

718. *An X-Ray Diffraction Determination of the Crystal and Molecular Structure of Pentaphenylantimony.*

By P. J. WHEATLEY.

A two-dimensional X-ray diffraction analysis of pentaphenylantimony, $\text{Sb}(\text{C}_6\text{H}_5)_5$, confirms that the molecule, unlike the phosphorus and arsenic homologues, approximates to a square pyramidal structure. The Sb-C bond lengths vary from 2.05 to 2.23 Å, with a standard deviation of 0.07 Å. The mean value of the length is 2.14 Å. There is no evidence that the axial Sb-C bond has a length different from the other four.

A RECENT communication¹ listed the crystallographic constants and some of the physical properties of the pentaphenyls of phosphorus, arsenic, and antimony. It was stated that pentaphenyl antimony has a square pyramidal structure, and it was concluded, from the trend in the dipole moments, that the lower homologues would have similar structures. It has now been confirmed that the structure proposed for the antimony compound is correct, but a parallel three-dimensional analysis of the phosphorus compound has demonstrated that the two lower homologues, which are isomorphous, adopt trigonal bipyramidal configurations.

EXPERIMENTAL

$\text{C}_{30}\text{H}_{25}\text{Sb}$. $M = 507.3$. Triclinic. $a = 10.27_7 \pm 0.05$, $b = 10.57_4 \pm 0.05$, $c = 13.59_4 \pm 0.07$ Å, $\alpha = 79^\circ 00' \pm 30'$, $\beta = 79^\circ 34' \pm 30'$, $\gamma = 119^\circ 37' \pm 30'$. $U = 1139.4$ Å³. $D_m = 1.42$. $Z = 2$. $D_c = 1.412$. $F(000) = 512$. Space group $P\bar{1}$ (C_2^1 , No. 2). Cu- K_α radiation ($\lambda = 1.542$ Å), single crystal rotation and Weissenberg photographs.

The crystals (m. p. 171—172°) are white and beautifully formed. Each crystal exhibits many faces, and no two crystals appear alike under the microscope. Multiple-film Weissenberg

¹ Wheatley and Wittig, *Proc. Chem. Soc.*, 1962, 251.

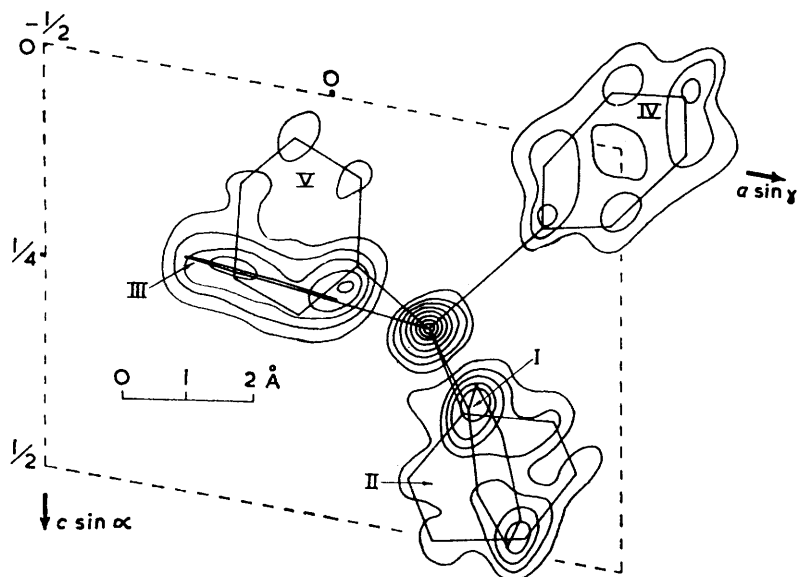


FIG. 1. Fourier projection down $[b]$ calculated with antimony phases only. Contours are in steps of $2.5 \text{ e}/\text{\AA}^2$, starting at $5.0 \text{ e}/\text{\AA}^2$, except in the antimony peak where the contours are in steps of $10.0 \text{ e}/\text{\AA}^2$, starting at $10 \text{ e}/\text{\AA}^2$.

TABLE I.

Atomic co-ordinates and orthogonal atomic co-ordinates in \AA .

Atom	X	Y	Z	X'	Y'	Z'
Sb	1.6865	0.4090	3.4364	2.5548	0.2312	3.1928
C(1)	2.380	2.081	4.730	3.568	1.807	4.395
C(2)	2.573	1.660	6.034	4.148	1.540	5.606
C(3)	3.068	2.769	6.744	4.803	2.540	6.266
C(4)	3.333	4.301	6.237	4.873	3.844	5.795
C(5)	2.951	4.643	4.931	4.128	4.125	4.582
C(6)	2.543	3.636	4.225	3.549	3.185	3.925
C(7)	2.306	-0.997	4.740	3.506	-1.232	4.404
C(8)	1.253	-2.269	5.967	2.980	-1.749	5.544
C(9)	1.721	-3.184	6.851	3.667	-2.727	6.366
C(10)	3.419	-2.507	6.579	5.057	-2.942	6.113
C(11)	4.394	-1.163	5.436	5.542	-2.297	5.051
C(12)	3.951	-0.552	4.660	4.911	-1.615	4.330
C(13)	-0.184	-1.840	3.256	0.871	-1.127	3.025
C(14)	-1.672	-2.196	3.133	-0.461	-0.771	2.911
C(15)	-2.685	-3.651	3.057	-1.366	-1.740	2.840
C(16)	-2.461	-4.872	3.064	-1.169	-3.071	2.847
C(17)	-1.061	-4.445	3.146	0.075	-3.321	2.923
C(18)	0.069	-2.906	3.254	1.091	-2.319	3.023
C(19)	3.723	1.677	1.526	3.720	0.129	1.418
C(20)	3.756	0.991	0.528	3.433	-0.765	0.491
C(21)	4.947	1.807	-0.880	4.022	-0.806	-0.817
C(22)	6.258	3.303	-1.035	5.112	0.013	-0.962
C(23)	6.281	4.009	-0.138	5.417	0.879	-0.128
C(24)	4.940	3.151	1.302	4.707	0.958	1.209
C(25)	0.437	1.325	2.655	1.221	1.616	2.467
C(26)	-0.637	1.306	3.449	0.539	2.278	3.204
C(27)	-1.777	1.954	3.002	-0.594	3.405	2.789
C(28)	-1.628	2.292	1.665	-0.888	3.415	1.547
C(29)	-0.670	1.389	0.746	-0.346	2.862	0.693
C(30)	0.505	1.708	1.211	0.822	1.689	1.125

atom were found from sharpened Patterson syntheses, and Fourier projections calculated with the antimony phases sufficed to define the approximate positions of the carbon atoms. The original $h0l$ electron density projection, calculated with the antimony phases only, is reproduced in Fig. 1, since it shows, despite the severe overlapping, that the molecule cannot be a trigonal bipyramid. Refinement of the two projections was carried out initially by hand calculations of successive Fourier and difference maps. It soon became apparent that many of the stronger low-order reflexions were suffering badly from extinction. These planes are marked by asterisks in Table 2. 10 $0kl$ reflexions and 21 $h0l$ reflexions were so affected. Extinction corrections were applied to these planes,² but they were omitted completely from the subsequent refinement cycles.

The hand calculations had reduced the R factor to about 15% for each projection. At this stage an Elliott 803B computer became available, and the later refinement was carried out with the programming system constructed by Daly, Stephens, and Wheatley.³ Several more difference maps were calculated for each projection with the non-extinguished planes only, and finally the co-ordinates and individual isotropic temperature factors were refined by a least-squares analysis, each projection being treated quite independently. The final R factor for the $0kl$ projection was 6.5%, and for the $h0l$ projection 8.4%. The z co-ordinates were then meaned and, since it was felt that the number of variables was too large, an overall isotropic temperature factor was selected for the carbon atoms in each projection. A final set of structure factors was calculated which gave an R factor of 11.1% for the $0kl$ and 12.3% for the $h0l$ projection. These figures include the extinguished planes but omit non-observed reflexions. The scattering factors were taken from International Tables, with the antimony curve corrected for the real part of the dispersion. The temperature factors used for the antimony atom were 3.77 and 2.98, and for the carbon atoms 5.68 and 4.90 Å² for the $0kl$ and $h0l$ projections respectively.

RESULTS

The co-ordinates of the atoms are given in Table 1, together with the orthogonal co-ordinates referred to a set of axes in which $[b']$ coincides with the original triclinic axis $[b]$; $[a']$ is the projection of the triclinic axis $[a]$ on the plane perpendicular to $[b']$; and $[c']$ is perpendicular to $[a']$ and $[b']$. Table 2 gives the observed and calculated structure

TABLE 3.

Bond lengths (Å) and bond angles (°) at the antimony atom.

Sb-C(1)	2.23	C(1)SbC(7)	89	C(7)SbC(19)	101
Sb-C(7)	2.12	C(1)SbC(25)	91	C(13)SbC(19)	109
Sb-C(13)	2.17	C(7)SbC(13)	88	C(19)SbC(25)	95
Sb-C(19)	2.13	C(13)SbC(25)	84	C(1)SbC(13)	147
Sb-C(25)	2.05	C(1)SbC(19)	104	C(7)SbC(25)	163

factors. Fig. 2 shows the molecule and the labelling of the atoms. Table 3 gives the bond lengths and angles at the antimony atom. The standard deviation of the co-ordinates of the antimony atoms are 0.003 Å, and of the carbon atoms about 0.07 Å. Thus the standard deviation of the Sb-C bond lengths is about 0.07 Å and of the C-C lengths about 0.10 Å. Angles involving antimony have a standard deviation of about 3° and those involving only carbon atoms about 6°. These standard deviations were obtained by normal least squares procedure from the residuals, but, since they involve projections, may well be over-optimistic. The C-C bond lengths vary between 1.15 and 1.71 Å, and have a mean value of 1.37 Å with a standard deviation of 0.02 Å. The mean value of the Sb-C bond length is 2.14 Å which agrees well with the distance found in dichlorotris-2-chlorovinylstibine, $(\text{ClCH}=\text{CH})_3\text{SbCl}_2$.⁴ It should be noticed, however, that the configuration of the bonds round the antimony atom found in this stibine is trigonal bipyramidal. There is no evidence that the axial bond in antimony pentaphenyl differs in length from the other four Sb-C bonds.

² James, "The Optical Principle of the Diffraction of X-rays," G. Bell and Sons, Ltd., London, p. 292.

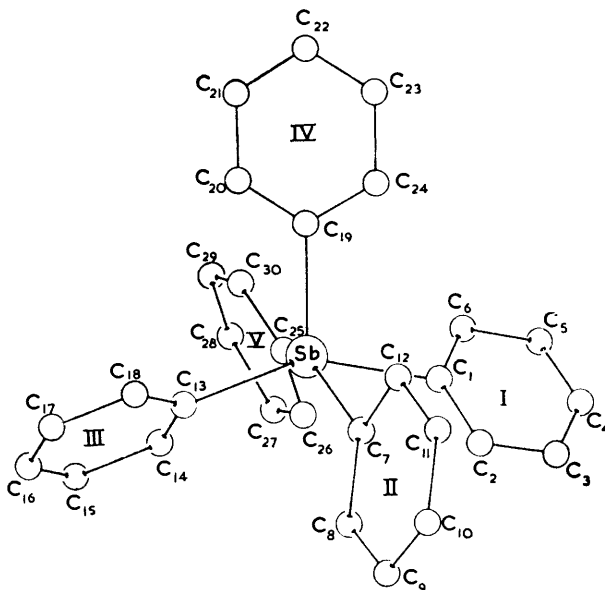
³ Daly, Stephens, and Wheatley, in course of publication.

⁴ Struchkov and Khotsanova, *Doklady Akad. Nauk S.S.S.R.*, 1953, **91**, 565.

[1964] *Crystal and Molecular Structure of Pentaphenylantimony.* 3723

The molecule has, within the limits of error, a two-fold axis of symmetry through the axial bond, as can be seen in Fig. 2. However the description of the molecule as being a square pyramid is a slight over-simplification, as there does seem to be a significant difference between the angles C(1)SbC(13) and C(7)SbC(25). The difference is such that the two atoms C(1) and

FIG. 2. Drawing of the molecule and labelling of the atoms.



C(13) lie further below the antimony atom than the two atoms C(7) and C(25). The mean least-squares plane through the four atoms forming the base of the pyramid is given, in terms of the orthogonal co-ordinates listed in Table 1, by the equation

$$-0.5452X' + 0.1144Y' + 0.8305Z' = 1.7483.$$

The departure of the four carbon atoms from this plane are: C(1), 0.16; C(7), -0.14; C(13), 0.16; C(25), -0.18 Å. The distance of the antimony atom from this plane is 0.46 Å.

The benzene rings are all planar within the limits of error. The mean planes through the five rings are given by the equations

$$\begin{aligned} \text{I} & \quad 0.8407X' - 0.1930Y' - 0.5060Z' = 0.3862 \\ \text{II} & \quad 0.2605X' + 0.7793Y' + 0.5700Z' = 2.5039 \\ \text{III} & \quad -0.0769X' - 0.0111Y' + 0.9970Z' = 2.9546 \\ \text{IV} & \quad 0.6412X' - 0.6622Y' + 0.3877Z' = 2.8557 \\ \text{V} & \quad 0.6926X' + 0.7110Y' - 0.1219Z' = 1.6556 \end{aligned}$$

The greatest departure of any carbon atom from its mean plane is 0.07 Å. The angles between the rings I and III is 124°, and between the rings II and V 48°.

The intermolecular contacts are all between benzene rings. There are 27 contacts less than 4.0 Å, the shortest being 3.55 Å.

I thank Professor G. Wittig of the University of Heidelberg who kindly provided the samples of the pentaphenyls of phosphorus, arsenic, and antimony.

MONSANTO RESEARCH S.A.,
BINZSTRASSE 39, ZÜRICH 3/45, SWITZERLAND.

[Received, November 4th, 1963.]