

With the orthogonality conditions discussed by Crowther (1972) this reduces to

$$R(\kappa, \psi, \pi + \varphi) = \sum_{lmm'} (\sum_n a_{lmn}^* b_{lm'n}) \sum_q d_{qm}^l(\beta) d_{qm'}^l(\beta) e^{i\gamma q} e^{i(m'-m)\alpha}.$$

Now substituting the equivalent polar angles for the Eulerian angles

$$R(\kappa, \psi, \varphi) = \sum_{lmm'} (\sum_n a_{lmn}^* b_{lm'n}) \times \sum_q d_{qm}^l(\psi) d_{qm'}^l(\psi) e^{i\kappa q} e^{i(m'-m)\varphi} (-1)^{(m'-m)}. \quad (1)$$

This result should be compared with that of Crowther's which corresponds to the special case where the Patterson function $P_1(\mathbf{x})$ remains stationary. In that case

$$R(\alpha, \beta, \gamma) = \sum_{lmm'} (\sum_n a_{lmn}^* b_{lm'n}) d_{m'm}^l(\beta) e^{im'\gamma} e^{im\alpha}. \quad (2)$$

The small modification which will be necessary to alter the Crowther fast-rotation function program to use

spherical coordinates can be seen by comparing expressions (1) and (2).

The procedure has been satisfactorily tested by comparing the results of a 'slow' rotation function with a modified 'fast' rotation function program.

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The Role of Coulombic Interactions in Explaining the Anomalous Structure of Pentaphenylantimony

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The observation of anomalous square-pyramidal geometry for pentaphenylantimony, $(C_6H_5)_5Sb$, has long been rationalized as a packing effect. The analogous P and As molecules are trigonal-bipyramidal in the solid state as expected. In this work calculations have been made of the energies resulting from intra- and intermolecular nonbonded interactions in both observed and hypothetical crystal structures of square-pyramidal and trigonal-bipyramidal pentaphenylantimony, pentaphenylarsenic, and pentaphenylphosphorus in order to determine if the solid state does indeed stabilize a non-equilibrium molecular geometry of $(C_6H_5)_5Sb$, and if so, how much energy is involved. The energies have been taken as pairwise sums over nonbonded atoms; the atom-atom potential functions used include repulsive, van der Waals, and Coulombic terms. Results of these calculations have been compared with work in which the potential functions did not include such $1/r$ terms. Both observed and hypothetical structures of all three molecules lie in true minima of the energy surface with respect to variations in cell constants and molecular position and orientation whether or not electrostatic terms are included. However, only the potential functions with Coulombic terms predict the crystallization of pentaphenylantimony as a square pyramid. The lattice-energy stabilization is then calculated to be about 15 kJ mol^{-1} .

Introduction

Considerable attention has been focused on pentaphenylantimony, $(C_6H_5)_5Sb$, since its observed geometries, square-pyramidal in one crystal form and trigonal-bipyramidal in another (a cyclohexane solvate) are thought to be strongly influenced by crystal packing forces. A comparison of the five known X-ray structures of penta-aryl Group V molecules (Brock & Webster, 1976) shows that $(C_6H_5)_5Sb$ is alone in ex-

hibiting a square-pyramidal form. It is, in fact, unique among all five-coordinate molecules having identical ligands and a spherical shell of d -electrons in displaying a non-trigonal-bipyramidal geometry.

Since the results of solid-state structure determinations are often used to interpret molecular behavior in the gaseous and liquid states, it is important to understand the extent to which crystal packing forces may influence molecular geometry. In this and previous work (Brock & Ibers, 1976) an attempt has been made

to assess the magnitudes of any lattice effects involved in the $(C_6H_5)_5Sb$ problem. In the earlier paper, calculations of intramolecular strain energies and of lattice energies were reported for square-pyramidal pentaphenylantimony as observed in the crystal, and for a trigonal-bipyramidal molecule and hypothetical unsolvated crystal structure derived from data on $(C_6H_5)_5P$ and $(C_6H_5)_5As$. These calculations were based on potential functions which included terms for repulsive and van der Waals interactions between non-bonded atoms. Comparisons showed that while the square-pyramidal structure is computed to have a more favorable lattice energy than the trigonal-bipyramidal one, the difference (4.6 kJ mol^{-1}) is not large enough to offset the more dominant intramolecular interactions (30.5 kJ mol^{-1}) favoring trigonal-bipyramidal geometry. At that time we suggested that the failure to predict the observed structure might be a result of neglecting Coulombic interactions.

Recently, Williams (1974) has published a new set of nonbonded potential functions for C and H atoms which includes Coulombic terms, and has shown (Hall & Williams, 1975) that these functions reproduce the pressure-induced phase transition in benzene while the set without Coulombic terms (Williams, 1967) does not. Therefore, the calculations of the intra- and intermolecular nonbonded energies of $(C_6H_5)_5Sb$ have been repeated using Williams's newest set of potential functions in order to determine whether the observed $P\bar{1}$ structure having square-pyramidal molecular geometry is then predicted to be the more stable one. In addition, both sets of potential functions have been employed in similar calculations for pentaphenylphosphorus and pentaphenylarsenic. The former substance is known (Wheatley, 1964) to crystallize as a trigonal bipyramid in space group Cc while the latter has a very similar unit cell and is presumed to have the same structure (Wheatley & Wittig, 1962). A comparison of the results of all of these calculations should indicate whether or not the addition of Coulombic terms to the atom-atom potentials significantly improves the predictive power of the functions in problems of this type. An analysis of the results should also lead to an estimate of the magnitude of the lattice-energy stabilization of the square-pyramidal form of pentaphenylantimony.

Description of the calculations

Calculations of the molecular and lattice energies were made using Busing's (1972) program *WMIN*. In this program the energy is taken as the sum of pairwise interactions between nonbonded atoms, and is computed using a form of the Buckingham potential (Gilbert, 1968) which incorporates the geometric-mean combining law:

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

Truncation errors in the van der Waals and Coulombic

contributions are virtually eliminated by use of the Ewald-Bertaut-Williams technique for accelerated convergence (Bertaut, 1952; Williams, 1971); limits were set to ensure convergence to 0.1 kJ mol^{-1} . This program also allows for minimization of the energy with respect to the structural parameters, that is the cell constants and rigid-body positions and orientations, by Newton's method.

Two sets of potential function parameters were used. The first set was derived (Williams, 1967) assuming the atoms to be electrically neutral, while the second (Williams, 1974) includes Coulombic interactions. The repulsive and van der Waals parameters for the As and Sb atoms were taken respectively from Kr and Xe potentials (Mason & Rice, 1954), while the parameters for the P atom were adapted from an Ar potential (Mason & Kreevoy, 1955). When these latter potentials were used in conjunction with the C and H functions including Coulombic terms, the charge on the Group V atom was adjusted to give molecular electroneutrality. Parameters for the two sets of functions are given in Table 1.

Table 1. *Nonbonded potential parameters*

Units are kJ mol^{-1} , Å, and electrons.				
Set I	A	B	C	q
H ^a	1.42	0.134	10.7	0.
C ^a	1.95	0.139	48.7	0.
P ^b	2.07	0.138	77.3	0.
As ^c	2.25	0.165	107.0	0.
Sb ^c	2.49	0.171	166.5	0.
Set II				
H ^d	1.43	0.134	13.0	0.179
C ^d	1.93	0.139	43.2	-0.179
P				0.895*
As		(As above)		0.895*
Sb				0.895*

References: (a) Williams (1967). (b) Mason & Kreevoy (1955). (c) Mason & Rice (1954). (d) Williams (1974).

* Adjusted to give electroneutrality for $(C_6H_5)_5M$ species.

Lattice-energy calculations were made in a manner described previously (Brock & Ibers, 1976) for both the observed and hypothetical $P\bar{1}$ and Cc structures of the three pentaphenyl molecules. Intermolecular nonbonded energy minimizations were performed with respect to the cell constants and molecular rigid-body translations and rotations. To save computer space the Cc cell was transformed as described before to a primitive cell in which $a=b$ and $\alpha=\beta$. In Cc only translations along the y axis affect the energy; consequently, there are only eight independent variables for minimizations in this space group. Upon transformation, however, the x and y directions are mixed. The resulting redundancy leads to a zero eigenvalue in the Newton-Raphson iteration; this redundancy is removed by omitting the corresponding eigenvector when the parameter shifts are calculated.

Of the six structures for which calculations were made, only two are known experimentally in full detail. The initial cell constants and molecular positions and orientations for all the $P\bar{1}$ structures were those found for $(C_6H_5)_5Sb$ while the same parameters for the Cc structures were taken from the data for $(C_6H_5)_5P$. The molecular conformations for the hypothetical crystals were also taken from these two basic structures. Trigonal-bipyramidal $(C_6H_5)_5As$ and $(C_6H_5)_5Sb$ molecules having the same phenyl ring orientations as pentaphenylphosphorus were formed by lengthening the P-C bonds in the Cc structure. The average axial and equatorial bond lengths chosen, 2.106 and 1.966 Å in the As and 2.256 and 2.150 Å in the Sb molecule, reproduce experimental results for related structures, e.g. the cyclohexane solvates (Brock & Webster, 1976). Similarly, hypothetical square-pyramidal $(C_6H_5)_5P$ and $(C_6H_5)_5As$ molecules were derived from the known pentaphenylantimony geometry by shortening the Sb-C bonds in the $P\bar{1}$ crystal. The decrements used were 0.18 and 0.14 Å for the axial and basal bonds of pentaphenylarsenic, and 0.29 and 0.24 Å for the corresponding bonds of pentaphenylphosphorus. These numbers reflect changes in radii between the three atoms (Pauling, 1960) and were also chosen so that the axial-to-basal bond length ratios in the P and As square pyramids would approximate the corresponding equatorial-to-axial ratios in the trigonal bipyramids as is the case for pentaphenylantimony.

The energy differences between the two molecular geometries resulting from differences in intramolecular nonbonded interactions were also computed. The

Table 2. Results of the energy minimizations of the $P\bar{1}$ pentaphenylantimony structure

Cell	Observed ^a	Set II	Set I
		(Coulombic) potentials $\Delta(\text{calc.}-\text{obs.})$	potentials $\Delta(\text{calc.}-\text{obs.})^b$
a (Å)	10.286	-0.109	-0.093
b	10.600	-0.046	-0.004
c	13.594	-0.074	0.011
α (°)	79.20	0.49	0.10
β	79.47	-0.85	-0.07
γ	119.52	-0.60	-1.08
V (Å ³)	1200	-19 (-1.6%)	5 (0.4%)
Molecule			
x^*	0.1631	0.0012	-0.0016
y	0.0394	0.0037	0.0037
z	0.2522	0.0003	0.0005
δ (°)†	-32.4	-0.1	-0.5
ϵ	-149.3	0.3	-0.6
η	-46.5	-0.1	-0.8

References: (a) Beauchamp, Bennett & Cotton (1968). (b) Brock & Ibers (1976).

* Fractional coordinates of central Sb atom.

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

molecular geometries described above were used for these calculations, and it should be noted that they do not necessarily correspond to stationary points on the energy surface.

Results

The experimentally determined parameters of the $P\bar{1}$ crystal structure of pentaphenylantimony and the parameter shifts after energy minimization using the potential functions of set II are given in Table 2. For comparison, the shifts reported previously (Brock & Ibers, 1976) for calculations without Coulombic contributions are shown as well. Similar data for the observed Cc structures of the analogous As and P molecules are displayed in Tables 3 and 4 respectively. The calculated molecular position and orientation for $(C_6H_5)_5As$ are not given since these numbers are not known from experiment. The cell constants for the three hypothetical structures after energy minimizations using the two potential function sets are found in

Table 3. Results of the energy minimizations of the Cc pentaphenylarsenic structure

Cell†	Observed*	Set II	Set I
		(Coulombic) potentials $\Delta(\text{calc.}-\text{obs.})$	potentials $\Delta(\text{calc.}-\text{obs.})$
a (Å)	10.058	-0.034	0.004
c	14.227	0.037	0.199
α (°)	79.21	0.08	-0.20
γ	119.89	-0.51	-0.48
V (Å ³)	1157	4 (0.3%)	21 (1.8%)

* Wheatley & Wittig (1962).

† Cell constants refer to the primitive cell defined in Brock & Ibers (1976).

Table 4. Results of the energy minimizations of the Cc pentaphenylphosphorus structure

Cell†	Observed*	Set II	Set I
		(Coulombic) potentials $\Delta(\text{calc.}-\text{obs.})$	potentials $\Delta(\text{calc.}-\text{obs.})$
a (Å)	9.962	-0.026	0.009
c	14.170	-0.014	0.152
α (°)	79.11	0.21	-0.07
γ	119.55	-0.01	-0.02
V (Å ³)	1134	-3 (0.3%)	13 (1.1%)
Molecule			
x^\ddagger	0.1139	0.0000	-0.0001
y	-0.1114	0.0001	0.0024
δ (°)§	76.7	-3.1	-1.9
ϵ	101.2	-0.3	-0.2
η	-136.5	2.7	1.7

* Wheatley (1964).

† Cell constants refer to the primitive cell defined in Brock & Ibers (1976).

‡ Fractional coordinates of the P atom; in this space group the energy is independent of the z coordinate.

§ Angles are those described in Table 2.

the signs and magnitudes of the energies clearly identify the *Cc* structure as the stable form.

Both the potential function sets calculate true minima for the known crystal structures with acceptably small changes in the cell constants and molecular translations and rotations. Only the set II potentials, however, predict the crystallization of pentaphenylantimony as a square pyramid. A consideration of the cell volumes calculated for the known structures also favors the Coulombic potentials. In all three compounds the cell calculated with the set II functions is smaller than that calculated with the first set; for the P and Sb cases the calculated cell is smaller than the observed one. Since these energy minimizations ignore vibrational effects, they correspond to a temperature of absolute zero (zero-point vibrational energy being neglected). Consequently, the cell should contract from the volume observed at room temperature.

A third argument favoring the set II potentials is based on the size of the intramolecular energy difference between the square-pyramidal and trigonal-bipyramidal geometries. If this difference is as large as 30 kJ mol⁻¹, as is calculated for pentaphenylantimony using the parameters of set I, it seems likely that the interchange of axial and equatorial phenyl rings through a square-pyramidal intermediate would be strongly hindered. The energy difference for pentaphenylarsenic is even larger, by a factor of about 1.5. However, the ¹³C NMR solution spectra of both (C₆H₅)₅Sb and (C₆H₅)₅As show all rings to be magnetically equivalent to 173 K (S. L. Smith & C. P. Brock, unpublished work).^{*} Therefore, the energy difference of 8 kJ mol⁻¹ calculated with the set II functions appears to be more reasonable.

Inspection of the energy curves drawn for atom-atom interactions shows the two sets of potential functions to differ dramatically. The large Coulombic terms of the set II potentials are dominant in the regions in which nonbonded contacts most often occur. It would not be possible to reproduce the set II curves with any reasonable nonbonded potential which did not include interactions of a Coulombic type. The 1/*r* terms cause the potentials to act over distances nearly an order of magnitude larger than those important for electrically neutral species. Although the partial charges of ±0.18 e⁻ on the C and H atoms and those of nearly 0.90 e⁻ on P, As, and Sb seem quite large considering the relative electronegativities of the different atoms, it must be remembered that the criterion for a potential function is its success in reproducing known structures. The set II potentials with Coulombic terms meet this requirement more fully than do the set I functions.

It should be noted that the assignment of Coulombic-type parameters to the atoms for the purpose of semi-

empirical calculations of intra- and intermolecular nonbonded interactions need not imply actual localization of charges in these amounts on individual atoms. Rather, the success of such potentials indicates that there is some deficiency in the non-Coulombic functions which is at least partially remedied by inclusion of an inverse distance term. That the derived parameters for this term are found to be of a sign and magnitude consistent with their interpretation as partial charges is then evidence that the deficiency in the earlier functions may indeed be the neglect of Coulombic interactions.

If the Coulombic potentials are accepted as more successful for this problem, the lattice-energy stabilization due to intermolecular nonbonded interactions of the *P* $\bar{1}$ structure over the *Cc* one is calculated to be 13–15 kJ mol⁻¹. If less than this amount of energy separates the square-pyramidal and trigonal-bipyramidal geometries of (C₆H₅)₅M, as is apparently the case for M=Sb, and if entropy effects are not important, then a seemingly anomalous crystal structure results. Since *RT* at 300 K is 2.5 kJ mol⁻¹, only a very small percentage of the (C₆H₅)₅Sb molecules in solution would be expected to possess the square-pyramidal geometry found in the solid state. Thus these calculations indicate that the crystallization process can be responsible for isolating a molecular conformation in the solid state which may not even be readily observable in solution.

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^{*} Observation of this pseudorotational motion might be expected for pentaphenylphosphorus, but we were unable to obtain ¹³C spectra of this compound which could be readily interpreted.