

Some Comparisons among Ring Compounds of Phosphorus and Arsenic

BY JERRY DONOHUE

Department of Chemistry, University of Southern California, Los Angeles 7, California, U.S.A.

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Numerous comparisons among various structural features in compounds containing 4- and 5-membered phosphorus rings and 5- and 6-membered arsenic rings are made. The molecular structure of $(PCF_3)_4$ indicates that the torsion angle about P-P bonds tends to be different from 0° , a conclusion confirmed by the results on the other molecules. The observed conformations of $(PCF_3)_5$ and $(AsCH_3)_5$ are very similar, and apparently result mainly from intra-, rather than inter-, molecular forces. The stable form of these five-membered rings is intermediate between symmetry m and 2. The P-C-F bond angles in $(PCF_3)_4$ and $(PCF_3)_5$ are explainable in terms of repulsion between non-bonded atoms. The stable orientation about P-C single bonds is the staggered one. The observed irregularities in the torsion angles about the As-C bonds in the $(AsC_6H_5)_6$ molecule may be ascribed to efficient molecular packing in the crystal. Some interesting but as yet unexplained differences exist among bond distances and bond angles in arsenic ring compounds.

Introduction

Recent structure determinations of compounds containing rings of phosphorus and arsenic include $(AsCH_3)_5$ (Burns & Waser [BW], 1957), $(PCF_3)_5$ (Spencer & Lipscomb [SL], 1961), $(AsC_6H_5)_6$ (Hedberg, Hughes & Waser [HHW], 1961), and $(PCF_3)_4$ (Palenik & Donohue [PD], 1962). Because many comparisons among the various structural features in these compounds were not made by the above authors, it is of interest to examine them in more detail than has been done previously.

$(PCF_3)_4$ and $(PCF_3)_5$

The primary purpose of the studies on the tetramer and pentamer of PCF_3 was to confirm the presence of the phosphorus rings, and because these two studies were carried out at the same time in several different widely separated laboratories the individual results were not examined for similarities and differences between the two molecules. Molecular quantities for

the tetramer and pentamer* are presented in Table 1. It is seen that those quantities, particularly the three different kinds of bond distances, which are not subject to constraint by ring formation are remarkably similar; the P-P-P bond angles and the P-P-P-P torsion angles are not, of course, the same in both compounds. Noteworthy also is the fact that the bond angles to the fluorine atoms which project inside the rings (F_i of Table 1) are significantly greater than the bond angles to the fluorine atoms which project outside the rings (F_o of Table 1). This effect undoubtedly arises from repulsion between non-bonded fluorine and phosphorus atoms. Moreover, in both rings the rotation of the CF_3 groups about the P-C bonds is such that the staggered conformation is achieved, as may be seen in Figs. 1 and 2. The exactly staggered conformation is imposed in the tetramer by the space group, and, although in the pentamer

Table 1. Comparison of molecular quantities in PCF_3 tetramer and pentamer

	Tetramer	Pentamer	
		Range	Average e.s.d.*
P-P	$2.213 \pm 0.005 \text{ \AA}$	2.202 to 2.252 \AA	$2.223 \pm 0.017 \text{ \AA}$
P-C	1.867 ± 0.014	1.873 to 1.925	1.906 ± 0.020
C-F	1.335 ± 0.015	1.281 to 1.401	1.346 ± 0.032
P-P-P	84.7°	93.9° to 108.3°	$101.3 \pm 4.9^\circ \dagger$
P-P-C	97.8	94.2 to 107.8	$97.6 \pm 3.9^\circ \dagger$
P-C- F_i	118.1	114.5 to 120.0	116.4 ± 1.9
P-C- F_o	109.6	107.0 to 111.0	109.2 ± 1.2
F-C-F	105.7 and 107.5	103.6 to 111.9	107.1 ± 2.4
P-P-P-P	34	18 to 58	$37 \pm 16^\circ$

* Standard deviation of the individual values from the average.

† Significant differences exist among the individual values.

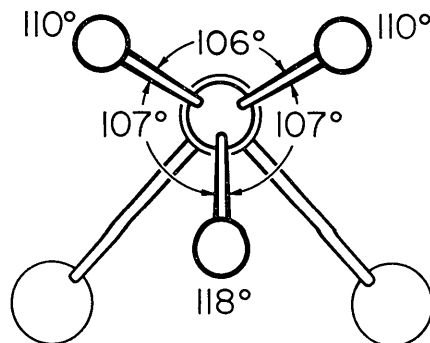


Fig. 1. View down the P-C bond in $(PCF_3)_4$, showing the two phosphorus atoms bonded to phosphorus, and the CF_3 group. The P-C-F angles are indicated by the numbers next to the F atoms (smallest circles).

* The revised values for the bond angles in the pentamer (Spencer, Simpson & Lipscomb, 1962) are used in Table 1 and elsewhere in this paper.

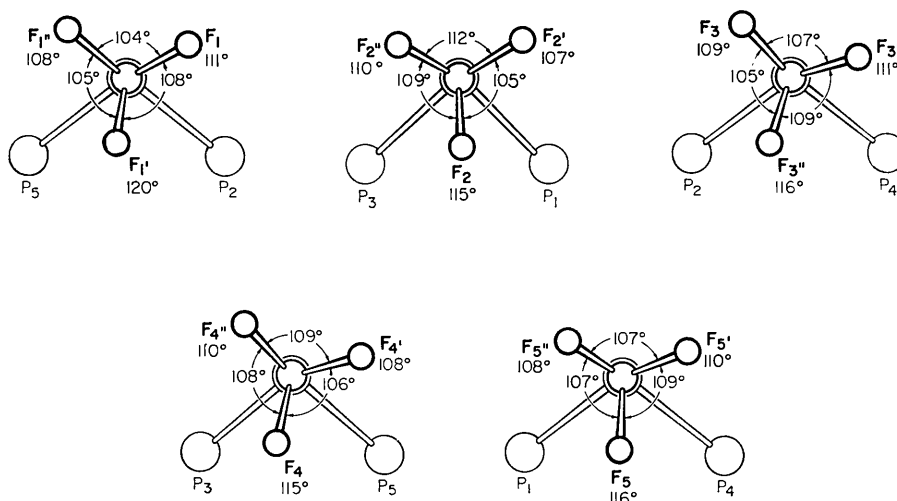


Fig. 2. Views down the five P-C bonds in $(PCF_3)_5$, showing the phosphorus and carbon ligands and the bond angles, as in Fig. 1.

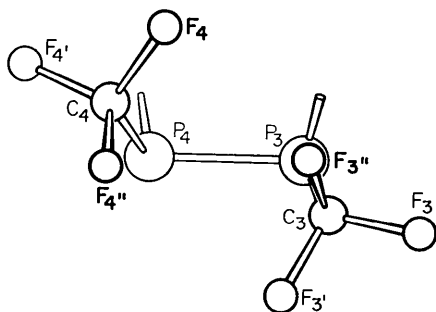


Fig. 3. Part of the $(PCF_3)_5$ molecule, showing the interaction between the two CF_3 groups on the same side of the ring.

no such restriction exists, the conformations in that molecule are all remarkably similar, and quite like that in the tetramer, as may be seen in Figs. 1 and 2. The greatest deviations occur in the case of the rotations about P_3-C_3 and P_4-C_4 , and the two trifluoromethyl groups here are those which are on the same side of the ring, and therefore interact more strongly than any of the other adjacent pairs, all of which lie on opposite sides of the ring. This interaction shows clearly in Fig. 3, from which it is evident that the small observed rotations, seen in Fig. 2, which move F_3'' away from P_4 and F_4 toward P_3 , lead to an increase in the $F_3'' \cdots F_4'$ distance between the two trifluoromethyl groups, and at the same time do not reduce the $F_3'' \cdots F_4$ and $F_3' \cdots F_4'$ distances to unacceptably short values. It may therefore be concluded that for the orientation about P-C bonds the staggered conformation is the stable one.

$(PCF_3)_5$ and $(AsCH_3)_5$

The determination of the crystal structure of arsenomethane by BW was the first in which the existence

of an arsenic ring structure was unequivocally established, and, incidentally, confirmed the pentameric formula which had been suggested, but not proven, by earlier electron diffraction and vapor density studies (Waser & Shomaker, 1945). In the later determination of the crystal structure of $(PCF_3)_5$, SL compared their P_5 ring with the As_5 ring by remarking that the latter was 'far less distorted', a 'result not surprising, since the relative sizes of the ring atoms and the substituent groups are reversed in the two compounds.'

As pointed out by BW, the only equilateral isogonal pentagon is planar. Deviations from planarity lead to an average angle of less than 108° , and since the normal bond angles at both phosphorus and arsenic are in the vicinity of 100° , non-planar rings are to be expected. This is precisely what is observed, but more striking is the fact that the average angles and their average deviations are virtually same in both molecules: $101.3 \pm 4.2^\circ$ in the P_5 ring and $101.8 \pm 3.0^\circ$ in the As_5 ring. This result, which is at variance with the opinion of SL, suggests that the forces leading to the non-planar rings must be quite similar in both molecules.

A second effect which causes the rings to assume a non-planar structure is relief of Pitzer (torsion) strain, which is expected to be at a maximum for planar rings. Evidence that this effect is in fact operative is found in the result for $(PCF_3)_4$, where the P-P-P bond angles are compressed to 84.7° as compared with 90° in a planar ring, with a consequent increase of the P-P-P torsion angles from 0° to 34° . This is shown in Fig. 4, which is a view down the P-P bond, and includes the two other ligands of each phosphorus atom. The non-planarity of the P_5 and As_5 rings accordingly cannot be ascribed solely to the requirement of bond angles smaller than 108° . Examination of the five torsion angles in these rings reveals an astonishing

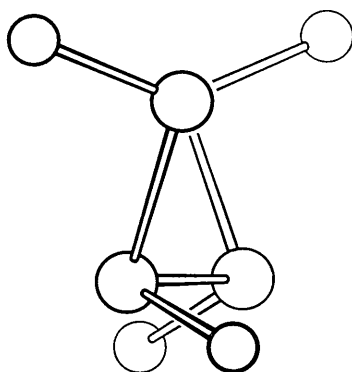


Fig. 4. The $(PCF_3)_4$ molecule, as viewed down a P-P bond. The larger circles are phosphorus atoms, the smaller are carbon atoms; the fluorine atoms are not shown.

resemblance between the two molecules, as shown in Fig. 5. (The numberings of the atoms in these figures are those of the respective original authors.) It is seen that when successive views of the two molecules are brought into the appropriate juxtaposition, the remarkable similarity is apparent. Since the intermolecular forces in the two crystals are certainly quite dissimilar, it may be concluded that the conformations are largely a result of similar intramolecular forces in the two molecules. The angular quantities for the two molecules are compared in Table 2.

The carbon atoms on the same side of the ring are

Table 2. Comparison of angular quantities in $(PCF_3)_5$ and $(AsCH_3)_5$

$(X=P \text{ or } As)$	$(PCF_3)_5$		$(AsCH_3)_5$	
	Atoms		Atoms	
X-X-X	4-3-2	102.7°	5-1-2	100.4°
	3-2-1	93.9	1-2-3	100.0
	2-1-5	103.4	2-3-4	105.6
	1-5-4	108.3	3-4-5	105.4
	5-4-3	98.0	4-5-1	97.5
	Average	101.3°	Average	101.8°
C-X-X	4-4-3	107.8°	5-5-1	102.8°
	4-4-5	96.9	5-5-4	98.0
	3-3-2	99.4	1-1-2	98.2
	3-3-4	100.5	1-1-5	96.9
	2-2-1	94.6	2-2-3	95.6
	2-2-3	95.1	2-2-1	94.4
	1-1-5	95.6	3-3-4	95.8
	1-1-2	94.2	3-3-2	97.6
	5-5-4	95.7	4-4-5	96.4
	5-5-1	96.6	4-4-3	95.3
Average	97.6°	Average	96.9°	
X-X-X-X*	4-5-1-2	+18°	5-4-3-2	-10°
	5-1-2-3	-44	4-3-2-1	-24
	1-2-3-4	+58	3-2-1-5	+49
	2-3-4-5	-47	2-1-5-4	-55
	3-4-5-1	+19	1-5-4-3	+38
Average	37°	Average	35°	

* The sense of a torsion angle is defined by an arbitrary convention which is obvious on referral to Fig. 5.

C_1 and C_5 in the arsenic compound and C_3 and C_4 in the phosphorus compound, and it is interesting that the angles $C_5-As_5-As_1$ and $C_4-P_4-P_3$ are the largest such angles in the two molecules, and, curiously, much larger than their respective opposites, namely, $C_1-As_1-As_5$ and $C_3-P_3-P_4$.

The torsion angles in the two rings are not in quite as close correspondence as are the bond angles. In fact, the twist about the bond P_1-P_5 is in the opposite sense to that about the bond As_3-As_4 , as may be noted in Fig. 5. More significant, probably, is the fact that none of the torsion angles is zero, the probable value for maximum energy.

The actual conformations assumed by each molecule must result from a balance among the strains in the bond angles and torsion angles plus repulsions across the rings and between the substituent groups, but complete treatment of the problem is difficult even if the repulsive effects are neglected, because the geometry of non-planar equilateral* pentagons is rather complicated. Four angles are required to specify the shape of such a pentagon. This inconveniently large number of variables is reduced to two for a pentagon of symmetry m or 2, these two cases having been analyzed by BW, the former in some detail. They noted that the actual shape of the arsenic five-ring is about midway between symmetries m and 2. This fact is apparent from examination of Fig. 5: symmetry m requires one torsion of angle of 0°, approximated by this molecule as shown in the view down As_3-As_4 ; symmetry 2 requires that one atom lie on the bisector of the projected torsion angle, approximated as shown in the view down As_5-As_1 . Also apparent from Fig. 5 is the fact that the P_5 ring likewise is intermediate, having neither symmetry m nor 2, as well as the fact that approximation to symmetry 2 occurs at a bond, P_2-P_3 , which is not the corresponding bond in the As_5 ring, unless the substituent groups are ignored, a fact which is perhaps suggestive that the effect of those groups is relatively minor with regard to ring conformation.

From their electron diffraction study of $(AsCH_3)_5$ vapor, Waser & Schomaker (1945) concluded that 'the molecule would carry out large-amplitude librations which would affect the cross-ring distances about its equilibrium conformations (probably with frequent transitions from one to another).' A similar conclusion in the case of the C_5 ring (cyclopentane) was later reached by Kilpatrick, Pitzer & Spitzer (1947), namely, 'that the puckering of the ring is not of a definite type, but that the angle of maximum puckering rotates around the ring.' They also found that both the angle strain and the torsion strain were virtually identical regardless of whether the molecule had symmetry m , 2, or an intermediate conformation. It is not possible to carry out the more detailed

* None of the bond distances in either ring differs significantly from the average.

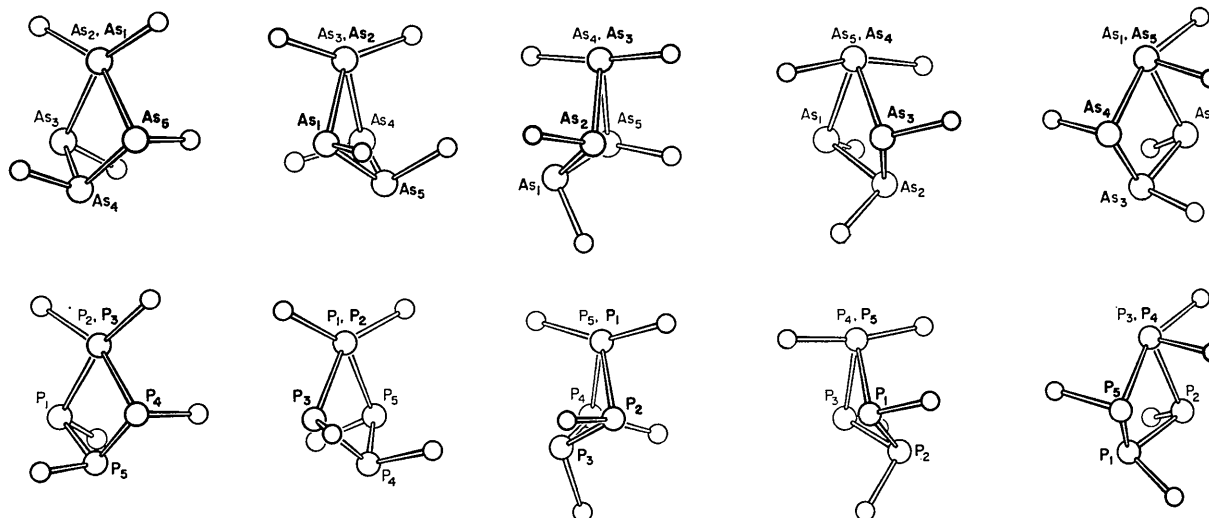


Fig. 5. Successive views down the five As-As and P-P bonds in the $(\text{AsCH}_3)_5$ and $(\text{PCF}_3)_5$. The fluorine and hydrogen atoms are not shown.

calculations, such as were made by Pitzer & Donath (1959) on cyclopentane, for the case of the As_5 and P_5 rings because of lack of sufficient knowledge of the bond bending force constants, the height and shapes of the barriers restricting rotation, the normal bond angles, and the normal torsion angles. Meanwhile, the present results indicate that the equilibrium conformation has neither symmetry m nor 2, but is intermediate between the two.

$(\text{AsC}_6\text{H}_5)_6$, $(\text{AsCH}_3)_5$, and As

The structure determination of arsenobenzene by HHW led to the unexpected result that this molecule is a hexamer. The As_6 ring was found to be in the chair conformation, with average bond angle $91.0 \pm 2.6^\circ$. In a regular As_6 ring, this value leads to torsion angles of 89.0° ; the actual torsion angles are shown in Fig. 6, in which it may also be noted that carbon and arsenic ligands associated with a particular As-As bond are always almost *trans*. Metallic arsenic also contains As_6 rings, as part of infinite puckered hexagonal sheets (Bradley, 1924). The bond angles are 97° , the torsion angles 82° , values which are different both to those in arsenobenzene and in arsenomethane. Furthermore, it is odd that while the As-C distances in $(\text{AsCH}_3)_5$ and $(\text{AsC}_6\text{H}_5)_6$ are not significantly different, the As-As distances are, and, moreover, are both different from that in metallic arsenic, but not from that found

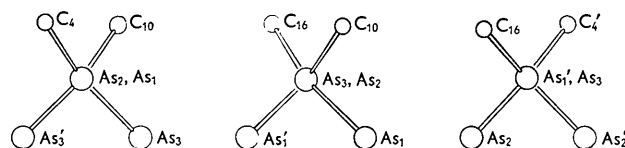


Fig. 6. Views down the three As-As bonds in $(\text{AsC}_6\text{H}_5)_6$, showing the carbon and other arsenic ligands of the arsenic atoms of the bond.

in gaseous As_4 by Maxwell, Hendricks & Moseley (1935). The relevant data are compared in Table 3. Some of the values given in Table 3 are subject to strain, the effect of which is, unfortunately, unknown.

The crystal symmetry of the $(\text{AsC}_6\text{H}_5)_6$ molecule is $\bar{1}$, and HHW pointed out that four small rotations and two moderate rotations about the As-C bonds would give the molecule the higher symmetry of $\bar{3}m$. This fact is illustrated in Fig. 7, which shows views down the three crystallographically independent As-C bonds.

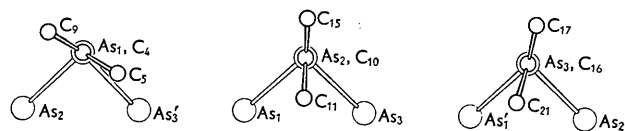


Fig. 7. Views down the three As-C bonds in $(\text{AsC}_6\text{H}_5)_6$ showing the orientation of the phenyl groups about these bonds. The planes of the C_6H_5 groups are perpendicular to the plane of the paper, and pass through the three respective carbon atoms shown in each part of the figure.

Table 3. Comparison of molecular quantities in arsenic rings

	$(\text{AsCH}_3)_5$	$(\text{AsC}_6\text{H}_5)_6$	$(\text{As}_6)_\infty$	As_4
As-As	$2.428 \pm 0.008 \text{ \AA}$	$2.456 \pm 0.005 \text{ \AA}$	2.51 \AA	2.44 \AA
As-As-As	$101.8 \pm 3.2^\circ$	$91.0 \pm 2.6^\circ$	97°	(60°)
As-As-As-As	35° (av.)	89° (av.)	82°	$(0^\circ \text{ and } 82^\circ)$
As-C	$1.95 \pm 0.02 \text{ \AA}$	$1.97 \pm 0.02 \text{ \AA}$	—	—
As-As-C	$96.9 \pm 2.2^\circ$	$100.1 \pm 1.1^\circ$	—	—

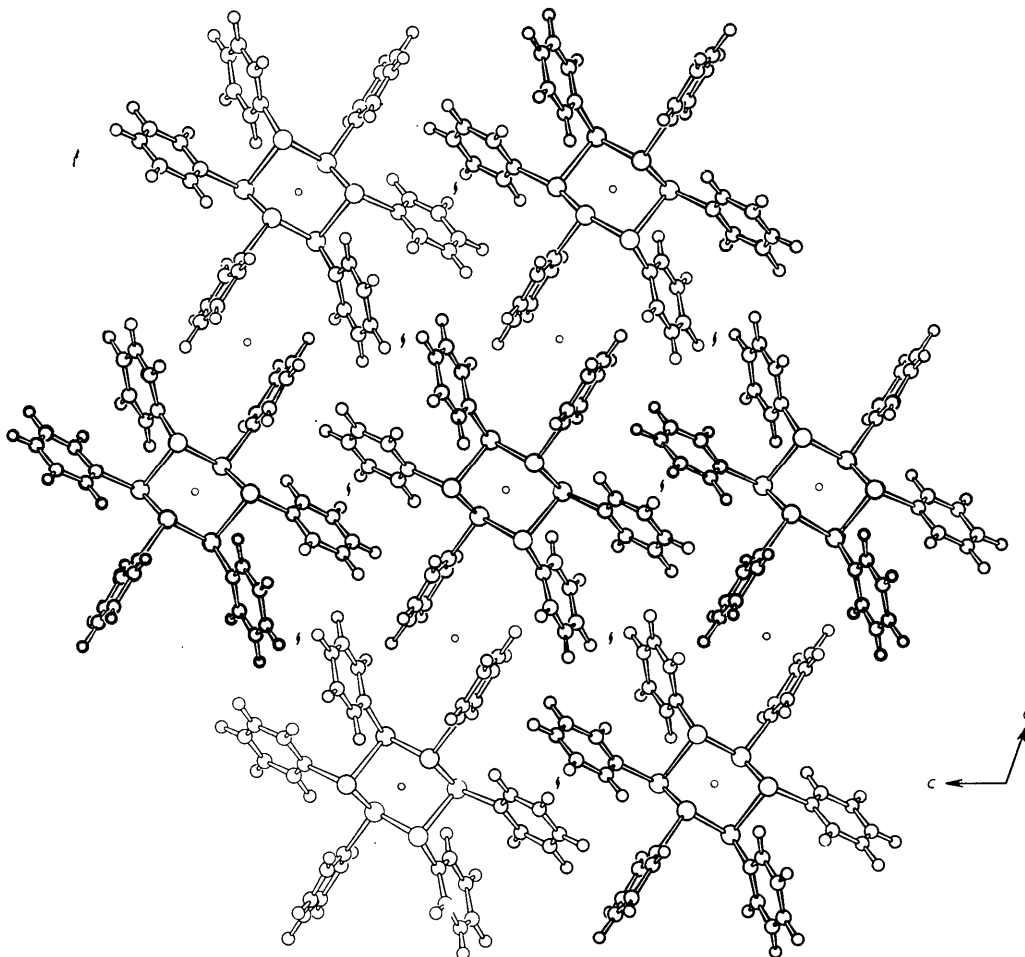


Fig. 8. Projection of the $(\text{AsC}_6\text{H}_5)_6$ structure down the b axis, showing the close neighbors of one molecule. The positions of the hydrogen atoms were assumed.

Moderate rotation about $\text{As}_1\text{-C}_4$ and small rotation about the other two As-C bonds would give the higher symmetry. One might inquire as to why these torsion angles vary so much more than those in the other ring compounds, since it might be expected that all three of them would be nearly equal and, perhaps, symmetrical, as is the case for the bond $\text{As}_2\text{-C}_{10}$. A plausible answer to this question is that the barrier to rotation about these bonds, which are in a similar situation to the C-CH_3 bond in toluene or the C-N bond in nitromethane, is very low, as it is in those molecules, i.e., less than a few tenths of a kilocalorie, so that only a small amount of crystal energy resulting from an efficient packing of these rather large and complex molecules is enough to give rise to the observed irregularities. This conclusion represents an exception, but a reasonable one, to the opinion of Pitzer (1957) who stated that 'one should be very cautious about postulating a change in structure of the molecule in order to accommodate the lattice arrangement.' The complexity of the molecular packing is shown in Fig. 8, examination of which reveals that the packing of the

molecules is indeed very efficient, and that it is unlikely that the phenyl groups can all be brought to the same angle of rotation without giving rise to unacceptably short distances elsewhere in the structure. Also evident in Fig. 8 is the tendency for some of the hydrogen atoms to interact with neighboring phenyl groups in such a way as to suggest that phenyl groups are crater-like, a property of aromatic rings first noted by Waser & Lu (1944) in crystalline biphenylene. The combination of these factors doubtless causes the observed results which at first sight might seem to be somewhat unexpected.

Conclusion

The discussion above is necessarily qualitative, largely because of the limited structural data which is available, and because of a lack of quantitative knowledge of many of the molecular properties. It seems certain, nevertheless, that the preferred orientation about phosphorus-carbon single bonds, like that about carbon-carbon single bonds, is the staggered one.

Also, the stable conformation of both phosphorus and arsenic five-membered rings is intermediate between symmetries m and 2; whether this situation is also true for cyclopentane and its derivatives remains to be shown. Finally, the question of why PCF_3 forms a tetramer and a pentamer, AsCH_3 a pentamer, and AsC_6H_5 a hexamer is still open.

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The Crystal Structure of $\text{Pd}_{17}\text{Se}_{15}$

BY S. GELLER

Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey, U.S.A.

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The crystal structure of $\text{Pd}_{17}\text{Se}_{15}$, with which $\text{Rh}_{17}\text{S}_{15}$ (formerly alleged to be Rh_9S_8) is isostructural, has been determined from single crystal data. The crystal belongs to one of the three space groups $O_h\text{-}Pm\bar{3}m$, $T_h\text{-}P\bar{4}3m$ or $O^1\text{-}P432$ with a lattice constant of 10.606 Å and two $\text{Pd}_{17}\text{Se}_{15}$ per unit cell. It is shown that the X-ray data do not lead to a choice of the most probable of the above space groups although refinement based on $Pm\bar{3}m$ leads to convergence with the lowest standard errors for all positional parameters. In $P432$, the x and y positional parameters of the palladium atoms in general positions do not converge with the data used; this is consistent with the large correlation between these two parameters.

The structure is described mainly on the basis of its belonging to space group $Pm\bar{3}m$. There are four kinds of palladium and three kinds of selenium atoms in the structure. The palladium atom in $1b$ has a regular octahedron of selenium atoms about it at 2.58 Å. A palladium atom in $3d$ has a square of selenium atoms about it at 2.53 Å and two palladium atoms at 2.78 Å in a line perpendicular to the plane of the square. The palladium atoms in $6e$ have a square of selenium atoms at 2.44 Å about them and one palladium at 2.78 Å on a line perpendicular to the plane of the selenium square. The palladium atoms in $24m$ have a 'buckled' square or 'flattened' tetrahedron of selenium atoms about them at distances 2.43, 2.49 and 2.51(2) Å. Other than the metal-metal bonds mentioned, there are no others in the ideal structure.

Introduction

Some years ago, Juza, Hülsmann, Meisel & Biltz (1935) studied the rhodium-sulfur system and reported the existence of a compound 'Rh₉S₈'. The powder pattern of this compound indicated that it had primitive cubic symmetry. In a search for superconductors among compounds of the $4d$ transition metals, Matthias, Corenzwit & Miller (1954) prepared 'Rh₉S₈' as well as 'PdSe' at about the same time. The powder pattern of the latter melt indicated that

the predominant phase present was isostructural with 'Rh₉S₈'. The compound allegedly Rh₉S₈ was found to be superconducting with a transition temperature of 5.8 °K. whereas the 'Pd₉Se₈' remained normal down to 1.4 °K. At the time, a small crystal of 'Rh₉S₈' was isolated from material prepared by Matthias *et al.* with intended stoichiometry RhS. Photographs taken with a Buerger precession camera confirmed the cubicity of the phase. A [100] Patterson projection misleadingly indicated a close relation to the Co₉S₈ structure (Lindqvist, Lundqvist & Westgren, 1936).