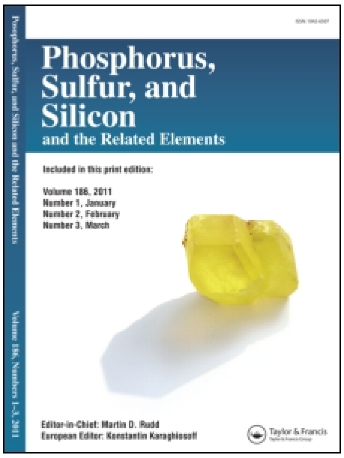

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SYNTHESIS AND MOLECULAR STRUCTURE OF SPIROARSORANES DIFFERING IN RING UNSATURATION. DISTORTION COORDINATES FOR FIVE-COORDINATED ARSENIC

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SYNTHESIS AND MOLECULAR STRUCTURE OF SPIROARSORANES DIFFERING IN RING UNSATURATION. DISTORTION COORDINATES FOR FIVE-COORDINATED ARSENIC[1]

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The new compound 2-phenyl-2,2′-spirobi(1,3,2-naphthodioxarsole), $(C_{10}H_6O_2)_2AsPh$, **6**, was prepared by reacting phenylarsonic acid and 2,3-dihydroxynaphthalene, similar to the preparation of the arsolanes $(Me_2C_2O_3)_2AsPh$, **5**, and $(C_2H_4O_2)_2AsPh$, **7**. The X-ray structures of **5–7**, which were determined, varied from near trigonal bipyramidal (TBP), **5**, to an intermediate geometry, **7**, to rectangular pyramidal (RP), **6**. For phenyl-substituted spirocyclic arsoranes containing like ring atoms directly bound to arsenic, the order of increasing displacement from the TBP toward RP parallels the order of increasing ring electron delocalization. It is found that the structures of arsoranes followed the C_{2v} constraint of the Berry pseudorotational coordinate similar to that reported for phosphoranes. The "limiting" RP for arsoranes has a trans basal angle, θ, of 151.4° similar to that found for other main-group five-coordinated elements. Arsolane **5** crystallizes in the monoclinic space group *C*2/*c* with a = 11.622 (3) Å, b = 17.480 (4) Å, c = 7.372 (1) Å, β = 93.12 (2)°, and Z = 4. Arsole **6** crystallizes in the orthorhombic space group *Cmc*2$_1$ with a = 22.213 (6) Å, b = 11.418 (3) Å, c = 8.180 (1) Å, and Z = 4. Arsolane **7** crystallizes in the monoclinic space group *C*2/*m* with a = 7.683 (2) Å, b = 24.221 (7) Å, c = 6.986 (2) Å, β = 124.77 (2)°, and Z = 4. The final conventional unweighted residuals were 0.023 (**5**), 0.031 (**6**), and 0.044 (**7**).

INTRODUCTION

With the recent advance in the structural chemistry of new five-coordinated arsenic compounds,[1] it is apparent that arsoranes form a continuous series of geometries extending from the trigonal bipyramid (TBP) to the square or rectangular pyramid (RP). Various ligand alterations and their influence on the geometry at arsenic in the pentacoordinated state have been studied.[2–7] These include varying the number of rings attached to arsenic,[2] varying the kind of directly attached ring atom,[4,5] changing the nature of the acyclic ligand,[1,3,4,6] and the inclusion of hydrogen bonding[1,3] and steric effects.[1] Saturated and unsaturated rings also have been studied.[1,3,4]

As with phosphoranes, the square-pyramidal structure is reached[4] only when a spirocyclic derivative contains unsaturated five-membered rings with like atoms in any one ring directly attached to the central atom. The reasons for this stabilization, which were formulated earlier,[8] are found to apply to all main-group elements where pentacoordination has been adequately studied. Specifically, this "rule" applies to the main-group 14[41] elements, silicon,[9–11] germanium,[12–14] and tin[15,16] and to the main-group 15[41] elements, phosphorus[17–19] and arsenic.[1,4] It would be

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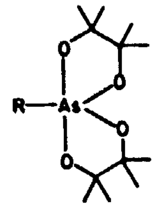
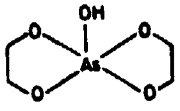
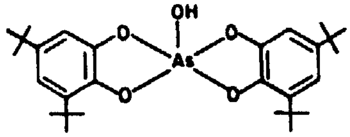


1[1], R = Me
2[3], R = Ph



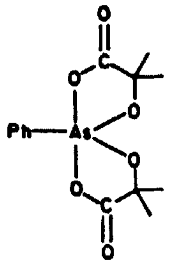
3[3]



4[1]

interesting to learn if the extent of ring unsaturation correlates with the degree of structural displacement toward the rectangular pyramid. Of the factors mentioned above for arsoranes the effect of ring saturation is not clear since the derivatives, which contain ring saturation (**1**–**3**), have either extensive ring substitution or hydrogen bonding present as complicating features. The hydroxyarsorane **4** also has hydrogen bonding as a structural influence.

To provide a more detailed assessment of ring saturation vs. unsaturation, the phenyl arsoranes $(Me_2C_2O_3)_2AsPh$, **5**, $(C_{10}H_6O_2)_2AsPh$, **6**, and $(C_2H_4O_2)_2AsPh$, **7**, were prepared and their X-ray structures determined. These derivatives, along with **2** and **8**,[4] provide a series of arsoranes with electron delocalization increasing in the order **2**, **7**, **5**, **8**, and **6**.



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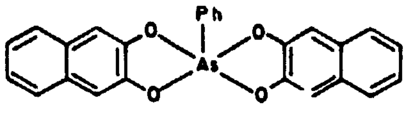

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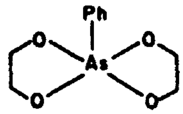
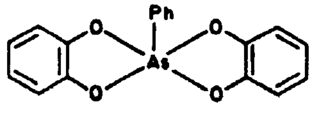


7



8[4]

EXPERIMENTAL

Proton NMR spectra were recorded on a Varian Model A-60 spectrometer on 10% (w/v) solutions of the samples in appropriate solvents using tetramethylsilane as the internal standard.

All X-ray crystallographic studies were done by using an Enraf-Nonius CAD4 diffractometer and graphite-monochromated molybdenum radiation ($\lambda(K\alpha_1)$ = 0.709 30 Å, $\lambda(K\alpha_2)$ = 0.713 59 Å) at an ambient temperature of 23 ± 2 °C. Details of the experimental and computational procedures have been described previously.[16]

2-Phenyl-2,2'-spirobi(4,4-dimethyl-5-oxo-1,3,2-dioxa-λ^5-arsolane), $(Me_2C_2O_3)_2AsPh$, **5**. To a solution of 2-hydroxyisobutyric acid (1.04 g, 10 mmol) in benzene (50 mL) was suspended phenylarsonic acid (1.01 g, 5 mmol), and the resulting mixture was heated under reflux with vigorous stirring for 1 h to obtain a clear solution. The water liberated in the reaction was azeotropically removed from the reaction flask by a Dean–Stark separator. Evaporation of solvent from the reaction mixture in vacuo gave a viscous liquid which solidified when hexane (5 mL) was added and shaken. The white solid left after evaporating the added hexane *in vacuo* was dissolved in a minimum volume of acetone at room temperature, and the solution was filtered. On cooling the filtrate at 0 °C overnight in a refrigerator, well-defined white crystals of **5** deposited: mp 141–142 °C (lit.[20] mp 138.2 °C) (yield 1.67 g, 94%); ^1H NMR ($CDCl_3$) 8.15 (m, 2 H, ortho protons of AsPh), 7.75 (m, 3 H, meta and para protons of AsPh), 1.65 (s, 6 H, CH_3 protons on the spirocyclic rings and away from the AsPh group), 1.45 (s, 6 H, CH_3 protons on the spirocyclic rings and adjacent to the AsPh group) ppm. Anal. Calcd for $C_{14}H_{17}O_6As$: C, 47.2; H, 4.81. Found: C, 47.32; H, 4.97.

2-Phenyl-2,2'-spirobi(1,3,2-naphthodioxarsole), $(C_{10}H_6O_2)_2AsPh$, **6**. To a suspension of pheynlarsonic acid (1.01 g, 5 mmol) in benzene (100 mL) was added 2,3-dihydroxynaphthalene (1.6 g, 10 mmol), and the resulting mixture was heated under reflux for 4 h. The water liberated in the reaction was removed azeotropically by a Dean–Stark separator. After 15 min of refluxing the reaction mixture, a clear pale yellow solution was obtained. On continuing to reflux further, a pale yellow crystalline precipitate formed. Evaporation of the benzene from the reaction mixture gave a pale yellow powder which was dissolved in 150 mL of boiling toluene, and the pale yellow solution was filtered hot. The amorphous residue was rejected. On cooling the solution, finely divided pale yellow crystals of **6** deposited; mp >250 °C (yield 1.0 g, 43%). The relative insolubility of **6** in common organic solvents at room temperature precluded NMR measurements. Anal. Calcd for $C_{26}H_{17}O_4As$: C, 66.7; H, 3.66. Found: C, 68.03; H, 3.79.

2-Phenyl-2,2'-spirobi(1,3,2-dioxa-λ^5-arsolane), $(C_2H_4O_2)_2AsPh$, **7**. The arsorane **7** was prepared according to Salmi et al.[21] similar to the procedure outlined for **5**. The white solid product that formed in benzene was recrystallized from acetone at 0 °C. After several days, white crystals of **7** deposited: mp 106–107 °C (lit.[20] mp 105.5 °C); ^1H NMR ($CDCl_3$) 8.0 (m, 2 H, ortho protons of AsPh), 7.6 (m, 3 H, meta and para protons of AsPh), 3.55–4.25 (complex multiplet, 8 H, CH_2 protons of ethylenedioxy groups) ppm.

The separation of the ortho proton resonances from those of meta and para protons indicated the pentacoordination of the arsenic atom in $PhAs(C_2H_4O_2)_2$.[21]

X-ray Crystallographic Studies for $(Me_2C_2O_3)_2AsPh$, **5**. Crystal data: $C_{14}H_{17}O_6As$, colorless crystal (0.28 × 0.30 × 0.35 mm), monoclinic space group $C2/c[C^6_{2h}$—No. 15],[22] a = 11.622 (3) Å, b = 17.480 (4) Å, c = 7.372 (1) Å, β = 93.12 (2)°, Z = 4, and $\mu_{MoK\bar{\alpha}}$ = 2.425 mm^{-1}. A total of 1718 independent reflections ($+h, +k, \pm l$) were measured by using the θ–2θ scan mode for $2° \leq 2\theta_{MoK\bar{\alpha}} \leq 55°$. No corrections were made for absorption.

The structure was solved by using a combination of direct methods (MULTAN) and difference Fourier techniques and was refined by full-matrix least squares.[23] The 12 independent non-hydrogen atoms were refined anisotropically. The 9 independent hydrogen atoms (coordinates obtained by a combination of difference Fourier techniques and calculation) were included in the refinement as fixed isotropic scatters. Calculated coordinates were updated as refinement converged so that the final C—H bond lengths were 0.98 Å. The final agreement factors[24] were R = 0.023 and R_w = 0.035 for the 1583 reflections having $I \geq 2\sigma_I$. A final difference Fourier synthesis showed a maximum density of 0.283 e/Å^3.

X-ray Crystallographic Studies for $(C_{10}H_6O_2)_2AsPh$, **6**. Crystal data: $C_{26}H_{17}O_4As$, colorless crystal (0.16 × 0.22 × 0.33 mm), orthorhombic space group $Cmc2_1$ [C^{12}_{2v}—No. 36],[25] a = 22.213 (6) Å, b = 11.418 (3) Å, c = 8.180 (1) Å, Z = 4, and $\mu_{MoK\bar{\alpha}}$ = 1.763 mm^{-1}. A total of 951 independent reflections ($+h, +k, +l$) were measured in the same manner as for **5**. No corrections were made for absorption.

The structure was solved by using standard Patterson and difference Fourier techniques and was refined by full-matrix least squares.[23] The 19 independent non-hydrogen atoms were refined anisotropically, while the 11 independent hydrogen atoms were included in the refinement as fixed isotropic scatters (calculated coordinates, updated as for **5**). The final agreement factors[24,26] were $R = 0.031$ and $R_w = 0.039$ for the 826 reflections having $I \geq 2\sigma_I$. A final difference Fourier synthesis showed a maximum density of 0.305 e/Å^3.

X-ray Crystallographic Studies for $(C_2H_4O_2)_2AsPh$, *7*. Crystal data: $C_{10}H_{13}O_4As$, colorless crystal (0.15 × 0.18 × 0.37 mm), monoclinic space group $C2/m[C^3_{2h}$—No. 12],[27] $a = 7.683$ (2) Å, $b = 24.221$ (7) Å, $c = 6.986$ (2) Å, $\beta = 124.77$ (2)°, $Z = 4$, and $\mu_{\mathrm{MoK}\bar{\alpha}} = 3.350$ mm^{-1}. A total of 964 independent reflections $(+h, +k, \pm l)$ were measured by using the θ–2θ scan mode for $2° \leq 2\theta_{\mathrm{MoK}\bar{\alpha}} \leq 50°$. No corrections were made for absorption.

The structure was solved and refined in the same manner as for **5**. The As, O, and phenyl ring atoms conform to the $C2/m$ space group symmetry and these atoms (seven independent non-hydrogen atoms anisotropic and three independent H atoms isotropic, fixed) were included in the refinement in full occupancy for their respective positions. The ethylene groups conform to the twofold symmetry but are disordered, having two sets of positions. Each independent pair of ethylene carbon atoms was refined anisotropically in half occupancy. Ethylene H atoms were omitted from the refinement. The final agreement factors[24] were $R = 0.044$ and $R_w = 0.057$ for the 868 reflections having $I \geq 2\sigma_I$. A final difference Fourier synthesis showed a maximum density of 0.719 e/Å^2.

RESULTS

The atom labeling scheme for **5** is given in the ORTEP plot of Figure 1. Atomic coordinates are given in Table I, while selected bond lengths and angles are given in Table II. The corresponding information for **6** is given in Figure 2, Table III,

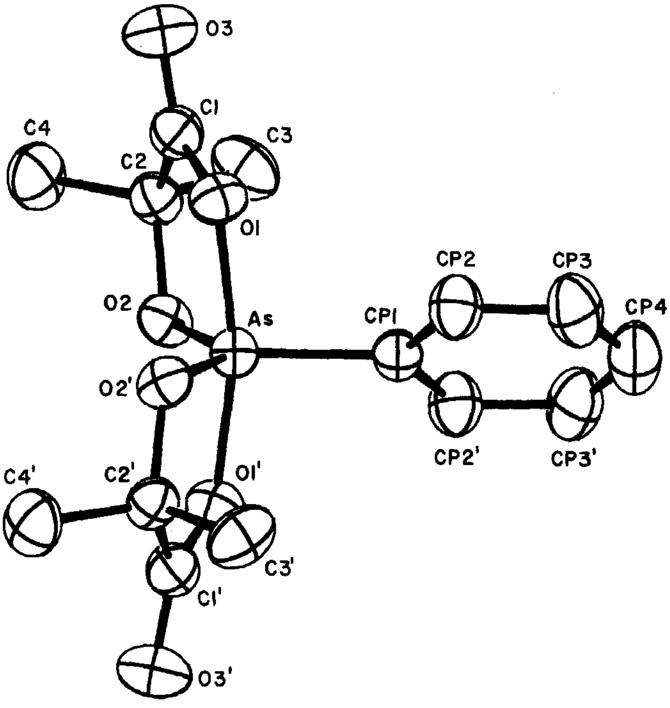


FIGURE 1 ORTEP plot of $(Me_2C_2O_3)_2AsPh$, **5**, with thermal ellipsoids at the 50% probability level. Primed atoms are related to unprimed ones by $-x, y, \frac{1}{2} - z$. Hydrogen atoms are omitted for purposes of clarity.

TABLE I

Atomic Coordinates in Crystalline $(Me_2C_2O_3)_2AsPh$, 5[a]

atom type[b]	coordinates 10^4x	 10^4y	 10^4z
As	0[c]	3284.2 (2)	2500[c]
O1	1569 (1)	3405 (1)	3095 (2)
O2	210 (1)	3752 (1)	457 (2)
O3	3173 (2)	3803 (1)	1881 (3)
C1	2155 (2)	3684 (1)	1740 (3)
C2	1406 (2)	3826 (1)	11 (3)
C3	1659 (3)	3225 (2)	−1409 (4)
C4	1582 (3)	4635 (2)	−686 (4)
CP2	554 (3)	1809 (1)	3939 (4)
CP3	538 (3)	1014 (2)	3920 (4)
CP1	0[c]	2194 (2)	2500[c]
CP4	0[c]	617 (2)	2500[c]

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 1.
[c] Fixed.

TABLE II

Selected Bond Lengths (Å) and Bond Angles (deg) for $(Me_2C_2O_3)_2AsPh$, 5[a]

type[b]	length	type	angle
As-CP1	1.905 (3)	O1-As-O1'	167.0 (1)
As-O1	1.864 (2)	O2-As-O2'	124.0 (1)
As-O2	1.743 (1)	O2-As-CP1	118.0 (1)
C1-O3	1.200 (3)	O1-As-CP1	96.5 (1)
C1-O1	1.332 (3)	O1-As-O2	88.3 (1)
C2-O2	1.452 (3)	O1-As-O2'	85.7 (1)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 1.

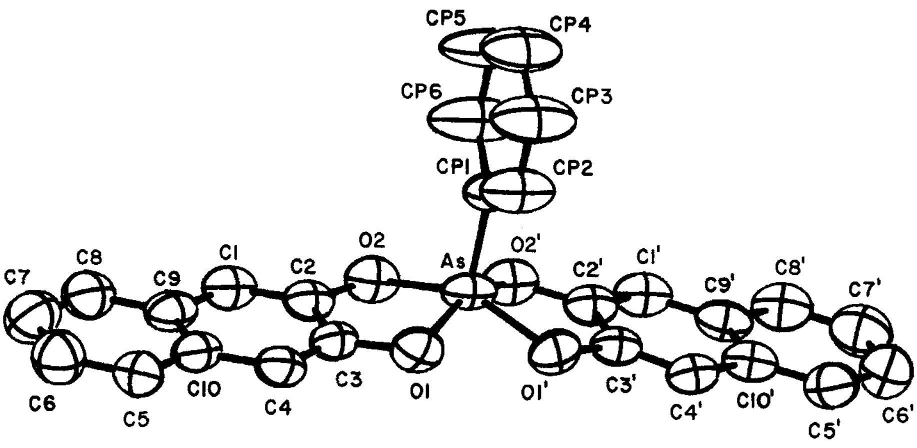


FIGURE 2 ORTEP plot of $(C_{10}H_6O_2)_2AsPh$, 6, with thermal ellipsoids at the 50% probability level. Primed atoms are related to unprimed ones by $2 - x, y, z$. Hydrogen atoms are omitted for purposes of clarity.

TABLE III

Atomic Coordinates in Crystalline $(C_{10}H_6O_2)_2AsPh$, 6[a]

atom type[b]	coordinates 10⁴x	10⁴y	10⁴z
As	10000[c]	8338.5 (5)	7500[c]
O1	9456 (2)	9490 (3)	7229 (6)
O2	9456 (3)	7592 (3)	8759 (5)
CP1	10000[c]	7529 (6)	5491 (9)
CP2	10000[c]	8140 (7)	4089 (12)
CP3	10000[c]	7600 (9)	2601 (22)
CP4	10000[c]	6457 (8)	2514 (28)
CP5	10000[c]	5816 (10)	3886 (17)
CP6	10000[c]	6345 (9)	5410 (13)
C1	8372 (4)	7603 (5)	9127 (7)
C2	8886 (4)	8059 (5)	8563 (7)
C3	8887 (3)	9148 (4)	7701 (11)
C4	8377 (3)	9734 (4)	7413 (16)
C5	7275 (4)	9803 (5)	7603 (20)
C6	6747 (4)	9328 (7)	8082 (10)
C7	6741 (5)	8242 (7)	8960 (12)
C8	7272 (5)	7692 (6)	9299 (9)
C9	7821 (4)	8164 (5)	8824 (8)
C10	7821 (4)	9261 (5)	7933 (7)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 2.
[c] Fixed.

TABLE IV

Selected Bond Lengths (Å) and Bond Angles (deg) for $(C_{10}H_6O_2)_2AsPh$, 6[a]

type[b]	length	type	angle
As-CP1	1.886 (8)	O1-As-O2′	150.0 (2)
As-O1	1.800 (4)	O1-As-O2	88.0 (2)
As-O2	1.802 (4)	O1-As-O1′	84.4 (3)
O1-C3	1.377 (8)	O2-As-O2′	84.2 (3)
O2-C2	1.383 (8)	CP1-As-O1	104.5 (2)
		CP1-As-O2	105.4 (2)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 2.

and Table IV, while the corresponding information for 7 is given in parts a and b of Figure 3, Table V, and Table VI. Anisotropic thermal parameters, parameters for hydrogen atoms, remaining bond lengths and angles, and deviations from selected least-squares mean planes are provided as supplementary material.

DISCUSSION

Basic Structures

The oxoarsolane 5 has crystallographic C_2 symmetry with As, CP1, and CP4 lying on a crystallographic twofold axis. The geometry about the As atom is close to a trigonal bipyramid which has O1 and O1′ in axial positions and CP1, O2, and O2′

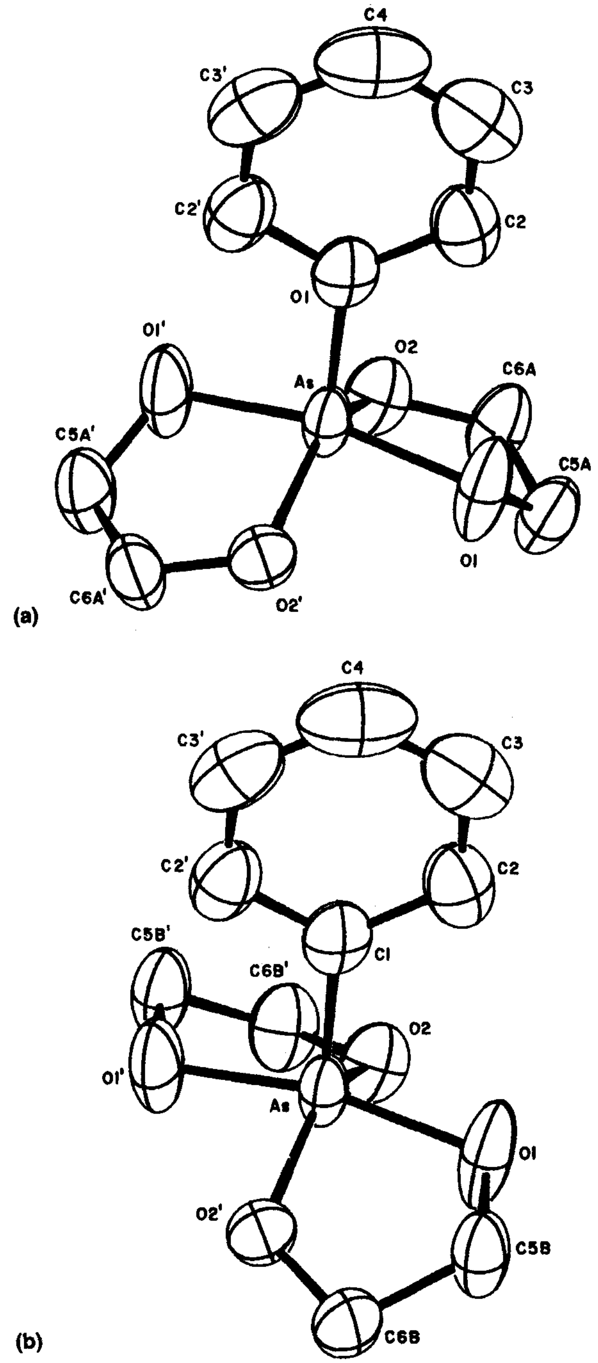


FIGURE 3 (a) ORTEP plot of the "A" conformation of $(C_2H_4O_2)_2AsPh$, 7, with thermal ellipsoids at the 50% probability level. Primed atoms are related to unprimed ones by $-x, y, -z$. Hydrogen atoms are omitted for purposes of clarity. (b) ORTEP plot of the "B" conformation of $(C_2H_4O_2)_2AsPh$, 7, with thermal ellipsoids at the 50% probability level. Primed atoms are related to unprimed ones by $-x, y, -z$. Hydrogen atoms are omitted for purposes of clarity.

TABLE V

Atomic Coordinates in Crystalline $(C_2H_4O_2)_2AsPh$, 7[a]

atom type[b]	**coordinates**		
	10^4x	**10^4y**	**10^4z**
As	**0[c]**	**1050.0 (3)**	**0[c]**
O1	**1629 (6)**	**949 (2)**	**3113 (6)**
O2	**2117 (5)**	**753 (1)**	**27 (6)**
C1	**0[c]**	**1843 (3)**	**0[c]**
C2	**1605 (9)**	**2130 (3)**	**1896 (9)**
C3	**1578 (11)**	**2700 (3)**	**1868 (12)**
C4	**0[c]**	**2980 (4)**	**0[c]**
C5A[d]	**3282 (17)**	**613 (5)**	**3864 (17)**
C6A[d]	**3861 (16)**	**635 (5)**	**2113 (18)**
C5B[d]	**203 (17)**	**883 (5)**	**3921 (17)**
C6B[d]	**−1861 (16)**	**612 (5)**	**2035 (17)**

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 3. [c] Fixed. [d] Half occupancy.

TABLE VI

Selected Bond Lengths (Å) and Bond Angles (deg) for $(C_2H_4O_2)_2AsPh$, 7[a]

type[b]	**length**	**type**	**angle**
As-O1	**1.803 (4)**	**O1-As-O1′**	**164.4 (3)**
As-O2	**1.769 (3)**	**O2-As-O2′**	**132.0 (2)**
As-C1	**1.921 (7)**	**O1-As-O2**	**86.0 (2)**
		O1-As-O2′	**87.7 (2)**
		C1-As-O1	**97.8 (2)**
		C1-As-O2	**114.0 (3)**

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 3.

in equatorial sites. The geometry actually lies between trigonal bipyramidal (TBP) and a rectangular pyramid (RP) having four basal oxygen atoms. In terms of the Berry coordinate,[28] the geometry is displaced 21.4% (23.3% using unit vectors) from the TBP to the RP based on the dihedral angle method,[17,18,29] where CP1 is the pivotal atom in the Berry pseudorotation process. The trigonal-bipyramidal nature of the geometry is in evidence in the As—O bond lengths. The axial As—O1 bonds [1.864 (2) Å] are significantly longer than the equatorial As—O2 bonds [1.743 (1) Å].

The atoms As, CP1, O1, and O1′ (plane 2, Table D) are required by symmetry to be coplanar. Similarly the atoms As, CP1, O2, and O2′ (plane 1, Table D) are required to be coplanar. The dihedral angle between these two planes is 88.5°, which is in the expected range for geometries which follow the C_{2v} constraint[30] of the Berry coordinate.

The phenyl ring (plane 6, Table D) is rotated about 45° out of the equatorial plane. The dihedral angles between the plane of the phenyl group and planes **1** and **2** mentioned above are 41.0° and 47.6°, respectively.

The five-membered rings in the structure are not planar, but envelope shaped.

The atoms As, O1, C1, C2, and O3 (plane 3, Table D) are coplanar to within ±0.006 Å, while O2 is displaced 0.245 Å out of this plane in a direction toward O2′.

The naphthodioxarsole **6**, which represents a new substance, has crystallographic C_s symmetry, with the As atom and the phenyl group lying on the crystallographic mirror plane. The geometry about the As atom is essentially rectangular pyramidal (oxygen atoms basal, CP1 apical). This is demonstrated by the value of the two trans basal angles, 150.0 (2)°. These angles are required by symmetry to be equal. Similarly, the four basal oxygen atoms are required by symmetry to be coplanar. The As atom is displaced 0.466 Å out of this plane (plane 3, Table H) in the direction of the phenyl group. In agreement with the RP geometry of **6**, the As—O bond lengths [1.802 (4), 1.800 (4) Å] are equal within the limits of the error.

The arsolane **7** has crystallographic C_2 symmetry with As, C1, and C4 lying on a crystallographic twofold axis. The geometry about the As atom lies on the coordinate connecting TBP (O1 and O1′ in axial positions; C1, O2, and O2′ in equatorial sites) to the RP (4 basal oxygen atoms), where C1 is the pivotal atom in the Berry pseudorotation process. The percent displacement along this coordinate is 39.6% (41.9% using unit vectors) from the TBP to the RP.

The atoms As, O1, O1′, and C1 (plane 2, Table L) are required by symmetry to be coplanar as are the atoms As, O2, O2′, and C1 (plane 1, Table L). The dihedral angle between these two planes is 89.1°, in agreement with a displacement along the Berry coordinate. The plane of the phenyl ring (plane 3, Table L), planar to within ±0.001 Å, makes dihedral angles of 23.3° and 65.8° with these planes, respectively.

Residual trigonal-bipyramidal character is apparent in the As—O bond lengths, which are longer for the axial bonds [1.803 (4) Å] than for the equatorial ones [1.769 (3) Å].

While the As, O, and phenyl ring atoms conform (in an experimentally determinable sense) to the *C2/m* space group symmetry, the molecules have two possible conformations which differ only in the positions of the atoms of the ethylene bridges. On the average, these conformers are superposed to conform to the space group symmetry. Examination of intermolecular contacts indicates that each conformer should be present in 50% abundance. Translationally related molecules along *c* must have opposite conformations while translationally related molecules along *a* must have the same conformation (Figure 4). At first sight, this ordering in a given layer would seem to imply that the *c* axis should be doubled. However, the packing in the *b* direction involves stacking of inversion related phenyl rings whose positions are not sensitive to the conformation (Figure 5). Therefore, the ordered layers are stacked in a random fashion, resulting in the observed average structure.

Ligand Influences

The geometries of phenyl-substituted arsoranes containing directly attached ring oxygen atoms show increasing displacement from the trigonal bipyramid toward the rectangular pyramid in the order **2** < **5** < **7** < **8** ~ **6** (Table VII). This order parallels the order of increasing electron delocalization provided by the ring system

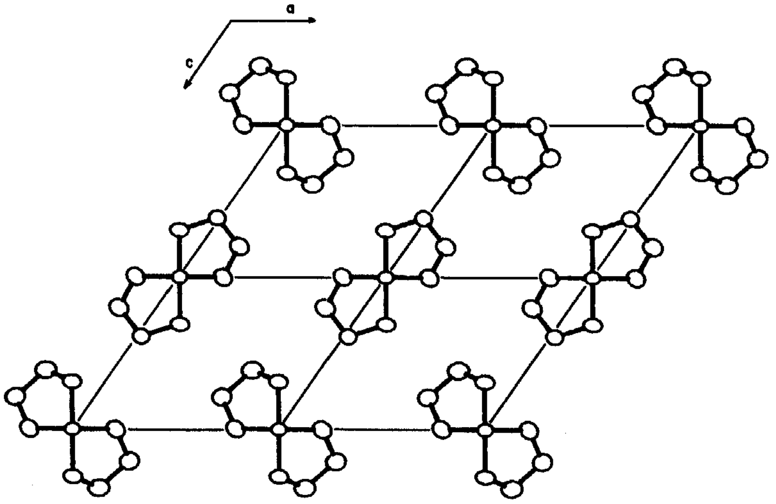


FIGURE 4 ORTEP plot of $(C_2H_4O_2)_2AsPh$, 7, showing the ordered alternation of conformation along c for layers parallel to the ac plane. Phenyl groups are omitted. A layer passing through four unit cells is shown.

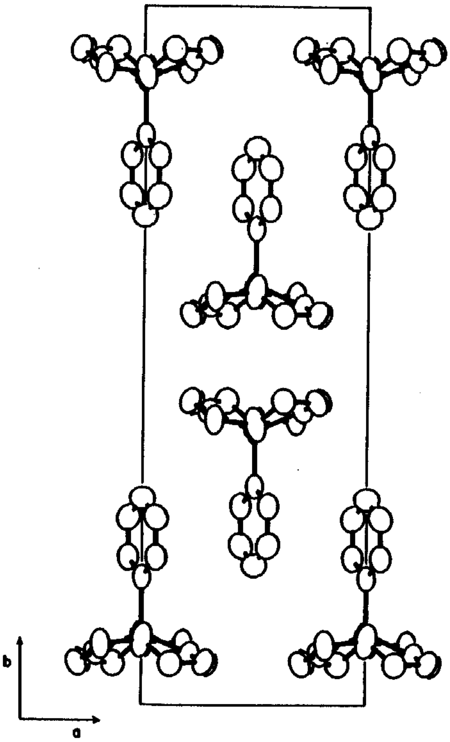
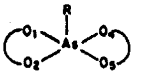


FIGURE 5 Unit cell diagram of $(C_2H_4O_2)_2AsPh$, 7, with the "A" and "B" conformations superimposed. Layers of conformationally insensitive phenyl groups separate the ordered layers and permit translationally related molecules along b to have different conformations.

TABLE VII

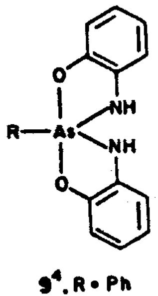
Axial and Equatorial Angles (θ), Dihedral Angles (δ) (deg), and As—O Bond Lengths (Å) for Arsoranes



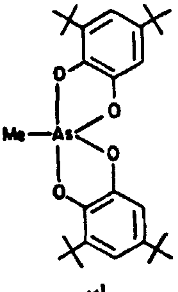
compd	δ_{24}	θ_{15}	θ_{24}	As-O$_{ax}$[a]	As-O$_{eq}$[a]	Δ(ax − (eq)	% (TBP→RP)[b]	ref[c]
14[d]	53.3	175.4	111.4	2.770 (5)				2
1	45.7	173.1	122.6	1.822 (1) 1.816 (5)	1.761 (2) 1.758 (4)	0.061 0.058	12.9	1
2	42.6	169.8	123.0	1.792 (1) 1.817 (5)	1.737 (2) 1.763 (4)	0.055 0.054	18.0	3
11[e]	40.3	168.3	124.3	1.835 (1) (5)	1.784 (2) (4)	0.051	22.5	1
9	41.0	171.8	127.3	1.896 (1) 1.863 (5)			22.9	4
10	40.2	169.6	125.9	1.860 (1) 1.893 (5)			23.3	5
5[e]	39.5	167.0	124.0	1.864 (1) (5)	1.743 (2) (4)	0.121	23.3	this work
7[e]	30.6	164.4	132.0	1.803 (1) (5)	1.769 (2) (4)	0.034	41.9	this work
4	30.3	167.8	135.8	1.785 (1) 1.830 (5)[g]	1.770 (2) 1.768 (4)	0.015	44.4	1
3	22.8	164.0	140.4	1.792 (1) 1.775 (5)	1.755 (2) 1.792 (4)[g]	0.037	58.6	3
13	15.2	158.6	143.1	1.834 (1) 1.798 (5)	1.794 (2) 1.798 (4)	0.040 0.000	72.2	6
8A[f]	2.8	152.1	149.3	1.816 (1) 1.816 (5)	1.809 (2) 1.797 (4)	0.007 0.019	94.8	4
8B[f]	0.3	151.0	150.7	1.809 (1) 1.806 (5)	1.809 (2) 1.810 (4)	0.000 −0.004	99.2	4
12	1.1	150.8	149.8	1.806 (1) 1.825 (5)	1.799 (2) 1.784 (4)	0.007 0.041	97.8	7
6[e]	0.0	150.0	150.0	1.802 (1) (5)	1.800 (2) (4)	0.002	99.4	this work

[a] The numbers in parentheses are atom identifications relative to the figure given below the table heading. [b] Based on unit bond distances. [c] These are references to the X-ray studies. [d] Compound 14 has a non-Berry distortion where both the axial and equatorial ligands move in the same direction. 14 also has a very long As–O bond length consistent with the fact that it is an arsonium ylide. Accordingly, data for 14 are not included in Figures 4–6. [e] Compounds 11, 5, and 7 contain crystallographic twofold axes about arsenic while 6 has a crystallographic mirror plane containing the arsenic atom and phenyl group. [f] There are two independent molecules per unit cell for arsorane 8. [g] Hydrogen bonded As–O bonds.

except for **5**. The latter arsorane, however, is the only member of the series that has asymmetrically substituted rings. The ligands are correctly positioned with the more electronegative carboxylate end situated axially in the trigonal bipyramid, in keeping with the electronegativity rule for this geometry.[31–33] In this sense, **5** behaves like the oxazarsoles **9**[4] and **10**[5], which are comparably displaced trigonal bipyramids (Table VII), having the less electronegative nitrogen atoms at equatorial sites, similar to that observed for phosphoranes.[34,35] Consequently, this study supports the finding that when like atoms directly attached to the central atom are involved in a spirocyclic system of five-membered rings, the rectangular pyramidal geometry is progressively approached as electron delocalization increases in the ring system.[8,18]



9[4], R = Ph
10[5], R = Me



11'[1]

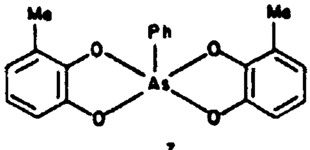
As already discussed,[1] the presence of electron donating groups substituted on the rings, as in **11**, is expected to enhance the charge at arsenic producing greater As—O bond electron pair repulsion effects which causes the structure to shift toward the trigonal bipyramid (Table VII).[36]

The structure of the phenylarsolane **7** provides an interesting comparison with the structure of the related anionic siliconate $[(C_2H_4O_2)_2SiPh]_2[H_3N(CH_2)_6NH_3]$.[10] The latter is displaced 72.1% toward the trigonal bipyramid compared to 41.9% for **7**. Besides the negative charge residing on the siliconate, three of the Si—O bonds are involved in hydrogen bonding with N—H linkages of the cation. Because **7** lacks these intermolecular perturbances, it is suggested that their influence in the siliconate is to further displace the structure toward the RP.

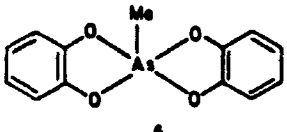
Distortion Coordinate

A convenient measure of structural distortion for pentacoordinated molecules[17,29,37] is obtained by plotting the values of the trans basal angles θ_{15} and θ_{24} of the RP (which are axial and equatorial angles with reference to the TBP) vs. the dihedral angle δ_{24}.[38]

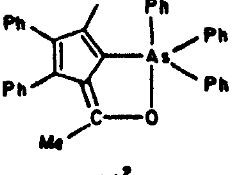
Figure 6 shows a θ vs. δ_{24} plot for pentacoordinated arsenic compounds which have been structurally characterized by X-ray analysis. These data are summarized in Table VII. The formulas **12–14** not previously identifed are shown below. The lines shown are determined by the θ values of 120° and 180° for the ideal trigonal bipyramid, which has δ_{24} = 53.1°, and θ values of 151.4° for the "limiting" rec-



12[7]



13[6]



14[2]

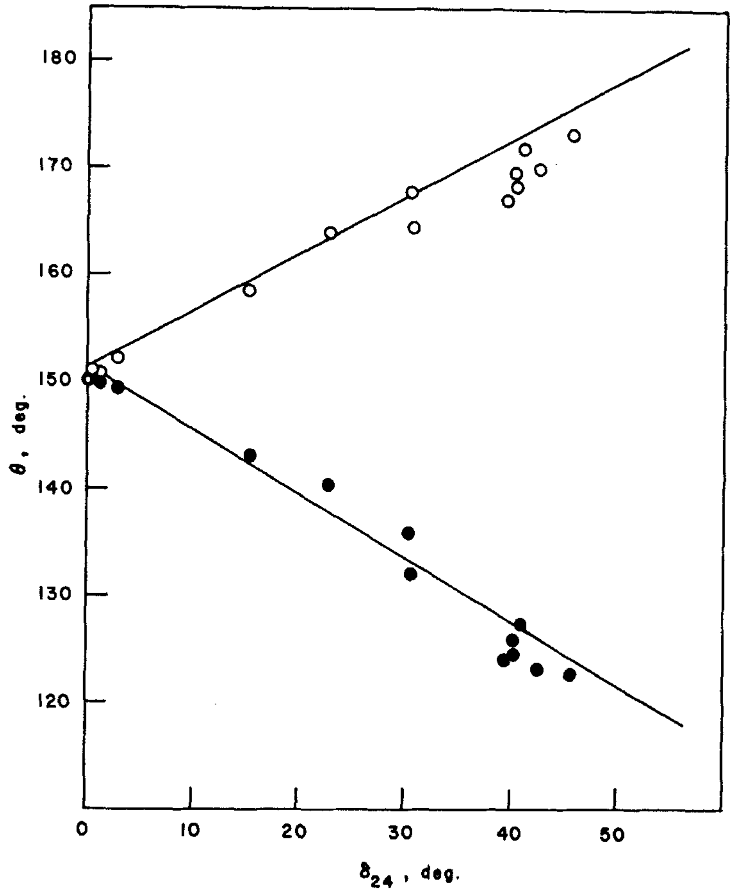


FIGURE 6 Variations of the axial angle θ_{15} (open circles) and equatorial angle θ_{24} (filled circles) vs. the dihedral angle δ_{24} as structural distortion for pentacoordinated arsenic(V) compounds listed in Table VII proceeds along the Berry coordinate from a rectangular pyramid toward a trigonal bipyramid. The partially filled circle is a θ_{15} and a θ_{24} point. Arsorane **14** which has a non-Berry distortion (see footnote *d* to Table VII) is not included. The least-squares lines, $\theta_{15} = 0.4666\delta_{24} + 151.0$ and $\theta_{24} = -0.6605\delta_{24} + 151.8$, give a value of 151.4° for the θ angle for the "limiting" rectangular pyramid.

tangular pyramid. The latter value is obtained from a least-squares fit to the data. The least-squares lines are given in the caption for Figure 6. It is seen that the Berry coordinate is well followed for arsoranes. A comparison of this type of plot for phosphoranes[17,18,29] and five-coordinated silicon compounds[10] indicates a similar scatter of points as well as a "limiting" rectangular pyramid with a trans basal θ angle of 152°.

A more elaborate means of expressing geometrical distortion is to use the sum of dihedral angle method which has been adequately described.[17] Comparison of the dihedral angle sum for a compound of interest $\Sigma_i|\delta_i(\mathrm{C}) - \delta_i(\mathrm{TBP})|$ with a similar sum, $R = \Sigma_i|\delta_i(\mathrm{TBP}) - \delta_i(\mathrm{RP})|$ (which is equal to 217.7° when $\theta = 150°$), for the two "idealized" geometries for pentacoordinated derivatives allows the calculations of a percent displacement between these two geometries from the TBP to the RP. A dihedral angle plot obtained from application of this method on a common reference scale[17] is given in Figure 7 for the arsoranes listed in Table VII. Again, the Berry coordinate is seen to be followed closely.

As the structures become more rectangular pyramidal, the axial and equatorial ring As—O bond lengths converge (Table VII). This is shown graphically in Figure 8 where the axial-equatorial bond difference, Δ, is expressed as a function of the dihedral angle δ_{24}. Since hydrogen bonding causes a lengthening of the affected As—O bonds,[11] these bonds are not included in obtaining Δ values. Such interactions are present for one of the ring As—O bonds in each of the hydroxyl derivatives **3** and **4** (Table VII).

By treating the axial and equatorial ring As—O bond length data separately, a range of 0.06 Å is obtained for As—O equatorial bond lengths and a value of 1.805 Å is indicated for the "limiting" RP. The least-squares equation is $\text{As—O}_{eq} = -0.00107\delta_{24} + 1.803$. A comparison with phosphoranes[17] and the isoelectronic five-coordinated anionic silicates[11] shows a 0.04 and 0.05 Å range, respectively, for equatorial ring M—O bond lengths. The axial As—O bond lengths in Table VII exhibit too much scatter to obtain a meaningful comparison.

In summary, it is found that arsoranes exhibit solid-state structural distortions paralleling distortions reported for phosphoranes and five-coordinated anionic silicates.[10,11] For the most part, the structural variations are understandable in terms

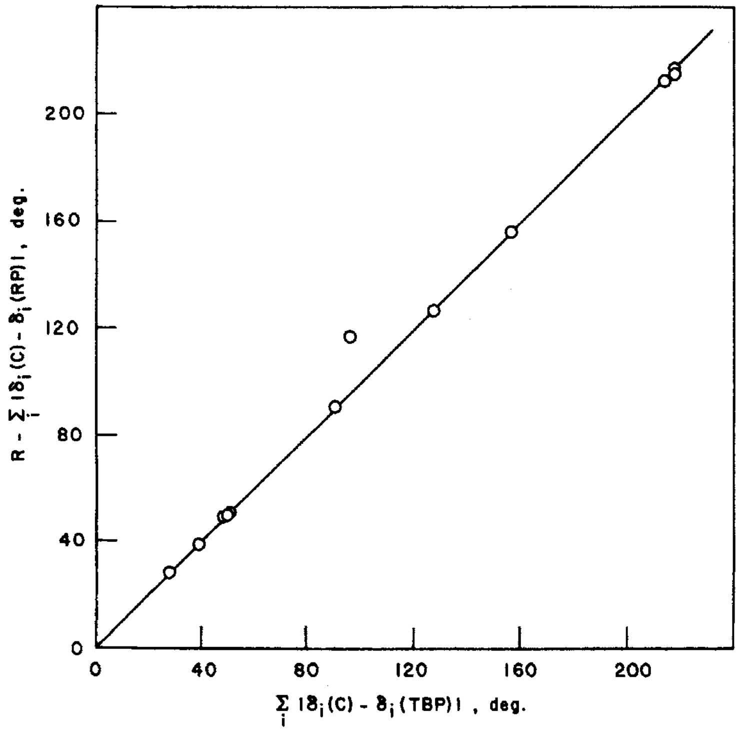


FIGURE 7 The sum of dihedral angles for pentacoordinated arsenic(V) compounds listed in Table VII from a rectangular-pyramidal geometry vs. the sum from a trigonal bipyramid on a common reference scale. The fifth circle from the left represents coincident data from two compounds.

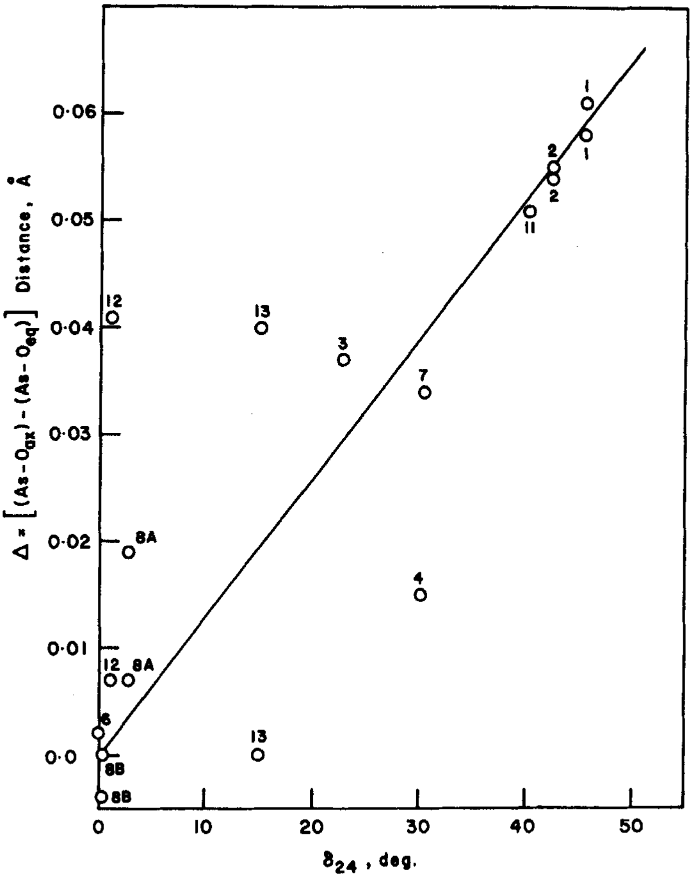


FIGURE 8 The differences in axial and equatorial ring As—O bond lengths (Δ) for the non-hydrogen-bonded As—O bonds vs. the dihedral angle δ_{24}. The numbers refer to compound entries in Table VII. The least-squares line is $\Delta = 0.001032\delta_{24} + 0.007458$. Entry 5 was excluded since it deviated greatly from the least-squares line.

of substituent effects.[1,4] The "limiting" rectangular pyramid, like that for five-coordinated phosphorus[18,29] and silicon,[10] has a trans basal angle close to 152°. This contrasts with the geometry of five-coordinated transition-metal complexes where θ values for the rectangular pyramid are found to vary in the range of 140°–175° depending on d orbital configurations.[39,40]

ACKNOWLEDGEMENT

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Registry No. **5**, 32049-50-6; **6**, 94843-94-4; **7**, 61381-30-4; 2-hydroxyisobutyric acid, 594-61-6; phenylarsonic acid, 98-05-5; 2,3-dihydroxynaphthalene, 92-44-4.

Supplementary Material Available: Table A, thermal parameters for $(Me_2C_2O_3)_2AsPh$, **5**, Table B, hydrogen atom parameters for **5**, Table C, additional bond lengths and angles for **5**, Table D, deviations from selected least-squares mean planes for **5**, Table E, thermal parameters for $(C_{10}H_6O_2)_2AsPh$, **6**, Table F, hydrogen atom parameters for **6**, Table G, additional bond lengths and angles for **6**, Table H, deviations from selected least-squares mean planes for **6**, Table I, anisotropic thermal parameters for $(C_2H_4O_2)_2AsPh$, **7**, Table J, hydrogen atom parameters for **7**, Table K, additional bond lengths and angles for **7**, Table L, deviations from least-squares mean planes for **7**, and a listing of observed and calculated structure factor amplitudes for **5–7** (26 pages). Ordering information is given on any current masthead page.

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but becomes 0° as edge 24 disappears on forming the RP.

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