

## Preliminary Communication

### Biphenyl-2,2'-diylphenylantimony dibromide; a new square pyramidal antimony(V) compound

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#### Abstract

In contrast to the trigonal bipyramidal geometry of triphenylantimony dibromide, the related biphenyl-2,2'-diylphenylantimony dibromide has a distorted square pyramidal arrangement of ligands about antimony and is dimeric in the solid state.

**Key words:** Group 15; Antimony; Bromide; Crystal structure; Square pyramid

In general, five coordinate complexes of Group 15 elements have trigonal bipyramidal structures, although the energy difference between this arrangement and the alternative square pyramidal structure is small. The two arrangements are linked by the Berry pseudo-rotation coordinate, and over the years, by careful choice of ligands, it has been possible to stabilise solid state structures distorted to various distances along the coordinate. Phosphorus(V) compounds have been most widely investigated and a number of square pyramidal molecules have been identified, most requiring the presence of at least one unsaturated chelating dioxo groups [1].

Arsenic systems have been less widely investigated but square pyramidal species containing dioxo groups are also known [2]. The situation with antimony(V) is clouded by the unexpected square pyramidal geometry of pentaphenylantimony [3], and pentaphenylbismuth also has this structure [4]. The probable importance of dioxo chelating groups in promoting square pyramidal geometry about antimony is, however, shown as one of the independent antimony atoms in triphenylantimony

catecholate hemihydrate has this geometry [5]. In contrast, the related biphenyl-2,2'-diyltriphenylantimony [6] has slightly distorted trigonal bipyramidal geometry about antimony. This change in geometry might result from the different bites of the two groups, 2.60 and 2.84 Å respectively, for catecholate and biphenyl, but certainly the two ligands produce different constraints at antimony. It should be noted in passing that in the square pyramidal mixed biphenyl/ catecholate,  $\text{PhSb}(\text{O}_2\text{C}_6\text{Cl}_4)(\text{C}_{12}\text{H}_8)$ , both chelating groups occupy *cis* basal positions [7].

With these points in mind, it is not surprising that both triphenylantimony dichloride and dibromide are trigonal bipyramidal [8] and, in keeping with the decrease in Lewis acidity of antimony(V) halides with successive substitution of halide by phenyl groups, both  $\text{Ph}_3\text{SbCl}_2$  and  $\text{Ph}_3\text{SbBr}_2$  are unassociated in the solid. The related diphenylantimony trihalides,  $\text{Ph}_2\text{SbCl}_3$  [9] and  $\text{Ph}_2\text{SbBr}_3$  [10], on the other hand, are associated in the solid and react with a range of Lewis bases.

We have recently synthesised biphenyl-2,2'-diylphenylantimony dibromide, an analogue of triphenylantimony dibromide, from phenylantimony dichloride and TMEDA stabilised dilithium biphenyl-2,2'-diyl, followed by bromine oxidation. Its crystal structure\* (see Fig. 1) clearly shows that the geometry about antimony

\* The compound was prepared by oxidising biphenylphenylantimony with bromine and crystals suitable for X-ray studies were obtained by slow recrystallisation from chloroform-hexane.

Crystal data:  $\text{C}_{18}\text{H}_{13}\text{Br}_2\text{Sb}$ ,  $M = 510.9$ , monoclinic, space group  $P2_1/c$ ,  $a = 11.924(2)$ ,  $b = 13.164(4)$ ,  $c = 11.067(2)$  Å,  $\beta = 109.83(2)^\circ$ ,  $V = 1634.0$  Å<sup>3</sup>,  $Z = 4$ ,  $\mu(\text{Mo-K}\alpha) = 65.4$  cm<sup>-1</sup>,  $D_c = 2.08$  g cm<sup>-3</sup>,  $F(000) = 968$ , crystal size  $0.5 \times 0.4 \times 0.2$  mm. Intensity data for 3022 reflections were measured (Hilger and Watts Y290 diffractometer using graphite monochromatised Mo-K $\alpha$  radiation) of which 2194 reflections with  $I > 3 \sigma(I)$  were used in the refinement. Data were corrected for Lorentz and polarisation effects and an empirical absorption correction (DIFABS) was applied. The position of the antimony atom was obtained from a three dimensional Patterson synthesis, and the other non-hydrogen atoms were revealed by a series of full-matrix least-squares refinements and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed at their calculated positions,  $d(\text{C-H})$  1.0 Å and were refined riding on the appropriate carbon atom. Final convergence occurred at  $R = 3.95\%$  ( $R_w = 4.40\%$ ) after application of a four coefficient Chebyshev weighting scheme. Atomic co-ordinates, thermal parameters and tables of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

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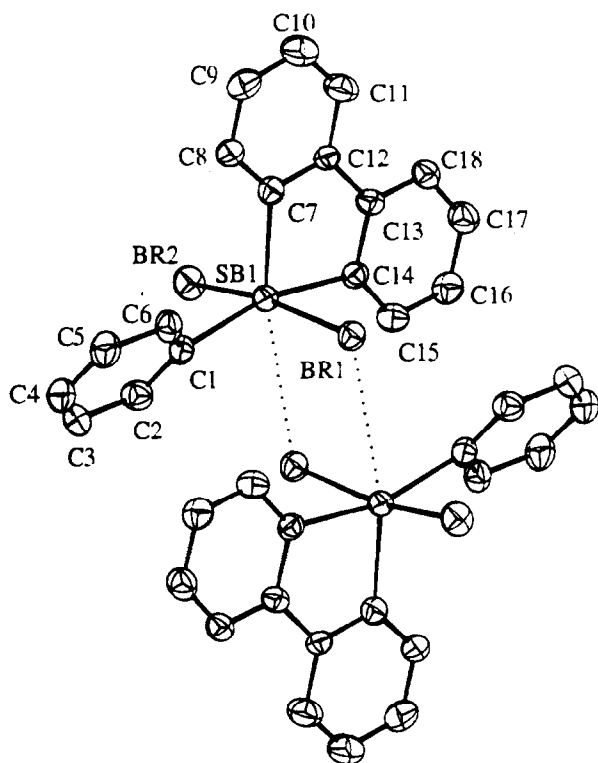


Fig. 1. Structure of (biphenyl-2,2'-diyl)phenylantimony(V) dibromide.

in the monomeric unit is basically square pyramidal. This is necessarily distorted as the atoms forming the basal plane are either of different types or in different environments, but using Muetterties and Guggenberger's criterion [11] ( $\delta e_1 = 83.0$ ,  $\delta e_2 = 79.2$  and  $\delta e_3 = 3.5^\circ$ ) square pyramidal geometry is confirmed. Unusually, however, the biphenyl group occupies apical and basal positions, with C(7) of the biphenyl group in the apical position and Br(1) (+0.031), Br(2) (+0.033), C(1) (-0.032) and C(14) (-0.032 Å) in the basal plane; antimony is 0.25 Å above the plane. (Values in parentheses are deviations of individual atoms from the mean plane through the four basal atoms.) As expected, the apical Sb-C distance is shorter, 2.104(6) Å, than those for the two *trans* basal carbons, 2.123(6) and 2.119(6) Å to C(1) and C(14), respectively, which are effectively equal.

On the other hand, the bromine atoms, which also occupy *trans* basal positions, show different antimony-bromine distances, *i.e.* 2.708(1) and 2.593(1) Å to Br(1)

and Br(2), respectively. The longer Br(1) separation is undoubtedly associated with weak intermolecular interaction with a centrosymmetrically related antimony atom at 3.346(1) Å leading to weak dimer formation in the solid state. The Sb(1)  $\cdots$  Br(1') separation, which is well within the sum of the antimony and bromine van der Waals' radii (*ca.* 4.1 Å), surprisingly, is shorter than that (3.477(3) Å) in Ph<sub>2</sub>SbBr<sub>3</sub>.

The observation of both square pyramidal geometry and apparently enhanced Lewis acidity in this biphenyl analogue of triphenylantimony dibromide poses problems. It is difficult to see that sufficiently large electronic effects would follow substitution of two phenyl groups by one biphenyl group to enhance the Lewis acidity. Equally, it is not easy to propose that incorporation of a biphenyl group would distort the antimony geometry toward the square pyramidal alternative, when replacement of two of the phenyl groups in square pyramidal pentaphenylantimony gives a trigonal bipyramidal biphenyl product. On the other hand, such distortion is attractive as a more accessible coordination site, *trans* to the apical carbon atom, becomes available for any weak intermolecular interaction. Clearly, energy differences between alternative structures in these systems are small and very small changes in individual parameters can lead to large structure changes.

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