

The Crystal Structure of Pentaphenylarsenic: Implications for the Role of Crystal Packing Forces in the Structures of Penta-aryl Group V Molecules

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The structure of the cyclohexane solvate of pentaphenylarsenic has been determined by X-ray crystallographic analysis. The substance crystallizes in space group $P\bar{1}$, cell dimensions $a=10.448$ (19), $b=10.566$ (21), $c=14.903$ (25) Å, $\alpha=121.09$ (5), $\beta=106.38$ (4), $\gamma=92.44$ (5)°, with one $(C_6H_5)_5As$ and one-half C_6H_{12} molecule in the asymmetric unit. The structural model, in which the phenyl rings were treated as rigid bodies, refined to a conventional R of 0.072 with 843 data collected on a Paired Weissenberg-geometry diffractometer. The pentaphenylarsenic molecule is an undistorted trigonal bipyramid with average axial and equatorial As-C bond lengths of 2.105 (7) and 1.964 (11) Å, respectively. In spite of the different intermolecular interactions involved, the molecular conformation, as measured by phenyl ring rotations, of $(C_6H_5)_5As$ is very similar to that of the analogous phosphorus compound and to that of the antimony molecule in the cyclohexane solvate. Comparisons of this preferred conformation with the distorted trigonal-bipyramidal structure found for penta-*p*-tolylantimony and with the square-pyramidal geometry observed for unsolvated pentaphenylantimony illustrate the types of distortions which can result from solid-state packing interactions.

Introduction

The determination of the crystal structure of pentaphenylarsenic, $(C_6H_5)_5As$, was undertaken in order to help answer questions raised by the unexpected observation of square-pyramidal geometry for pentaphenylantimony in one of its crystalline forms (Wheatley, 1964*b*; Beauchamp, Bennett & Cotton, 1968). In contrast, the predicted trigonal-bipyramidal arrangement of the phenyl rings was found for the corresponding phosphorus molecule (Wheatley, 1964*a*), and for the cyclohexane solvate of the antimony compound (Brabant, Blanck & Beauchamp, 1974). The very similar penta-*p*-tolylantimony also displays this trigonal-bipyramidal geometry (Brabant, Hubert & Beauchamp, 1973), which is expected if intramolecular nonbonded interactions are to be minimized. The anomalous square-pyramidal form of $(C_6H_5)_5Sb$ has long been rationalized as a packing effect, by which it is meant that attractive intermolecular interactions in the crystal stabilize a molecular geometry which would not predominate at equilibrium in the gas phase or in solution.

Calculations of intra- and intermolecular nonbonded interactions have been made for pentaphenylantimony in order to explore the origin and magnitude of these packing effects (Brock & Ibers, 1976). Previously, the unit cell of $(C_6H_5)_5As$ had been reported (Wheatley & Wittig, 1962), and from these data it had been concluded that the compound crystallizes in a structure very similar to that found for pentaphenylphosphorus. Consequently, the energy calculations focused on understanding why unsolvated $(C_6H_5)_5Sb$ crystallizes with square-pyramidal geometry in a triclinic cell

rather than in the monoclinic Cc cell observed for the arsenic and phosphorus molecules. Such calculations would be aided by more detailed knowledge of the structure of pentaphenylarsenic, especially in terms of the changes in intermolecular contacts resulting from the replacement of the phosphorus atom by the larger arsenic atom. Therefore, a structural study was initiated.

Pentaphenylarsenic was synthesized by the method reported by Wittig & Clauss (1952) and referenced by Wheatley & Wittig (1962). However, in spite of a number of recrystallization attempts under varying conditions, we were not able to obtain crystals suitable for X-ray analysis which were free of solvent. Rather, the crystals finally chosen for study were found to have a unit cell of symmetry $P\bar{1}$ and a density corresponding to the inclusion of one-half molecule of cyclohexane per $(C_6H_5)_5As$ unit. Since this cell was analogous to that observed for the solvated form of $(C_6H_5)_5Sb$, we decided to continue; the effect on intermolecular contacts of changing the radius of the central atom would still be determined. It was also hoped that a comparison of the molecular conformations of these related molecules would provide insight into types and magnitudes of distortions from idealized trigonal-bipyramidal geometry that could be expected to occur as a result of crystal packing forces.

Experimental

Crystals were grown from cyclohexane and were mounted in capillaries under nitrogen to prevent decomposition and loss of solvent. Preliminary photographs indicated that the crystals were triclinic.

Initially, the space group was assumed to be the centrosymmetric $P\bar{1}$. The successful refinement of the structure supports this assignment. Axes were chosen to correspond to strong lines on the Weissenberg photographs and to crystal morphology; as a result, they define a primitive, but not reduced, cell. A clear, colorless crystal with faces of the forms $\{100\}$, $\{1\bar{1}0\}$, $\{010\}$, $\{01\bar{1}\}$, and $\{001\}$, and of approximate dimensions $0.18 \times 0.12 \times 0.55$ mm was mounted on a Philips Pailred Weissenberg-geometry diffractometer with the elongated c direction aligned parallel to the rotation (ω) axis. Cell constants were determined from a least-squares procedure using diffractometer measurements made with Mo $K\alpha_1$ radiation ($\lambda = 0.70926$ Å). Cell constants thus determined were $a = 10.448$ (19), $b = 10.566$ (21), $c = 14.903$ (25) Å, $\alpha = 121.09$ (5), $\beta = 106.38$ (4), $\gamma = 92.44$ (5)°. These dimensions give a calculated density based on two $(C_6H_5)_5As$ and one C_6H_{12} molecule per unit cell of 1.27 g cm $^{-3}$. The density measured by flotation in aqueous $ZnCl_2$ was somewhat lower, 1.18 (2) g cm $^{-3}$, perhaps as a result of loss of solvent from crystals left exposed to the air.

Diffracted intensities for layers from $l=0$ to $l=11$ were measured with silicon-monochromated Mo $K\alpha$ radiation, a scintillation counter, and pulse height analyzer to a maximum $\sin \theta/\lambda$ of 0.46. The half-width of the omega scan varied from 1.0° on the zero level to 2.2° for the reflections near the origins of the highest levels; the scan speed was constant at 0.5° min $^{-1}$. Stationary backgrounds, measured at both ends of the scan, were counted for 40 and 100 s for $l \leq 6$ and > 6 respectively. A total of 2173 intensities were measured of which 2003 were independent. After averaging, 843 reflections had $I \geq 3\sigma(I)$ where $\sigma(I)$ is given by $\sigma(I) = [CT + 0.25(t_c/t_b)^2 (B_1 + B_2) + (pI)^2]^{1/2}$. In this expression CT , B_1 , and B_2 are the total background counts, t_c and t_b are times (in s) spent measuring peak and background, and p was taken as 0.04. The relatively low number of reflections with $I \geq 3\sigma(I)$ is probably a result of the significant attenuation of the incident beam by the silicon monochromator.

Three zero-level reflections were measured manually every six to eight hours. A plot of these intensities shows a complicated variation with time of about 10% which appears to reflect crystal decomposition, instrumental instabilities, and laboratory temperature fluctuations. Owing to the complexity of the pattern, no corrections for these variations were made. The data were corrected for Lorentz and polarization effects. An absorption correction was made ($\mu = 13.9$ cm $^{-1}$) using an adaptation of the program of Burnham (1966); transmission factors ranged from 0.79 to 0.87.

Solution and refinement

The position of the arsenic atom was determined from the Patterson function, which was computed with

Dellaca & Robinson's *FOURIER*, a program based on Zalkin's *FORDAP*. A subsequent electron density map phased by the arsenic revealed the positions of the phenyl rings. Full-matrix least-squares refinement followed using Doedens & Ibers's program *NUCLS*, which in its non-group form closely resembles Busing, Martin & Levy's (1962) *ORFLS* program. The phenyl rings were treated as rigid groups of D_{6h} symmetry ($C-C = 1.40$, $C-H = 1.00$ Å) with individual isotropic temperature factors for each carbon atom. Scattering factors for C, H and As atoms were taken from Cromer & Waber (1974), while the anomalous contributions for the As atom were calculated from the $\Delta f'$ and $\Delta f''$ values given by Cromer & Liberman (1970). In this refinement the function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$; only the 843 reflections for which $F_o^2 \geq 3\sigma(F_o^2)$ were included.

At this stage in the refinement it became apparent that one of the three independent carbon atoms of the cyclohexane molecule was disordered between two positions. Carbon atoms in these positions with occupancy factors of 0.5 were refined successfully. In the final cycles, contributions from fixed hydrogen atoms were included ($C-H = 1.00$ Å, $H-C-H = 105^\circ$) for the two orientations of the ring. All hydrogen atoms were given temperature factors 1 Å 2 larger than that of the attached carbon atom. At convergence, $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.072$ and $RW = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2} = 0.070$. The largest parameter shift in the final cycle was 0.03σ . No evidence of extinction was observed and no correction was applied.

Further refinements were performed in which the occupancy factor of the entire solvent molecule and the ratio of the occupancy factors for the two positions of the disordered carbon atom were varied. In neither case did the converged value differ significantly from unity. In another refinement the carbon atoms were allowed to vary independently. In this calculation the number of variables increased from 86 to 146 and the R values fell to $R = 0.067$ and $RW = 0.063$. This decrease is significant at the 0.005 level according to Hamilton's (1965) R ratio test; however, the resulting lengths and angles within the phenyl rings (calculated using Busing, Martin & Levy's (1964) *ORFFE* error function program) differ significantly. The C-C bond lengths vary from 1.31 to 1.44 Å (average, 1.38 Å) and the bond angles vary from 116 to 126° (average, 120°). Since these differences are much larger than would be expected chemically, if not necessarily statistically, it was concluded that the phenyl ring geometry is known from other experiments better than it can be determined using a data set of this size and quality. Therefore, the rigid body model was retained.

At the completion of the rigid body refinement the error in an observation of unit weight was calculated to be 1.55. A final difference electron density map showed no important features, the highest peak being 0.58 e Å $^{-3}$ or about 15% of a carbon atom. Of the reflections omitted from the refinement, none had

$|F_o^2 - F_c^2| > 4.8\sigma(F_o^2)$. * Atomic and thermal parameters are given in Table 1. In this list, each carbon atom is

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31649 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Positional ($\times 10^3$) and thermal parameters and standard deviations for $(C_6H_5)_5As$

	x	y	z	B (\AA^2)
As	122.4 (3)	38.6 (3)	285.3 (2)	*
C(1A)	473 (6)	393 (6)	28 (4)	6.6 (14)
C(1B)	375 (5)	382 (6)	-51 (4)	5.7 (13)
C(2)	418 (3)	521 (4)	72 (2)	9.3 (9)
C(3)	506 (4)	654 (3)	84 (2)	9.4 (9)
C(11)	159 (1)	217 (1)	452 (1)	4.7 (6)
C(12)	134 (1)	355 (2)	470 (1)	4.1 (6)
C(13)	161 (1)	480 (1)	578 (1)	6.6 (7)
C(14)	213 (1)	467 (1)	670 (1)	5.3 (6)
C(15)	238 (1)	329 (2)	652 (1)	5.7 (6)
C(16)	211 (1)	204 (1)	544 (1)	5.1 (6)
C(21)	89 (2)	-139 (1)	120 (1)	3.3 (6)
C(22)	-26 (1)	-260 (2)	63 (1)	5.4 (6)
C(23)	-42 (1)	-387 (1)	-42 (1)	5.0 (6)
C(24)	55 (2)	-394 (1)	-91 (1)	4.7 (6)
C(25)	169 (1)	-273 (2)	-35 (1)	5.9 (6)
C(26)	186 (1)	-146 (1)	71 (1)	5.3 (6)
C(31)	255 (2)	174 (2)	284 (1)	4.0 (6)
C(32)	387 (2)	240 (1)	365 (1)	4.5 (6)
C(33)	479 (1)	336 (2)	361 (1)	4.7 (6)
C(34)	439 (2)	366 (2)	277 (1)	5.4 (6)
C(35)	306 (2)	300 (1)	197 (1)	6.1 (7)
C(36)	214 (1)	204 (2)	201 (1)	4.6 (6)
C(41)	187 (2)	-100 (2)	329 (1)	3.2 (5)
C(42)	318 (2)	-126 (1)	333 (1)	4.8 (6)
C(43)	365 (1)	-255 (2)	363 (1)	6.6 (7)
C(44)	281 (2)	-300 (2)	389 (1)	5.7 (6)
C(45)	150 (2)	-273 (1)	384 (1)	5.4 (6)
C(46)	103 (1)	-173 (2)	354 (1)	5.0 (6)
C(51)	-73 (1)	46 (4)	248 (1)	6.4 (7)
C(52)	-139 (2)	58 (3)	321 (1)	5.0 (6)
C(53)	-278 (1)	62 (2)	296 (1)	5.1 (6)
C(54)	-350 (1)	54 (4)	198 (1)	5.6 (7)
C(55)	-285 (2)	42 (3)	125 (1)	6.0 (7)
C(56)	-146 (1)	38 (2)	150 (1)	5.1 (6)

* Anisotropic temperature factor of the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$, where $\beta_{11} = 0.0060$ (4), $\beta_{22} = 0.0106$ (5), $\beta_{33} = 0.0055$ (2), $\beta_{12} = 0.0026$ (3), $\beta_{13} = 0.0023$ (2), $\beta_{23} = 0.0027$ (3).

assigned a label C(*ij*), where *i* denotes the number of the phenyl ring and *j* gives the position within the ring, numbering beginning at the α -carbon atom (carbon bonded to central arsenic atom). The standard deviations of the positional parameters of the phenyl ring carbon atoms quoted therein are derived from the standard deviations of the ring positions and orientations calculated in the refinement. Fixed hydrogen positions and thermal parameters for the two orientations of the cyclohexane molecule are listed in Table 2.

Table 2. Calculated hydrogen positional parameters ($\times 10^3$)

	x	y	z	B (\AA^2)
H(1A)	411	305	15	7.2
H'(1A)	562	409	84	7.2
H(2A)	322	500	24	10.1
H'(2A)	415	551	147	10.1
H(3A)	462	742	108	10.4
H'(3A)	597	691	145	10.4
H(1B)	308	400	-104	6.7
H'(1B)	324	291	-60	6.7
H(2B)	337	551	93	9.1
H'(2B)	471	497	126	9.1
H(3B)	447	687	38	10.4
H'(3B)	536	743	163	10.4

Results and discussion

A stereoscopic drawing of the unit cell, made using Johnson's (1965) thermal ellipsoid plotting program ORTEP, is shown in Fig. 1. The structure consists of well-separated trigonal-bipyramidal $(C_6H_5)_5As$ molecules. There are no important interactions other than normal van der Waals contacts within or between neighboring pentaphenylarsenic molecules or between these units and the cyclohexane molecule. A few close contacts exist in the structure involving hydrogen atoms; there are five such contacts shorter than 2.4 \AA . Only one of these is between atoms belonging to the arsenic molecules, the distance between two axial hydrogen atoms [H(14) and H(25)] related by translation along the [011] direction being 2.33 \AA . This direction corresponds very closely [to within 10 (1°)] to the axial direction of the molecule. Four other short

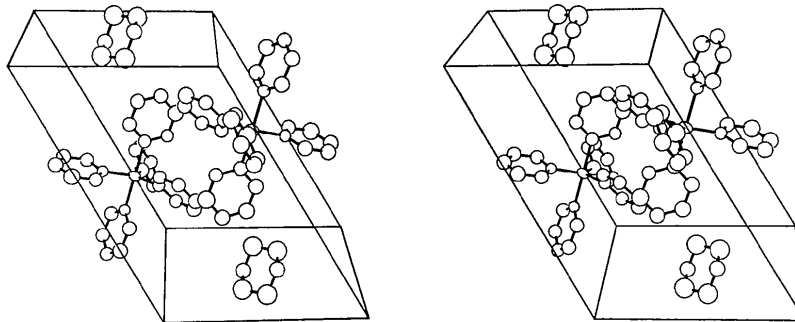


Fig. 1. A stereoscopic view of the unit cell of $(C_6H_5)_5As \cdot \frac{1}{2}C_6H_{12}$. The *y* axis is horizontal, the *z* axis is vertical and the *x* axis points out of the paper. The shapes of the atoms in this and Fig. 2 represent 50% probability contours of thermal motion. Hydrogen atoms are omitted for the sake of clarity, and only one orientation of the disordered C_6H_{12} molecule is shown.

contacts involve the C_6H_{12} molecule and range from 2.27 to 2.16 Å. Since the hydrogen atoms were not located experimentally, and since small displacements of the cyclohexane hydrogen atoms from their idealized positions would lengthen the interatomic distances considerably without the expenditure of significant amounts of energy, these short contacts were not considered to be a serious problem.

The structure described herein is very similar to that found by Brabant *et al.* (1974) for $(C_6H_5)_5Sb \cdot \frac{1}{2}C_6H_{12}$. The transformation matrix relating the two unit cells is

$$a_{As} \approx M a_{Sb} \quad \text{where} \quad M = \begin{bmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ -1 & -1 & 0 \end{bmatrix}.$$

The unit-cell dimensions for the antimony compound after transformation are $a=10.579$, $b=10.569$, $c=15.117$ Å, $\alpha=120.55$, $\beta=106.93$, $\gamma=92.08^\circ$. Comparison with the $(C_6H_5)_5As \cdot \frac{1}{2}C_6H_{12}$ cell shows that the angles for the two cells differ by less than a degree, and that the b axes have the same length to within experimental error. The major differences between the two cells are an increase of 0.131 Å in the length of the a axis and of 0.214 Å in the length of the c axis when antimony is substituted for arsenic. The transformation given above also relates the fractional coordinates of the atoms:

$$x_{As} \approx x_{Sb} M^{-1} + [\frac{1}{2}, \frac{1}{2}, \frac{1}{2}],$$

the average difference between corresponding coordinates being 0.007. In the following discussion the antimony structure is referred to this transformed cell.

A comparison of the differences in the cell constants of these two structures with the differences in bond lengths shows that the changes in molecular size and shape resulting from the substitution of a larger central atom are partially, but not completely, reflected in the increased unit-cell dimensions. The bond lengths necessary for this comparison may be found in Table 3. In both the arsenic and antimony structures the axial direction of the trigonal bipyramid is nearly coincident [10 (1) and 9 (1) $^\circ$ respectively] with the [011] direction.

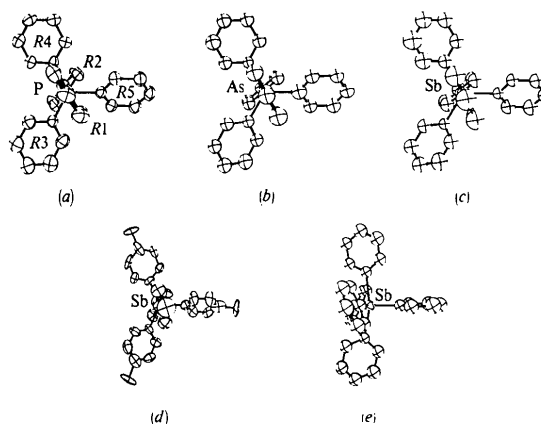


Fig. 2. Penta-aryl molecules of Group V elements viewed [(a) through (d)] perpendicular to the trigonal plane of the bipyramid, and (e) in such a way as to maximize the similarities between this square-pyramidal molecule and the four trigonal-bipyramidal ones. (a) $(C_6H_5)_5P$: Wheatley (1964a). (b) $(C_6H_5)_5As$, C_6H_{12} solvate: this work. (c) $(C_6H_5)_5Sb$, C_6H_{12} solvate: Brabant *et al.* (1974). (d) $(p-CH_3C_6H_4)_5Sb$: Brabant *et al.* (1973). (e) $(C_6H_5)_5Sb$: Beauchamp *et al.* (1968).

Table 3. Dimensions of the penta-aryl molecules of the Group V elements

	Distances are in (Å) and angles in ($^\circ$).				
	$(C_6H_5)_5P^{(a)}$	$(C_6H_5)_5As \cdot \frac{1}{2}C_6H_{12}^{(b)}$	$(C_6H_5)_5Sb \cdot \frac{1}{2}C_6H_{12}^{(c)}$	$(p-CH_3C_6H_4)_5Sb^{(d)}$	$(C_6H_5)_5Sb^{(e)}$
Bond lengths					
M-C(11)	1.99 (1)	2.11 (1)	2.25 (1)	2.25 (1)	2.22 (1)
M-C(21)	1.99 (1)	2.10 (1)	2.24 (1)	2.24 (1)	2.20 (1)
M-C(31)	1.87 (1)	1.96 (2)	2.12 (2)	2.15 (2)	2.21 (1)
M-C(41)	1.83 (1)	1.96 (2)	2.15 (1)	2.18 (1)	2.22 (1)
M-C(51)	1.85 (1)	1.98 (2)	2.13 (1)	2.14 (1)	2.13 (1)
Bond angles					
C(11)-M-C(21)	177 (1)	179 (1)	179 (1)	178 (1)	149 (1)
C(31)-M-C(41)	123 (1)	119 (1)	120 (1)	130 (1)	164 (1)
C(41)-M-C(51)	118 (1)	120 (2)	118 (1)	114 (1)	96 (1)
C(51)-M-C(31)	120 (1)	121 (2)	122 (1)	116 (1)	100 (1)
Conformation angles					
C(12)-C(11)-M-C(41)	7 (1)	-1 (2)	-3 (1)	-15 (1)	17 (1)
C(22)-C(21)-M-C(31)	14 (1)	22 (2)	22 (1)	10 (1)	14 (1)
Dihedral angles					
R1-R2	73 (1)	78 (2)	74 (2)	49 (2)	55 (1)
R3-R4	41 (1)	45 (2)	51 (2)	23 (3)	45 (1)
[C(31), C(41), C(51)]-R3	27 (1)	38 (1)	41 (1)	32 (2)	20 (1)
[C(31), C(41), C(51)]-R4	18 (1)	13 (1)	16 (1)	-7 (2)	28 (1)
[C(31), C(41), C(51)]-R5	-56 (1)	-50 (2)	-52 (1)	-64 (2)	-96 (1)

(a) Wheatley (1964a). (b) This work. (c) Brabant *et al.* (1974). (d) Brabant *et al.* (1973). (e) Beauchamp *et al.* (1968).

While the axial dimension of the molecule increases by 0.28 Å when arsenic is replaced by antimony, the repeat distance along [011] increases by only 0.25 Å. Similarly, the *a* axis is close [18 (1) and 15 (1)° for M=As and Sb, respectively] to the direction of one of the equatorial M–C bonds. This M–C bond increases by 0.17 Å, and the overall molecular dimension changes by 0.25 Å, but the repeat distance changes by only 0.13 Å. Calculations show that changes in the cell constants account for only 30% of the increases in the axial M–C bond lengths and for less than 10% of those in the equatorial bond lengths.

Clearly, the packing in the $(C_6H_5)_5M \cdot \frac{1}{2}C_6H_{12}$ cell is much more efficient for M=Sb than for M=As. The volume ratio for the two unit cells is 1.03, while a ratio of molecular volumes calculated assuming non-penetrating ellipsoids with major and minor axes corresponding to molecular dimensions along the axial and equatorial directions is 1.08. Evidently there is more interpenetration and meshing of the phenyl rings in the antimony than in the arsenic structure. The relatively large change in the repeat distance along [011] probably indicates that the packing is particularly dense in this direction. This conclusion is supported by the observation of a short intermolecular contact between axial ring hydrogen atoms which is discussed above. Since the packing density is quite different in the two structures, it seems likely that different intermolecular contacts are important in determining the unit-cell dimensions. The variations between the two structures in the repeat distances along the three directions are also evidence for this supposition.

A number of interesting comparisons can be made between $(C_6H_5)_5As$ and the other four penta-aryl molecules of Group V elements for which X-ray structures have been determined. These others include: $(C_6H_5)_5P$ (space group *Cc*); the cyclohexane solvates of $(C_6H_5)_5As$ and $(C_6H_5)_5Sb$ ($P\bar{1}$) described above; $(p-CH_3C_6H_4)_5Sb$ ($P2_1/c$); and the unsolvated form of $(C_6H_5)_5Sb$ ($P\bar{1}$, apparently unrelated to the $P\bar{1}$ cells found for the solvates). The first three listed are undistorted trigonal bipyramids, the fourth shows a minor distortion in one bond angle, and the last is so distorted that it is classified as having square-pyramidal geometry. All five are pictured in Fig. 2 and a consistent numbering scheme for the phenyl rings is defined. In each case the view direction is parallel to a vector between opposite α -carbon atoms. In the first four molecules these pairs are the axial atoms; in the fifth the pair was chosen to maximize similarities with the other four. The important bond lengths and angles for the five molecules, and angles describing their molecular conformations, are given in Table 3. The average C–C bond length found for the disordered cyclohexane solvent molecule is 1.51 (3) Å and the average C–C–C bond angle is 112 (1)°.

Considering only the data from the four trigonal-bipyramidal molecules, it is apparent that the bond

lengths change in a regular manner in accord with predictions made from covalent radii. Taking averages over chemically equivalent bonds, it is seen that the M–C_{eq} bond length increases by 0.11 Å when phosphorus is replaced by arsenic, and by 0.19 Å when arsenic is changed to antimony. These differences are those predicted from a consideration of Pauling's (1960) covalent radii. The M–C_{ax} bond lengthens in a similar fashion, 0.11 Å, when phosphorus is exchanged for arsenic, but the change is smaller, 0.14 Å, when antimony is substituted for arsenic. This result is in agreement with Gillespie's (1972) observation that axial–equatorial bond length ratios decrease down the periodic table as inter-ligand steric crowding at the axial site is relieved by the increase in the radius of the central atom.

In $(C_6H_5)_5As$ the angle defined by the arsenic atom and the axial α -carbon atoms does not deviate significantly from 180°, nor do the angles in the equatorial plane differ from 120°. These angles also approach their ideal values in the other three trigonal-bipyramidal molecules. In none of these four cases does a C_{ax}–M–C_{eq} angle differ by more than 4° from perpendicularity, nor is a central atom displaced significantly from the plane defined by the equatorial α -carbon atoms. All rings are nearly coplanar with their respective M–C bonds, the largest such deviation being less than 10°.

All five molecules have an approximate C_2 axis defined by *R5* and the central atom. In each case each axial ring eclipses one of the equatorial M–C bonds. The conformation angles quoted in Table 3 describe this aspect of the geometry. As a result of steric interactions between the hydrogen atoms on the *o*-carbon atoms, all three equatorial rings are rotated away from coplanarity with the trigonal plane. These rotations are described by the dihedral angles given in Table 3. This angle is largest for *R5* in all five molecules, and in the undistorted molecules the sense of rotation of this ring is different from that of the equatorial rings *R3* and *R4*.

The three undistorted molecules pictured in Fig. 2 can be seen to have nearly identical conformations in spite of the fact that they represent three different substances arranged in two different space groups and that the energy involved in rotating a phenyl ring about the M–C bond must not be very great. Even the two molecules which crystallize in the same space group are probably exposed to different sets of intermolecular interactions as has been argued above. It can therefore be concluded that this conformation is the one which would most likely be observed in the absence of solid-state interactions. The conformations exhibited by the $(p-CH_3C_6H_4)_5Sb$ molecule and by the unsolvated form of $(C_6H_5)_5Sb$ demonstrate the types of deviations from solution or free-state equilibrium conformations which might result from packing effects. In the former case the angle in the equatorial plane opposite the unique ring *R5* is opened up to 130°.

Presumably the simultaneous rotation of *R*5 by 10° away from the equatorial plane allows for the closer approach of the equatorial rings *R*3 and *R*4. In the unsolvated (C₆H₅)₅Sb structure this same type of distortion is carried much further, and also involves displacement of the *R*1 and *R*2 rings away from *R*5 in the plane perpendicular to the original equatorial plane. Furthermore, in this final example the Sb–C(31) and Sb–C(41) bonds are significantly lengthened.

It could be argued that the distortions described above outline the mechanism of pseudo-rotation proposed by Berry (1960) for five-coordinate molecules. It has been suggested (Bürgi, 1973; Bürgi, Dunitz & Shefter, 1974) that an analysis of geometric parameters describing similar molecular units in a variety of environments can be used to experimentally map the minimum energy pathways involved in chemical transformations. In this study the pathway corresponds to a normal mode of the penta-aryl molecule. In any event, the energy changes required to distort the molecules in this way cannot be large since ¹³C NMR solution spectra (S. L. Smith & C. P. Brock, unpublished work) show the α-carbons of pentaphenylarsenic and pentaphenylantimony to be magnetically equivalent to 173 K. This equivalence implies rapid interconversion between axial and equatorial sites, presumably through an intermediate square-pyramidal geometry. It can thus be concluded that the first three molecules pictured in Fig. 2 define the preferred conformation of the penta-aryl Group V molecules, and that the last two show the types of distortions that are observed as a result of packing interactions.

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The Crystal and Molecular Structure of the 2:1 Complex between Triphenylarsine Oxide and Selenous Acid

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(Ph₃AsO)₂H₂SeO₃ crystallizes in space group *Fdd*2, *a* = 20·59, *b* = 32·95, *c* = 10·05 Å, with eight formula units in the unit cell. The structure has been determined by three-dimensional X-ray methods from 959 visually estimated independent reflexions, and refined by full-matrix least squares; *R* = 0·11. The molecules of the complex are held together by hydrogen bonds; each hydrogen of the selenous acid is bonded to one triphenylarsine oxide.

Introduction

During an investigation into the reaction between selenium dioxide and triphenylarsine in various organic

solvents a colourless crystalline compound was obtained (El Sheikh, Patel, Smith & Waller, 1976). Since the chemical analysis and physical properties of this compound could not be explained in terms of a simple