LAWSON, C. L. & HANSON, R. J. (1974). *Solving Least-Squares Problems*. New Jersey: Prentice-Hall.
LE ROY, J., MOREAU, J. M., PACCARD, D. & PARTHÉ, E. (1977). *Acta Cryst.* B**33**, 2414–2417.
MCNEAR, E., VINCENT, M. & PARTHÉ, E. (1976). *Amer. Min.* **61**, 831–838.
MOREAU, J. M. & PACCARD, D. (1976). *Acta Cryst.* B**32**, 1654–1657.
MOREAU, J. M., PACCARD, D. & PARTHÉ, E. (1976). *Acta Cryst.* B**32**, 496–500; 1767–1771.
RICE, J. R. (1966). *Math. Comput.* **20**, 325.
STEWART, J. M. (1976). *X-RAY system, version of* 1976. Technical Report TR-446 of The Computer Science Center, University of Maryland.
THORNLEY, F. R. & NELMES, R. J. (1974). *Acta Cryst.* A**30**, 748–757.
VINCENT, M. G. (1976). Private communication.
WIND, H. (1972). *Proc.* 1972 *Cern Computing and Data Processing School*, Report Cern 72-21, pp. 53 106.
YVON, K. (1976). Private communication.

Acta Cryst. (1977). A**33**, 898–902

Lattice Energy Calculations for $(C_6H_5)_5M.\frac{1}{2}C_6H_{12}$, M = P, As, and Sb: Towards an Understanding of Crystal Packing in the Pentaphenyl Group V Compounds

BY CAROLYN PRATT BROCK

Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506, *USA*

(*Received* 22 *February* 1977; *accepted* 12 *May* 1977)

Semi-empirical calculations of the energy due to intermolecular interactions have been made for crystals of $(C_6H_5)_5M.\frac{1}{2}C_6H_{12}$, M = P, As, and Sb. This energy has been calculated as a pairwise sum over nonbonded atoms; energy minimizations have been performed with respect to the unit-cell parameters and molecular positions and orientations. Two sets of potential functions including repulsive and van der Waals terms have been employed; one of the sets also contains r^{-1} (Coulombic) contributions to the energy. The experimentally determined structures of the arsenic and antimony compounds have been well reproduced, as has the disorder observed for the solvent molecule in the former; it is suggested that this disorder is also present in the latter crystal. A comparison of the energies calculated for these solvates with those computed previously for unsolvated species predicts the stability of $(C_6H_5)_5P.\frac{1}{2}C_6H_{12}$, for which no crystallographic data have been previously reported. Crystals of this compound have now been identified. These comparisons also show the relative lattice energies of the three possible crystal structures seen in this system (Cc, $P\bar{1}$, and the $P\bar{1}$ cyclohexane solvate considered here) to be the same for all three molecules, suggesting that the molecular packing is not greatly affected by a change in the central group V atom.

Introduction

The study of molecular packing in crystals is important if the influence of intermolecular nonbonded interactions on molecular geometry or conformation is to be understood. We have attacked this problem by considering the pentaphenyl compounds of phosphorus, arsenic, and antimony. Three different structures have been reported for these molecules (see Table 1). In one of these, that of the unsolvated pentaphenylantimony crystal, the molecule adopts anomalous square-pyramidal geometry; in the others, the expected trigonal-bipyramidal conformation is observed. In previous work (Brock & Ibers, 1976; Brock, 1977) we modeled the unsolvated $P\bar{1}$ and Cc structures with a semi-empirical force field describing intermolecular nonbonded interactions; those cell constants and molecular positions and orientations which had been found experimentally were well reproduced after energy minimization. Correlations were drawn between the relative magnitudes of the calculated energies and the observed crystal form for the three compounds, and the observation of square-pyramidal geometry for unsolvated pentaphenylantimony was explained as a packing effect.

Table 1. *Crystal structures reported for* $(C_6H_5)_5M$ *compounds,* M = P, As, *and* Sb

Cc:	$(C_6H_5)_5P^a$	$(C_6H_5)_5As^b$	
$P\bar{1}$:			$(C_6H_5)_5Sb^c$
$P\bar{1}$ (solvate):		$(C_6H_5)_5As.\frac{1}{2}C_6H_{12}{}^d$	$(C_6H_5)_5Sb.\frac{1}{2}C_6H_{12}{}^e$

References: (*a*) Wheatley (1964). (*b*) Wheatley & Wittig (1962) (unit-cell data only). (*c*) Beauchamp, Bennett & Cotton (1968). (*d*) Brock & Webster (1976). (*e*) Brabant, Blanck & Beauchamp (1974).

In this work we have attempted to describe the cyclohexane solvated structure of these compounds in a similar fashion. In the pentaphenylarsenic solvate the cyclohexane molecule is disordered; in a successful model the two orientations of this species must have

comparable energies. Calculations should indicate to what degree the solvate structure is stabilized relative to the other arrangements, and it should be possible to predict whether or not the pentaphenylphosphorus solvate can be formed. Comparisons between lattice energies calculated for the three compounds should also give information about the extent to which homologous molecules within a family of the periodic table can be expected to form isostructural crystals.

Description of the calculations

Lattice energy minimizations for the cyclohexane solvates of the pentaphenyl compounds of antimony, arsenic, and phosphorus were carried out in a manner described in detail previously (Brock, 1977). As before, two sets of functions were used to describe the intermolecular nonbonded interactions (Williams, 1967; Williams, 1974). The first set, of the Buckingham form,

Table 2. *Results of the energy minimizations of the* $(C_6H_5)_5Sb.\frac{1}{2}C_6H_{12}$ *structure*

	Observed*	Δ(Calc − Obs)	Δ(Calc − Obs)
Coulombic interactions?		no	yes
Cell:			
a (Å)	10·579 (5)	0·035, 0·038†	−0·019, −0·006†
b	10·569 (4)	−0·166, −0·170	−0·283, −0·287
c	15·117 (8)	0·095, 0·051	0·087, 0·037
α (°)	120·55 (4)	0·11, 0·06	0·13, 0·08
β	106·93 (4)	0·95, 0·79	0·79, 0·56
γ	92·08 (3)	−0·67, −1·42	−0·76, −1·38
V (Å^3)	1357·2	−16·2, −12·9 (−1·2%, −1·0%)	−36·7, −32·8 (−2·7%, −2·4%)
$(C_6H_5)_5Sb$ molecule:			
x‡	0·1206 (1)	−0·0018, 0·0029	−0·0028, 0·0012
y	0·0343 (2)	0·0007, −0·0028	0·0039, 0·0009
z	0·2825 (1)	0·0003, −0·0030	0·0036, 0·0015
δ (°)§	−37·20	0·12, 2·00	−1·65, 0·06
ε	−107·86	−0·69, −0·35	−0·27, 0·05
η	153·04	0·16, 1·70	−1·14, 0·36

* Brabant, Blanck & Beauchamp (1974). Numbers in parentheses are standard deviations.
† The two values are for structures which differ only in the orientation of the disordered cyclohexane molecule.
‡ 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).

Table 3. *Results of the energy minimizations of the* $(C_6H_5)_5As.\frac{1}{2}C_6H_{12}$ *structure*

	Observed*	Δ(Calc − Obs)	Δ(Calc − Obs)
Coulombic interactions?		no	yes
Cell:			
a (Å)	10·448 (19)	0·051, 0·092†	0·002, 0·048†
b	10·566 (21)	−0·118, −0·134	−0·291, −0·305
c	14·903 (25)	0·050, −0·001	0·018, −0·050
α (°)	121·09 (5)	0·11, 0·10	−0·10, −0·19
β	106·38 (4)	0·48, 0·32	0·33, 0·01
γ	92·44 (5)	−0·03, −0·86	−0·15, −0·87
V (Å^3)	1315·8	−10·7, −4·7 (−0·8%, −0·4%)	−35·3, −28·1 (−2·7%, −2·1%)
$(C_6H_5)_5As$ molecule:			
x‡	0·1224 (3)	−0·0020, 0·0023	−0·0031, 0·0010
y	0·0386 (3)	0·0015, −0·0024	0·0048, 0·0013
z	0·2853 (2)	−0·0007, −0·0037	0·0036, 0·0020
δ (°)§	−33·54	−0·28, 1·12	−2·21, −0·98
ε	−110·06	0·31, 0·59	0·66, 0·97
η	158·51	0·19, 1·32	−1·40, −0·35

* Brock & Webster (1976). Numbers in parentheses are standard deviations.
† The two values are for structures which differ only in the orientation of the disordered cyclohexane molecule.
‡ Fractional coordinates of central As atom.
§ Angles are those described in Table 2.

contains exponential and r^{-6} terms; in the second, Coulombic (r^{-1}) contributions are included as well. With one exception the parameters for these functions were those used in the earlier work (Brock, 1977); however, application of Williams's (1974) charge separation parameter of $0{\cdot}358e^-$ for hydrocarbons to cyclohexane results in the localization of charges of $-0{\cdot}238$ and $0{\cdot}119e^-$ respectively on the carbon and hydrogen atoms of this molecule rather than the $\pm 0{\cdot}179e^-$ calculated for the atoms of phenyl rings.

Like the pentaphenyl molecules, the cyclohexanes were treated as rigid bodies in the calculations. They were idealized in the chair conformation with geometric parameters: $r_{C-C} = 1{\cdot}54$ Å, $r_{C-H} = 1{\cdot}04$ Å, $\theta_{CCC} = 111°$, and $\theta_{HCH} = 108°$. Except for the C–H distance, these values are those used by Wiberg & Boyd (1972) in a conformational study; the C–H distance, however, was shortened to satisfy the requirements of Williams's (1967, 1974) potential functions. The starting points for the minimizations of the As and Sb compounds were the known unit cells, known $(C_6H_5)_5M$ molecular positions, orientations, and geometries, and the two orientations of the cyclohexane molecule refined in the $(C_6H_5)_5As.\frac{1}{2}C_6H_{12}$ crystal structure determination. The coordinates of the center of the C_6H_{12} ring are fixed in all cases by symmetry and were not varied during the minimizations. Pentaphenylantimony and -arsenic were idealized as before from the conformations found experimentally. Since the conformation of pentaphenylphosphorus in the cyclohexane solvate is not known, this molecule was derived by shortening the axial and equatorial bond lengths of $(C_6H_5)_5As.\frac{1}{2}C_6H_{12}$ by 0·114 and 0·110 Å respectively. All minimization data for the three compounds are given with respect to unit cells similar to that defined in the structure determination of $(C_6H_5)_5As.\frac{1}{2}C_6H_{12}$; the transformation between this cell and that originally

Table 4. *Unit-cell data calculated for the* $(C_6H_5)_5P.\frac{1}{2}C_6H_{12}$ *structure*

Coulombic interactions?	no	yes
a (Å)	10·408, 10·458*	10·364, 10·412*
b	10·418, 10·395	10·230, 10·216
c	14·837, 14·778	14·792, 14·723
α (°)	121·68, 121·68	121·44, 121·40
β	106·62, 106·31	106·49, 106·05
γ	92·46, 91·69	92·34, 91·66
V (Å^3)	1274·5, 1281·0	1248·4, 1255·7

* The two values are for structures which differ only in the orientation of the disordered cyclohexane molecule.

Table 5. *Observed and calculated orientation angles* (°) *for the disordered solvent molecule in* $(C_6H_5)_5M.\frac{1}{2}C_6H_{12}$, M = Sb *and* As

	M = Sb			M = As		
	Observed[a]	Calculated		Observed[b]	Calculated	
Coulombic interactions?		no	yes		no	yes
Orientation A:						
δ*	†	−16·0	−19·2	−17·7	−19·2	−21·2
ε	†	−14·1	−14·3	−10·8	−14·5	−15·9
η	†	−114·0	−116·8	−111·6	−114·8	−116·9
Orientation B:						
δ	−48·3	−48·4	−45·3	−49·4	−47·6	−45·7
ε	5·3	−0·9	−2·1	2·8	−1·2	−2·9
η	−110·9	−109·8	−106·8	−113·9	−108·8	−107·8

References: (*a*) Brabant, Blanck & Beauchamp (1974). (*b*) Brock & Webster (1976).

* Angles are those described in Table 2.

† Disorder of the cyclohexane molecule was not included in the crystallographic model.

Table 6. *Calculated lattice energies* (in kJ/mol) *of* $(C_6H_5)_5M$ *crystals*, M = P, As, *and* Sb

	Set I potentials			Set II (Coulombic) potentials		
Space group	P	As	Sb	P	As	Sb
Cc*	−138·5	−139·3	−140·6	−147·1	−148·5	−150·4
$P\bar{1}$*	−141·7	−142·7	−145·2	−160·2	−161·9	−165·5
$P\bar{1}$ (C_6H_{12} solvate)†	−163·7	−165·1	−170·7	−190·6	−192·1	−195·7
	−162·3	−163·7	−170·0	−188·8	−190·1	−194·6

* Brock (1977).

† The two values are for structures which differ only in the orientation of the disordered cyclohexane molecule.

chosen for the antimony solvate has been reported previously (Brock & Webster, 1976).

The results of the energy minimizations for the pentaphenylantimony and -arsenic solvates are compared with the experimental data in Tables 2 and 3 respectively, while unit-cell data calculated for the phosphorus structure are given in Table 4. In each case results are given for the two different orientations of the cyclohexane ring and for the two sets of potential functions. Orientation angles for the cyclohexane molecules in $(C_6H_5)_5Sb.\frac{1}{2}C_6H_{12}$ and $(C_6H_5)_5As.\frac{1}{2}C_6H_{12}$ after minimization are collected in Table 5. The corresponding experimental values are not very accurate since the cyclohexane ring was not particularly well described in either determination. Table 6 contains the calculated energy values for all three compounds in the three crystal structures which are known for this system.

Discussion

The experimentally determined cell constants of the pentaphenylantimony and -arsenic solvates are reproduced to better than 1% except for the length of the *b* axis, which is calculated to be considerably shorter than is observed. It is not clear why the agreement is worse in this direction. Inadequacies in the model may be especially important along [010], or perhaps thermal expansion of the crystal is particularly large in this direction. In determining the parameters of his most recent potential functions, Williams (1974) fit crystallographic data for 18 hydrocarbons. Seven of these structures were determined at low temperature; the average temperature for the 18 experimental determinations was *ca* 240 K. Similarly, the average temperature of the seven structures fit by the other set of potentials (Williams, 1967) is *ca* 190 K. Since vibrational effects are ignored in the calculations reported herein, the unit cells measured at room temperature should contract during energy minimization. Another measure of the agreement between observed and calculated structures is based on an examination of the second derivatives of the energy evaluated at the point on the energy surface corresponding to the experimentally determined crystal structure. If the fit is good, all the eigenvalues of the matrix of the second derivatives will be positive; that is, the experimental structure will be within the range of curvature of the calculated minimum. Such was the case for all the minimizations reported in this work. In previous calculations of the unsolvated crystals in this system (Brock, 1977) it was argued that the interatomic potentials including Coulombic terms provided a substantially better model for the system than did the other set of potential functions. There is, however, no evidence in this study to differentiate between the two sets.

The disorder of the solvent molecule observed in $(C_6H_5)_5As.\frac{1}{2}C_6H_{12}$ is quite well described in these calculations. In the arsenic structure the ratio of the occupancy factors of the two sites was unity to within experimental error; minimum-energy structures calculated in this work for the two orientations of the cyclohexane ring differ by at most 2 kJ/mol over the three compounds. This agreement is remarkable considering that this readily deformable molecule was assumed to have a strict chair conformation. Furthermore the shapes of the two minima are not exactly the same so that entropy considerations may be important. The two calculated orientations of the cyclohexane molecule are well defined and vary little between the three compounds. The major difference between the two is the position of one carbon atom and its symmetry-related partner. This model is in good agreement with that refined from crystallographic data for $(C_6H_5)_5As.\frac{1}{2}C_6H_{12}$, and may fit the data for the antimony solvate better than the ordered model reported for that structure. The cyclohexane molecule refined in the latter determination has rather short C–C bonds [1·43 to 1·46 (5) Å] and large C–C–C angles [115 to 117 (3)°], and may well represent a 'flattened' average of two disordered positions.

For all three compounds the C_6H_{12} solvate is calculated to be considerably lower in energy than the unsolvated structures whether or not Coulombic terms are included in the potential functions. The energy differences between the solvated structure and observed unsolvated form are 25–30 kJ/mol without, and 30–45 kJ/mol with the inclusion of Coulombic terms. Any entropy contributions would not be of this magnitude, so that these calculations predict that the solvated form should precipitate from cyclohexane solutions in all three cases. No such solvate of pentaphenylphosphorus has been reported previously. We have found, however, that $(C_6H_5)_5P$ crystals grown from cyclohexane belong to space group $P\bar{1}$ and have a cell volume of 1286 (5) Å^3. This volume is in line with the values for the arsenic and antimony solvates, and is 76 Å^3 per molecule larger than that of the unsolvated *Cc* cell. Measurements of rotation and zero-level Weissenberg pictures give values for a^*, b^*, γ^*, and c which agree well with unit-cell data for the other two solvated crystals. The axial lengths of the $(C_6H_5)_5M.\frac{1}{2}C_6H_{12}$ crystals change by about 1% as Sb is changed to As, and As to P; the angle γ^* is the same between the three cells to within 0·3°.

A consideration of the energy values given in Table 6 indicates that the energy differences between the three compounds for a single structure type are quite small relative to the energy differences between packing arrangements. The relative ordering of energies ($P\bar{1}$ solvate $< P\bar{1} < Cc$) is the same in all cases. Additionally, an examination of interatomic distances shows the same short contacts to be present in the three compounds. In the cyclohexane solvates, for example, the 10 to 15 shortest intermolecular contacts are very similar between the pentaphenylantimony, -arsenic, and -phosphorus crystals. These similarities do *not* imply, however, that the overall packing is the same in the three cases; changes in packing with change

in molecular size are by no means isotropic in this triclinic cell. Consequently, while many of the intermolecular contacts in the $(C_6H_5)_5M.\frac{1}{2}C_6H_{12}$ structure shorten as M = Sb is changed to As and then to P, other such distances are increased. For instance the very important intermolecular contact along [011] between two axial ring hydrogen atoms lengthens from *ca* 2·2 Å in the antimony structure to *ca* 2·3 Å in $(C_6H_5)_5P.\frac{1}{2}C_6H_{12}$. Even though this particular contact is one of the two shortest in all the structures considered, the energy involved is less than 1·5 kJ/mol. In structures of this complexity it is probably not realistic to look at a few short contacts and consider them as structure determining. Rather, the relative stabilities of molecular crystals are determined by hundreds of intermolecular interactions, the most important of which may have an energy of less than several kJ/mol.

It is now possible to present a unified view of the crystal structures of the pentaphenyl compounds of phosphorus, arsenic, and antimony. For all three molecules the equilibrium geometry in solution is trigonal-bipyramidal; this geometry is observed if crystals grown from cyclohexane (from our experience the most convenient solvent for this system) are studied. If crystals are grown from a solvent which does not enter the lattice, two structures of comparable energies are possible. The $P\bar{1}$ structure is slightly more stable than the *Cc* arrangement in terms of lattice energy, but requires the pentaphenyl molecules to assume a higher energy square-pyramidal geometry. The energy of this conformational change decreases down the family; only in $(C_6H_5)_5Sb$ is it small enough that the $P\bar{1}$ structure is formed. The initial observation of the 'anomalous' square-pyramidal geometry for pentaphenylantimony then was a result of efforts to crystallize the compound in an unsolvated form. Such attempts are quite standard since solvates are often unstable in air, and the solvent molecules often complicate least-squares refinements. This system serves as a reminder, however, that in flexible molecules the observed geometry or conformation may depend on the crystal form studied, and that a comparison of alternate crystalline forms or of a series of closely related molecules must be made before a seemingly anomalous effect is considered to be established.

Acknowledgement is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also thank the Computing Center of the University of Kentucky for providing generous amounts of time on the local IBM 370/165, and Ms M.-S. Kuo for preparing the pentaphenylphosphorus sample.

References

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

BRABANT, C., BLANCK, B. & BEAUCHAMP, A. L. (1974). *J. Organometal. Chem.* **82**, 231–234.

BROCK, C. P. (1977). *Acta Cryst.* A**33**, 193–197.

BROCK, C. P. & IBERS, J. A. (1976). *Acta Cryst.* A**32**, 38–42.

BROCK, C. P. & WEBSTER, D. F. (1976). *Acta Cryst.* B**32**, 2089–2094.

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

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

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

WIBERG, K. B. & BOYD, R. H. (1972). *J. Amer. Chem. Soc.* **94**, 8426–8430.

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

WILLIAMS, D. E. (1974). *Acta Cryst.* A**30**, 71–77.