The Role of Crystal Packing Forces in the Structure of Pentaphenylantimony

By Carolyn Pratt Brock

Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506, U.S.A.

and James A. Ibers

Department of Chemistry, Northwestern University, Evanston, Illinois 60201, U.S.A.

Pentaphenylantimony, $(C_6H_5)_5Sb$, possesses square-pyramidal, rather than the expected trigonal-bipyramidal geometry in the solid state; an attempt has been made to determine whether the observed conformation results from crystal packing forces. A semi-empirical strain-energy minimization procedure has been used in which the energy is taken as a sum of bond and angle deformation terms and of repulsive and van der Waals interactions between non-bonded atoms. The phenyl rings were treated as rigid bodies having D_{6h} symmetry. Calculations of intramolecular and lattice energies were made for $(C_6H_5)_5Sb$ as observed in the crystal and for a hypothetical trigonal-bipyramidal molecule and crystal structure derived from data on $(C_6H_5)_5P$ and $(C_6H_5)_5As$. Comparisons show that intermolecular forces favor the square-pyramidal crystal structure by 4·6 kJ/mole but that intramolecular interactions favor trigonal-bipyramidal molecular geometry by 30·5 kJ/mole. We suggest that the failure to predict the experimentally observed structure may result from the neglect of Coulombic interactions.

Introduction

The observed structure of pentaphenylantimony, $(C_6H_5)_5Sb$, is of unusual interest. Five-coordinate molecules having identical monodentate ligands, a spherical shell of d electrons, and no sterically active lone pairs are expected to adopt trigonal-bipyramidal geometries in order to minimize ligand–ligand repulsions (Gillespie, 1963). Pentaphenylantimony, however, is an important exception to this rule, as two crystallographic studies have shown that it possesses square-pyramidal geometry in the solid state (Wheatley, 1964b; Beauchamp, Bennett & Cotton, 1968). On the other hand, the analogous pentaphenylphosphorus molecule has been shown to be a trigonal bipyramid (Wheatley, 1964a) and pentaphenylarsenic presumably has a similar structure since it crystallizes in a unit cell very similar to that of the phosphorus compound (Wheatley & Wittig, 1962). Cell data for these three compounds are given in Table 1.

Table 1. *Crystal data for* $(C_6H_5)_5M$ *molecules*

	M = P*	M = As†	M = Sb‡
Space group	Cc	Cc	$P\bar{1}$
Z	4	4	2
a	10·029	10·075	10·286 Å
b	17·215	17·412	10·600 Å
c	14·170	14·227	13·594 Å
α	90°	90°	79° 12′
β	112° 03′	111° 57′	79° 28′
γ	90°	90°	119° 31′

* Wheatley (1964a). † Wheatley & Wittig (1962). ‡ Beauchamp, Bennett & Cotton (1968).

The occurrence of the anomalous pentaphenylantimony structure has usually been ascribed to crystal packing effects; that is, it is suggested that the crystallization process stabilizes a molecular conformation different from that which exists at equilibrium in the free state or in solution. The reported structure of penta-*p*-tolylantimony, in which the molecule adopts a trigonal-bipyramidal conformation, supports this view (Brabant, Hubert & Beauchamp, 1973). Replacement of the *para* hydrogen atoms of the phenyl rings by methyl groups alters the intermolecular interactions, and hence the packing of the molecule, without significantly changing the electronic structure or the intramolecular interactions. An additional indication that packing effects are important comes from the recent structure determination of a cyclohexane solvate of pentaphenylantimony, in which the molecule displays undistorted trigonal-bipyramidal geometry (Beauchamp, 1974).

Since the results of solid-state structure determinations are often used to interpret molecular behavior in the gaseous or liquid states, it is important to understand the extent to which crystal packing forces may affect observed molecular structures. Such forces are particularly important when the energy differences separating possible structures are small, as for five-coordinate molecules. In such molecules the trigonal-bipyramidal and square-pyramidal geometries may be separated by less than ten kilojoules per mole (1 kJ/mole = 0·2390 kcal/mole = 83·61 cm^{-1}), and the interconversion of the two forms corresponds to one of the normal modes of molecular motion. We therefore have made calculations of the conformational and lattice energy of pentaphenylantimony in an attempt to assess the possible magnitude of any lattice effects and in order to determine whether such effects could be responsible for the stabilization of a non-equilibrium molecular geometry.

Description of the calculations

Conformational and lattice-energy calculations for molecules in both the free and solid states were carried out using methods described previously (Brock & Ibers, 1973). Use was made of Busing's (1972) program *WMIN*, which combines calculation of molecular strain energy arising from bond and angle deformation terms and from intramolecular non-bonded interactions with the possibility for summing the intermolecular contributions to the energy (van der Waals, repulsive, and Coulombic) over the crystal lattice. The form of the Buckingham potential for non-bonded interactions used in this program is that of Gilbert (1968):

$$E_{ij} = (B_i + B_j) \exp\left[(A_i + A_j - r_{ij})/(B_i + B_j)\right] - (C_i C_j)/r_{ij}^6.$$

The non-bonded potential parameters for the carbon and hydrogen atoms were those developed by Williams (1967), while the potential for the antimony atom was adapted from a xenon potential given by Mason & Rice (1954). The values of these parameters are given in Table 2. The expression allows the geometric-mean combining law to be used to represent interactions between unlike atoms. In order to avoid forcing the bonds into any preconceived pattern, bond-angle deformation terms were omitted and the same harmonic bond-stretching potential was used for all the carbon–antimony bonds. The force constant of this potential was set at 3·00 mdyn/Å and the hypothetical strain-free bond distance was taken as 2·10 Å. Initially it was assumed that the atoms were electrically neutral and no Coulombic interactions were included.

Table 2. *Non-bonded potential function parameters*

Energy in kJ/mole

	A (Å)	B (Å)	C (kJ Å^6/mole)$^{1/2}$
H*	1·421	0·1337	10·7
C*	1·951	0·1389	48·7
Sb†	2·494	0·1712	166·5

* Williams (1967). † Mason & Rice (1954).

Starting atomic coordinates were taken from results of the crystal structure determination of Beauchamp *et al.* (1968). In order to make the problem tractable we assumed that the energy required to distort the phenyl rings is much larger than that required to translate or rotate them, and therefore we treated the rings as rigid bodies. Idealized phenyl rings having D_{6h} symmetry, $d_{C-C} = 1·40$ Å and $d_{C-H} = 1·04$ Å, were placed in average positions derived from the observed ring-carbon coordinates.

The summations of the non-bonded interactions were carried out to 6·75 Å for energy minimizations of the isolated molecule. Interactions beyond this limit affect the calculated energies (by *ca.* 2 kJ/mole) but have little influence on calculated geometries. Energies

quoted for specific molecular conformations were carried further to assure convergence to 0·1 kJ/mole. For the lattice calculations the program utilizes the Ewald–Bertaut–Williams method for accelerated convergence (Bertaut, 1952; Williams, 1971); limits were set to assure that the truncation error was less than 0·1 kJ/mole. The energy minimization procedure was continued until the energy change after a given cycle was of this magnitude or less. Owing to storage and time requirements the energy calculations were carried out on the Lawrence Berkeley Laboratory CDC 7600 computer, both on site and *via* remote transmission from the Northwestern University CDC 200 Series User Terminal. Less demanding computations, including geometrical analyses of results using the Busing, Martin, Levy (1964) *ORFFE* program, were carried out on the University of Kentucky IBM 360/65 computer.

Results

The energy of the pentaphenylantimony molecule was minimized by varying simultaneously the three translational and three rotational degrees of freedom of each of the rings starting from the observed square-pyramidal structure. The molecule converted smoothly to a trigonal bipyramid, encountering no barrier in the process; the square pyramid is not in a local minimum of the energy surface. The resulting trigonal-bipyramidal geometry is very similar to that found for pentaphenylphosphorus (Wheatley, 1964a). This same conformation is also obtained starting from an arbitrary square-pyramidal or trigonal-bipyramidal geometry, suggesting that the rotations of the rings are quite restricted. The values of the antimony–carbon bond distances and angles before and after energy minimization of the isolated molecule are given in Table 3; the observed conformations of the phosphorus and antimony species and that of pentaphenylantimony after minimization are shown in Fig. 1.

Table 3. *Bond distances (Å) and angles (°) in the penta-phenylantimony molecule*

	Square-pyramidal structure*	After energy minimization†
Sb–C$_{ax}$	2·128	2·190, 2·190
Sb–C$_{eq}$	2·202, 2·213, 2·225, 2·225	2·178, 2·179, 2·180
∠C$_{ax}$–Sb–C$_{eq}$	105, 106, 100, 97	96, 90, 84
		84, 90, 96
∠C$_{ax}$–Sb–C$_{ax}$	–	179
∠C$_{eq}$–Sb–C$_{eq}$	149, 164	120, 120, 120
	88, 87, 88, 88	

* Beauchamp, Bennett & Cotton (1968). † This work.

The results of this minimization point up a shortcoming in the force field used to represent the molecule. In the observed square-pyramidal structure the axial Sb–C bond is about 0·1 Å shorter than the average basal Sb–C bond, and a similar difference between the equatorial and axial bonds would be expected in the

trigonal-bipyramidal structure. However, after minimization the difference in the lengths of these two sets of bonds is at most 0·02 Å. Attempts were made to remedy this problem by using an anharmonic stretching potential based on Badger's rule, but they were not successful. It appears that in order to produce the observed bond-length differences two bond-stretching potentials having different equilibrium bond lengths would have to be employed. Since such a procedure would bias the calculation towards a preconceived bonding pattern, the potential, although inadequate, was retained.

Calculations of the energy of the pentaphenylantimony crystal were next performed. The adequacy of the force-field description was first tested by varying the cell constants and the six rigid-body translations and rotations of the molecule to minimize the energy and thus to determine if the observed structure was well reproduced. The shifts in the 12 variables, given in Table 4, are all small, and tests on calculated values of the second derivatives of the energy with respect to these variables show that the structure lies in a true minimum of the energy surface rather than on a saddle point or maximum.

The next level of energy minimization of the crystal structure, that of allowing the positions of the individual rings of the molecule to vary independently, was less successful. Owing to the inadequacy of the Sb–C stretching potential, the positions of the rings shifted significantly and the Sb–C bond lengths changed by up to 0·07 Å. These changes alter the non-bonded contacts, both intra- and intermolecular, of the molecule. Since the cell constants are very sensitive to changes in these contacts, the shifts in the cell dimensions were large and the stability of the minimization decreased. In order to stabilize the calculation, the positions of the individual rings were varied while the cell constants were fixed at their experimentally determined values. Although the bond lengths changed significantly and in fact adopted a trigonal-bipyramidal distribution (three shorter, two longer), the bond angles retained a distinctly square-pyramidal pattern.

Table 4. *Results of the energy minimization of the P1 pentaphenylantimony structure*

	Experimental*	Calculated†	Difference
		Cell constants	
a	10·286 (7)	10·193	−0·093 Å
b	10·600 (7)	10·596	−0·004 Å
c	13·594 (9)	13·605	+0·011 Å
α	79·20 (5)	79·30	+0·10°
β	79·47 (5)	79·40	−0·07°
γ	119·52 (5)	118·44	−1·08°
	Fractional coordinates and orientation angles‡		
x	0·16313 (6)	0·16156	−0·00157 (0·016 Å)
y	0·03940 (6)	0·04306	+0·00366 (0·39 Å)
z	0·25224 (4)	0·25271	+0·00047 (0·006 Å)
δ	−32·4	−32·9	−0·5°
ε	−149·3	−149·9	−0·6°
η	−46·5	−47·3	−0·8°

* Beauchamp, Bennett & Cotton (1968).
† This work.
‡ The angles δ, ε, and η are those which bring about alignment (except for translation) of an internal Cartesian coordinate system within the group with a fixed external Cartesian coordinate system based on the crystal axes (La Placa & Ibers, 1965).

In order for these calculations of the energy of the crystal to be helpful in deciding if packing forces are indeed responsible for the observed square-pyramidal molecular geometry, comparisons must be made with calculations of the energy of the most likely trigonal-bipyramidal structure. Since the antimony compound is prepared in the same way as are the phosphorus and arsenic analogues (Wittig & Clauss, 1952), and since pentaphenylphosphorus is known to be a trigonal bipyramid and pentaphenylarsenic is assumed to be one, a hypothetical trigonal-bipyramidal structure of pentaphenylantimony in the monoclinic space group Cc was derived from the structural data for the two analogous compounds (see Table 1). The increase in the van der Waals radius between arsenic and antimony is twice that between phosphorus and arsenic (Pauling, 1960); the cell lengths of the derived monoclinic cell for pentaphenylantimony were therefore calculated ac-
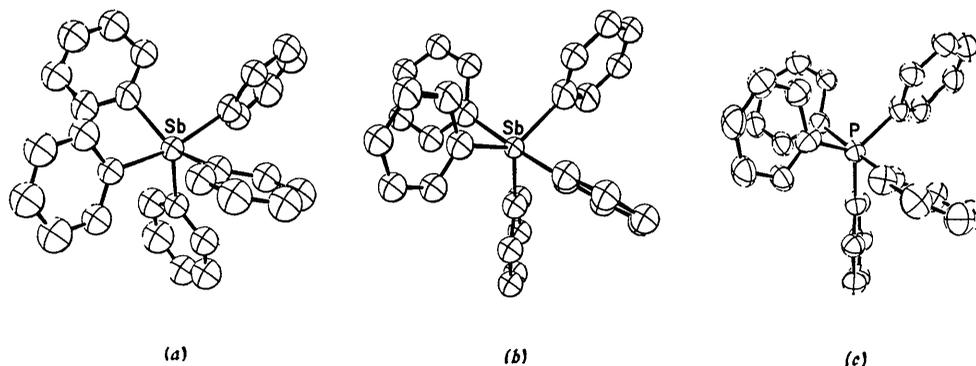
Fig. 1. (*a*) (C₆H₅)₅Sb as observed in P1 crystal (Beauchamp *et al.*, 1968). (*b*) (C₆H₅)₅Sb after minimization of the isolated molecule. (*c*) (C₆H₅)₅P as observed in *Cc* crystal (Wheatley, 1964*a*).

cording to the following formula:

$$a_{i,Sb} = a_{i,As} + 2(a_{i,As} - a_{i,P}), \quad i = 1, 3,$$

where $a_{i,As}$ is the ith dimension of the unit cell of pentaphenylarsenic. The monoclinic angles of the phosphorus and arsenic unit cells are experimentally equal; this same value was used for the hypothetical antimony cell. In order to save computer space, this centered cell a was transformed to a primitive cell a' for the energy calculations. The transformation is

$$a' = Ma, \quad \text{where} \quad M = \begin{bmatrix} -\frac{1}{2} & \frac{1}{2} & 0 \\ -\frac{1}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

It is interesting that upon transformation the new cell ($a = b = 10.252$, $c = 14.341$ Å, $\alpha = \beta = 79.30$, $\gamma = 120.55°$) has dimensions very similar to those of the $P\bar{1}$ cell. There is, however, no obvious relationship between the symmetry and molecular arrangements of the two unit cells.

The molecular geometry in this hypothetical structure was based on the geometry found for pentaphenylphosphorus (Wheatley, 1964a). Starting from the $(C_6H_5)_5P$ crystal coordinates, each ring was shifted in the direction defined by the phosphorus atom and the ring center such that the P(Sb)–C distance was increased to 2.25 Å for the axial rings and to 2.15 Å for the equatorial rings (Brabant, Hubert & Beauchamp, 1973; Beauchamp, 1974). In this way valence and torsion angles involving the rings of the pentaphenylphosphorus structure were preserved. Starting fractional coordinates and molecular orientation angles for the hypothetical structure were those of the pentaphenylphosphorus structure. The results of the energy minimization varying the four cell constants and six molecular degrees of freedom are given in Table 5. Again the shifts are not large and tests of the second derivatives of the energy with respect to these variables show that the structure is in a true minimum. This hypothetical structure is a reasonable one.

Table 5. *Results of the energy minimization of the hypothetical Cc pentaphenylantimony structure*

Cell constants and coordinates refer to primitive cell defined in text.

	Derived	Calculated	Difference
		Cell constants	
a	10.252	10.229	−0.023 Å
c	14.341	14.564	+0.223 Å
α	79.30	78.94	−0.36°
γ	120.55	119.28	−1.27°
	Fractional coordinates and orientation angles*		
x	0.1139	0.1299	+0.0160 (0.16 Å)
y	−0.1114	−0.0922	+0.0192 (0.28 Å)
z	0.0019	−0.0118	−0.0137 (−0.20 Å)
δ	74.5	73.6	−0.9°
ε	101.2	100.9	−0.3°
η	−135.6	−134.5	+1.1°

* Angles are those described in Table 4.

Finally calculations were made of the intramolecular energy of square-pyramidal pentaphenylantimony as in the crystal and of the trigonal-bipyramidal form as in the hypothetical structure. The difference between these two energies is given in Fig. 2 along with the lattice energies, which do not include intramolecular contributions, calculated for the $P\bar{1}$ and Cc crystal structures.

Square-pyramidal   −30.5 kJ/mole   Trigonal-bipyramidal
molecule   →   molecule
↓ −145.2 kJ/mole   ↓ −140.6 kJ/mole
Square-pyramidal   Hypothetical
crystal structure   trigonal-bipyramidal
($P\bar{1}$)   crystal structure
                 (Cc)

Fig. 2. Energy contributions from non-bonded interactions for $(C_6H_5)_5Sb$ species.

Conclusions

From the results of the calculations displayed in Fig. 2 we see that the lattice energy of the $P\bar{1}$ square-pyramidal crystal structure is indeed lower than that of the trigonal-bipyramidal Cc structure, but that the difference of 4.6 kJ/mole is not large enough to overcome the energy difference of 30.5 kJ/mole favoring the trigonal bipyramid for the isolated molecule. It is difficult to assess the uncertainties in these calculations, but we believe that within the framework of the method relative errors greater than about ±1.5 kJ/mole are unlikely. Hence we expect that pentaphenylantimony should crystallize under equilibrium conditions as a trigonal bipyramid in space group Cc. Since it does not, either crystal packing forces are not the deciding factor, the calculations have neglected some important effect, or equilibrium conditions do not prevail. In order for this latter situation to occur, two conditions must be met. First, the rate of precipitation of the $P\bar{1}$ crystal must be very large relative to the rate of formation of the Cc crystals times the equilibrium constant for the conversion of a square-pyramidal molecule to a trigonal-bipyramidal one. Secondly, the rate of dissolution of the $P\bar{1}$ crystal must be very small relative to the time scale of the crystallization so that equilibrium is not attained. It does not seem likely that these two conditions would be met. The recent structural evidence on the penta-p-tolylantimony crystals and on the cyclohexane solvate of pentaphenylantimony supports the supposition that the observed $P\bar{1}$ square-pyramidal structure in fact results from packing forces; the calculations must therefore be examined further.

Is the neglect of an entropy term in the calculations important? Both space groups have two equivalent positions in the primitive unit cell and in neither structure is any symmetry imposed on the molecule; entropy contributions arising from symmetry should be the same in both cases. Molecular motion also contributes to the entropy, but in this regard the two structures do not

appear to differ significantly. The average root-mean-square amplitude of vibration in the $P\bar{1}$ pentaphenyl-antimony structure is 0·28 Å while in the Cc phosphorus structure it is 0·25 Å. The entropy difference between the isolated molecules is not known, but is unlikely to be large enough to overcome the energy difference.

Two other explanations occur to us. First, in the calculations Coulombic interactions were neglected since the atoms were taken to be electrically neutral. Given electronegativities of 2·5, 2·1, and 1·9 for the C, H, and Sb atoms, respectively (Pauling, 1960), this neglect seems reasonable. If, however, Coulombic interactions are included through assignment of partial charges to each of the atoms the energies do change. If the charges on the H and C atoms are taken to be equal but opposite and the charge on the Sb atom is adjusted to yield electroneutrality the energy difference between the square-pyramidal and trigonal-bipyramidal geometries is decreased and the lattice-energy stabilization of the $P\bar{1}$ over the Cc structure is increased as the charge is increased. At a charge of about 0·17 e$^-$ on C the $P\bar{1}$ structure is favored thermodynamically. Although direct comparisons cannot be made owing to the use of slightly different non-bonded potential parameters for C and H atoms, it is interesting to note that Hall & Williams (1975) found that charges of a similar magnitude (0·18 e$^-$) must be placed on the C and H atoms of benzene in order that the observed structures at atmospheric and 25 kbar pressure may be reproduced.

Secondly, it is possible that the energy difference between the square-pyramidal and trigonal-bipyramidal geometries of the molecule in the free state or in solution has been overestimated. A variable-temperature proton magnetic resonance study of partially deuterated pentaphenylantimony in light petroleum–ethyl bromide shows the rings to be equivalent magnetically to 173 °K; the exchange was slowed but not stopped at 131 °K (Beattie, Livingston, Ozin & Sabine, 1972). If it is assumed that the exchange involves pseudorotation of the trigonal bipyramid through a square-pyramidal transition state, then this behavior suggests that the energy difference between the two geometries has an upper limit of 10–12 kJ/mole. Note that if there is a charge of about 0·15 e$^-$ on the C atoms then the energy difference between the two conformations of pentaphenylantimony is reduced to about this range.

However, note that the derived partial charges on the atoms are clearly correlated with the potential constants and may, in fact, be simply manifestations of insufficiencies in these constants.

References

BEATTIE, J. R., LIVINGSTON, K. M. S., OZIN, G. A. & SABINE, R. (1972). *J. Chem. Soc. Dalton*, pp. 784–786.

BEAUCHAMP, A. L. (1974). *J. Organometall. Chem.* **82**, 231–234.

BEAUCHAMP, A. L., BENNETT, M. J. & COTTON, F. A. (1968). *J. Amer. Chem. Soc.* **90**, 6675–6680.

BERTAUT, F. (1952). *J. Phys. Radium*, **13**, 499–505.

BRABANT, C., HUBERT, J. & BEAUCHAMP, A. L. (1973). *Canad. J. Chem.* **51**, 2952–2957.

BROCK, C. P. & IBERS, J. A. (1973). *Acta Cryst.* B**29**, 2426–2433.

BUSING, W. R. (1972). *Acta Cryst.* A**28**, S252–S253.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE*. Report ORNL-TM-306, Oak Ridge National Laboratory, Tennessee.

GILBERT, T. L. (1968). *J. Chem. Phys.* **49**, 2640–2642.

GILLESPIE, R. J. (1963). *J. Chem. Soc.* pp. 4672–4678.

HALL, D. & WILLIAMS, D. E. (1975). *Acta Cryst.* A**31**, 56–58.

LA PLACA, S. J. & IBERS, J. A. (1965). *Acta Cryst.* **18**, 511–519.

MASON, E. A. & RICE, W. E. (1954). *J. Chem. Phys.* **22**, 843–851.

PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.

WHEATLEY, P. J. (1964a). *J. Chem. Soc.* pp. 2206–2222.

WHEATLEY, P. J. (1964b). *J. Chem. Soc.* pp. 3718–3723.

WHEATLEY, P. J. & WITTIG, G. (1962). *Proc. Chem. Soc.* pp. 251–252.

WILLIAMS, D. E. (1967). *J. Chem. Phys.* **47**, 4680–4684.

WILLIAMS, D. E. (1971). *Acta Cryst.* A**27**, 452–455.

WITTIG, G. & CLAUSS, K. (1952). *Liebigs Ann.* **577**, 26–38.