The structure of amorphous Ph_3SbO: information from EXAFS (extended X-ray absorption fine structure) spectroscopy

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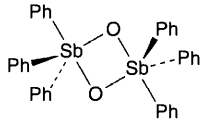
EXAFS data for amorphous Ph_3SbO are consistent with a structure in which trigonal-bipyramidal $SbPh_3O_2$ units share their axial oxygens to form a chain kinked at the oxygen atoms.

Phosphine oxides, R_3PO, and diorganosulfoxides, R_2SO, are generally monomeric in the solid state with four- and three-coordinate phosphorus and sulfur atoms respectively. In contrast, few structures have been reported for the heavier congeneric compounds, such as those involving antimony and tellurium, despite their value in synthesis (particularly in the latter case) as oxo-transfer reagents.[1] From the structural data which are available, however, it is clear that these materials are usually associated into oligomeric or polymeric, oxo-bridged forms, with a concomitant increase in the element coordination number, as observed, for example, in the dimeric structures of crystalline Ph_3SbO (**1a**)[2] and Ph_2TeO.[3] The main factors responsible for this trend as the group is descended are likely to be the increasing polarity of the element–oxygen bond, weaker element–oxygen multiple bonding (*i.e.* two single bonds are preferred over one double bond) and greater element atomic size, but it is clear that further structural data are required in order to more fully understand the nature and hence reactivity of these species.



1a

Triphenylantimonyoxide, Ph_3SbO **1**, is known to exist in crystalline form as a dimer (**1a**), the structure of which has been determined by single-crystal X-ray diffraction revealing a central, four-membered Sb_2O_2 ring.[2] However, as described and discussed in detail by Doak and co-workers,[2] various amorphous forms of **1** of unknown structure can also be prepared, which are assumed to be polymeric in nature on the basis of their insolubility. Prompted by our recent success in characterising the polymeric structure of amorphous iodosylbenzene, PhIO, and the related iodine(III) imido compound $PhINSO_2(C_6H_4Me\text{-}4)$ using iodine EXAFS (extended X-ray absorption fine structure) spectroscopy,[4]‡ we sought to use the same approach to probe the nature of amorphous **1**.

Amorphous **1** (**1b**) was prepared as a white powder according to one of the methods described by Doak and co-workers in ref. 2 by treating Ph_3Sb with H_2O_2 in acetone, the nature of the resulting material being confirmed by elemental analysis and melting point.§ EXAFS spectra¶ were recorded at both 300 and 77 K on a solid sample of **1b**. Analysis of these spectra (Fig. 1 and Table 1) indicate the presence of two oxygen atoms and three carbon atoms directly bonded to the antimony at distances of *ca.* 2.04 and 2.12 Å respectively (Table 1). Longer range Sb–C_{ortho}, Sb–C_{meta}, Sb–C_{para} shells may also be successfully modelled at distances of 3.09, 4.21 and 4.90 Å. These dimensions are in excellent agreement[7] with those of the central $SbPh_3O_2$ moiety in the compound $\{(RSO_3)SbPh_3O\}_2SbPh_3$ [R = $C_6H_3(NO_2)_2$-2,4],[8] (**2**, Scheme 1) in which the Sb–O distance is 2.032 Å, the average Sb–C_{ipso} distance is 2.11 Å and average Sb–C_{ortho}, Sb–C_{meta}, Sb–C_{para} distances are 3.05, 4.37 and 4.88 Å. In **2** the central $SbPh_3O_2$ moiety has the antimony trigonal bipyramidally coordinated with the oxygens in the axial sites and phenyls in the equatorial positions. Finally the EXAFS data analysis for **1b** shows a significant Sb···Sb shell at 3.78 Å (see Table 1, *cf.* Sb···Sb in **2** is 3.72 Å). Triangulation of the Sb–O and Sb···Sb distances, assuming the oxygens to be bridging two antimony atoms, gives an Sb–O–Sb angle of 136° (with an

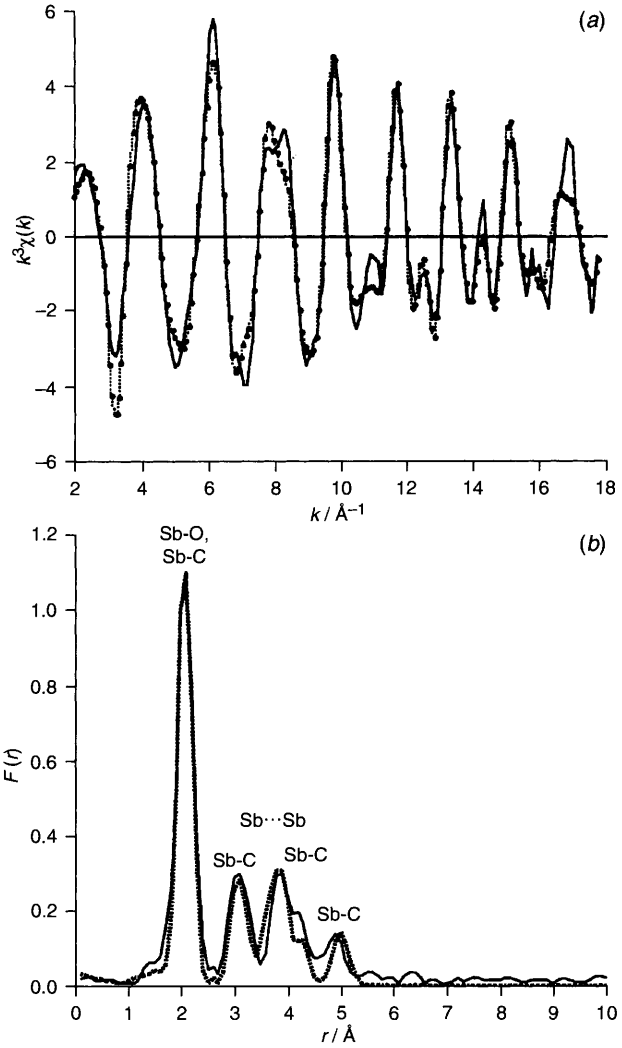


Fig. 1 (*a*) Observed (—) and calculated (-*-) k^3-weighted antimony K-edge EXAFS spectrum for solid **1b** at 77 K; (*b*) observed (—) and calculated (...) Fourier-transform magnitudes (quasi-radial distribution function, arbitrary units)

uncertainty *ca.* 3° assuming precision *ca.* 0.02 Å in the distances), compared with Sb–O–Sb 140.8° in **2**.

The analysis of the EXAFS data is therefore consistent with a structure for **1b** as shown in Fig. 2, in which trigonal-bipyramidal $SbPh_3O_2$ units share their axial oxygens to form a chain kinked at the oxygen atoms although these data do not permit a distinction between oligomeric and polymeric structures for **1b**. Indeed some of the variability in composition and properties noted[2] for **1b** and other amorphous forms of 'Ph_3SbO' may be related to differing degrees of polymerisation and chain-terminating groups being present. Doak and coworkers[2] also note the possibility that amorphous Ph_3SbO is not a pure material and hence any conclusion regarding the structure of **1b** drawn here must be tentative and relate to the predominant (and average) local structure. Nevertheless, within these limits it seems clear that amorphous Ph_3SbO **1b** consists of a linear oligomeric or polymeric array of the form shown in Fig. 2.

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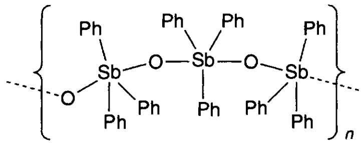
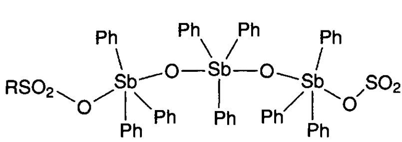
Table 1 Details of Sb K-edge EXAFS data and analysis for Ph_3SbO **1b**

Contact	300 K		77 K	
N atom	R/Å[a]	σ/Å^2	R/Å	σ/Å^2
2 O	2.030(3)	0.0021(4)	2.045(8)	0.0044(11)
3 C	2.133(2)	0.0027(4)	2.114(7)	0.0026(7)
6 C	3.091(6)	0.0086(10)	3.092(6)	0.0073(10)
2 Sb	3.779(5)	0.0132(9)	3.785(3)	0.0087(5)
6 C	4.215(6)	0.0041(11)	4.213(6)	0.0017(8)
3 C	4.905(21)	0.0096(30)	4.900(24)	0.0092(42)
Correlations between R and σ >0.50	$\sigma_1:\sigma_2 = 0.69$; $\sigma_1:R_2 = -0.76$; $\sigma_2:R_1 = 0.75$		$R_1:R_2 = -0.76$; $R_1:\sigma_2 = 0.78$; $R_2:\sigma_1 = -0.82$	
k_{max}/Å^{-1}	17.80		17.80	
R (%)[b]	6.56		7.69	
R' (%)	6.51		8.18	

[a] The estimated standard deviation in the least significant digit as calculated by EXCURV92 model fitting is given in parentheses. We note that such estimates (of precision) are likely to overestimate the accuracy of parameter values (since they do not include the effects of systematic errors and of correlation of these parameters with others not refined). [b] Residual indices R and R' were calculated as: $R = \sum_i[k^3(\chi^{obs}_i - \chi^{calc}_i)]^2/\sum_i(k^3\chi^{obs}_i)^2$. R' was calculated as for R' with final model parameters, but with data Fourier-filtered with r_{max} = 6.0 Å to remove noise.



1b



2 [R = $C_6H_3(NO_2)_2$-2,4]

Fig. 2

Footnotes

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‡ The polymeric natures of $PhINSO_2(C_6H_4Me\text{-}4)$,[5] 2,4,6-$Me_3C_6H_2$-$INSO_2(C_6H_4Me\text{-}4)$[5] and 2-$MeC_6H_4INSO_2(C_6H_4Me\text{-}4)$[6] have recently been confirmed by single-crystal X-ray diffraction studies.

§ A sample of amorphous **1** (**1b**) was prepared according to one of the methods described in ref. 2 by treating Ph_3Sb with H_2O_2 in acetone. Compound **1b** prepared by this route is reported to have a melting point of 170–180 °C;[2] the melting point for our material was 164 °C. The sample of **1b** as prepared here was subjected to elemental analysis. $C_{18}H_{15}OSb$ requires C, 58.60; H, 4.10. Found C, 57.50; H, 4.00%.

¶ EXAFS data were collected and analysed by normal procedures[4] at the Daresbury synchrotron radiation source (SRS) on station 9.2 in transmission mode, to 17.8 Å^{-1} in *k*-space at the antimony K-edge. The solid samples were diluted with boron nitride in order to achieve changes in log (I_0/I) in the range 1–1.5 at the absorption edge. Raw data were corrected for dark currents and converted to *k*-space (with EXCALIB[9]), and backgrounds subtracted (with EXBACK[9]) to yield EXAFS functions $\chi^{obs}_i(k)$. These were Fourier-filtered to remove features at distances below *ca.* 1.2 Å, but not to remove long-distance features of the quasi-radial distribution function (*i.e.* no noise removal was attempted). Model fitting was carried out with EXCURV92,[9] using curved wave theory. Only shells significant[10] at the 95% level were included in the final models, *i.e.* shells added to the model were only retained if they caused a reduction in the R index of >4% of the previous value. Details of the final models are listed in Table 1, which gives interatomic distances (r), Debye–Waller factors (σ) and the 'coordination' numbers, *i.e.* the number of atoms in a given shell. *Ab initio* phase shifts and back-scattering factors using spherical wave theory were used throughout.

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