

## Synthesis, Characterization and Conductivity Studies of Tetraphenylstibonium Halides and Trihalides

ABDULLAH KHAN<sup>†</sup>, ABUL K. AZAD<sup>‡</sup>, IZHAR HUSSAIN<sup>¶</sup> and FAHIM UDDIN<sup>\*</sup>

Department of Chemistry, University of Karachi, Karachi, Pakistan

E-mail: fahim\_uddin01@yahoo.com

A series of tetraphenylstibonium halides and tetraphenylstibonium trihalides compounds of type  $\text{Ph}_4\text{SbX}$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ) and  $\text{Ph}_4\text{SbX}_3$  ( $\text{X}_3 = \text{Br}_3, \text{IBr}_2, \text{ICl}_2$ ) have been synthesized as crystalline solids. The electrolytic conductivity measurement in acetonitrile show that  $\text{Ph}_4\text{SbF}$  is very weak,  $\text{Ph}_4\text{SbCl}$  and  $\text{Ph}_4\text{SbBr}$  are weak but  $\text{Ph}_4\text{SbI}$  is a strong electrolyte. All of the trihalides show strong electrotytic conductivity. The calculation of molar conductivity supports the experimental results. The conductometric titrations studies of  $\text{Ph}_4\text{SbCl}$  with  $\text{ICl}$ ,  $\text{Ph}_4\text{SbBr}$  with  $\text{Br}_2$  and  $\text{IBr}$  indicate that the trihalides  $\text{Ph}_4\text{SbX}_3$  are formed readily in acetonitrile solution.

**Key Words:** Synthesis, Characterization, Tetraphenylstibonium halides, Tetraphenylstibonium trihalides, Conductivity.

### INTRODUCTION

Organic derivatives of type  $\text{R}_4\text{EX} = \text{R}_4\text{E}^+ + \text{X}^-$  ( $\text{R} = \text{aryl group}; \text{E} = \text{P, As}$ ) are well known for phosphines and arsines. Trialkyl and triaryl phosphines and arsines generally react fairly readily with alkyl or aryl halides to form quaternary salts.



where  $\text{R}'\text{X} = \text{alkyl/aryl halide}$ . Quaternization becomes more difficult with antimony and bismuth, especially when the organic group is electron withdrawing *e.g.*, phenyl or  $\text{CF}_3$ .

These compounds of type ( $\text{R}_4\text{EX}$ ) are usually having high melting-point, crystalline solids, soluble in polar solvents in which they give highly conducting solutions, suggesting therefore that they are ionic both in the solid state and in solutions. A crystal structure analysis<sup>1</sup> of  $\text{Ph}_4\text{PI}$  confirmed that the structure is built from  $\text{Ph}_4\text{P}^+$  and  $\text{I}^-$  ions. Clark *et al.*<sup>2</sup> have reported that  $\text{Ph}_4\text{PF}$  can exist in a molecular covalent as well as normal ionic form. However, the chemical constitution of the analogous antimony derivatives has not been established. Less work has been reported on the structure of tetraphenylstibonium halides.  $(\text{C}_6\text{H}_5)_4\text{SbCl}$  and  $(\text{C}_6\text{H}_5)_4\text{SbBr}$  are thought

<sup>†</sup>Department of Chemistry, University of Balochistan, Quetta, Pakistan.

<sup>‡</sup>School of Chemistry, University of St Andrews, St Andrews, Scotland, UK.

<sup>¶</sup>Department of Pharmacy, COMSATS, Institute of Information Technology, Abbotabad, Pakistan.

to be ionic on the basis of their infrared spectra<sup>3</sup>. The tetraphenylstibonium halides are generally regarded as having an ionic structure as  $(R_4Sb^+X_3^-)$ . Schmidbaur and co-workers<sup>4</sup> have suggested a covalent trigonal bipyramidal structure<sup>5</sup> for  $Me_4SbF$  and  $Me_4SbOH$ .

On the other hand, the crystal structure<sup>6</sup> of  $Ph_4SbOH$  by X-ray diffraction has shown that the hydroxyl derivatives of this compound is covalent in nature and possesses a structure with the hydroxyl group occupying an axial position. The axial Sb-C distance (2.218 Å) is longer than the equatorial Sb-C distance (2.116-2.140 Å). This result is consistent with the generally accepted rule that the more electronegative substituent groups occupy axial positions and that the axial bond lengths are greater than the equatorial ones. X-ray diffraction analysis suggests<sup>7</sup> distorted trigonal-bipyramidal coordination for Sb atom in tetraphenylstibonium fluoride with a Sb-C bond length of 2.102 Å while the Sb-F distance is equal to 2.0530 Å.

In view of the published covalent molecular nature of tetraphenylstibonium hydroxide ( $Ph_4SbOH$ ), tetramethylstibonium hydroxide and fluoride ( $Me_4SbOH$ ,  $Me_4SbF$ ) and to establish the nature of tetraphenylstibonium halogen organometallic derivatives of group 15 elements in the +5 oxidation state, it seemed worth to carry out the preparation and conductivity study of the tetraphenylstibonium halides  $Ph_4SbX$  ( $X = F, Cl, Br, I$ ) in acetonitrile solution. As a preliminary to present investigation of the electrolytic conductance of the trihalides  $Ph_4SbX_3$ , we carried out conductometric titrations of  $Ph_4SbX-X_2$  systems ( $X = Cl, Br, I$  and  $X_2 = Br_2, IBr, ICl$ ) to obtain information on the stoichiometry of the adducts formed in acetonitrile and to gain preliminary information on their conducting properties. Also to identify any trihalide ions formed in each reaction, the ultra-violet spectrum of the solution being titrated was recorded at selected stages. These techniques have previously proved to be very informative when applied to other similar systems<sup>8-10</sup>. In this paper the results of infrared spectra and molar conductance studies on tetraphenylstibonium halides and -trihalides are reported.

## EXPERIMENTAL

Stibonium halides have been conveniently prepared in good yields from the reactions of halogen halides with aqueous tetraphenylstibonium hydroxide ( $Ph_4SbOH$ ), which was obtained by treating an aqueous solution of tetraphenylstibonium bromide with aqueous ammonia. A number of alternative preparative methods have been described earlier<sup>11-14</sup>. Standard reagents used in this work were of the analytical grade available commercially and were purified by conventional methods. Acetonitrile of a purity suitable for conductance measurement was obtained using the method described by Smit and Witten<sup>15</sup>. Iodine monobromide was freshly prepared from a 1:1 molar mixture of purified bromine and iodine.

**Preparation of tetraphenylstibonium halides and -trihalides:**  $(C_6H_5)_4SbF$  was prepared by adding an excess of hydrofluoric acid (40 %) to an aqueous solution

of  $(C_6H_5)_4SbOH$ . A white crystalline solid was formed. This was filtered and dried in a desiccator. m.p. 153-155 °C. (literature m.p. 145-160 °C)<sup>16</sup>. Found: C, 64.07; H, 4.45 %  $C_{24}H_{20}SbF$  requires: C, 64.17; H, 4.49 %.

$(C_6H_5)_4SbCl$  was prepared by an adding an excess of conc. HCl to the suspension of tetraphenylstibonium hydroxide in water until clear solution was obtained. The volume of the solution was reduced by boiling. On cooling, it gave a white crystalline solid which was filtered and pumped to dryness. m.p. 200-204 °C (literature m.p. 204-205 °C)<sup>17</sup>. Found: C, 61.75; H, 4.26 %  $C_{24}H_{20}SbCl$  requires: C, 61.91; H, 4.33 %.

For preparation of  $(C_6H_5)_4SbBr$ , a mixture of triphenylstibine (10 g, 28.323 mmol) bromobenzene (4.50 g, 74.985 mmol) was heated to 230 °C. A black mixture was formed which was poured into water. The solution was boiled until a small quantity of black deposit remained, charcoal was added and the solution was filtered hot. Potassium bromide (20.00 g, 168.196 mmol) was added to the filtrate. White crystals of tetraphenylstibonium bromide was obtained when the solution was cooled. It was filtered and dried on the vacuum line (yield 85 %). m.p. 202-208 °C (literature m.p. 200-213 °C)<sup>17</sup>. Found: C, 56.46; H, 3.88 %  $C_{24}H_{20}SbBr$  requires: C, 56.51; H, 3.95 %.

$(C_6H_5)_4SbI$  was made by adding conc. HCl to an aqueous suspension of  $(C_6H_5)_4SbOH$  until the solution was acidic. The solution was then heated and filtered. On cooling, an off-white crystalline solid was formed. This was filtered off. After re-crystallization from water, colorless needle-like crystals of  $(C_6H_5)_4SbI$  were obtained. m.p. 209-211 °C. Found: C, 51.88; H, 3.58 %  $C_{24}H_{20}SbI$  requires: C, 51.74; H, 3.62 %.

$(C_6H_5)_4SbOH$  was obtained in excellent yield by adding ammonia solution to a hot solution of  $(C_6H_5)_4SbBr$  in water. Upon cooling, the solution gave a white solid. This was filtered and dried in a desiccator. m.p. 216-224 °C. Found: C, 64.23; H, 4.62 %  $C_{24}H_{21}SbO$  requires: C, 64.46; H, 4.73 %.

For preparation of  $(C_6H_5)_4SbBr_3$ , bromine (0.2775 g, 1.7363 mmol) in acetonitrile (10 mL) was added drop wise to a solution of  $(C_6H_5)_4SbBr$  (0.8858 g, 1.7365 mmol) in acetonitrile (15 mL). After freeze-drying the solution, an orange-yellow solid was obtained. m.p. 112-114 °C. Found: C, 42.55; H, 2.93; Br, 35.65 %  $C_{24}H_{20}SbBr_3$  requires: C, 43.03; H, 3.01; Br, 35.78 %.

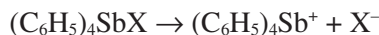
For preparation of  $(C_6H_5)_4SbIBr_2$ , bromine (1.1300 g, 0.8134 mmol) in acetonitrile (15 mL) was added to the solid  $(C_6H_5)_4SbI$  (0.48 g, 0.8100 mmol). A clear light-yellow solution was formed. On freeze-drying, it gave an orange colored crystalline solid. m.p. 148-150 °C. Found: C, 40.16; H, 2.73; Br, 22.02; I, 17.10 %  $C_{24}H_{20}SbIBr_2$  requires: C, 40.21; H, 2.81; Br, 22.29; I, 17.70 %.

For preparation of  $(C_6H_5)_4SbICl_2$ , iodine chloride (0.1499 g, 0.9235 mmol) in acetonitrile (7.00 mL) was added drop wise with shaking to a solution of  $(C_6H_5)_4SbCl$  (0.4300 g, 0.9235 mmol) in the same solvent (20 mL). A clear yellow solution was formed which gave a yellow powdery solid after freeze-drying; this was pumped on the vacuum line. m.p. 116-119 °C. Found: C, 46.85; H, 3.23; Cl, 11.14; I, 19.94 %  $C_{24}H_{20}SbICl_2$  requires: C, 45.90; H, 3.21; Cl, 11.29; I, 20.21 %.

Conductivity measurements were made at 25 °C in a sealed cell. A standard pair of smooth platinum dipping electrodes were used. The cell constant was determined using standard potassium chloride solution and was checked from time to time. The conductivity was measured using a Philips PR9500 resistance bridge and molar conductivity values were then calculated and plotted against the square-root of molar concentration. Ultra-violet spectra were recorded on a Unicam SP800 UV-visible recording spectrometer; measurements were made in stoppered quartz cells of path lengths in the range 5.0-0.1 mm, measurements being made at room temperature (*ca.* 20 °C). Trihalide ions ( $\text{Br}_3^-$ ,  $\text{IBr}_2^-$  and  $\text{ICl}_2^-$ ) have characteristics absorption in the UV which enables their identification<sup>18</sup>. Microanalysis for carbon, hydrogen and nitrogen were performed on a Perkin-Elmer Model 240 elemental analyzer and a Carlo Erba Strumentazione Mod 1106. Halogen analysis was carried out potentiometrically using an adoption of the method described by Lingane<sup>19</sup>. Melting points were measured with a Gallenkamp melting point apparatus in glass melting point tubes with one open end.

## RESULTS AND DISCUSSION

**$\text{Ph}_4\text{SbX}$  ( $\text{X} = \text{F, Cl, Br, I}$ ):** The conductivity of these adducts in acetonitrile at 25 °C was measured (Table-1) over a range of concentrations and the molar conductivity was calculated. A plot of molar conductivity ( $\Lambda_m$ ) against the square root of molar concentration ( $\sqrt{C_m}$ ) was constructed for each compound (Fig. 1). For the purpose of comparison, values of  $\Lambda_m$  at  $C_m$  0.01 mol dm<sup>-3</sup> were obtained from the graphs and these are given in Table-2. All these stibonium halides are crystalline solids. Their properties are shown in Table-3. Table-2 indicates that the molar conductivity of  $(\text{C}_6\text{H}_5)_4\text{SbF}$  is very low, demonstrating that the compound is virtually a non-electrolyte in acetonitrile. This suggests that this compound is likely to be covalent molecular in the solid state. The values of molar conductivity for  $(\text{C}_6\text{H}_5)_4\text{SbCl}$  and  $(\text{C}_6\text{H}_5)_4\text{SbBr}$  lie between those expected for a strong electrolyte and a weak electrolyte in acetonitrile; thus they both must be regarded as weak electrolytes:



where ( $\text{X} = \text{Cl, Br}$ ). It may therefore be concluded that the bromide and chloride, like the fluoride, are covalent molecular in the solid state and ionize only to a certain extent under the influence of the strongly ionizing solvent. The molar conductivity value for  $(\text{C}_6\text{H}_5)_4\text{SbI}$  from Table-2 suggests that this compound is a strong electrolyte in acetonitrile solution and there is a possibility of an ionic structure for this compound in the solid state. The behaviour of this compound is thus analogous<sup>1</sup> to  $(\text{C}_6\text{H}_5)_4\text{PI}$

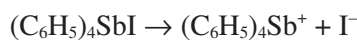


TABLE-1  
CONDUCTIVITY STUDY OF  $\text{Ph}_4\text{SbX}$  AND  $\text{Ph}_4\text{SbX}_3$  IN ACETONITRILE AT 25 °C

Compound	$C_m$ (mol dm <sup>-3</sup> )	$\sqrt{C_m}$ (mol <sup>1/2</sup> dm <sup>-3/2</sup> )	$10^4 K$ (S cm <sup>-1</sup> )	$\Lambda_m$ (S cm <sup>2</sup> mol <sup>-1</sup> )
$(\text{C}_6\text{H}_5)_4\text{SbF}$	0.0005456	0.0230	0.0065	1.20
	0.0028930	0.0540	0.0830	2.80
	0.0078570	0.8800	1.0500	1.90
	0.0100000	0.1000	1.1900	1.80
$(\text{C}_6\text{H}_5)_4\text{SbCl}$	0.0011080	0.0230	0.4340	39.20
	0.0028750	0.0620	0.8720	22.50
	0.0100000	0.1010	0.1920	15.00
	0.0118390	0.1080	1.5640	13.21
$(\text{C}_6\text{H}_5)_4\text{SbBr}$	0.0021980	0.0460	2.4080	109.55
	0.0041100	0.0640	3.8980	94.80
	0.0100000	0.1000	5.2375	70.00
	0.0134600	0.1160	8.1970	60.90
$(\text{C}_6\text{H}_5)_4\text{SbI}$	0.0022560	0.0470	3.4850	154.50
	0.0068860	0.0830	8.9650	130.20
	0.0100000	0.1000	11.5630	119.00
	0.0113000	0.1060	13.1050	115.90
$(\text{C}_6\text{H}_5)_4\text{SbBr}_3$	0.0027170	0.0520	4.3390	159.60
	0.0079470	0.0890	10.900	137.20
	0.0100000	0.1000	14.870	131.00
	0.0136870	0.1160	17.164	125.40
$(\text{C}_6\text{H}_5)_4\text{SbBr}_2\text{I}$	0.0009270	0.0096	1.5430	166.50
	0.0067560	0.0259	8.7119	128.90
	0.0100000	0.1000	15.6237	110.00
	0.0168900	0.0411	20.4440	121.00
$(\text{C}_6\text{H}_5)_4\text{SbICl}_2$	0.0009630	0.0310	1.5180	157.60
	0.0026230	0.0510	3.8330	146.10
	0.0075920	0.0870	9.3870	123.60
	0.0100000	0.1000	14.2850	118.00

TABLE-2  
MOLAR CONDUCTIVITY OF  $(\text{C}_6\text{H}_5)_4\text{SbX}$  AND  $\text{Ph}_4\text{SbX}_3$  AT MOLAR  
CONCENTRATION ( $C_m$ ) = 0.01 mol dm<sup>-3</sup> IN ACETONITRILE

Compound	$\Lambda_m$ (S cm <sup>2</sup> mol <sup>-1</sup> )
$(\text{C}_6\text{H}_5)_4\text{SbF}$	1.8
$(\text{C}_6\text{H}_5)_4\text{SbCl}$	15.0
$(\text{C}_6\text{H}_5)_4\text{SbBr}$	70.0
$(\text{C}_6\text{H}_5)_4\text{SbI}$	119.0
$(\text{C}_6\text{H}_5)_4\text{SbBr}_3$	131.0
$(\text{C}_6\text{H}_5)_4\text{SbBr}_2\text{I}$	110.0
$(\text{C}_6\text{H}_5)_4\text{SbCl}_2\text{I}$	118.0

### Conductometric titrations studies of the tetraphenylstibonium halides with halogens and interhalogens

**Reaction of tetraphenylstibonium bromide with bromine:** The result of the conductometric titration of  $(\text{C}_6\text{H}_5)_4\text{SbBr}$  with  $\text{Br}_2$  in acetonitrile is illustrated in

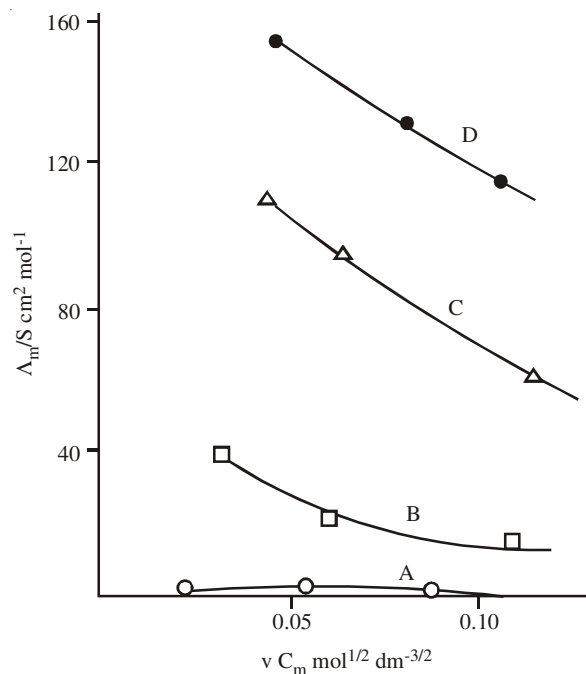
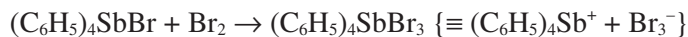


Fig. 1. Conductometric titration of  $(C_6H_5)_4SbX$  in acetonitrile at 25 °C. chloride. (X = F, Cl, Br or I), (A)  $(C_6H_5)_4SbF$ , (B)  $(C_6H_5)_4SbCl$ , (C)  $(C_6H_5)_4SbBr$ , (D)  $(C_6H_5)_4SbI$

Fig. 2, curve A. The conductivity increased steadily up to the 1:1 mole ratio when bromine was added to the tetraphenylstibonium bromide. Further addition of bromine to the solution resulted in a decrease of the conductivity. Thus a distinct 1:1 mol ratio break was observed in the titration graph, indicating the formation of 1:1 adduct  $\{(C_6H_5)_4SbBr_3\}$  in solution. The colour of the solution turn yellow during the course of the titration and its ultraviolet spectrum showed that a tribromide ion ( $Br_3^-$  at  $\lambda_{max} = 269 \mu m$ ) was present from the start of the reaction. The molar conductivity value at 1:1 mol ratio was  $125.9 S cm^2 mol^{-1}$  ( $C_m = 0.004293 mol dm^{-3}$ ) indicating that the compound is a strong electrolyte in acetonitrile. The reaction occurring is: 0:1  $\rightarrow$  1:1 mol ratio



**Reaction of tetraphenylstibonium bromide with iodine bromide:** The result of the conductometric titration of  $(C_6H_5)_4SbBr$  with  $IBr$  in acetonitrile is shown in Fig. 2, curve B. It is seen that that the graph is similar to that of the  $(C_6H_5)_4SbBr-Br_2$  system and displays a break at the 1:1 ratio. The originally colorless solution turned yellow after the first addition of  $IBr$  solution and the ultraviolet spectrum of the solution showed the presence of  $IBr_2^-$  ion ( $\lambda_{max} = 257 \mu m$ ). The molar conductivity values at the 1:1 mol ratio was  $123.0 S cm^2 mol^{-1}$ , ( $C_m = 0.0039109 mol dm^{-3}$ ) indicating that the adduct  $(C_6H_5)_4SbIBr_2$  is a strong electrolyte. The reaction may be represented:

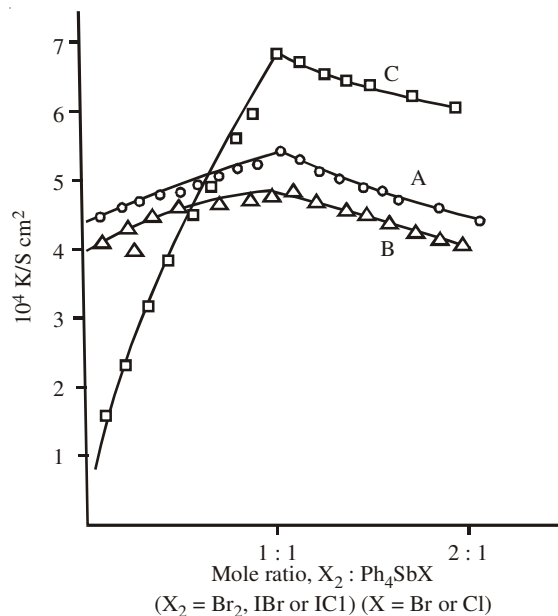
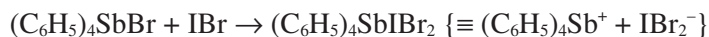
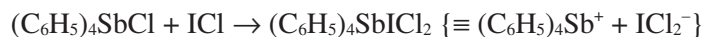


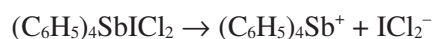
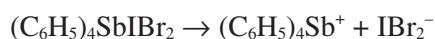
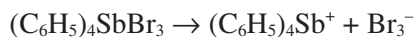
Fig. 2. Conductometric titration of  $(\text{C}_6\text{H}_5)_4\text{SbBr}$  with bromine, iodine bromide and iodine chloride. (A)  $(\text{C}_6\text{H}_5)_4\text{SbBr}-\text{Br}_2$ , (B)  $(\text{C}_6\text{H}_5)_4\text{SbBr}-\text{IBr}$ , (C)  $(\text{C}_6\text{H}_5)_4\text{SbCl}-\text{ICl}$



**Reaction of tetraphenylstibonium chloride with iodine chloride:** The result of the conductometric titration of  $(\text{C}_6\text{H}_5)_4\text{SbCl}$  with  $\text{ICl}$  in acetonitrile is illustrated graphically in Fig. 2, curve C. Again a distinct 1:1 break was observed in the conductometric titration graph of this system, showing that the compound of stoichiometry  $(\text{C}_6\text{H}_5)_4\text{SbICl}_2$  is forming in solution. The solution acquired a light yellow colour from the beginning of the reaction and its ultraviolet spectrum showed absorption due to the  $\text{ICl}_2^-$  ion ( $\lambda_{\text{max}} = 227 \mu\text{m}$ ). The molar conductivity  $\{ \Lambda_{\text{m}}(1:1) = 102.6 \text{ S cm}^2 \text{ mol}^{-1} \text{ at } C_{\text{m}} = 0.005554 \text{ mol dm}^{-3} \}$  indicates that the adduct is a strong electrolyte in acetonitrile. The reaction occurring is: 0:1  $\rightarrow$  1:1 mol ratio



The molar conductivity values for tetraphenylstibonium trihalides in acetonitrile have been obtained by the same procedure as for tetraphenyl stibonium halides. The values obtained are shown in Table-3. These high values are typical of strong electrolytes in acetonitrile.



The trihalide ions ( $\text{Br}_3^-$ ,  $\text{IBr}_2^-$ ,  $\text{ICl}_2^-$ ) have been confirmed from the ultraviolet spectrum of the solutions.

TABLE-3  
 PROPERTIES OF  $\text{Ph}_4\text{SbX}$  AND  $\text{Ph}_4\text{SbX}_3$  COMPOUNDS

Compound	Colour	m.p. (°C)
$(\text{C}_6\text{H}_5)_4\text{SbF}$	White	153-155
$(\text{C}_6\text{H}_5)_4\text{SbCl}$	White	200-204
$(\text{C}_6\text{H}_5)_4\text{SbBr}$	White	202-208
$(\text{C}_6\text{H}_5)_4\text{SbI}$	Pale-yellow	209-211
$(\text{C}_6\text{H}_5)_4\text{SbBr}_3$	Orange-yellow	112-114
$(\text{C}_6\text{H}_5)_4\text{SbBr}_2\text{I}$	Orange-yellow	148-150
$(\text{C}_6\text{H}_5)_4\text{SbCl}_2\text{I}$	Pale-yellow	116-119

### Conclusion

The molar conductivity of the tetraphenylstibonium halides follows the sequence  $(\text{C}_6\text{H}_5)_4\text{SbF} < (\text{C}_6\text{H}_5)_4\text{SbCl} < (\text{C}_6\text{H}_5)_4\text{SbBr} < (\text{C}_6\text{H}_5)_4\text{SbI}$ . This follows the pattern observed in other systems such as  $\text{R}_3\text{AsX}$  ( $\text{R} = \text{aryl group}$ )<sup>8-10</sup>. For example the molar conductivity of  $(\text{C}_6\text{H}_5)_3\text{AsF}_2 < (\text{C}_6\text{H}_5)_3\text{AsCl}_2 < (\text{C}_6\text{H}_5)_3\text{AsBr}_2$ . This trend is likely to be due to the bond strength variation  $\text{Sb-F} > \text{Sb-Cl} > \text{Sb-Br} > \text{Sb-OH}$  and to the electro-negativity effect.

### ACKNOWLEDGEMENTS

The authors thank HEC, Islamabad for financial support to Abdullah Khan and the School of Chemistry, University of St Andrews, Scotland, U.K. for providing laboratory facilities.

### REFERENCES

- G.L. Khotsyanova and Y.T. Strukov, *Kristallografiya*, **1**, 669 (1956).
- S.J. Brown and J.H. Clark, *J. Chem. Soc., Chem. Commun.*, 1256 (1983).
- K.M. Mackay, D.B. Sowerby and W.C. Young, *Spectrochim. Acta*, **24A**, 611 (1968).
- H. Schmidbaur, J. Weidlein and K.-H. Mitschke, *Chem. Ber.*, **102**, 4136 (1969).
- H.E. Affsprung and H.E. May, *Anal. Chem.*, **32**, 1164 (1960).
- A.L. Beauchamp, M.J. Bennett and F.A. Cotton, *J. Am. Chem. Soc.*, **91**, 297 (1969).
- V.V. Sharutin, O.K. Sharutina, A.P. Pakusina, S.A. Smirnova and M.A. Pushilin, *Russ. J. Coord. Chem.*, **31**, 108 (2005).
- G.S. Harris and M.F. Ali, *Inorg. Nucl. Chem. Lett.*, **4**, 5 (1968).
- M.F. Ali and G.S. Harris, *J. Chem. Soc., Dalton Trans.*, 1545 (1980).
- G.S. Harris, A. Khan and A. Mahomedy, *Polyhedron*, **14**, 1953 (1995).
- A.J. Downs and I.A. Steer, *J. Organometal. Chem.*, **8**, 21 (1967).
- J. Chatt and F.C. Mann, *J. Chem. Soc.*, 1192 (1940).
- A.R. Davis, J.W. Macklin and R.A. Plane, *J. Chem. Phys.*, **50**, 1478 (1969).
- G.O. Doak, G.G. Long and L.D. Freedman, *J. Organometal. Chem.*, **12**, 443 (1968).
- J.W. Smith and L.B. Witten, *Trans. Faraday Soc.*, **47**, 1304 (1951).
- R.G. Goel, *Can. J. Chem.*, **47**, 4607 (1969).
- G. Witting and K. Torssel, *Acta Chem. Scand.*, **7**, 1293 (1955).
- A.I. Popov and R.F. Swenson, *J. Am. Chem. Soc.*, **77**, 3724 (1955).
- J. J. Lingane, *Electroanalytical Chemistry*, Interscience Publishers Inc. New York, Ch. VI (1955).