3) in reasonably high yields. Group IV B mercaptides [6, 19] reacted in a similar manner with these electrophiles.

$$3\,MeI + Sb(SC_6H_4Me\text{-}p)_3 \rightarrow 3MeSC_6H_4Me\text{-}p + SbI_3 \qquad (1)$$

$$3o\text{-}NO_2C_6H_4SCl + Sb(SC_6H_4Me\text{-}p)_3 \rightarrow 3o\text{-}NO_2C_6H_4SSC_6H_4Me\text{-}p + SbCl_3 \qquad (2)$$

$$3SCl_2 + 2Sb(SC_6H_4Me\text{-}p)_3 \rightarrow 3(p\text{-}MeC_6H_4)_2S_3 + 2\,SbCl_3 \qquad (3)$$

Spectra

The i.r. and, in outline, the mass spectra of $Sb(SC_6H_5)_3$ were reported by Brill and Campbell [4] in a study of the spectra of $E(YR)_3$; E = As and Sb, Y = O and S. However their investigation was essentially concerned with the arsenic derivatives. Only the general features in the mass spectra were indicated; however specific mention was made of the ion, $[SbSC_6H_4]^+$. In our study, the mass spectra of $Sb(SC_6H_4X\text{-}p)_3$; X = H, Me, Br, NO_2 and NH_2 were investigated at 20 eV. The parent ions were present for all the compounds, although only for X = H, Me and Br were they present to any significant extent (>0.2%). The mass spectra of the amino and nitro derivatives were particularly disappointing with very few antimony containing ions apparent and then only in low abundance. Ions derived from the sulphide (and also the corresponding disulphide) moieties were however more prominant.

TABLE II. Major Ions in the Mass Spectra of $Sb(SC_6H_4X\text{-}p)_3$.

Ion	Abundance (%)		
	X = H	Me[a]	Br[b]
$[Sb(SC_6H_4X\text{-}p)_3]^+$	16	22	5
$[SbS_2(C_6H_4X\text{-}p)_3]^+$	1½	½	0.2
$[Sb(SC_6H_4X\text{-}p)_2]^+$	100	100	100
$[SbS(C_6H_4X\text{-}p)_2]^+$	2	1	1½
$[SbS_2(C_6H_3X\text{-}p)]^+$	2	1	1
$[SbSC_6H_4X\text{-}p]^+$	14	1½	5
$[SbSC_6H_3X\text{-}p]^+$	67	32	60
$[SbS]^+$	7	–	32
$[(SC_6H_4X\text{-}p)_2]^+$	4	–	6
$[HSC_6H_4X\text{-}p]^+$	14	5	4
$[SC_6H_4X\text{-}p]^+$	8	2½	11

[a] Other ions: $[C_7H_7]^+$ (10%). [b] Other ions: $[BrSb(SC_6H_4Br)_2]^+$ (2%); $[BrSb(SC_6H_4Br)]^+$ (9%); $[SbSC_6H_4]^+$ (11%).

There are similarities in the mass spectra of $Sb(SC_6H_4X\text{-}p)_3$; X = H, Me and Br with analogous base ions, $[Sb(SC_6H_4X\text{-}p)_2]^+$ and with fragmentations following the same pathways – namely loss of successive mercaptide units (the major pathway) and elimination of sulphur from $SbSC_6H_4X$ units (Table II). The type of ion reported by Brill and Campbell [4] – $[SbSC_6H_3X]^+$ – was also abundant. For the bromo derivative, the ions $[BrSb(SC_6H_4Br)_n]^+$, n = 1, 2 were also obtained.

Infrared Spectra

Brill and Campbell quoted for pyramidal $Sb(SC_6H_5)_3$, the Sb–S stretching frequencies at 367 (symmetric) and 338 (antisymmetric) with the bending frequencies at 282 (symmetric) and 250 cm^{-1} (antisymmetric). In addition to that of $Sb(SC_6H_5)_3$, the i.r. spectra of $Sb(SC_6H_4X\text{-}p)_3$; X = Me, Br, NO_2 and NH_2 were recorded in this study. While our spectrum for $Sb(SC_6H_5)_3$ agreed with that reported, we do not feel sufficiently confident to specify the particular Sb–S frequencies of all these compounds. In Table III, we list what we consider to be the most probable Sb–S frequencies [stretching at 340–380 cm^{-1} (either one or a group of bands) and bending at 240–290 cm^{-1}]. The values, obtained from comparisons of the i.r. spectra of $Sb(SC_6H_4X\text{-}p)_3$ with those of the appropriate disulphides, $(p\text{-}XC_6H_4S)_2$, are presented with the usual reservations.

TABLE III. Antimony–Sulphur, Vibrational Assignments in Triaryl Thioantimonites.

$Sb(SC_6H_4X\text{-}p)_3$ X	Sb–S Stretch		Bend
H	340, 370 (s)		250, 288 (w)
Me	356, 364 375, 382 (s)		244 (w), 285 (s)
Br	368, 379 (m)	330 (w)?	260, 284 (w)
NH_2	375, 380 (s)		288 (s)
NO_2	368 (s)	239 (w)?	266 (s)

TABLE IV. ^{121}Sb Mössbauer Parameters for $Sb(SC_6H_4X\text{-}p)_3$ at 4K.

Compound $Sb(SC_6H_4X\text{-}p)_3$ X	δ (mm/s)[a]	e^2qQ (mm/s)[b]	Full Width at Half Peak Height (mm/s)	Resonance Dip (%)
H	[−11.7][c]	12.7[d]	5.9[c]	9
Me	−12.3	13.6	3.1	6
Bu^t	−12.3	13.9	3.1	6
Br	−12.8	13.4	3.2	3
NO_2	−12.5	11.8	3.1	8
NH_2	−12.2	13.8	3.4	11

[a] Relative to $CaSnO_3$: errors ± 0.1 mm/s. [b] Errors ± 0.2 mm/s. [c] The spectrum gave a very poor computer fit, see text. [d] From n.q.r. data: ref. 4.

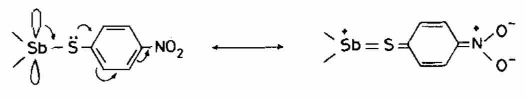
Mössbauer Spectra

The Mössbauer spectra were obtained at 4 K and the Mössbauer parameters are given in Table IV. The pyramidal $Sb(SC_6H_4X\text{-}p)_3$; X = Me, Br, NO_2, NH_2, Bu^t, H, gave positive values for the quadrupole coupling constants, (e^2qQ = 11.8–13.9 mm/sec) indicating excess p-electron density in the lone pair [20], which occupies the vertex of the trigonal pyramid and which lies along the z axis. The values of e^2qQ for $Sb(SC_6H_4X\text{-}p)_3$ are lower than those [21] for $Sb(OR)_3$ (R = alkyl; e^2qQ = 19 mm/s) and for [22] $Sb(C_6H_4X\text{-}p)_3$ (X = H, Me and Cl; e^2qQ = 18 mm/s at 80 K). In Table IV the value quoted for $Sb(SC_6H_5)_3$ is that obtained from an n.q.r. study [4]. The Mössbauer spectrum of this compound gave a very poor computer fit due to the presence of excessive background noise arising from a malfunction of the multichannel analyser. It was considered unnecessary to rerun the spectrum.

The negative values of the isomer shifts, δ [relative to $Ba^{121}SnO_3$], suggest considerable s electron density about the antimony. However compared to the isomer shifts for $Sb(C_6H_4X\text{-}p)_3$ (X = H, OMe and Cl: δ = −8.5, −9.3 and −8.9 mm/s), it appears that more s electron density is removed from antimony when it is directly attached to an aryl ring compared to the situation when a sulphur atom intervenes. Other antimony–sulphur compounds studied have been Sb_2S_3 [δ at 80 K = −14.6 mm/s] [23], SbSBr [δ = −14.9 and e^2qQ 10.4 mm/s] and [24] SbSI [δ = −14.8 and e^2qQ 12.3 mm/s].

There are only slight variations within both the isomer shift values and the quadrupole splitting values, except for the X = NO_2 derivative. This consistancy indicates little transmission of electronic effects of the substituent, X, through the ring and sulphur to the antimony atom and furthermore it is the atom directly attached to antimony in SbY_3 compounds which effectively dictates the values of the Mössbauer parameters. The variations of δ and e^2qQ values in general are too small, considering the errors involved, to make any serious attempt to correlate them with the electronic parameters of the groups, X.

The NO_2 group is a powerful electron withdrawing group. The values of δ and e^2qQ for $Sb(SC_6H_4NO_2\text{-}p)_3$ suggest that the total s electron density about antimony in this compound is about that in the other mercaptides yet the p-electron density in the lone pair is less. This would arise from use of more p_z-



(I)

electrons in bonding with $SC_6H_4NO_2$-*p* as a result of a contribution from (I) to the overall bonding. None of the other substituents, X, is a sufficiently powerful electron withdrawing group to act in a similar way.

References

1 H. J. Bielig, G. Lützel and A. Reidies, *Ber., 89,* 775 (1956).
2 R. Klement and R. Reuber, *Ber., 68,* 1761 (1935); R. Klement and A. May, *ibid., 71,* 890 (1938).
3 P. F. Wiley, *J. Org. Chem., 16,* 810 (1951).
4 T. B. Brill and N. C. Campbell, *Inorg. Chem., 12,* 1884 (1973).
5 A. G. Davies and S. C. W. Hook, *J. Chem. Soc. B,* 735 (1970).
6 J. L. Wardell and D. W. Grant, *J. Organometal. Chem., 20,* 91 (1969).
7 T. Zincke and F. Farr, *Annalen, 391,* 57 (1912).
8 E. E. Colichman and D. L. Love, *J. Am. Chem. Soc., 75,* 5736 (1953).
9 I. Danielson, J. E. Christian and G. L. Jenkins, *J. Am. Pharm. Assoc. Sci. Ed., 36,* 257 (1947).
10 B. Holmberg, *Ber., 43,* 226 (1910).
11 C. H. Huang, O. Knop and F. W. D. Woodhams, *American Mineralogist, 55,* 115 (1970).
12 S. L. Ruby, G. M. Kalvius, R. E. Snyder and G. B. Beard, *Phys. Rev., 148,* 176 (1966).
13 J. G. Stevens and S. L. Ruby, *Phys. Lett. (A), 32,* 91 (1970).
14 R. C. Mehrotra, V. D. Gupta and S. Chatterjee, *Aust. J. Chem., 21,* 2929 (1968).
15 H. Schmidbaur and K. H. Mitschke, *Chem. Ber., 104,* 1837 (1971).
16 H. Schmidbaur and K. H. Mitschke, *Chem. Ber., 104,* 1842 (1971).
17 J. L. Wardell and D. W. Grant, unpublished observation.
18 P. L. Clarke, *Ph.D. Thesis, University of Aberdeen* (1973).
19 J. L. Wardell, R. D. Taylor and T. J. Lillie, *J. Organometal. Chem., 33,* 25 (1971).
20 T. B. Brill, G. E. Parris, G. G. Long and L. H. Bowen, *Inorg. Chem., 12,* 1888 (1973).
21 L. H. Bowen, G. G. Long, J. G. Stevens, N. C. Campbell and T. B. Brill, *Inorg. Chem., 13,* 1787 (1973).
22 S. E. Gukabyan, V. P. Gor'kov, P. N. Zaikin and V. S. Shpinel, *J. Struct. Chem., 14,* 603 (1973).
23 T. Birchall and B. D. Valle, *Chem. Comm.,* 675 (1970).
24 J. D. Donaldson, A. Kjekshus, D. G. Nicholson, and J. T. Southern, *Acta Chem. Scand., 29A,* 220 (1975).