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CRYSTAL STRUCTURES OF TWO PHENYL SPIROARSORANES. THE FIRST TRULY RECTANGULAR-PYRAMIDAL ARSENIC(V) COMPOUND

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CRYSTAL STRUCTURES OF TWO PHENYL SPIROARSORANES. THE FIRST TRULY RECTANGULAR-PYRAMIDAL ARSENIC(V) COMPOUND¹

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Single-crystal X-ray analysis of 2-phenyl-2,2'-spirobi(1,3,2-benzodioxarsole), (C₆H₄O₂)₂AsPh (**5**), and 2-phenyl-2,2'-(3*H*,3'*H*)-spirobi(1,3,2-benzoxazarsole), (C₆H₄ONH)₂AsPh (**6**), reveals, respectively, a rectangular-pyramidal structure and a trigonal-bipyramidal structure. **5** crystallizes in the monoclinic space group, *P*2₁/*c*, with *a* = 16.787 (5) Å, *b* = 6.767 (3) Å, *c* = 27.374 (6) Å, β = 90.37 (2)°, and *Z* = 8. The structure was refined to *R* = 0.041, *R*_w = 0.060 and showed two independent molecules per asymmetric unit. The displacement along the Berry coordinate for the two molecules, based on unit bond distances, is 99.2% and 94.8% from the trigonal bipyramid toward the rectangular pyramid. For **6**, the orthorhombic space group, *Pbca*, is obtained with *a* = 10.933 (1) Å, *b* = 10.726 (1) Å, *c* = 26.710 (3) Å, and *Z* = 8. The structure refined to *R* = 0.032, *R*_w = 0.043 and is displaced 22.9% from the trigonal bipyramid toward the rectangular pyramid. Comparisons between related group 5A pentacoordinated compounds indicate that structural principles found for phosphoranes apply thus far to arsenic(V) and antimony(V) derivatives. Molecular mechanics calculations on related spirocyclic phosphoranes and arsoranes support this conclusion.

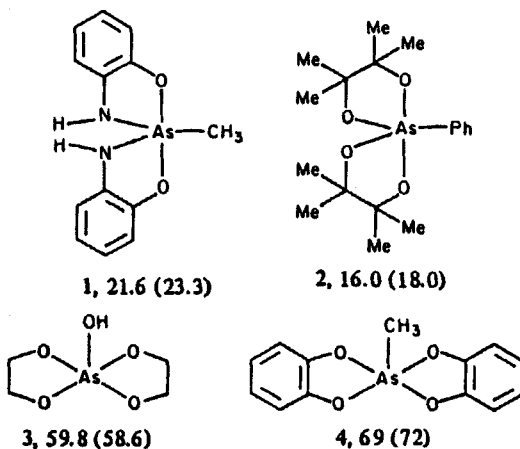
Consideration of dynamic stereochemistry of pentacoordinated arsenic(V) compounds has been hampered by a lack of a well-defined structural basis. In the case of phosphoranes, the extensive structural basis that was developed² provided a quantitative model³ upon which dynamic behavior inferred from NMR investigations² could be systematically correlated. It is of interest to ascertain to what extent the underlying structural principles found for phosphoranes apply to arsoranes.

Some effort has been made in the latter context in learning if a range of structures exists for arsoranes like that for phosphoranes, which extends between the two prevalent five-coordinated geometries, the trigonal bipyramid and the rectangular pyramid.^{4,5} Thus far, only a few structures are known for five-coordinated arsenic(V) compounds. Ph₅As⁶ and AsF₅⁷ are trigonal bipyramids. The spiroarsoranes **1**⁸ and **2**⁹ are close to the ideal trigonal bipyramid, while the structures of **3**⁹ and **4**¹⁰ are displaced progressively more toward the rectangular pyramid. The numbers below the structures following the compound identification are a measure of the structural placement along the Berry coordinate from the trigonal bipyramid toward

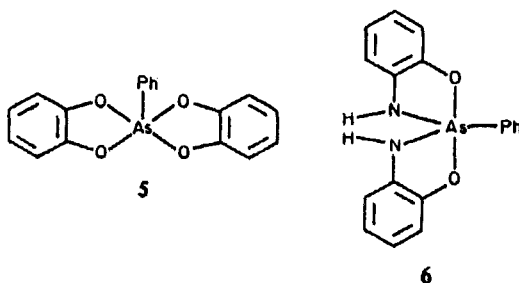
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the rectangular pyramid based on a dihedral angle method.⁴ Percentage displacement using actual bond distances is followed by the value in parentheses based on unit bond vectors. Owing to hydrogen bonding, **3** is dimeric in the solid⁹ and, consequently, may have some lattice distortions that enter into its structural placement.



To explore substituent effects to a greater extent, we report the X-ray analysis of the two spiroarsoranes, **5** and **6**, which are the phenyl derivatives of **4** and **1**, respectively. The structures of **5**¹¹ and **6**¹² in solution are indicated to be penta-coordinated from NMR data.

EXPERIMENTAL

All X-ray crystallographic studies were done with an Enraf-Nonius CAD4 diffractometer and graphite-monochromated molybdenum radiation (fine-focus tube, λ $K\alpha_1$ = 0.70930 Å, λ $K\alpha_2$ = 0.71359 Å). Details of the experimental procedures have been previously described.¹³

Crystallography of $(C_6H_4O_2)_2AsPh$ (5**).** 2-Phenyl-2,2'-spirobi(1,3,2-benzodioxarsole) (**5**) was prepared by the reaction of phenylarsonic acid and catechol in benzene solution according to our previous procedure.¹¹ A crystal having dimensions of 0.25 × 0.30 × 0.42 mm was cut from a larger light yellow lath and mounted inside a sealed thin-walled glass capillary as a precaution against moisture sensitivity. The diffraction symmetry ($2/m$) and the observed extinctions ($0k0$, $k = 2n + 1$, $h0l$, $l = 2n + 1$) were consistent with the uniquely determined space group $P2_1/c$ [C_{2h}^2 No. 14].¹⁴ The lattice constants based on 25 reflections having $10.31^\circ \leq \theta_{MoK\alpha} \leq 13.88^\circ$ and determined at $23 \pm 1^\circ C$ are $a = 16.787$ (5) Å, $b = 6.767$ (3) Å, $c = 27.374$ (6) Å, and $\beta = 90.37$ (2)°. A unit cell content of eight molecules gives

a calculated volume of 16.9 Å³ per nonhydrogen atom. The assignment of $Z = 8$ (two molecules per asymmetric unit) was confirmed by solution and refinement of the structure.

A total of 4050 independent reflections ($+h$, $+k$, $\pm l$) were measured by using the θ - 2θ scan mode for $2^\circ \leq 2\theta_{\text{MoK}\alpha} \leq 45^\circ$. Scan speeds varied from 0.74 to 4.0°/min, and six intensity control reflections were monitored. No corrections were made for absorption ($\mu_{\text{MoK}\alpha} = 2.33 \text{ mm}^{-1}$). The structure was solved by using Patterson and difference Fourier techniques and refined by full-matrix least squares.^{15a} The 46 independent nonhydrogen atoms were refined anisotropically. The 26 independent hydrogen atoms (calculated coordinates) were included as fixed isotropic scatterers, whose positional parameters were updated as refinement converged so that the final C—H bond lengths were 0.98 Å. During the last cycle of refinement the largest Δ/σ was 0.01, and a final difference Fourier showed a maximum density of 0.402 e/Å³. The final agreement factors^{15b} were $R = 0.041$, $R_w = 0.060$, and GOF = 1.890 for the 3107 reflections having $I \geq 2\sigma_I$.

Crystallography of (C₆H₄ONH)₂AsPh (6). 2-Phenyl-2,2'-(3*H*,3'*H*)-spirobi(1,3,2-benzoxazarsole) (**6**) was prepared by the reaction of phenylarsonic acid and *o*-aminophenol in benzene according to a procedure of Mallon and Wieber.¹⁶ A colorless to pale yellow crystal which was approximately a cube with an edge length of 0.33 mm was cut from a larger rodlike crystal and mounted as described for **5**. The diffraction symmetry (*mmm*) and the observed extinctions ($0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; hkl , $h = 2n + 1$) were consistent with the uniquely determined space group *Pbca* [D_{2h}^{15} No. 61].¹⁷ The lattice constants based on 25 reflections having $10.25^\circ \leq \theta_{\text{MoK}\alpha} \leq 13.92^\circ$ and determined at $23 \pm 1^\circ\text{C}$ are $a = 10.933$ (1) Å, $b = 10.726$ (1) Å, and $c = 26.710$ (3) Å. A unit cell content of eight molecules gives a calculated volume of 17.0 Å³ per nonhydrogen atom. The assignment of $Z = 8$ was confirmed by solution and refinement.

A total of 2741 independent reflections ($+h$, $+k$, $+l$) were measured by using the θ - 2θ scan mode for $2^\circ \leq 2\theta_{\text{MoK}\alpha} \leq 50^\circ$. Scan speeds varied from 0.80 to 4.0°/min, and six intensity control reflections were monitored. No corrections were made for absorption ($\mu_{\text{MoK}\alpha} = 2.30 \text{ mm}^{-1}$).

The structure was solved and refined in the same manner as for **5**. The 23 independent nonhydrogen atoms were refined anisotropically. The 13 aromatic hydrogen atoms were treated as described for **5**. Coordinates for the two N—H hydrogen atoms were obtained from a difference Fourier synthesis based on the remaining 36 independent atoms. Thermal parameters for both of these H atoms were fixed, and only the coordinates for one of these (HN) proved refineable. During the last cycle of refinement the largest Δ/σ was 0.07, and a final difference Fourier showed a maximum density of 0.313 e/Å³. The final agreement factors¹⁸ were $R = 0.032$, $R_w = 0.043$, and GOF = 1.318 for the 2023 reflections having $I \geq 2\sigma_I$.

RESULTS AND DISCUSSION

Molecular Structures of 5 and 6

The atom labeling schemes for **5** and **6**, respectively, are given in the ORTEP plots of Figures 1 and 2. For **5**, atomic coordinates are given in Table I. The corresponding information for **6** is given in Table II. Bond lengths and angles are presented in Tables III and IV for **5** and **6**, respectively. Anisotropic thermal parameters (Tables A and B), parameters for hydrogen atoms (Tables C and D), and least-square planes (Tables E and F) for both **5** and **6** are provided as supplementary materials.

Arsorane **6** lies on the Berry coordinate¹⁹ connecting the trigonal bipyramid (TP) to the rectangular pyramid (RP) and is displaced 21.5% (22.9% by using unit vectors) from the TP toward the RP. The oxygen atoms are axial, the nitrogen atoms are equatorial, and C7 of the phenyl group occupies the equatorial pivotal site. As is often the case for molecules lying on the Berry coordinate, **6** has a pseudo-2-fold axis coincident with the As—C7 bond.² For facilitation of the examination of this pseudosymmetry, atoms are named so that the primed ones go into the unprimed ones by the pseudo-2-fold axis.

In the case of tricoordinated N atoms directly bonded to phosphorus, it has been observed² that the geometry about the N atom is planar rather than tetrahedral.

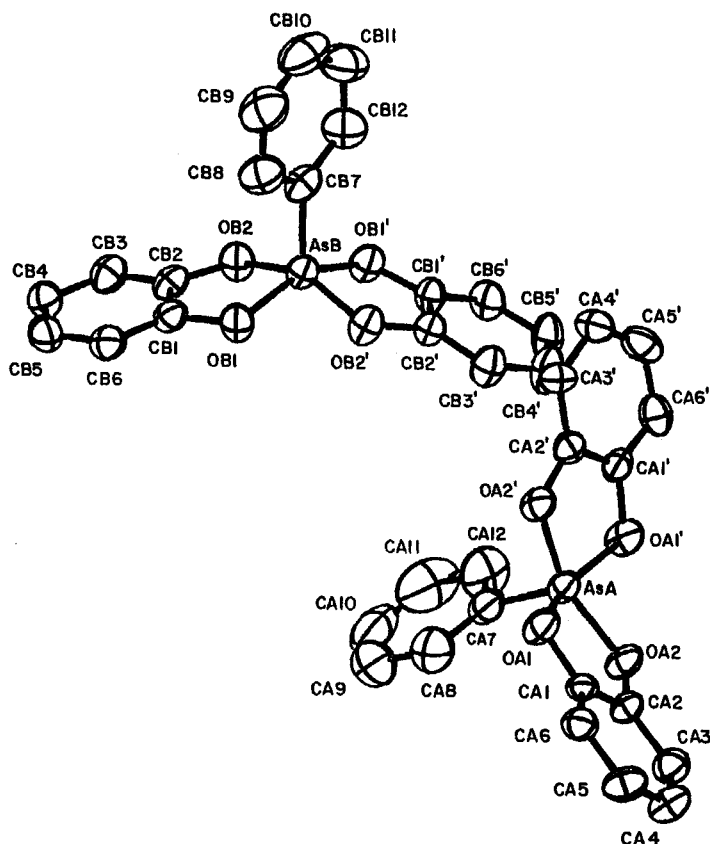


FIGURE 1 ORTEP plot showing the two independent molecules of $(C_6H_4O_2)_2AsPh$ (5). Hydrogen atoms are omitted for purposes of clarity. Thermal ellipsoids are at the 50% probability level.

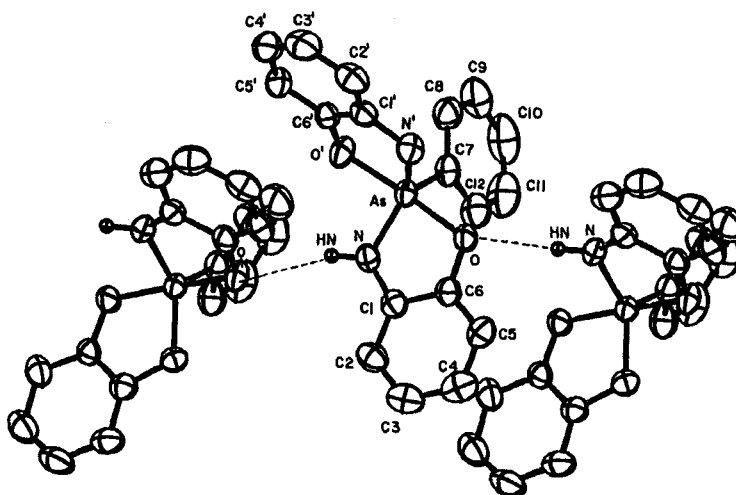


FIGURE 2 ORTEP plot of $(C_6H_4ONH)_2AsPh$ (6) with thermal ellipsoids at the 50% probability level. Hydrogen atoms except for HN have been omitted for purposes of clarity. Two *b*-glide related molecules are also shown to illustrate the hydrogen bonding.

TABLE I
Atomic Coordinates in Crystalline $(C_6H_4O_2)_2AsPh$, 5°

atom type ^b	coordinates		
	10 ⁴ x	10 ⁴ y	10 ⁴ z
ASA	-102.8 (3)	6894.1 (8)	3848.5 (2)
ASB	4883.1 (3)	3126.8 (8)	3602.9 (2)
OA1	-421 (2)	9438 (6)	3903 (1)
OA2	-1114 (2)	6298 (5)	3662 (1)
OA1'	-80 (2)	4425 (5)	4090 (1)
OA2'	635 (2)	7587 (5)	4305 (1)
OB1	4886 (2)	5540 (5)	3322 (1)
OB2	5630 (2)	2367 (5)	3168 (1)
OB1'	4604 (2)	545 (5)	3602 (1)
OB2'	3864 (2)	3743 (5)	3750 (1)
CA1	-1234 (3)	9612 (7)	3810 (2)
CA2	-1610 (3)	7905 (7)	3671 (2)
CA3	-2417 (3)	7859 (9)	3581 (2)
CA4	-2834 (3)	9591 (9)	3630 (2)
CA5	-2463 (4)	11326 (9)	3775 (2)
CA6	-1641 (3)	11357 (8)	3869 (2)
CA1'	506 (3)	4235 (8)	4449 (2)
CA2'	899 (3)	5967 (8)	4557 (2)
CA3'	1486 (3)	6012 (9)	4915 (2)
CA4'	1679 (3)	4251 (10)	5150 (2)
CA5'	1284 (4)	2567 (9)	5035 (2)
CA6'	677 (4)	2469 (8)	4680 (2)
CA7	503 (3)	6711 (11)	3260 (2)
CA8	543 (4)	8316 (13)	2956 (3)
CA9	1000 (5)	8234 (18)	2525 (3)
CA10	1406 (5)	6525 (20)	2447 (3)
CA11	1380 (5)	4904 (18)	2747 (3)
CA12	924 (4)	5040 (12)	3171 (3)
CB1	5526 (3)	5730 (8)	3011 (2)
CB2	5933 (3)	3963 (8)	2925 (2)
CB3	6569 (3)	3896 (9)	2612 (2)
CB4	6793 (3)	5698 (10)	2392 (2)
CB5	6382 (4)	7419 (9)	2476 (2)
CB6	5738 (3)	7475 (8)	2785 (2)
CB1'	3819 (3)	338 (8)	3736 (2)
CB2'	3419 (3)	2069 (8)	3819 (2)
CB3'	2617 (3)	2063 (8)	3932 (2)
CB4'	2228 (3)	255 (9)	3955 (2)
CB5'	2627 (4)	-1493 (9)	3867 (3)
CB6'	3442 (4)	-1479 (8)	3740 (2)
CB7	5450 (4)	3536 (9)	4201 (2)
CB8	5697 (4)	5386 (10)	4327 (2)
CB9	6102 (4)	5635 (12)	4765 (3)
CB10	6278 (4)	4044 (14)	5063 (3)
CB11	6038 (5)	2215 (12)	4935 (3)
CB12	5616 (4)	1869 (10)	4497 (2)

^a Numbers in parentheses are estimated standard deviations in the last significant figure. ^b Atoms are labeled to agree with Figure 1.

In the present study, only one of the H atoms bonded to nitrogen (HN) was refined, but the indication is that the geometry about N in **6** is closer to planar than to tetrahedral. For planar geometry the sum of the angles about N would be 360°, whereas for tetrahedral geometry the sum would be 328.4°. In **6**, the sum of the angles about atom N (HN refined) is 352 (8)°.

TABLE II
 Atomic Coordinates in Crystalline (C₆H₄ONH)₂AsPh, 6^a

atom type ^b	coordinates		
	10 ⁴ x	10 ⁴ y	10 ⁴ z
As	1280.2 (3)	2062.7 (3)	1142.4 (1)
O	1919 (2)	3426 (2)	1511 (1)
O'	652 (2)	602 (2)	866 (1)
N	2704 (3)	1288 (3)	1286 (1)
N'	-85 (3)	2155 (3)	1523 (1)
Cl	3438 (3)	1923 (3)	1632 (1)
C2	4510 (3)	1507 (4)	1842 (1)
C3	5141 (4)	2285 (5)	2167 (2)
C4	4707 (4)	3462 (4)	2279 (1)
C5	3597 (3)	3880 (3)	2073 (1)
C6	2980 (3)	3111 (3)	1749 (1)
C7	1252 (3)	2957 (3)	522 (1)
C8	225 (4)	2890 (3)	218 (2)
C9	240 (5)	3513 (4)	-239 (2)
C10	1276 (5)	4163 (5)	-381 (2)
C11	2278 (5)	4220 (4)	-76 (2)
C12	2277 (4)	3626 (4)	387 (2)
C1'	-802 (3)	1033 (3)	1482 (1)
C2'	-1829 (3)	742 (4)	1757 (1)
C3'	-2440 (4)	-367 (4)	1653 (2)
C4'	-2027 (4)	-1162 (4)	1285 (2)
C5'	-978 (4)	-874 (4)	1005 (2)
C6'	-379 (3)	226 (3)	1110 (1)

^a See footnote a of Table I. ^b Atoms are labeled to agree with Figure 2.

 TABLE III
 Bond Lengths (Å) and Bond Angles (Deg) for (C₆H₄O₂)₂AsPh, 5^a

type ^b	bond lengths		type	bond lengths	
	molecule A	molecule B		molecule A	molecule B
As-O1	1.809 (4)	1.806 (4)	C6-C1	1.374 (7)	1.381 (7)
As-O1'	1.797 (4)	1.809 (4)	C1'-C2'	1.377 (7)	1.370 (7)
As-O2	1.816 (3)	1.810 (4)	C2'-C3'	1.386 (7)	1.383 (8)
As-O2'	1.816 (4)	1.809 (3)	C3'-C4'	1.391 (8)	1.389 (8)
As-C7	1.914 (6)	1.908 (6)	C4'-C5'	1.355 (9)	1.381 (8)
O1-C1	1.391 (6)	1.380 (6)	C5'-C6'	1.403 (9)	1.413 (8)
O1'-C1'	1.391 (6)	1.378 (6)	C6'-C1'	1.382 (8)	1.383 (8)
O2-C2	1.370 (6)	1.368 (6)	C7-C8	1.371 (10)	1.363 (8)
O2'-C2'	1.367 (6)	1.371 (6)	C8-C9	1.412 (11)	1.385 (9)
C1-C2	1.369 (7)	1.398 (7)	C9-C10	1.361 (14)	1.381 (10)
C2-C3	1.375 (8)	1.375 (8)	C10-C11	1.371 (14)	1.347 (11)
C3-C4	1.372 (8)	1.411 (8)	C11-C12	1.398 (10)	1.408 (9)
C4-C5	1.387 (9)	1.374 (8)	C12-C7	1.357 (9)	1.417 (9)
C5-C6	1.401 (8)	1.379 (8)			

type	bond angles		type	bond angles	
	molecule A	molecule B		molecule A	molecule B
O1-As-O1'	149.3 (2)	151.0 (2)	O2'-C2'-C3'	124.5 (5)	124.4 (5)
O2-As-O2'	152.1 (2)	150.7 (2)	C6-C1-C2	121.9 (5)	121.9 (5)
O1-As-O2	87.6 (2)	88.4 (2)	C1-C2-C3	121.4 (5)	121.1 (5)
O1'-As-O2'	88.5 (2)	88.7 (2)	C2-C3-C4	117.8 (5)	116.5 (6)
O1-As-O2'	84.1 (2)	83.8 (2)	C3-C4-C5	121.5 (5)	121.8 (5)
O1'-As-O2	85.1 (2)	84.6 (2)	C4-C5-C6	120.3 (5)	121.5 (6)
C7-As-O1	106.9 (3)	103.4 (2)	C5-C6-C1	117.1 (5)	117.2 (5)
C7-As-O1'	103.8 (3)	105.6 (2)	C6'-C1'-C2'	122.7 (5)	122.3 (5)
C7-As-O2	104.4 (2)	105.2 (2)	C1'-C2'-C3'	120.6 (5)	120.9 (5)
C7-As-O2'	103.5 (2)	104.1 (2)	C2'-C3'-C4'	118.0 (5)	118.1 (5)
As-O1-C1	110.8 (3)	110.5 (3)	C3'-C4'-C5'	120.1 (5)	121.2 (5)
As-O1'-C1'	111.1 (3)	110.2 (3)	C4'-C5'-C6'	123.5 (6)	120.5 (5)
As-O2-C2	112.7 (3)	110.9 (3)	C5'-C6'-C1'	115.1 (5)	116.8 (5)
As-O2'-C2'	111.0 (3)	110.9 (3)	As-C7-C8	119.3 (6)	120.0 (5)
O1-C1-C2	115.4 (4)	114.1 (5)	As-C7-C12	119.1 (6)	118.1 (4)
O1'-C1'-C2'	114.1 (5)	115.4 (5)	C12-C7-C8	121.5 (7)	121.9 (6)
O2-C2-C1	113.3 (4)	114.2 (5)	C7-C8-C9	120.4 (8)	118.5 (7)
O2'-C2'-C1'	114.9 (5)	114.5 (5)	C8-C9-C10	116.1 (9)	121.2 (7)
O1-C1-C6	122.6 (5)	124.0 (5)	C9-C10-C11	124.6 (8)	120.0 (7)
O1'-C1'-C6'	123.2 (5)	122.1 (5)	C10-C11-C12	117.7 (9)	121.4 (7)
O2-C2-C3	125.2 (5)	124.7 (5)	C11-C12-C7	119.6 (8)	116.8 (6)

^{a, b} See footnotes a and b of Table I.

TABLE IV
Bond Lengths (Å) and Bond Angles (Deg) for
(C₆H₄ONH)₂AsPh, 6^a

type ^b	bond length	type	bond length
As-O	1.896 (2)	C1'-C2'	1.378 (5)
As-O'	1.863 (2)	C2'-C3'	1.392 (6)
As-N	1.806 (3)	C3'-C4'	1.379 (6)
As-N'	1.807 (3)	C4'-C5'	1.403 (6)
As-C7	1.914 (4)	C5'-C6'	1.378 (5)
N-C1	1.401 (5)	C6'-C1'	1.397 (5)
O-C6	1.366 (4)	C7-C8	1.388 (5)
C1-C2	1.373 (5)	C8-C9	1.393 (6)
C2-C3	1.388 (6)	C9-C10	1.383 (7)
C3-C4	1.381 (6)	C10-C11	1.366 (7)
C4-C5	1.405 (5)	C11-C12	1.390 (6)
C5-C6	1.372 (5)	C12-C7	1.379 (5)
C6-C1	1.404 (4)	N-HN	0.87 (6)
N'-C1'	1.404 (4)	N'-HN'	1.041 (3) ^c
O'-C6'	1.362 (4)	HN--O	2.33 (5)
type	bond angle	type	bond angle
N-As-N'	127.3 (1)	C4-C5-C6	118.6 (4)
N-As-O'	90.9 (1)	C1-C6-C5	120.7 (3)
N-As-O	85.8 (1)	O-C6-C5	124.2 (3)
N-As-C7	115.4 (1)	O-C6-C1	115.1 (3)
N'-As-O'	86.8 (1)	As-C7-C8	119.5 (3)
N'-As-O	89.3 (1)	As-C7-C12	118.4 (3)
N'-As-C7	117.3 (1)	C8-C7-C12	122.0 (4)
O'-As-O	171.8 (1)	C7-C8-C9	118.6 (4)
O'-As-C7	94.2 (1)	C8-C9-C10	119.5 (4)
O-As-C7	94.0 (1)	C9-C10-C11	121.1 (4)
As-O-C6	111.4 (2)	C10-C11-C12	120.6 (5)
As-O'-C6'	111.4 (2)	C11-C12-C7	118.2 (4)
HN-N-C1	120 (4)	N'-C1'-C2'	126.9 (3)
HN-N-As	118 (4)	N'-C1'-C6'	112.6 (3)
As-N-C1	114.2 (2)	C2'-C1'-C6'	120.6 (4)
HN'-N'-C1'	116.4 (3) ^c	C1'-C2'-C3'	118.6 (4)
As-N'-C1'	113.0 (2)	C2'-C3'-C4'	120.9 (4)
HN'-N'-As	117.5 (2) ^c	C3'-C4'-C5'	120.8 (4)
N-C1-C2	126.9 (3)	C4'-C5'-C6'	117.9 (4)
C2-C1-C6	120.5 (4)	C5'-C6'-C1'	121.2 (3)
N-C1-C6	112.6 (3)	C5'-C6'-O'	123.3 (3)
C1-C2-C3	119.0 (4)	O'-C6'-C1'	115.5 (3)
C2-C3-C4	120.9 (4)	N-HN--O	159 (5)
C3-C4-C5	120.3 (4)		

^{a, b} See footnotes *a* and *b* of Table II. ^c Esd based on nonhydrogen atoms only.

The fact that HN in 6 was refinable (where HN' was not) may be due to the fact that it appears to be involved in a hydrogen bond. The distance between HN and O of the adjacent molecule (*b* glide related) is 2.33 (5) Å, which is 0.3 Å less than the van der Waals sum²⁰ of 2.6 Å. This phenomenon is propagated as a chain of hydrogen bonded molecules in the lattice as illustrated in Figure 2. Similar intermolecular hydrogen bonding was reported for 1.⁸

For the spiroarsorane 5, where there are two independent molecules, the geometry about As is seen to be essentially that of the rectangular pyramid. The average displacement along the Berry coordinate for the two molecules is 95.2% (97.0% by using unit vectors) from the TP toward the RP.

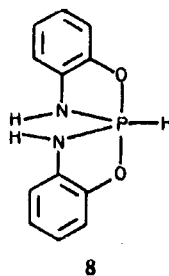
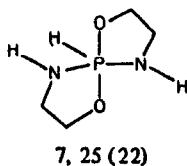
Molecule **5B** is essentially pure RP, 97.5% (99.2% by using unit vectors) from the TP toward the RP, with an average deviation from the Berry coordinate of $\pm 0.7\%$. The four oxygen atoms which form the basal plane (plane IIIB, Table E) are coplanar to within ± 0.002 Å, with the As atom displaced 0.455 Å out of this plane toward the phenyl group. There is no evidence of residual TP character in the As—O bond lengths which are identical within the limits of the error, and the trans basal angles are similarly identical (differ by 0.3° with an esd of 0.2°).

While molecule **5A** is very similar to molecule **5B**, it appears to have a small amount of residual TP character. Here the displacement along the Berry coordinate is 92.8% (94.8% by using unit vectors), with a very small deviation from the Berry coordinate averaging $\pm 0.2\%$. The atoms forming the basal plane for **5A** (plane IIIA, Table E) are less coplanar (± 0.02 Å) than those for **5B**, with the As atom displaced 0.457 Å out of the basal plane toward the phenyl group. The trans basal angles ($152.1(2)^\circ$, axial with respect to the TP; $149.3(2)^\circ$, equatorial with respect to the TP) differ by 2.8° , and while the four As—O bond lengths are nearly within three esd's of each other, the As—O_{ax} bonds average 0.013 Å longer than the equatorial ones.

It is interesting to compare the angle and bond length variations within the five-membered ring in **5** and **6**. The alternation in angle size and bond length for adjacent bonds in the more trigonal-bipyramidal arosane **6** complements that found in related phosphoranes and is a manifestation of the unequal lengths associated with apical and equatorial bonds of a trigonal bipyramid.^{21,22} In the rectangular-pyramidal arsorane **5B**, these alternations largely disappear in line with the equal character of ring basal As—O bonds. One consequence of the presence of the larger arsenic atom (relative to a phosphorus atom) is that the length of the mutual C—C bond of the associated fused six-membered ring averages several hundredths of an angstrom larger than in related phosphorane structures.^{2,21}

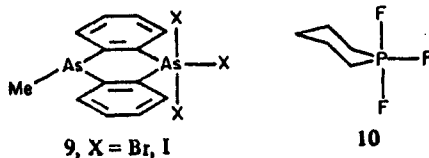
STRUCTURAL PRINCIPLES

Like that for the oxazaspiroarsorane **1**,⁸ the apical positions of **6** are occupied by the oxygen atoms, in agreement with the electronegativity rule.²³ The apical O—As—O and equatorial N—As—N bond angles are similar in the two derivatives as reflected in their almost equal structural displacement from the trigonal bipyramid. For **1**, these angles are 169.6° and 125.9° , respectively, with an esd of $0.2-0.4^\circ$, while the corresponding angle values for **6** are $171.8(1)^\circ$ and $127.3(1)^\circ$.



In the analogously structured phosphoranes **7**^{24,25} and **8**,²⁴ these apical and equatorial angles are 177.1 (1)° and 130.8 (1)° for **7** and 177.8 (1)° and 121.8 (1)° for **8**. the structure of **7** is displaced 25% (22%) from the trigonal bipyramid, similar to that of **1** and **6**. For lack of refinement of the equatorial proton position for **8**, the structural displacement based on the dihedral angle is not calculated but appears similar to that for **7**.

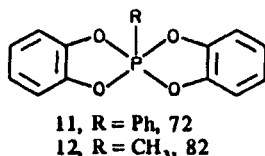
When a six-membered ring is included as part of the framework as in arsorane **9**, X-ray analysis²⁶ shows that the ring assumes diequatorial positions, presumably because of reduced ring strain relative to occupancy of an apical-equatorial pair.



X-ray analysis of an analogous phosphorane seems lacking, but ¹⁹F NMR data²³ indicate this geometry in (CH₂)₅PF₃ (**10**) with no evidence of ligand exchange.

In agreement with the factors found to stabilize the rectangular-pyramidal geometry for phosphoranes,^{2,5} the presence of unsaturated five-membered rings and like ligands bound to phosphorus in any one ring, and the presence of an acyclic ligand which is bulky and of low electronegativity, the structure of the spiroarsorane **5** is rectangular pyramidal. The related methyl derivative **4**¹⁰ is less so, 69% on the basis of bond distances.

The structures of the corresponding spiroposphoranes **11**²² and **12**²⁷ are available for comparison. Here the opposite situation prevails. The structure of the phenyl derivative **11** is less displaced toward the rectangular pyramid, 72%, than that for the methyl spiroposphorane **12**, 82%, both on the basis of bond distances. It is difficult to account for this reversal at present. Evidence thus far accumulated



shows that arsoranes are more nonrigid than phosphoranes both in their dynamic NMR behavior and in data derived from vibrational motions associated with intramolecular ligand exchange.⁵ Both lines of evidence indicate that the order of non-rigidity for group 5A pentacoordinated elements is Sb > As > P. The lower energy difference between the trigonal bipyramid and rectangular pyramid implied by these lines of evidence makes it easier to stabilize pentacoordinated arsenic in this structural form relative to phosphorus. This would rationalize the structure obtained for the phenylspiroarsorane **5** relative to the phenylphosphorane **11**. The subtle differences in bonding, possibly including some measure of lattice effect, is elusive at present in rationalizing the structural displacement between the phosphoranes **11** and **12** or the arsoranes **4** and **5**.

Following our previous method,^{28,29} we have carried out molecular mechanics

calculations on the series of model phosphoranes and arsoranes shown in Table V. The results are expressed as % displacement along the Berry coordinate and show two features that are in agreement with pentacoordinate structural principles.^{2,3,5,23} Increasing the steric requirements of the acyclic substituent from the proton to the methyl group drastically increases the % displacement toward the RP, in line with X-ray structural determinations.^{10,27,30,31}

When the ring atoms attached to phosphorus are made different, as in the methyl phosphorane containing ring oxygen and sulfur atoms in Table V, the calculation shows the structure is strongly displaced back toward the trigonal bipyramid with the more electronegative ligands occupying the apical sites. Although direct experimental verification is not available with this specific model derivative, the related arsoranes, **1**⁸ and **6**, and phosphoranes, **7**^{24,25} and **8**,²⁴ all have structures near this calculated displacement.

Even though the agreement between calculated and experimental structures in Table V is satisfactory, the calculation appears insensitive, in its present form, to differentiate between the substitution of ring oxygen for ring sulfur atoms or between substitution of arsenic for phosphorus.

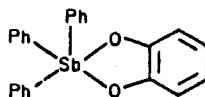
In line with the order of nonrigidity expressed above, Sb > As > P, pentacoordinated antimony in **13**³² apparently is stabilized in a near rectangular-pyramidal geometry with the presence of only one unsaturated five-membered ring containing like atoms bonded to it. This derivative, which is a hemihydrate (Ph₃SbO₂C₆H₄)₂·H₂O, has both pentacoordinated antimony, **13**, and hexacoordinated antimony in the unit cell.³² The latter has the water molecule occupying the sixth coordination site. The trans basal angles for **13** are 154.9 (1)° and 147.4 (2)°.

As with spirocyclic phosphoranes,^{2,5} the presence of saturated five-membered rings in related pentacoordinated arsenic and antimony derivatives allows the struc-

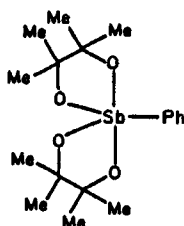
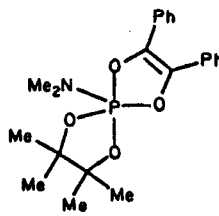
TABLE V
Comparison of Structural Distortions^a

model structure			exptl structure			
			M = P		M = As	
R	X	Y	calcd	exptl ^b	calcd	exptl ^b
CH ₃	O	O	92	82 ²⁷	93	(72) ¹⁰
H	O	O	13	(1.7) ^{30,c}		
CH ₃	S	S	93	79 ³¹		
H	S	S	-11			
CH ₃	O	S	23			

^a Displacement (%) along the Berry coordinate from the trigonal bipyramid toward the rectangular pyramid. The unparenthesized values are based on the use of actual bond distances; parenthesized values, on unit bond distances. ^b References are given as superscripts. ^c There are two independent molecules per unit cell with slightly different parameters.³⁰

**13, 84.0 (85.3)**

ture to go more toward the trigonal bipyramid. Presumably, ring puckering reduces ring strain and offsets any ring strain advantage that is encountered for unsaturated five-membered rings in dibasal positions of the rectangular pyramid relative to the apical-equatorial orientation in the trigonal bipyramid.²¹ The structures of the pentacoordinated arsenic derivative **2** and antimony derivative **14**,³³ like the phosphorane **15**,³⁴ are not too far from the ideal trigonal bipyramid.

**14, 13 (12.1)****15, 31**

In the case of **2** and **14**, dynamic ¹H NMR data give ligand exchange barriers (ΔG^\ddagger) of 22.2³⁵ and 19.1^{33,36} kcal/mol, respectively, for pseudorotation which has the phenyl group apical and one of the rings diequatorial in an intermediate trigonal bipyramid.³⁷

We conclude that the basic structural principles developed for phosphorane stereochemistry^{2,3,38} apply to the stereochemistry of pentacoordinated arsenic compounds and apparently also to pentacoordinated antimony.^{39,40} The ease of attainment of the rectangular-pyramidal geometry appears to be reflected in the relative fluxional character assigned to these elements in their pentacoordinated state.⁵

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Registry No. **5**, 79677-99-9; **6**, 72409-78-0.

Supplementary Material Available: Compilations of observed and calculated structure factor amplitudes and thermal parameters (Tables A and B), parameters for hydrogen atoms (Tables C and D), and least-squares planes (Tables E and F) for **5** and **6**, respectively (26 pages). Ordering information is given on any current masthead page.

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