Notes

Crystal Structure of Biphenyl-2,2′-diyltriphenylantimony

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An *X*-ray analysis of the title compound shows slightly distorted trigonal-bipyramidal geometry about the central atom in contrast to the square-pyramidal co-ordination in the related $SbPh_5$. The heavy-atom method was used with *X*-ray diffractometer data and refinement by full-matrix least squares converged at R 0.036 for 3 367 reflections. Crystals are monoclinic, space group $P2_1/n$, with a = 10.488(5), b = 16.561(8), c = 13.503(6) Å, β = 92.16(2)°, and Z = 4.

THE square-pyramidal geometry about antimony[1] in $SbPh_5$ is highly unexpected especially as trigonal-bipyramidal structures have been observed for the corresponding arsenic and phosphorus pentaphenyls,[2] for the cyclohexane adduct of $SbPh_5$,[3] and for penta(*p*-tolyl)antimony.[4] A completely satisfactory explanation for the unusual geometry is still lacking but it is clear that interactions between non-bonded atoms are important.[5]

Square-pyramidal structures have been identified for an increasing number of five-co-ordinate phosphorus(V) compounds by Holmes and his co-workers [6] and others,[7] and it appears that the incorporation of chelating dioxo-groups can stabilise this geometry at the expense of the more usual trigonal-bipyramidal alternative. Extension to arsenic chemistry has met with some success but the number of square-pyramidal structures observed so far is low [8] and it is not possible to assess the general validity of this approach. The situation with antimony is even more ambiguous, but square-pyramidal geometry has been found about one of the antimony atoms in the catechol hydrate $[SbPh_3(O_2C_6H_4)]_2{\cdot}H_2O$.[9]

In this context, the crystal structure of biphenyl-2,2′-diyltriphenylantimony, $Sb(C_{12}H_8)Ph_3$, was of interest. In the first instance it contains five aryl groups attached to the central antimony as in $SbPh_5$, and secondly the fact that two of these are interconnected in the chelating biphenyl group might serve to constrain the geometry as in the phosphorus work mentioned above.

EXPERIMENTAL

The compound was prepared following the method of Hellwinkel and Bach,[10] from triphenylantimony dibromide and 2,2′-dilithiobiphenyl in diethyl ether at −70 °C. Crystals suitable for *X*-ray analysis were obtained by slow recrystallisation from diethyl ether.

Crystal Data.—$C_{30}H_{23}Sb$, $M = 506.8$, Monoclinic, $a = 10.488(5)$, $b = 16.561(8)$, $c = 13.503(6)$ Å, $\beta = 92.16(2)°$, $U = 2\,343.7$ Å^3, $Z = 4$, $D_c = 1.44$ g cm^{-3}, $F(000) = 1\,016$, space group $P2_1/n$ from systematic absences, Mo-K_α radiation, $\lambda = 0.7107$ Å, $\mu = 11.9$ cm^{-1}.

Structure Determination.—A Hilger and Watts four-circle diffractometer was used to collect data for 4 406 independent reflections of which 3 367 with $I \geqslant 3\sigma(I)$ were considered observed. The data were corrected for Lorentz and polarisation effects but no absorption correction was necessary. Data reduction and subsequent calculations used the CRYSTALS programs;[11] scattering factors were those for neutral atoms.[12] The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares to R 0.065 with isotropic and 0.045 with anisotropic thermal parameters. Hydrogen atoms were placed at their calculated position but were not refined in subsequent cycles. Final convergence was at R 0.036 after using a four-coefficient Chebyshev weighting scheme.

Atomic co-ordinates are listed in Table 1, while anisotropic thermal parameters, calculated hydrogen-atom positions, bond distances and angles for the phenyl groups, and observed and calculated structure factors are listed in Supplementary Publication No. SUP 23081 (33 pp.).†

TABLE 1

Fractional co-ordinates (× 10^4), with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Sb(1)	3 010.4(2)	2 353.1(1)	2 356.7(2)
C(1)	1 194(4)	2 876(2)	2 831(3)
C(2)	1 157(4)	3 641(3)	3 248(3)
C(3)	40(6)	3 948(3)	3 611(4)
C(4)	−1 029(5)	3 491(4)	3 576(4)
C(5)	−1 019(5)	2 733(4)	3 169(4)
C(6)	105(5)	2 427(3)	2 804(3)
C(7)	3 711(4)	3 502(2)	1 882(3)
C(8)	2 898(5)	4 047(3)	1 397(4)
C(9)	3 339(5)	4 790(3)	1 091(4)
C(10)	4 581(6)	5 000(3)	1 265(4)
C(11)	5 394(5)	4 469(3)	1 742(4)
C(12)	4 970(4)	3 719(3)	2 049(3)
C(13)	2 105(4)	1 639(2)	1 216(3)
C(14)	1 191(4)	1 966(3)	574(3)
C(15)	652(4)	1 515(3)	−196(3)
C(16)	998(5)	728(3)	−315(3)
C(17)	1 888(5)	390(3)	328(4)
C(18)	2 450(4)	843(2)	1 090(3)
C(19)	3 410(4)	1 849(2)	3 808(3)
C(20)	2 674(4)	1 942(2)	4 622(3)
C(21)	3 048(4)	1 595(3)	5 522(3)
C(22)	4 147(5)	1 137(3)	5 595(3)
C(23)	4 886(4)	1 043(2)	4 776(3)
C(24)	4 549(4)	1 406(2)	3 869(3)
C(25)	5 324(4)	1 359(2)	2 980(3)
C(26)	4 863(4)	1 765(2)	2 131(3)
C(27)	5 544(4)	1 756(3)	1 276(3)
C(28)	6 689(5)	1 353(3)	1 249(4)
C(29)	7 139(5)	948(3)	2 081(4)
C(30)	6 479(4)	941(3)	2 940(3)

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† For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

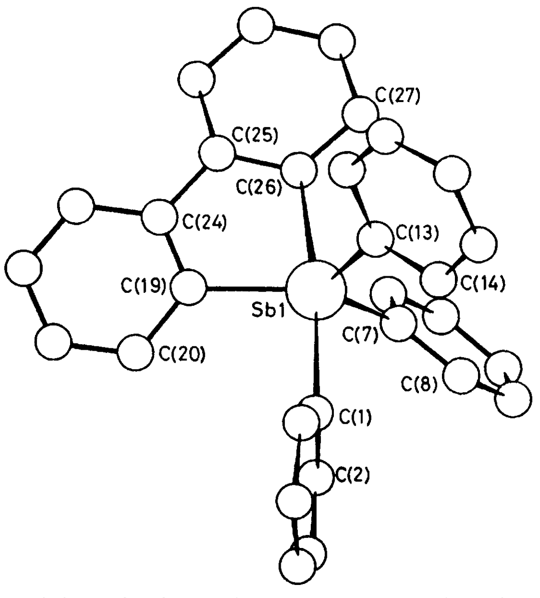
DISCUSSION

Bond-distance and -angle data for the compound are listed in Table 2 and the Figure shows the molecular structure and the atom-numbering scheme. From this it is clear that the best description of the geometry about the antimony atom is in terms of a trigonal bipyramid and the possibility of the alternative square pyramid is not in fact realised. The biphenylyl group, in keeping with its short bite, spans an equatorial and an axial position.

TABLE 2

Bond distances (Å) and angles (°) with estimated standard deviations in parentheses

Sb(1)–C(1)	2.209(4)	Sb(1)–C(19)	2.156(4)
Sb(1)–C(7)	2.146(4)	Sb(1)–C(26)	2.204(4)
Sb(1)–C(13)	2.136(4)		
C(19)–C(20)	1.375(5)	C(25)–C(26)	1.399(5)
C(20)–C(21)	1.388(6)	C(26)–C(27)	1.381(5)
C(21)–C(22)	1.380(7)	C(27)–C(28)	1.375(6)
C(22)–C(23)	1.384(7)	C(28)–C(29)	1.376(7)
C(23)–C(24)	1.398(5)	C(29)–C(30)	1.374(7)
C(19(–C(24)	1.401(5)	C(25)–C(30)	1.398(5)
C(24)–C(25)	1.476(5)		
C(1)–Sb(1)–C(7)	92.8(1)	C(7)–Sb(1)–C(13)	115.1(1)
C(1)–Sb(1)–C(13)	93.5(1)	C(7)–Sb(1)–C(19)	123.9(1)
C(1)–Sb(1)–C(19)	91.6(1)	C(7)–Sb(1)–C(26)	92.1(1)
C(1)–Sb(1)–C(26)	170.8(1)	C(13)–Sb(1)–C(19)	120.5(1)
C(19)–Sb(1)–C(26)	79.2(1)	C(13)–Sb(1)–C(26)	91.5(1)
Sb(1)–C(19)–C(20)	125.9(3)	Sb(1)–C(26)–C(25)	112.2(3)
Sb(1)–C(19)–C(24)	113.1(3)	Sb(1)–C(26)–C(27)	127.4(3)
C(20)–C(19)–C(24)	121.0(4)	C(25)–C(26)–C(27)	120.4(4)
C(19)–C(20)–C(21)	120.3(4)	C(26)–C(27)–C(28)	120.5(4)
C(20)–C(21)–C(22)	119.9(4)	C(27)–C(28)–C(29)	119.2(4)
C(21)–C(22)–C(23)	119.8(4)	C(28)–C(29)–C(30)	121.7(4)
C(22)–C(23)–C(24)	121.4(4)	C(24)–C(30)–C(25)	119.6(4)
C(23)–C(24)–C(19)	117.6(4)	C(26)–C(25)–C(30)	118.7(4)
C(19)–C(24)–C(25)	118.3(3)	C(24)–C(25)–C(26)	117.2(3)
C(23)–C(24)–C(25)	124.1(4)	C(24)–C(25)–C(30)	124.2(4)



View of the molecule showing the atom-numbering scheme

The three equatorial Sb–C distances, mean 2.146 Å, are equal within the error of the determination as are the two axial distances, mean 2.206 Å. As expected in this geometry, the axial distances are the longer but the difference between the axial and equatorial distances here is smaller than that for either penta(*p*-tolyl)antimony [4] or for the cyclohexane solvate of pentaphenylantimony.[3]

The antimony atom lies *ca.* 0.1 Å below the plane of the three equatorial atoms, and the axial carbon atoms C(1) and C(19) are respectively 2.31 Å below and 2.08 Å above this plane. These data give some indication of the distortion from trigonal-bipyramidal geometry by incorporation of the biphenylyl group. This is more clearly shown by the angles at antimony where, for example, that between the two biphenylyl carbon atoms C(19)–Sb(1)–C(26) is reduced to 79.2°. Although the C(1)–Sb(1)–C(19) angle (91.6°) is greater than the ideal angle, the axial–axial angle is well below the 180° expected for the unconstrained polyhedron. The major distortion in the equatorial plane is associated with the C(7) phenyl group which is displaced away from the biphenylyl group, leading to a value of 123.9° for the C(7)–Sb(1)–C(19) angle.

As expected all three phenyl groups are planar, the mean deviation from the appropriate least-squares best plane being 0.003 Å, and the two units of the biphenylyl group are also individually closely planar (maximum deviation 0.012 Å, mean deviation 0.005 Å). (Torsion angles describing the relative orientations of the five aromatic rings are listed in Table 3.) Perhaps surprisingly, the twist angle in this group is very small (3.1°), implying that chelation to antimony requires an almost planar conformation. In a related chlorobiphenyl compound, in which the organic group is singly bonded to antimony, the twist angle is *ca.* 65°,[13] a value similar to that in the gas-phase structure of 2,2′-dichlorobiphenyl (70°).[14] Among the dimensions of the biphenylyl group, the C–C distances adjacent to the C(24)–C(25) link are significantly longer and the angles about C(24) and C(25) show the greatest deviations from 120°. Finally, attention is drawn to the planarity of the

TABLE 3

Selected torsion angles (°)

C(7)–Sb(1)–C(1)–C(2)	−35.5
C(13)–Sb(1)–C(1)–C(2)	−150.8
C(19)–Sb(1)–C(1)–C(2)	88.5
C(26)–Sb(1)–C(1)–C(2)	86.4
C(1)–Sb(1)–C(7)–C(8)	−39.7
C(13)–Sb(1)–C(7)–C(8)	55.5
C(19)–Sb(1)–C(7)–C(8)	−133.5
C(26)–Sb(1)–C(7)–C(8)	148.1
C(1)–Sb(1)–C(13)–C(14)	46.5
C(7)–Sb(1)–C(13)–C(14)	−48.2
C(19)–Sb(1)–C(13)–C(14)	140.4
C(26)–Sb(1)–C(13)–C(14)	−141.3
C(1)–Sb(1)–C(19)–C(20)	−2.6
C(7)–Sb(1)–C(19)–C(20)	91.8
C(13)–Sb(1)–C(19)–C(20)	−97.6
C(26)–Sb(1)–C(19)–C(20)	177.1
C(1)–Sb(1)–C(26)–C(27)	−176.8
C(7)–Sb(1)–C(26)–C(27)	−54.8
C(13)–Sb(1)–C(26)–C(27)	60.2
C(19)–Sb(1)–C(26)–C(27)	−179.1

pentagon formed by Sb(1), C(19), C(24), C(25), C(26) where the angles sum to 540°.

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