kinetic *trans*-effect series. We have also observed a "*cis* influence" which is comparable in magnitude to the *trans* influence.

It appears that a mechanism based on the stabilization of the five-coordinate activated complex is the most reasonable to explain the kinetic *trans* effect for σ-bonding ligands. Our calculations strongly support this mechanism both qualitatively and quantitatively. However, it is possible that bond-weakening effects may also be important in some cases (for example, the methide ion).

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A Reinvestigation of the Crystal and Molecular Structure of Pentaphenylantimony[1]

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Abstract: The structure of pentaphenylantimony has been redetermined from three-dimensional X-ray diffraction data (2337 independent reflections) measured on a counter diffractometer. The results confirm the general structural features found earlier by Wheatley in a two-dimensional study. The improved accuracy obtained with three-dimensional data allows the following conclusions. (1) While the molecule as a whole has C_1 point symmetry, the five carbon atoms bound to the antimony atom are arranged with virtual C_{2v} symmetry. (2) The set of Sb–C bond lengths is consistent with a square-pyramidal geometry, *viz.*, Sb–C(axial) = 2.115 (5) Å; four Sb–C(basal) bonds with an average length of 2.216 (7) Å. (3) The C(axial)–Sb–C(basal) angles deviate alternately by about +4 and −4° from their mean, thus spoiling the ideal C_{4v} symmetry which would exist if all were equal. The principal crystallographic data are as follows: space group, $P\bar{1}$; unit cell dimensions: $a = 10.286 \pm 0.007$ Å; $b = 10.600 \pm 0.007$ Å ; $c = 13.594 \pm 0.009$ Å; $\alpha = 79° 12' \pm 3'$; $\beta = 70° 28' \pm 3'$; $\gamma = 119° 31' \pm 3'$; measured density, 1.42 ± 0.01 g cm^{-3}; calculated density (for $Z = 2$), 1.41 g cm^{-3}.

There has been only one reported exception to the generalization that five-connected group V (*i.e.*, P, As, Sb, Bi) elements in compounds with formally 10-electron valence shells have bonds directed to the vertices of a trigonal bipyramid,[3,4] and in fact this generalization seems to apply even more broadly,[4] covering EX_n compounds of group VI (*e.g.*, SF_4) and group VII (*e.g.*, ClF_3) provided "incomplete" trigonal bipyramids are recognized. The lone reported exception is pentaphenylantimony, which has been characterized as having a "distorted square-pyramidal" structure[5] although pentaphenylphosphorus,[6] pentaphenylarsenic,[6] and several $(C_6H_5)_4SbOR$ (R = CH_3,[7] H[8]) compounds are all trigonal bipyramidal.

In view of the exceptional nature of the reported structure of $(C_6H_5)_5Sb$, as well as the importance of the question of the relative stabilities of trigonal-bipyramidal and square-pyramidal structures in understanding the fluxional nature of many molecules with the former as their ground-state geometry,[9] it seemed to us to be of unusual importance to seek confirmation of the reported structure of $(C_6H_5)_5Sb$ and to obtain more accurate structural parameters.

The reported study[5] is based on only two-dimensional data and does not provide meaningful results concerning the relative lengths of the Sb–C bonds. Moreover, it does not appear that the possibility of a water molecule or some other small ligand molecule occupying a sixth coordination site about the antimony atom and thus forcing a square-pyramidal disposition of the phenyl groups is excluded by the reported study.

A redetermination of the structure of pentaphenylantimony, using three-dimensional counter-diffractometer data was therefore undertaken and is described here.

Experimental Section

Preparation. Pentaphenylantimony was prepared by reaction of C_6H_5Li with $(C_6H_5)_3SbCl_2$ (Eastman), as described by Wittig and Clauss.[10] It was recrystallized from isooctane as colorless crystals (mp 167–168°, lit.[10] 169–170°). Part of the crude product was first recrystallized from *n*-hexane to yield yellowish plates which melt at 167–169° with a definite change of phase about 130–135°. The former is probably a solvate similar to $(C_6H_5)_5Sb \cdot 0.5$cyclohexane, isolated by Wittig and Clauss.[10] This solvate was heated at 115° under vacuum for 6 hr (during which some decomposition occurred), and after recrystallization from isooctane the pure, unsolvated, colorless compound was recovered.

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[2] Hydro-Quebec Postdoctoral Fellow, 1966–1968.

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Anal. Calcd for $C_{30}H_{25}Sb$: C, 71.03; H, 4.97. Found: C, 71.01; H, 4.93.

Crystals suitable for X-ray work were obtained from isooctane. A few crystals were grown by addition of methanol to a saturated solution in carbon tetrachloride. They were shown to have the same cell parameters as the crystals from isooctane, which in turn are identical with those used in Wheatley's work and isolated from anhydrous ethyl ether.[11] Crystals from all sources exhibit a great variety of habits.

Data Collection. Pentaphenylantimony is not air sensitive, and the X-ray work was carried out on crystals mounted on a glass fiber and exposed to the atmosphere. Precession photographs ($h0l$, $h1l$, $\underline{h}2l$, $0kl$, $1kl$, $2kl$) indicated one of the triclinic space groups P1 or P$\bar{1}$ and served to establish the identity of our crystals with those of Wheatley. The same labeling of axes was adopted and the cell constants were obtained at 23° from the zero-level precession photographs and by linear extrapolation of cell edges against the function[12] $(\cos^2 \theta/2)[(1/\sin \theta) + (1/\theta)]$, with 2θ values measured on a General Electric XRD-5 manually operated single-crystal diffractometer using Cu Kα radiation ($\lambda(K\alpha_1) = 1.5405$ Å, $\lambda(K\alpha_2) = 1.5443$ Å): $a = 10.286 \pm 0.007$ Å, $b = 10.600 \pm 0.007$ Å, $c = 13.594 \pm 0.009$ Å, $\alpha = 79° 12' \pm 3'$, $\beta = 79° 28' \pm 3'$, $\gamma = 119° 31' \pm 3'$. The density measured by flotation in aqueous KI solutions (1.42 ± 0.01 g cm^{-3}) agrees well with the calculated density of 1.405 g cm^{-3} for a formula weight of 507.3, $Z = 2$, and a unit cell volume of 1199.5 Å^3.

Intensity data were collected on the General Electric XRD-5 manual diffractometer with the c^* axis coincident with the ϕ axis of the instrument. The crystals were placed 5.73 in. from the source, while the distance from the crystal to the detector with a circular aperture of 2° was 7.05 in. The integrated intensities of 2532 independent reflections within the sphere $\theta \leq 50.5°$ were measured using nickel-filtered Cu Kα radiation. The counts were measured by means of a scintillation counter with a pulse-height discriminator set to accept 95% of the Cu Kα radiation within the window centered on the Cu Kα peak. A $\theta/2\theta$ scan technique was employed at a 2θ scan rate of 4°/min. The peak counts, P, were obtained from a 2θ scan of 2.66° from $2\theta_{\text{calcd}} - 1.33°$ to $2\theta_{\text{calcd}} + 1.33°$. Stationary background counts, B_1 and B_2, of 20 sec each were taken at each limit of the scan. The integrated intensity I is given by $I = P - (B_1 + B_2)$. Using the two criteria (a) $I \leq 0$, (b) $I < 3(P + B_1 + B_2)^{1/2}$, 195 reflections were later rejected as statistically insignificant.

After a few hours of exposure to the X-ray beam, the regular decrease of intensity of the standard reflections indicated a slow decomposition of the crystal. The variety of crystal habits makes the search for the axes on new crystals very laborious. Consequently, only two crystals (of dimensions 0.30 × 0.25 × 0.30 mm and 0.35 × 0.17 × 0.25 mm) were used for data collection, and the decomposition process was followed carefully in order to apply a suitable correction.

Decomposition Correction. Decomposition was monitored by measuring eight standard reflections every 4 hr. Crystal no. 1 was discarded after all the standard reflections had fallen by ~28%. Then crystal no. 2 was mounted. The behavior of crystal no. 2 was rather different from that of crystal no. 1 and showed a pronounced $\sin \theta/\lambda$ dependence so that at the end of data collection the standard reflections showed decreases varying from 10 (200) to 28% (30$\bar{8}$). The decreases of all eight reflections are given in Table I for both crystals. It is interesting to note that the lower angle reflections showed an initial increase in intensity during the first approximately 5 hr, which may indicate that the initial decomposition enhanced the mosaic character of the crystal and hence reduced primary extinction. Twenty-five duplicate reflections, measured both at the beginning and at the end of data collection for both crystals, were added to the standard reflections in order to cover more effectively the entire range of $\sin \theta/\lambda$ values.

In attempting to rationalize the discrepancy in behavior of the two crystals, two possibilities were considered: (a) that the rates of decomposition varied with the morphology and (b) that the rate observed for crystal 1 corresponded to a much later stage of decomposition (crystal 1 had been used for about 50 hr during preliminary photographic work) and would have behaved like crystal 2 during its early exposure period. To test these hypotheses, crystal 2 was continuously exposed for a further 45 hr and the standard reflections were measured every 8 hr. The behavior of crystal 2 showed (b) to be the case. There was a discontinuity at ~50 hr at which time the $\sin \theta/\lambda$ dependence disappeared.

Table I. Decomposition Data

Standard reflection				Intensity loss when crystal was discarded and decay constants			
				Crystal no. 1		Crystal no. 2	
h	k	l	$\sin \theta/\lambda$	$\frac{(I_0 - I_t)^a}{I_0}$	$k \times 10^2$	$\frac{(I_0 - I_t)}{I_0}$	$k \times 10^2$
0	0	$\bar{2}$	0.158	0.30	0.84	0.11	0.32
2	0	0	0.236	0.28	0.79	0.10	0.31
0	0	$\bar{4}$	0.310	0.30	0.88	0.14	0.47
0	0	$\bar{6}$	0.474	0.32	0.95	0.19	0.65
0	$\bar{1}$	$\bar{6}$	0.523	0.29	0.83	0.22	0.73
0	5	0	0.573	0.27	0.79	0.27	1.01
6	0	0	0.708	0.28	0.82	0.24	0.69
3	0	$\bar{8}$	0.818	0.33	1.03	0.28	0.95

[a] Losses are referred to the beginning of diffractometer data collection. Estimating for the effects of *total* exposure time, the losses may range from 37 to 50%.

Plots of ln I_t *vs.* time showed that the intensity followed quite closely the equation $\ln (I_0/I_t) = kt$ for both crystals (the square of the coefficient of correlation, r^2, for the least-squares straight lines varied from 0.92 to 0.97). The values of the decay constants k are given in Table I. An additional 25 values of k were calculated from the duplicate reflections assuming the same exponential decay. The 32 values of k for crystal 1 gave an average value of 0.0086 ± 0.0021 hr^{-1}, and the intensities collected on crystal 1 were corrected for the later decomposition stage by means of the equation $I_0 = I_t \exp(0.0086t)$.

Various simple equations were tested to fit the $\sin \theta/\lambda$ dependence of the constant k for crystal 2. The linear equations $k = 0.000467 + 0.0213 \sin \theta/\lambda$ and $k = 0.00309 + 0.0359 \sin^2 \theta/\lambda^2$ were found to give a reasonable fit (r^2 of 0.84 and 0.83, respectively). The first equation was preferred because it gives a better fit with the lower angle reflections where the sampling is poorer. In view of its small value, the intercept was set equal to zero and the best value of k' in the equation $k = k' \sin \theta/\lambda$ was 0.024 ± 0.006 hr^{-1}. The intensities obtained from crystal 2 were then corrected by means of the equation $I_0 = I_t \exp(0.024t \sin \theta/\lambda)$.

The validity of these correction equations was checked. The intensities of the standard and duplicate reflections were corrected with the appropriate equation and compared to I_0 measured at the beginning of data collection. The ratios $I_0^{\text{calcd}}/I_0^{\text{measd}}$ were found to be 0.98 ± 0.10 and 1.02 ± 0.05 for crystal 1 and crystal 2, respectively. A second correction was applied to the data from crystal 1 to account for the early decomposition stage, by means of the equation used for crystal 2, assuming $t = 50$ hr.

After correction for decomposition, the intensities were further corrected for the Lorentz and polarization effects. Appreciable variation in the intensities of the $00l$ reflections were observed as a function of the crystal orientations, ϕ scans of several of these reflections indicating variations of ±50% (crystal 1) and ±20% (crystal 2). Consequently, absorption corrections ($\mu = 96.0$ cm^{-1}), based on the equations of the crystal faces, were applied to I_0. The transmission factors were in the ranges 0.60–0.28 and 0.35–0.19, respectively. The variations on ϕ scans were reduced to ±8% for both crystals after the absorption corrections were applied.

Refinement. The structure was refined by the full-matrix least-squares process. The scattering factors for carbon and antimony were those of Cromer and Waber,[13] while the form factors used for hydrogen were those experimentally determined by Mason and Robertson.[14] The anomalous dispersion corrections[15] ($\Delta f' = -0.9$ e, $\Delta f'' = 6.10$ e) of antimony were included in the calculated structure factors. The function minimized during the least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ is the observed structure

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(11) Private communication from Professor G. Wittig who supplied the crystals for Wheatley's work.

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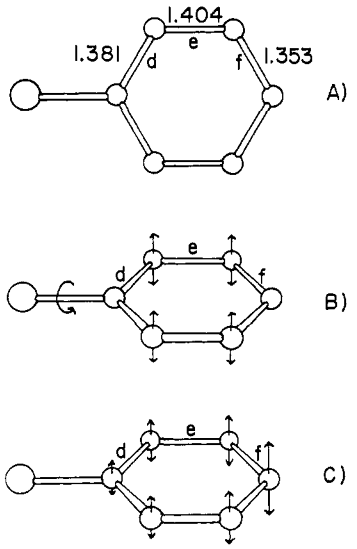

Figure 1. (A) The observed average bond lengths for the phenyl rings. (B) The tortional mode considered for the Sb–C_6H_5 groups. (C) The bending mode considered for the Sb–C_6H_5 groups.

amplitude, $|F_c|$ is the calculated structure amplitude, and w is the weighting factor.

The positional parameters obtained by Wheatley[5] were used as starting coordinates. Four cycles of least-squares refinement of scale factors and positional and thermal parameters for the antimony and carbon atoms led to a discrepancy index $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.069$. The weighted residual, $R_2 = \{\Sigma w[|F_o| - |F_c|]^2/\Sigma w|F_o|^2\}^{1/2}$ was 0.085. The antimony atom was next assigned an anisotropic temperature factor of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$, and two more cycles of refinement of all parameters for carbon and antimony resulted in $R_1 = 0.056$ and $R_2 = 0.073$. A difference Fourier map using all data revealed the positions of 24 of the 25 hydrogen atoms. These were fixed at the calculated position corresponding to a carbon–hydrogen distance of 1.08 Å and were assigned isotropic temperature factors 10% higher than those of the carbon atoms to which they are bound. Three cycles of refinement of the scale factor and the positional and thermal parameters of antimony and carbon atoms resulted in convergence with $R_1 = 0.051$ and $R_2 = 0.065$. At this point, a program for the refinement of the phenyl groups as rigid bodies became available.[16]

The rigid body refinement program as used was limited to planar regular bodies, *e.g.*, six carbon atoms of a phenyl group, or a limited but continuous sequence of atoms in such a body, such as the five hydrogen atoms of a phenyl group. The coordinates of the individual atoms are generated in the *XY* plane of an internal Cartesian coordinate system using the idealized radius of the body and are rotated by the angles *F*, *D*, and *E* radians about the axes *Z*, *X*, and *Y*, respectively. The internal coordinate system was conveniently defined by placing the origin at the center of the ring, the *X* axis parallel to a^*, the *Y* axis parallel to the line defined by the intersection of the plane containing a^* and b^* with the plane containing *b* and *c*, and the *Z* axis parallel to *c*. Individual temperature factors are assigned to each of the ring atoms.

The rigid body parameters (*X*, *Y*, *Z*, *D*, *E*, *F*, *B*'s) were generated from the parameters of the final cycle of individual atom refinement, assuming an ideal distance of 1.397 Å from the center of gravity of the phenyl ring to each carbon atom. The discrepancy factor obtained from the scattering factors calculated with these coordinates was 0.059, and the weighted residual R_2 was 0.079. Three cycles of refinement in which the scale factors, the positional and anisotropic temperature factors of antimony, and the parameters for five rigid bodies (no hydrogen atoms included) reduced R_1 to 0.057 and R_2 to 0.075. The hydrogen atoms were then fixed at the calculated positions (C–H distance = 1.08 Å) and the same parameters were allowed to refine. The hydrogen atoms were shifted after each cycle according to the carbon atom shifts. Two more cycles resulted in convergence with $R_1 = 0.052$ and $R_2 = 0.069$. A final difference Fourier map did not reveal peaks greater than 0.75 e Å^{-3}.

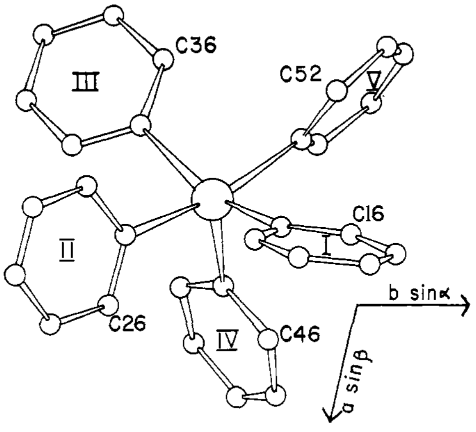

Figure 2. The molecular structure projected on a plane perpendicular to the *c* axis. Roman numerals are used to number the rings and the C_{ij}'s indicate numbering of carbon atoms within each ring, with C_{i1} always bonded to antimony.

The independent atom model appears to be significantly better than the rigid body approximation. An *R* factor test[17] rejected the rigid body model at the 0.995 confidence level, but this assumes no systematic errors in the data, which in Hamilton's definition would include the parameters of the model. It is worthwhile to consider (a) the observed average geometry of a ring in pentaphenylantimony (averaged assuming a mirror plane normal to the plane of the ring and passing through the atoms C_1 and C_4), (b) the effects expected for an oscillation about the C_1–C_4 axis, and (c) those expected for an approximation to an Sb–phenyl bending mode, as shown in Figure 1. The coordinate errors introduced by (b) would produce geometry errors such that $d = f < e$ (which should be unaffected) and a pattern of temperature factors $(B_1 = B_4) < (B_2 = B_3)$, while the effects of (c) could be summarized as $d > e > f$ (all reduced from the true value) and $B_1 < B_2 < B_3 < B_4$ (this assumes that the fulcrum of the vibration lies between Sb and C_1). The observed pattern in (a) then implies contributions from both (b) and (c) and suggests that a significant contribution to systematic errors in the refinement could result from the deficiency in representing group vibrations. If this is indeed the case, the confidence at which the rigid body model is rejected should decrease with a decrease in the temperature at which an investigation is carried out. For the present structure, a full anisotropic refinement is not justified in the light of the assumptions made for the decomposition correction and hence corrections for the effects of thermal motion of a rigid body[18] cannot be made. The presence of librations and the concomitant changes in geometry for which no valid correction is made decrease the utility of a benzene ring geometry as internal standard. Hence we consider that the use of the rigid body approximation is justified for this structure for the reasons proposed elsewhere.[19]

Results

A view of the molecule down the *c* axis is shown in Figure 2. The carbon atoms are assigned two indices, the first of which corresponds to the ring number (1 to 5). The second corresponds to sequential numbering of the ring vertices, the index 1 being assigned

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(16) Computer programs for the IBM 360 computer used in this study were: D. P. Shoemaker, MIXG2 (calculates diffractometer settings) and DISTAN (orthogonal cell coordinates, inter- and intramolecular contacts and angles); R. C. Elder, PDATA2 (corrects MIXG2 output for ϕ_0 and scan width and prints diffractometer settings in convenient format) and PUBTAB (prepares structure factors in proper format for publication); W. C. Hamilton, GONO9 (used for absorption correction); A. Zalkin, FORDAP (Fourier summation for Patterson or difference Fourier maps); C. T. Prewitt, SFLS5 (least-squares refinement of parameters) and SFLS5R (with rigid body routine, adapted by M. J. Bennett and B. M. Foxman); M. J. Bennett, PMMO (general data reduction program); J. S. Wood, MGEOM (bond lengths and angles with standard deviations and best least-squares planes).

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Table II. Final Atom Parameters for Free Atom Refinement[a] (R_1 = 5.1%, R_2 = 6.5%)

Atom	x	y	z	B, Å^2 [b]
Sb	0.16311 (6)	0.03937 (6)	0.25224 (4)	3.77[c]
C_{11}	0.2265 (9)	0.1960 (9)	0.3463 (7)	4.55 (16)
C_{12}	0.2536 (11)	0.1603 (11)	0.4424 (7)	5.48 (19)
C_{13}	0.2996 (12)	0.2657 (12)	0.4964 (9)	6.65 (23)
C_{14}	0.3200 (12)	0.4038 (12)	0.4590 (8)	6.44 (22)
C_{15}	0.2980 (11)	0.4426 (12)	0.3644 (8)	6.19 (21)
C_{16}	0.2499 (11)	0.3387 (11)	0.3092 (7)	5.28 (19)
C_{21}	0.2374 (10)	−0.0883 (9)	0.3500 (7)	4.38 (16)
C_{22}	0.1254 (11)	−0.2143 (11)	0.4397 (7)	5.71 (20)
C_{23}	0.1716 (12)	−0.2916 (12)	0.5073 (8)	6.34 (22)
C_{24}	0.3232 (13)	−0.2430 (13)	0.4858 (9)	6.78 (23)
C_{25}	0.4356 (13)	−0.1219 (14)	0.3966 (9)	7.31 (25)
C_{26}	0.3928 (11)	−0.0428 (11)	0.3276 (7)	5.68 (20)
C_{31}	−0.0082 (10)	−0.1833 (10)	0.2365 (7)	4.73 (17)
C_{32}	−0.1540 (11)	−0.2162 (11)	0.2275 (8)	5.82 (20)
C_{33}	−0.2578 (13)	−0.3649 (14)	0.2221 (9)	7.34 (25)
C_{34}	−0.2172 (14)	−0.4622 (14)	0.2262 (9)	7.66 (26)
C_{35}	−0.0722 (13)	−0.4307 (13)	0.2293 (9)	7.04 (24)
C_{36}	0.0300 (11)	−0.2887 (11)	0.2381 (7)	5.64 (20)
C_{41}	0.3593 (10)	0.1558 (10)	0.1109 (7)	4.71 (17)
C_{42}	0.3595 (13)	0.0832 (13)	0.0373 (9)	6.99 (24)
C_{43}	0.4895 (16)	0.1691 (16)	−0.0612 (11)	8.82 (31)
C_{44}	0.6090 (13)	0.3107 (13)	−0.0748 (9)	7.15 (24)
C_{45}	0.6064 (13)	0.3787 (14)	−0.0034 (10)	7.38 (26)
C_{46}	0.4807 (11)	0.3034 (11)	0.0907 (8)	5.79 (20)
C_{51}	0.0297 (10)	0.1335 (9)	0.1942 (7)	4.54 (17)
C_{52}	−0.0789 (10)	0.1418 (10)	0.2653 (7)	5.03 (18)
C_{53}	−0.1711 (11)	0.1906 (11)	0.2327 (8)	5.67 (20)
C_{54}	−0.1519 (13)	0.2299 (13)	0.1231 (9)	7.23 (25)
C_{55}	−0.0464 (13)	0.2212 (13)	0.0548 (9)	7.32 (25)
C_{56}	0.0448 (11)	0.1714 (11)	0.0892 (8)	5.78 (20)

[a] Standard deviations in the last figure of each parameter are given in parentheses. [b] Anisotropic parameters for Sb are as follows: β_{11}, 0.01365 (11); β_{22}, 0.01260 (10); β_{33}, 0.00541 (5); β_{12}, 0.00660 (8); β_{13}, −0.00372 (6); β_{23}, −0.00248 (5). [c] This is the equivalent B computed from the preceding anisotropic thermal parameter.

Table III. Final Atom Parameters from the Rigid Body Refinement[a] (R_1 = 5.2%, R_2 = 6.9%)

Atom	x	y	z	B, Å^2 [b]
Sb	0.16313 (6)	0.03940 (6)	0.25224 (4)	3.76[c]
C_{11}	0.2272 (7)	0.1967 (6)	0.3472 (4)	5.42 (17)
C_{12}	0.2518 (8)	0.1576 (5)	0.4430 (5)	5.59 (20)
C_{13}	0.2986 (7)	0.2616 (7)	0.4989 (4)	6.69 (24)
C_{14}	0.3207 (7)	0.4047 (6)	0.4592 (4)	6.52 (23)
C_{15}	0.2961 (8)	0.4438 (5)	0.3635 (5)	6.31 (22)
C_{16}	0.2493 (7)	0.3398 (7)	0.3075 (4)	5.14 (19)
C_{21}	0.2363 (9)	−0.0902 (8)	0.3502 (5)	4.43 (17)
C_{22}	0.1231 (9)	−0.2148 (8)	0.4400 (4)	5.64 (20)
C_{23}	0.1685 (10)	−0.2909 (6)	0.5071 (6)	6.50 (23)
C_{24}	0.3271 (9)	−0.2424 (8)	0.4841 (5)	6.82 (24)
C_{25}	0.4404 (9)	−0.1178 (8)	0.3946 (4)	7.56 (27)
C_{26}	0.3950 (10)	−0.0417 (6)	0.3275 (6)	5.62 (20)
C_{31}	−0.0078 (7)	−0.1810 (6)	0.2358 (4)	4.76 (18)
C_{32}	−0.1550 (8)	−0.2174 (7)	0.2279 (5)	5.82 (21)
C_{33}	−0.2604 (7)	−0.3610 (7)	0.2220 (4)	7.33 (26)
C_{34}	−0.2187 (7)	−0.4683 (6)	0.2240 (4)	7.70 (28)
C_{35}	−0.0716 (8)	−0.4320 (7)	0.2319 (5)	7.19 (25)
C_{36}	0.0339 (7)	−0.2883 (7)	0.2378 (4)	5.70 (21)
C_{41}	0.3577 (7)	0.1550 (10)	0.1115 (4)	4.69 (18)
C_{42}	0.3594 (8)	0.0827 (6)	0.0357 (7)	7.10 (25)
C_{43}	0.4855 (11)	0.1602 (11)	−0.0588 (8)	9.05 (33)
C_{44}	0.6098 (7)	0.3100 (10)	−0.0775 (4)	7.24 (26)
C_{45}	0.6081 (8)	0.3824 (11)	−0.0018 (7)	7.66 (27)
C_{46}	0.4821 (11)	0.3049 (11)	0.0927 (8)	5.95 (21)
C_{51}	0.0293 (8)	0.1324 (8)	0.1954 (8)	4.59 (17)
C_{52}	−0.0791 (10)	0.1415 (7)	0.2673 (5)	4.96 (18)
C_{53}	−0.1711 (8)	0.1903 (7)	0.2317 (5)	5.67 (21)
C_{54}	−0.1546 (8)	0.2300 (8)	0.1242 (8)	7.29 (26)
C_{55}	−0.0461 (10)	0.2209 (7)	0.0523 (5)	7.47 (27)
C_{56}	0.0458 (8)	0.1721 (7)	0.0879 (5)	5.89 (21)

[a] Standard deviations in the last digit of each parameter are given in parentheses. [b] Anisotropic thermal parameters for Sb are as follows: β_{11}, 0.01363 (12); β_{22}, 0.02158 (11); β_{33}, 0.00540 (5); β_{12}, 0.00660 (8); β_{13}, −0.00372 (6); β_{23}, −0.00247 (5). [c] This is the value of B equivalent to the preceding anisotropic thermal parameter.

Table IV. Coordinates of Rigid Phenyl Groups[a,b]

	Fractional coordinates			Angles, radians		
Ring no.	x	y	z	D	E	F
1	0.2739 (4)	0.3007 (5)	0.4032 (3)	3.310 (4)	1.806 (4)	0.642 (3)
2	0.2817 (5)	−0.1663 (5)	0.4173 (3)	5.571 (4)	0.176 (5)	1.737 (5)
3	−0.1133 (5)	−0.3247 (5)	0.2299 (3)	2.996 (4)	2.733 (4)	3.868 (3)
4	0.4837 (5)	0.2325 (6)	0.0170 (4)	0.822 (4)	0.783 (6)	3.259 (6)
5	−0.0626 (5)	0.1812 (5)	0.1598 (3)	2.408 (4)	1.252 (6)	1.779 (5)

[a] Standard deviations in the last digit of each coordinate are given in parentheses. [b] The coordinates given are for the C_6 groups, C_{i1}–C_{i6}. The sets H_{i2}–H_{i6} have the same x, y, z, D, and E coordinates, but their F angles are $2\pi/6$ radians greater since these bodies begin with H_{i2} which is 60° rotated from C_{i1}.

Table V. Final Molecular Dimensions as Given by the Independent Atom (IA) and Rigid Body (RB) Refinements[a]

	Sb–C bond lengths, A IA	RB
Sb–C_{41}	2.128 (8)	2.115 (5)
Sb–C_{11}	2.202 (8)	2.218 (5)
Sb–C_{21}	2.213 (8)	2.220 (7)
Sb–C_{31}	2.225 (9)	2.212 (5)
Sb–C_{51}	2.225 (8)	2.214 (7)

	C–Sb–C bond angles, deg IA	RB
C_{41}–Sb–C_{11}	104.8 (3)	105.0 (2)
C_{41}–Sb–C_{21}	99.6 (3)	99.8 (3)
C_{41}–Sb–C_{31}	106.0 (3)	105.7 (3)
C_{41}–Sb–C_{51}	96.4 (3)	96.7 (3)
C_{51}–Sb–C_{21}	164.0 (3)	163.5 (3)
C_{31}–Sb–C_{11}	149.2 (3)	149.3 (2)
C_{11}–Sb–C_{51}	88.4 (3)	88.5 (2)
C_{31}–Sb–C_{51}	88.6 (3)	88.1 (3)
C_{21}–Sb–C_{21}	86.7 (3)	86.7 (2)
C_{11}–Sb–C_{21}	87.8 (3)	87.2 (9)

		C–C distances,[b,c] C_{ij} − $C_{i(j+1)}$			
i	j	Distance	i	j	Distance
1	1	1.407 (13)	4	1	1.372 (14)
	2	1.383 (12)		2	1.368 (13)
	3	1.387 (14)		3	1.449 (17)
	4	1.351 (15)		4	1.339 (18)
	5	1.370 (15)		5	1.316 (17)
	6	1.389 (14)		6	1.394 (15)
2	1	1.399 (13)	5	1	1.386 (12)
	2	1.374 (12)		2	1.366 (13)
	3	1.415 (14)		3	1.384 (13)
	4	1.329 (15)		4	1.418 (15)
	5	1.377 (16)		5	1.345 (16)
	6	1.412 (15)		6	1.390 (15)
3	1	1.397 (13)			
	2	1.353 (13)			
	3	1.429 (15)			
	4	1.327 (17)			
	5	1.358 (16)			
	6	1.392 (15)			

[a] Standard deviations occurring in the last quoted figure are given in parentheses. [b] Only the IA values are given as the RB values were fixed at 1.397 Å. [c] Index j is modulo 6.

to the atom bound to antimony. Hydrogen atoms are referred to with the same pair of indices as the carbon atom to which they are attached.

Table II gives the final atom coordinates and temperature factors obtained in the conventional, free atom refinement process, while Table III gives the corresponding results from the rigid body refinement. The rigid body parameters as such are given in Table IV. All esd's were obtained from the inverse matrix of the final cycle of least-squares refinement.

Bond lengths and angles are given in Table V. Results from both refinements are given side by side for comparison. No anomalous nonbonded contacts, inter- or intramolecular, were found. Indeed the shortest intramolecular contacts were ~0.4 Å longer than corresponding ones in $(C_6H_5)_5P$.

Discussion

The over-all molecular structure reported by Wheatley[5] is confirmed by the present work. However, the more accurate three-dimensional treatment brings out interesting features unobserved in the two-dimensional study. The C_2 symmetry obtained in the latter work disappears in the light of our results. Although rings II and V almost coincide through 180° rotation about the Sb–C_{41} bond, rings I and III are so oriented that the twofold axis is not retained. As far as the coordination geometry about antimony is concerned, the molecule does come close to having C_{2v} symmetry. The angles defined by Sb–C_{41} and the other Sb–C_{i1} bonds are practically equal for opposite pairs, and the axial C_{41} atom is not greatly out of the planes through these pairs (0.09 Å out of C_{21}–Sb–C_{51} plane and 0.01 Å out of C_{11}–Sb–C_{31} plane). Packing forces are probably responsible for slight bending of the phenyl rings (*i.e.*, nonlinearity of Sb–C_{i1}–C_{i4}), the distance from antimony to the least-squares planes through the rings varying from 0.08 to 0.16 Å.

The molecules are packed in the crystal in such a way as to leave a free space opposite to the Sb–C_{41} bond, which might be considered as a potential sixth coordination site. This space is not effectively occupied by portions of the neighboring molecules. The shortest intermolecular contacts of antimony are Sb–C_{13} = 4.40 Å and Sb–H_{13} = 4.18 Å. The possibility of a small ligand filling this site was carefully considered. However, the size of the hole precludes the presence of bulky molecules, and even the oxygen of a water molecule placed at the 2.20-Å (Sb–OH_2) distance observed in hexacoordinate $(C_6H_5)_2SbCl_3 \cdot H_2O$)[20] on the prolongation of the C_{41}–Sb line would make an abnormally short contact of 2.2 Å with the C_{32} atom opposite to the hole. This and the absence of any significant indication of electron density on the final difference Fourier map confirm that pentaphenylantimony is a genuinely pentacoordinate, unsolvated species in this crystal.

The question of how best (or even *whether*) to describe the structure of this molecule as a distorted form of one of the idealized structures (*i.e.*, the trigonal bipyramid or the square pyramid) does not have an entirely straightforward answer. This is because the angles of

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(20) T. N. Polynova and M. A. Porai-Koshits, *Zh. Strukt. Khim.*, **8**, 112 (1967).

the square pyramid, unlike those of the trigonal bipyramid, are not uniquely defined. One may assume that C_{41} lies at the apex of a square pyramid and then calculate how much each of the C_{41}–Sb–C_{i1} angles deviates from the mean value of all four of them. One finds deviations of 3.2, 2.0, 3.9, and 5.1° for the angles to C_{11}, C_{21}, C_{31}, and C_{51}, respectively, the sum of which is 14.2°. For a trigonal bipyramid, assuming that C_{21} and C_{51} would be "axial," the C_{41}–Sb–C_{i1} deviations, listed in the same order, are 15.0, 9.0, 14.3, and 6.7°, the sum of which is 45.0°. On this basis, the structure appears to be much closer to square pyramidal than to trigonal bipyramidal. However, this argument really begs the question by assuming that the appropriate apex-to-base angle, that is, the one from which deviations should be measured, for a square pyramid is the one to which the observed angles most nearly correspond. Such an assumption is equivalent to assuming the conclusion, namely, that we are dealing with a distorted square pyramid. If, in fact, the "appropriate" angle for a square pyramidal $(C_6H_5)_5Sb$ with the lowest potential energy was ≤ 90 or ≥ 113°, then the sum of the deviations would be equal to or greater than those for the trigonal bipyramid.

In order to conclude that the observed structure is best described as a distorted square pyramid, it is necessary to have some reason to believe that the most "appropriate" apex-to-base angle ought to be >90 and <113°. Although this *seems* quite possible and even likely, the lack of axial symmetry in the Sb–C_6H_5 moieties together with intrinsic rotational freedom about the Sb–C_{i1} bonds makes it difficult to substantiate such a belief.

It is to be noted that the pattern of Sb–C bond lengths does unambiguously favor the view that we are dealing here with a distorted square pyramid. What would be the axial bond in such a structure is uniquely different (~2.12 Å) from the other four (basal bonds), all of which have essentially the same length (2.20–2.23 Å).

In conclusion, it may be said that even if the $(C_6H_5)Sb$ molecule is satisfactorily described as distorted square pyramidal *in the crystal*, there remains the question of what role intermolecular forces play in determining this result. It is, after all, of the essence of the fluxional, stereochemically nonrigid, or pseudo-rotating AB_5 molecules that there is little difference in the potential energy of the square-pyramidal and trigonal-bipyramidal structures. It is clear that the $(C_6H_5)_5Sb$ molecule and some of its derivatives should be examined in other environments in order to sort out the inherent structural preference from the influence of intermolecular forces. Such studies are being undertaken by A. L. B.